THE CHEMISTRY OF CYCLODIPHOSPHAZANES

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

DOCTOR OF PHILOSOPHY

by

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ACKNOWLEDGEMENTS

I wish to thank my supervisor, Dr. R. Keat, for the constant advice and encouragement he has given me throughout the preparation of this thesis.

Thanks are also due to my colleagues in the Chemistry Department for the interest they have shown in this work, especially Dr. D. S. Rycroft for obtaining the Fourier-transform n.m.r. spectra, and Dr. K. W. Muir and Mrs A. N. Keith for undertaking the X-ray diffraction studies.

I also wish to express my gratitude to Liz Prentice (typing) and Fiona and David (general solace and encouragement).

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

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ABSTRACT

A variety of bis(di)alkylaminocyclodiphosph(lll)azanes of the type, $(R^1R^2NPNR^3)_2$ (R^1=alkyl, R^2=alkyl or H, R^3=alkyl or aryl), have been prepared. In most cases synthesis has been effected by aminolysis of the dichloro-derivatives, $(ClPNR^3)_2$, exceptions being $(Me_2NPNC_6H_4OMe\text{-}\underline{p})_2$ which was prepared by dimethylaminolysis of the acyclic bis(dichlorophosphino)amine, $(C_6H_4OMe\text{-}\underline{p})N(PCl_2)_2$, and $(Me_3SiNMe.PNBu^t)_2$, which was prepared by treating $(ClPNBu^t)_2$ with heptamethyldisilazane. The novel cage compound, $\overline{P(NBu^t)_2PNMe.(CH_2)_2.NMe}$, has also been prepared, through the action of N,N´-dimethylethylene-diamine on $(ClPNBu^t)_2$. The synthesis of $Me_2N\overline{P.NBu^t.PCl.NBu^t}$ was repeated and other monodialkylamino-derivatives, $R^1_2N\overline{P.NR^2.PCl.NR^2}$ (R^1=Me, R^2=Ph; R^1=Pr^i, R^2=Bu^t), prepared by treating $(ClPNR^2)_2$ with two molar equivalents of the required amine. The action of excess antimony trifluoride or methylamine on $Me_2N\overline{P.NBu^t.PCl.NBu^t}$ afforded $Me_2N\overline{P.NBu^t.PF.NBu^t}$ and $Me_2N\overline{P.NBu^t.P(NHMe).NBu^t}$ respectively.

A series of alkoxycyclodiphosph(lll)azanes of the type, $RO\overline{P.NBu^t.PX.NBu^t}$ (R=alkyl; X=Cl or OR), plus the cage-derivatives, $\overline{P(NBu^t)_2PO.(CH_2)_n.O}$ (n=2 or 3) have been synthesised via alcoholysis of $(ClPNBu^t)_2$ in the presence of triethylamine. Attempts at isolating $(Bu^tOPNBu^t)_2$ were unsuccessful owing to butene elimination forming $Bu^tO\overline{P.NBu^t.P(O)H.NBu^t}$.

Many of the above cyclodiphosph(lll)azanes display geometrical isomerism and evidence is presented on the basis of n.m.r., i.r., Raman, and photoelectron spectroscopic data, dipole moment and basicity measurements, and X-ray diffraction studies to suggest that when t-butyl is attached to the ring-nitrogen the cis form is thermodynamically favoured, whereas when the smaller aryl-groups are attached, it is the trans form which is more stable. For the first

time, thermodynamically unstable cyclodiphosphazane isomers [trans-$(XPNBu^t)_2$ (X=Me_2N,MeO, and EtO)] have been isolated.

The compounds, $[Cl(X)PNBu^t]_2$ (X=O or S), were surprisingly unreactive towards dimethylamine; $[Me_2N(X)PNBu^t]_2$ finally being produced by treating $(Me_2NPNBu^t)_2$ with t-butylhydroperoxide (X=O) and elemental sulphur (X=S). Unlike $(ClPNBu^t)_2$, which is readily oxidised, $(Me_2NPNBu^t)_2$ is unaffected by dimethyl sulphoxide. These results prompted an investigation into the oxidation reactions of cyclodiphosph(lll)azanes. Cis and trans-$(XPNBu^t)_2$ (X=Me_2N or MeO) react stereospecifically with one or two molar equivalents of elemental sulphur and selenium to give the respective mono- and di- sulphides and selenides with retention of configuration at phosphorus. An X-ray diffraction study of cis-$[Me_2N(S)PNBu^t]_2$ confirmed the structural assignments. Neither cis nor trans-$(MeOPNBu^t)_2$ reacted with elemental tellurium, but both cis and trans-$(Me_2NPNBu^t)_2$ afforded the monotelluride, trans-$Me_2NP.NBu^t.P(Te)NMe_2.NBu^t$, which exhibited intermolecular tellurium exchange at an intermediate rate on the n.m.r. time-scale. No ditelluride could be isolated. Selenium exchange was not observed. However, mixing equimolar solutions of cis-$(XPNBu^t)_2$ (X=Me_2N or MeO) with cis or trans-$[X(Se)PNBu^t]_2$ yielded the analogous cis, or cis and trans (1:1) monoselenides, $XP.NBu^t.P(Se)X.NBu^t$. Treatment of both cis and trans-$(Me_2NPNBu^t)_2$ with methyl iodide produced the quaternary salts, cis and trans-$Me_2NP.NBu^t.P^+(Me)NMe_2.NBu^t$ (retention of configuration at phosphorus). On the other hand, the action of methyl iodide on both cis and trans-$(MeOPNBu^t)_2$ resulted in an Arbuzov-type rearrangement to $MeOP.NBu^t.P(O)Me.NBu^t$ and (after extended reaction periods) to cis and trans-$[Me(O)PNBu^t]_2$ respectively. Similarly, treatment of cis-$(EtOPNBu^t)_2$ with methyl iodide afforded $EtOP.NBu^t.P(O)Me.NBu^t$ and cis-$[Me(O)PNBu^t]_2$. Tentative evidence is presented to suggest these Arbuzov-type rearrangements occur with

inversion of configuration at phosphorus. Cis-$[Me(O)PNBu^t]_2$ may also be produced by heating cis-$(MeOPNBu^t)_2$ in an evacuated sealed tube. The thermodynamic instability of trans-$(XPNBu^t)_2$ ($X=Me_2N$ or MeO) is paralleled by their enhanced nucleophilicity relative to the cis isomers, as was shown by qualitative observations of the considerably faster rates of reaction of the trans isomers towards sulphur, selenium and methyl iodide. The compounds, $Et_2N(X)\overline{P.NBu^t.P(Y)NEt_2.NBu^t}$ (X=S or Se, Y=lone-pair; X=Y=S or Se), $C_5H_{10}N(Se)\overline{P.NBu^t.P(X)NC_5H_{10}.NBu^t}$ (X=lone-pair or Se), and $\overline{P(Se).(NBu^t)_2.PNMe.(CH_2)_2.NMe}$ were produced similarly from their respective parent cyclodiphosph(III)azanes. By contrast, the reactions of cis-$Me_2N\overline{P.NBu^t.PCl.NBu^t}$ with one molar equivalent of dimethyl sulphoxide or elemental sulphur gave a 1:1 mixture of $Me_2N(O)\overline{P.NBu^t.P(O)Cl.NBu^t}$ isomers plus starting material and a 1:1 mixture of $Me_2N(S)\overline{P.NBu^t.PCl.NBu^t}$ isomers respectively. The adduct, $Me_2N\overline{P.NBu^t.P^+.NBu^t}\ AlCl_4^-$, was formed (though not isolated) on reacting cis-$Me_2N\overline{P.NBu^t.PCl.NBu^t}$ with aluminium trichloride.

The magnitude and sign of the coupling constant, $^2J(PNP)$, has been obtained from the n.m.r. spectra of many of the aforementioned cyclodiphosphazanes by single, double, and triple-resonance methods. The manner in which this coupling is affected by geometrical isomerism, the electronegativity of the phosphorus substituents, and the oxidation state of phosphorus is discussed. Triple-resonance experiments used in determining the sign of $^2J(PNP)$ also permitted the sign and magnitude of $^3J(PNPSe)$ to be determined for the first time. ^{77}Se chemical shifts were calculated for a number of mono- and diselenide isomers; those in the cis isomers always being considerably upfield (ca. 35-120 p.p.m.) of the analogous trans isomers.

Slow rotation about both phosphorus(III)- and phosphorus(V)-nitrogen bonds in many of the dialkylamino-substituted cyclodiphosphazanes has been detected by variable-temperature ^{1}H and ^{13}C n.m.r. spectroscopy. The barriers to rotation about these bonds along with the preferred conformations of the amino-groups are discussed.

CHAPTER 1

GENERAL INTRODUCTION

HISTORICAL

The first preparation of relatively pure white elemental phosphorus is generally attributed to Hennig Brandt (in 1669)[1] as a result of his alchemical experiments with urine. Although Brandt's method is not entirely known, the method which developed from it was to heat a mixture of boiled-down urine, sand and charcoal - a process not dissimilar to today's electric furnace method:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \longrightarrow P_4 + 10\ CO + 6\ CaSiO_3.$$

Distillation of such a mixture affords white phosphorus which luminesces in the dark and led to the name 'phosphoros'(Gr. light bearing) which is synonomous with the ancient name for the planet Venus when appearing before sunrise. Phosphorus is never found free in nature, but is widely distributed in combination with a variety of minerals, one of the most important being apatite (above), an impure tri-calcium phosphate. Today, phosphates are mined worldwide on a large scale and used commercially in a range of products from fertilisers, detergents, and animal feedstuffs to pharmaceuticals and insecticides.

It was not until the middle of the nineteenth century, nearly two hundred years after Brandt's preparation, that there was the first report of the synthesis of a number of phosphorus-nitrogen compounds,[2] and by the early twentieth century only Michaelis had made a significant contribution to this field.[3,4] Indeed, after Michaelis there was little progress in phosphorus-nitrogen chemistry till the 1950s when, with the

aid of modern spectroscopic techniques (especially nuclear magnetic resonance), much of the early work was reinvestigated and greatly extended.

Today, phosphorus-nitrogen compounds are of some industrial use through their action as flameproofing agents, polymer plasticisers and antioxidants. There have also been numerous studies on the herbicidal and insecticidal activity possessed by such compounds, which in turn have led to their development as nerve agents. However, the most widespread application is the use of ammonium phosphates as fertilisers in the agricultural industry.

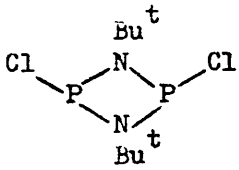
Finally, one of the most important aspects of phosphorus-nitrogen chemistry is its role in biological processes. For example, creatine phosphate which is present in high concentrations in both the muscle and nerve cells acts as a reserve store of energy by phosphorylating adenosine diphosphate (ADP) to adenosine triphosphate (ATP) which then acts as the central energy-transfer agent in the body.

NOMENCLATURE

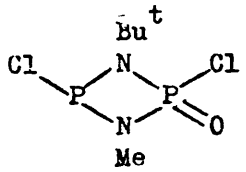
Two nomenclature systems are in current use for the naming of compounds containing the $\overline{\text{P-N-P-N}}$ unit. The basic four-membered ring may be termed a cyclodiphosphazane (as proposed by Shaw and co-workers[5]) or, according to the Chemical Abstracts system, as a 1,3,2,4-diazadiphosphetidine. The former system will be used here.

Compounds can be named as derivatives of cyclodiphosph(III)azanes or cyclodiphosph(V)azanes depending on the oxidation state of the ring phosphorus atoms. Nitrogen takes precedence over phosphorus in the

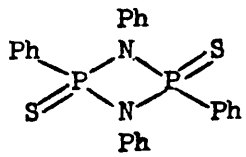
ring numbering, and nitrogen and phosphorus substituents are added as prefixes in alphabetical order. The ring geometry (if known) may also be indicated eg.,



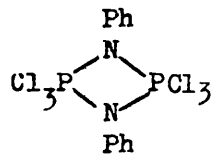
1,3-di-t-butyl-2-cis-4-dichlorocyclodiphosph(lll)azane



1-t-butyl-2-cis-4-dichloro-3-methyl-2-oxocyclodiphosphazane



1,3-diphenyl-2-trans-4-diphenyl-2,4-dithiocyclodiphosph(v)azane



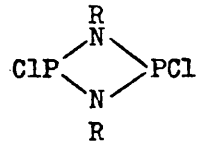
2,2,2,4,4,4-hexachloro-1,3-diphenylcyclodiphosph(v)azane.

CYCLODIPHOSPHAZANES

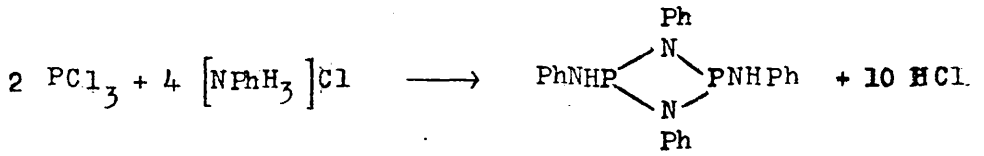
Although the first report[6] of the formation of a cyclodiphosphazane appeared towards the end of the last century, the detailed chemistry of these compounds has only been studied in the last twenty years. Reviews describing the chemistry of cyclodiphosphazanes have appeared,[7,8] but so great has been the proliferation of work this decade that a more recent review is desirable. The following survey outlines synthetic routes to cyclodiphosphazanes with three, four and five co-ordinate phosphorus and describes some of their structural features.

CYCLODIPHOSPH(III)AZANES (three co-ordinate phosphorus)

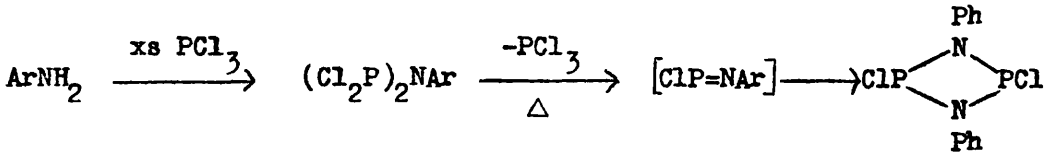
One of the earliest and most general routes to compounds of the type (1) is the reaction of excess phosphorus trichloride with primary amines or their hydrochlorides (the latter usually requiring more forceful conditions). When excess amine (or amine hydrochloride) is used, the partly or fully aminolysed product may be obtained. The study of such reactions, however, has resulted in a number of conflicting reports. For example, early work on the reaction of phosphorus trichloride with a large excess of aniline claimed[9-11] the formation and isolation of bis(anilino)chlorophosphine, $(PhNH)_2PCl$, and tris(anilino)phosphine, $(PhNH)_3P$. This has since been questioned[12] and has not been substantiated by other workers.[6,13-15] Instead, Michaelis and Schroeter[6] maintained that the reaction of phosphorus trichloride with excess aniline hydrochloride provided a compound of the general formula $(PhNPNHPh)_n$, for which n was found to be two.



(1)



Goldschmidt and Krauss[14] later corroborated this by studying the action of excess aromatic amine on phosphorus trichloride. They did, however, challenge the finding[6] that (1) (R=Ph) is the product of the reaction of aniline hydrochloride with excess phosphorus trichloride. They reported[14] the isolation of bis(dichlorophosphino)aniline, $(Cl_2P)_2NPh$, as the sole product. Haszeldine and co-workers[15] resolved the situation by showing that $(Cl_2P)_2NPh$ is isolated under low temperature work up conditions (at or below 30°) whereas (1) (R=Ph) is isolated at higher temperatures (100-150°) through thermal elimination of phosphorus trichloride from $(Cl_2P)_2NPh$. Other primary aromatic amines were found to behave similarly and the reaction scheme proposed involved the rapid dimerisation of an unstable phosphorus imide [phosph(lll)azene] intermediate - though no direct evidence of this was found.



The reactions of phosphorus trichloride with primary aliphatic amines and their hydrochlorides, though paralleling in some ways the reactions with aromatic amines, tend to be more dependent on the nature of the amine. Michaelis showed[3] that dichlorophosphinoalkylamines, $Cl_2P.NHR$ (2), are

the sole products of the reactions of primary aliphatic amines with excess phosphorus trichloride and yet the analogous reactions with amine hydrochlorides do not yield (2), but instead form bis(dichlorophosphino)alkylamines, $(Cl_2P)_2NR$, (R=Me or Et)[16] which unlike their aryl counterparts show no tendency to decompose thermally to cyclodiphosphazanes.

The products of the reactions of phosphorus trichloride with three molar equivalents of primary aliphatic amines vary depending on the amine.[17] These reactions may be summarised as follows:

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

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

$$PCl_3 + RNH_2 \longrightarrow ClP\begin{smallmatrix} N(R) \\ N(R) \end{smallmatrix}PCl \quad (R=Pr^i \text{ or } Bu^t)$$

The fact that largely acyclic products are formed in the reactions with methylamine and ethylamine, whereas with isopropylamine and t-butylamine cyclodiphosphazanes are the major products, suggests the mechanism of formation of (1) (R=aryl) is different from (1) (R=alkyl). Here the mechanism proposed [17] is condensation via an acyclic intermediate of the type $Cl_2P.NR.PCl.NHR$ ($R= Pr^i$ or Bu^t) which undergoes extremely ready cyclisation. A directive factor in the cyclisation of an intermediate

of the above type may well be the presence of relatively bulky R-substituents because of their ability to reduce the bond angles at nitrogen and so lower the activation energy for the formation of a four-membered ring system. (1) ($R=Bu^t$) may also be obtained by the reaction of phosphorus trichloride with $Bu^t.NLi.SiMe_3$, and (2) ($R=Bu^t$) with triethylamine.[18]

$$Bu^t.NH.SiMe_3 \xrightarrow[-Bu^nH]{Bu^nLi} Bu^t.NLi.SiMe_3 \xrightarrow[-LiCl\ -Me_3SiCl]{PCl_3} \tfrac{1}{2}\ (ClPNBu^t)_2$$

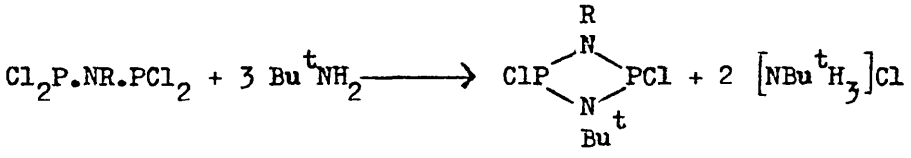
$$Bu^t.NH.PCl_2 + Et_3N \longrightarrow \tfrac{1}{2}\ (ClPNBu^t)_2 + [NEt_3H]Cl$$

Reactions with greater proportions of t-butylamine lead to aminolysis of the ring compound,

$$2\ PCl_3 + 8\ Bu^tNH_2 \longrightarrow Bu^tNHP\begin{matrix}N(Bu^t)\\ \diagdown\ \diagup\\ N(Bu^t)\end{matrix}PCl + 5\ [NBu^tH_3]Cl$$ [17]

$$2\ PCl_3 + 10\ Bu^tNH_2 \longrightarrow Bu^tNHP\begin{matrix}N(Bu^t)\\ \diagdown\ \diagup\\ N(Bu^t)\end{matrix}PNHBu^t + 6\ [NBu^tH_3]Cl.$$ [19]

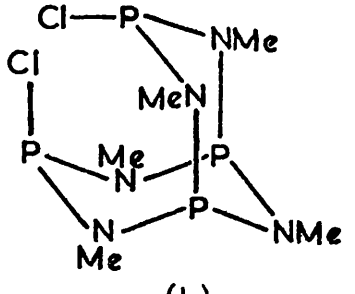
Only quite recently have cyclodiphosph(III)azanes with different alkyl groups on the ring nitrogens been prepared.[20] This was accomplished by the ready cyclisation of bis(dichlorophosphino)amines, $(Cl_2P)_2NR$ (R=Me or Et) with t-butylamine to yield (3).



(3) (R=Me or Et)

No direct evidence was found in the above reaction for the presence of the intermediates $Cl_2P.NR.PCl.NBu^t$, nor did the size of the R-group appear to affect the rate of cyclisation since little difference was observed in the ease with which $(Cl_2P)_2NMe$ and $(Cl_2P)_2NBu^t$ reacted.

The reactions of $(Cl_2P)_2NR$ (R=Me or Et) with other primary amines led to much reduced yields of cyclodiphosph(III)azanes.[20] For example, the reaction of $(Cl_2P)_2NMe$ with three molar equivalents of methylamine produced a mixture of products out of which $(ClPNMe)_n$ (n=2-4) and the cage compound (4) were assigned. (4) is probably a precursor in the formation of $P_4(NMe)_6$ (5) formed from the reaction of phosphorus trichloride with excess methylamine.[19]



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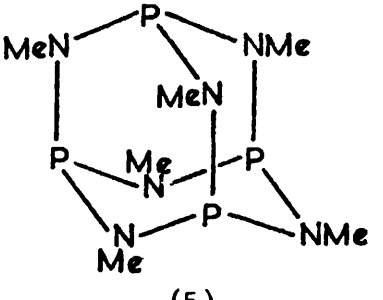


(5)

The corresponding reaction with ethylamine initially produced $(ClPNEt)_2$ which on standing rearranged to a mixture containing $(ClPNEt)_3$. The compounds $(ClPNEt)_3$ and $(ClPNEt)_4$ were originally reported[21] from the reaction of phosphorus trichloride with $EtN(SiMe_3)_2$.

One possible explanation[22] as to why t-butylamine gives rise to much higher yields of cyclodiphosph(III)azanes than other primary amines is that it is a relatively strong base, but a poor nucleophile,[23] and so will be more efficient at abstracting hydrogen chloride than effecting further aminolysis. In contrast, methylamine and ethylamine, being stronger nucleophiles will be more efficient at producing aminolysis products such as $R'NH(Cl)P.NR.P(Cl)NHR'$ which are probable precursors of the complex mixtures generally obtained with these amines. In fact, the compound (1) (R=Me) has not yet been synthesised by any route. It was reported[21] to be formed by the reaction,

$$2\,PCl_3 + 2\,(Me_3Si)_2NMe \longrightarrow ClP\begin{matrix}\diagup N(Me)\diagdown\\ \diagdown N(Me)\diagup\end{matrix}PCl + 4\,Me_3SiCl$$

but this has since been disputed by other workers[17,24] who verified an earlier report[25] which claimed the formation of dichlorophosphino(trimethylsilyl)methylamine, $Cl_2P.NMe.SiMe_3$.

Whereas, as outlined above, aminolysis reactions of phosphorus trichloride and bis(dichlorophosphino)amines frequently lead to cyclic products, the same is not true of the corresponding reactions with phosphorus trifluoride and aryl or alkyldichlorophosphines.

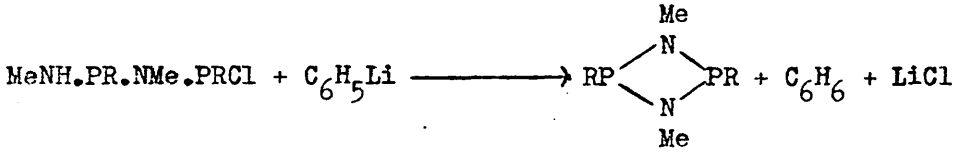
Difluorophosphinoalkylamines, $F_2P.NHR$, plus $(RNH)_2PF_2H$ are the products of reaction of phosphorus trifluoride with primary aliphatic amines[26] unless the amine is t-butylamine when bis(t-butylamino)fluorophosphine, $(Bu^tNH)_2PF$, is the product of further aminolysis. The best route to 2,4-difluorocyclodiphosph(III)azanes is by halogen exchange with the respective 2,4-dichloro compounds using, for example, antimony trifluoride.[27] Similarly, only the diamino-derivatives, $(RNH)_2PAr$, result from the reactions of dichlorophenylphosphine and dichloro(pentafluorophenyl)phosphine with excess primary aliphatic amines[28-30] or aniline,[31] and bis(methylamino)alkylphosphines, $RP(NHMe)_2$ ($R=Bu^t$ or CF_3), are the products from the reaction of dichloro(t-butyl)phosphine[32] or dichloro(trifluoromethyl)phosphine[33] with excess methylamine.

In contrast to the above is the recent report[34] of the reaction of dichloro(t-butyl)phosphine with bis(methylamino)(t-butyl)phosphine,

$$RP(NHCH_3)_2 + Bu^tPCl_2 \xrightarrow[-[NEt_3H]Cl]{Et_3N} MeNH.PR.NMe.PRCl$$

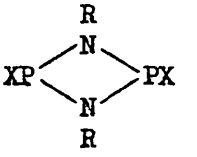
(6) ($R=Bu^t$)

which leads to a compound (6) of the same structure as the postulated intermediates[17,20] involved in the rapid cyclisation step in the aminolysis of phosphorus trichloride and bis(dichlorophosphino)amines. Indeed, the action of phenyllithium on (6) results in ring closure to the corresponding cyclodiphosph(III)azane (7).

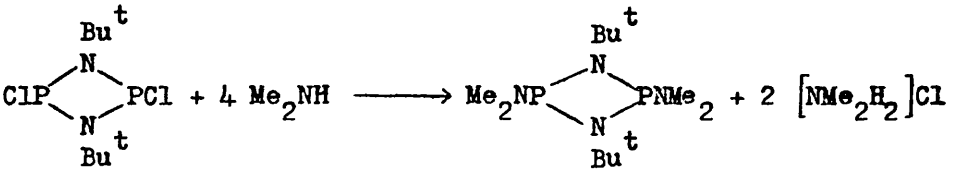


(7) (R=Bu^t)

To date this survey has been contained mainly to the synthesis of dichlorocyclodiphosph(III)azanes (1). However in recent years many ring compounds of the type (8) (X=amino, alkyl, alkoxy) have been prepared. As previously discussed, the reaction of phosphorus trichloride with excess amine[14,19] or amine hydrochloride[6] readily afforded (8) (X=NHR;R=Bu^t or Ph). A number of other amino-substituted cyclodiphosph(III)azanes have now been produced by a variety of routes, one of the most straightforward being aminolysis of (1). In contrast to an earlier report [35] that dimethylaminolysis of (1) (R=Bu^t) led to only complicated mixtures, it was found[22] that the 2,4-bis(dimethylamino)cyclodiphosph(III)azane (9) was the sole product of the reaction with excess amine.

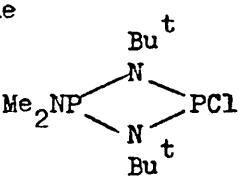


(8)



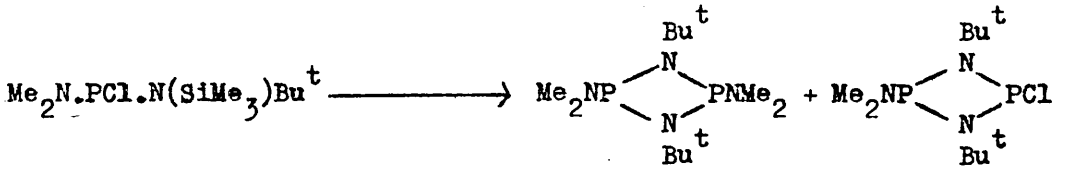
(9)

A similar reaction occurred with diethylamine [22] and the reaction with two molar equivalents of dimethylamine readily gave the monodimethylamino-derivative (10).



(10)

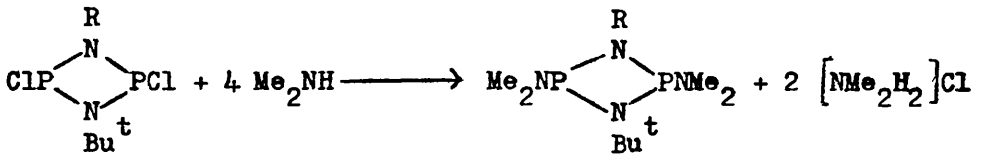
It was later discovered[36] that a mixture of (9) and (10) could be prepared by heating (dimethylamino)(t-butyl-trimethylsilylamino)chlorophosphine, $Me_2NP(Cl).N(SiMe_3)Bu^t$, with evolution of trimethylchlorosilane,



(9) (40%) (10) (60%)

+ Me_3SiCl.

It was found also [22] that ready dimethylaminolysis of (3) (R=Me or Et) occurred,



(11) (R=Me or Et)

though (11) (R=Me) could also be prepared[22] by the action of t-butylamine on bis(chlorodimethylamino phosphino)methylamine.

$$(Me_2N)ClP.NMe.PCl(NMe_2) + 3\ Bu^tNH_2 \longrightarrow Me_2NP\begin{smallmatrix}NMe\\ \diagup\ \diagdown\\ NBu^t\end{smallmatrix}PNMe_2 + 2\left[NBu^tH_3\right]Cl$$

(11) (R=Me)

The compound (8) (R=Ph,X=NMe_2) has also been reported[15] through the action of dimethylaminotrimethylsilane either on (1) (R=Ph) or on bis(dichlorophosphino)phenylamine, $PhN(PCl_2)_2$. Surprisingly, the reaction of dimethylamine with (1) (R=Ph) was not investigated. Haszeldine and co-workers also prepared[37] a number of N-arylsulphonyl-derivatives (8) [X=NMeR′ (R′=alkyl),R=R″SO_2 (R″=aryl)] by treating bis(dialkylamino)chlorophosphines with aryl sulphonamides in anhydrous pyridine,

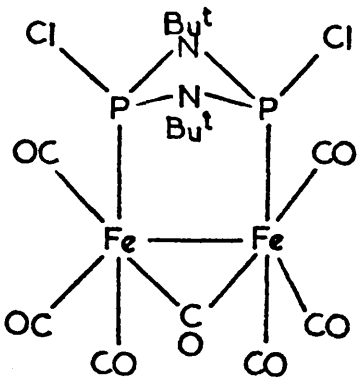
$$ArSO_2.NH_2 + (MeRN)_2PCl \xrightarrow{\text{pyridine}} Me(R)NP\begin{smallmatrix}SO_2Ar\\ \diagup\ \diagdown\\ NSO_2Ar\end{smallmatrix}PN(R)Me.$$

A series of compounds of the type (8) (R=$SiMe_3$,X=amino) has been synthesised by Zeiss and co-workers[38] through the action of sodium bis(trimethylsilyl)amide,$NaN(SiMe_3)_2$, on bis(alkylamino)chlorophosphines.

$$2\ X_2PCl + 2\ NaN(SiMe_3)_2 \longrightarrow (XPNSiMe_3)_2 + 2\ NaCl + 2\ SiMe_3X$$

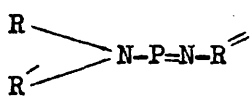
[X=Me_2N,Et_2N,Pr^i_2N, $C_5H_{10}N$,C_4H_8N,Ph(Me)N]

Interestingly, (8) ($R=SiMe_3$, $X=Me_2N$) may act as a bridging ligand between two $M(CO)_5$ units [39] (M=Cr,Mo), though this is not the first report of a cyclodiphosph(111)azane ring being used as a ligand: (1) ($R=Bu^t$) having been complexed[40] with $Fe_2(CO)_9$ to give the species (12), whose structure was proposed on the basis of infrared spectroscopic data.



(12)

A final route to amino-substituted cyclodiphosph(111)azanes is via monomeric tervalent phosphazenes (13).



(13)

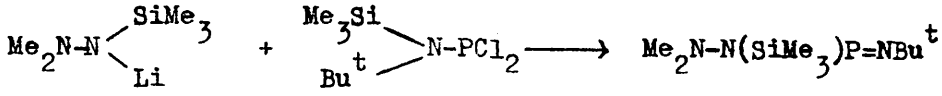
It is only quite recently that a number of such compounds have been made, the most common route involving lithiated silyl amines.[41-45]

$$R_2NPCl_2 + Li\text{-}NRR' \longrightarrow R_2NP{=}NR' + LiCl + RCl$$
$$(R,R' = Me_3Si, Bu^t)$$

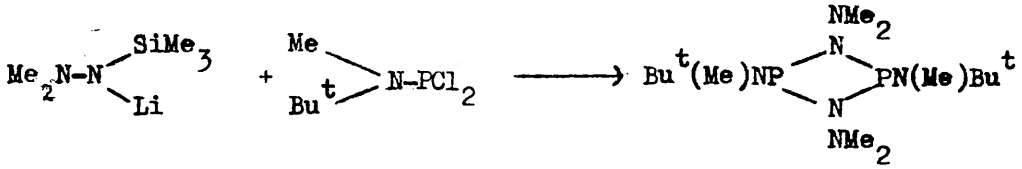
$$PCl_3 + 2\ Li\text{-}NRR' \longrightarrow RR'NP{=}NR' + 2\ LiCl + RCl$$
$$(R,R' = Me_3Si, Bu^t)$$

In the latter preparation, it was discovered [36] on using phosphorus tribromide that either a monomer or dimer could be formed depending on the

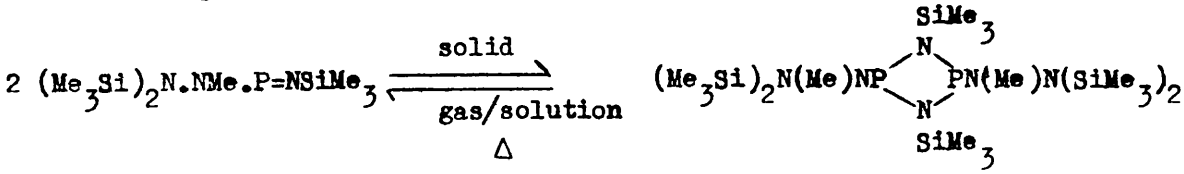
reaction conditions. It was also found [46] that the bulk of the nitrogen substituents affected not only the stability of the monophosph(lll)azene (when formed) but also the course of the reaction,



and yet,

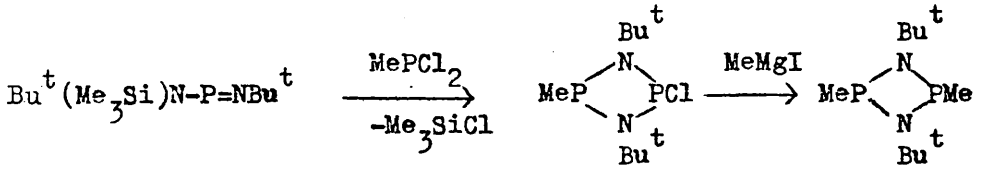


Indeed, the steric bulk of the nitrogen substituents and the possible lower basicity of the two co-ordinate nitrogen in these monomers is possibly why dimerisation of such compounds is either very slow or non-existent. The first report[47] of such a process was the slow cyclisation at 25°C under inert gas of bis(trimethylsilyl)-aminotrimethylsilylphosph(lll)azene, $(Me_3Si)_2NP{=}NSiMe_3$, to the dimeric 1,3-bis(trimethylsilyl)-2,4-bis[bis(trimethylsilyl)amino]-cyclodiphosph(lll)azane, $[(Me_3Si)_2NPNSiMe_3]_2$. More recently, however, a number of such dimerisations have been reported[36] which at ambient temperatures take from one or two weeks to over a year. Perhaps most interesting of all was the observation for the first time of the following monomer:dimer equilibrium,[36]



The compound (8) (R=Bu^t,X=Me) may also be prepared from the reaction of a

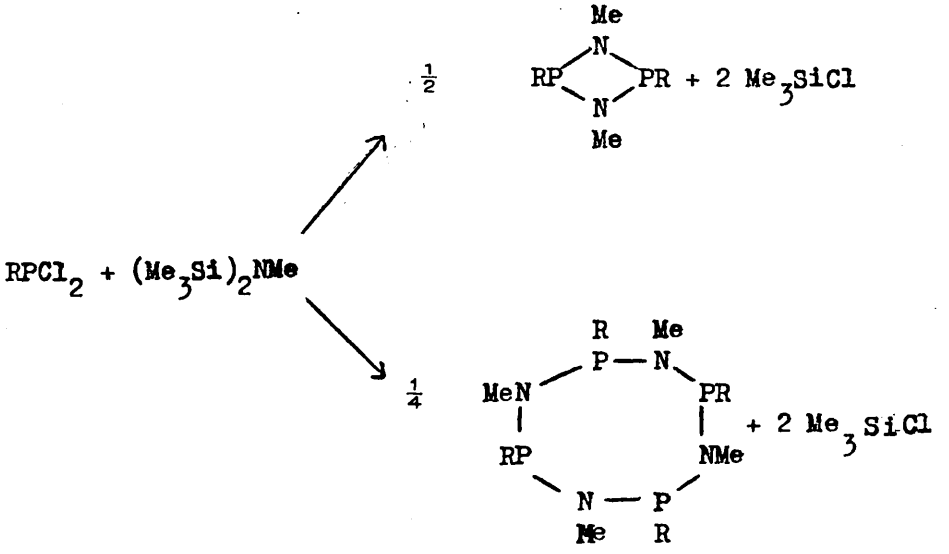
monomeric phosph(III)azene with dichloromethyl phosphine followed by a Grignard reaction.[48]



(14)

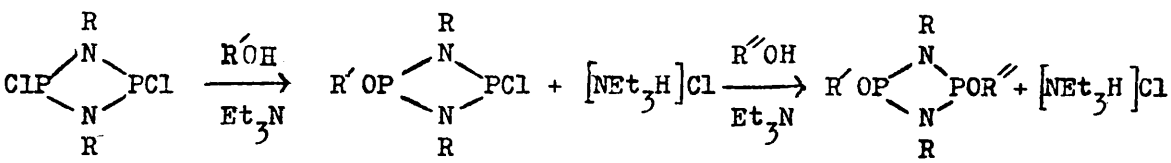
It is of note that (14) may also be synthesised through the action of two molar equivalents of methylmagnesium iodide, MeMgI, on 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(III)azane, $(ClPNBu^t)_2$,[48] or by an analogous route described earlier for (7), through the action of dichloromethylphosphine on bis(t-butylamino)methylphosphine, $MeP(NHBu^t)_2$ in triethylamine.[48]

A recent attempt[49] to prepare (8) (R=Me,X=Me or Et) from heptamethyldisilazane and the corresponding dichloroalkylphosphine led not to the four-membered, but the eight-membered ring system shown below.



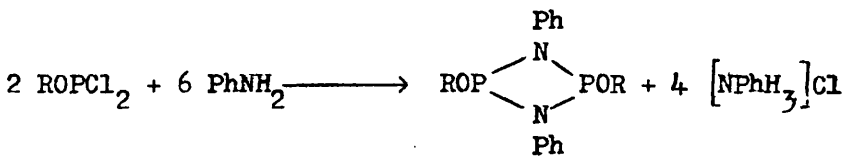
At present the only known compounds of the type (8) (X=alkyl) are the aforementioned (8) (R=Bu^t,X=Me;R=Me,X=Bu^t).

Several alkoxycyclodiphosph(lll)azanes (8) (X=alkoxy) have been reported and generally can be prepared either by the direct action of alcohol on (1) in the presence of triethylamine as hydrogen chloride acceptor,[50,51]



(R=Ph or Bu^t;R′,R″=alkyl)

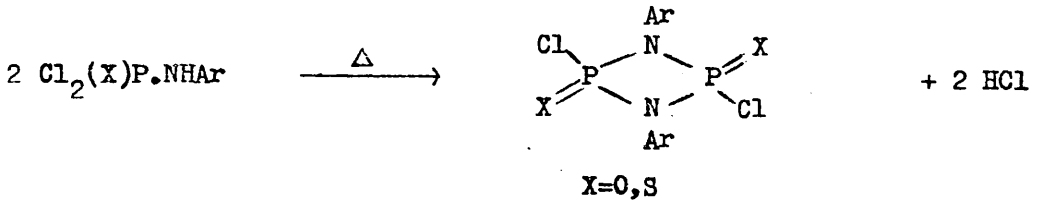
or by the action of aniline on the dichloroalkoxyphosphine, $ROPCl_2$[52,53] (R=Me or Et),



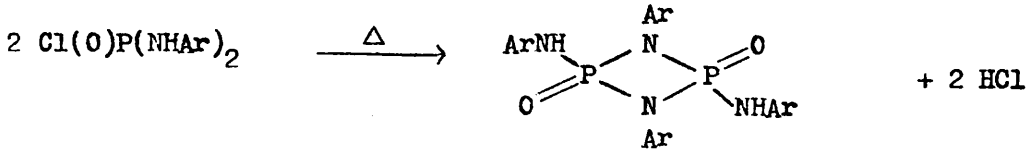
(R=Me or Et)

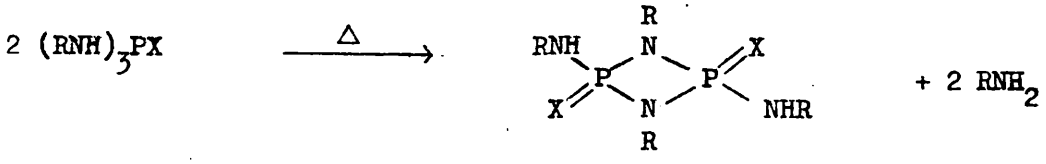
CYCLODIPHOSPH(V)AZANES (four co-ordinate phosphorus)

An extensive range of cyclodiphosph(v)azanes is now known. They may be prepared in a variety of ways, the first of which that will be considered being by the thermolysis of primary aminophosphinoyl and aminophosphinothioyl derivatives.[7,8] A few examples are given in Scheme 1.



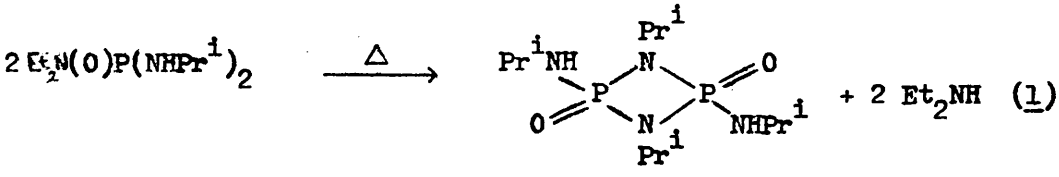
X=O,S



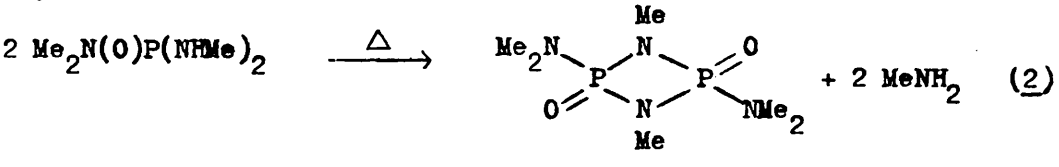


R=alkyl or aryl

X=O,S



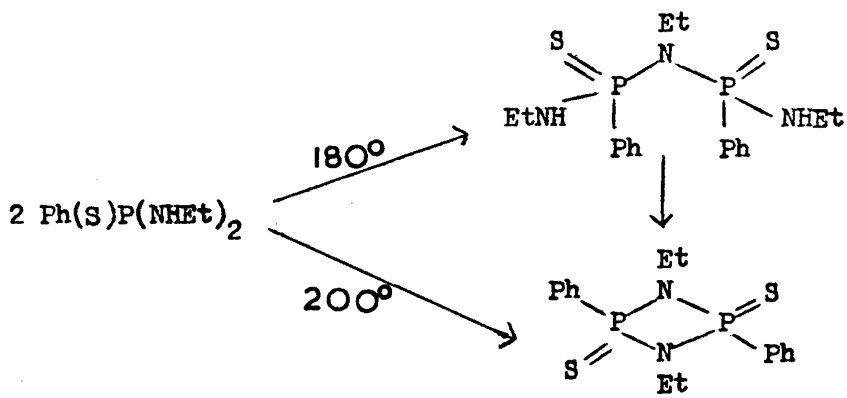
however,



Scheme 1[7,8]

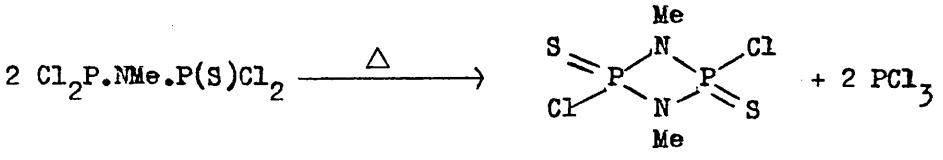
Tertiary amines have occasionally[a] been used to aid reactions in which hydrogen chloride is evolved[8,54] and there is also one report[55] of dehydrochlorination using Grignard reagents. Reactions (1) and (2), the thermolysis of the mixed triamino-derivatives $R_2N(O)P(NHR')_2$, are of interest in that either the primary or secondary amine may be lost; in fact, it is the more volatile which is eliminated. Similarly, the reaction of hexamethylphosphoramide, $(Me_2N)_3PO$, with primary aromatic amines yields on heating,[56] $\left[Me_2N(O)PNAr\right]_2$ plus dimethylamine, presumably via the intermediate $(Me_2N)_2(O)P.NHAr$.

Ibrahim and Shaw[57] found evidence to suggest that some of these thermolyses may proceed via nitrogen-bridged diphosphorus intermediates when they discovered that thermolysis of $Ph(S)P(NHEt)_2$ yields a nitrogen-bridged diphosphorus compound at a lower temperature than that generally required for cyclodiphosph(v)azane formation.



This behaviour was not observed, however, for the diamides, $Ph(S)P(NHR)_2$ (R=Me or CH_2Ph).[58]

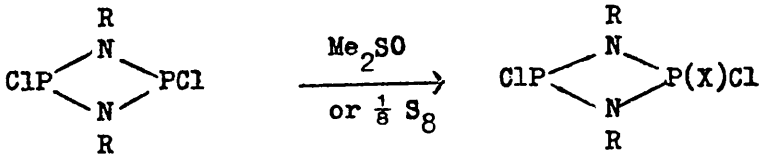
It was later shown that several chloro-derivatives of nitrogen-bridged diphosphorus compounds may cyclise: $Cl_2(O)P.NR.P(O)ClNHR$ (R=Me or aryl) cyclise with ease in the presence of tertiary amine[59] and $Cl_2P.NMe.P(S)Cl_2$ is thermally unstable, cyclising with loss of phosphorus trichloride on heating.[60]



Another common route to cyclodiphosph(v)azanes is by the oxidation of other cyclodiphosphazanes.

Sulphur dioxide easily converts the hexachlorocyclodiphosphazanes, $(Cl_3PNR)_2$, into the corresponding 2,4-dioxo compounds, $[Cl(O)PNR]_2$,[61] and similar reactions with hydrogen sulphide in the presence of tertiary amine produce the 2,4-dithio analogues.[7,8]

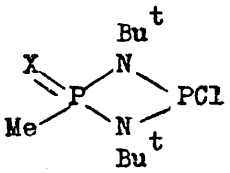
The first reported[17] route to mixed oxidation state cyclodiphosphazanes was the controlled oxidation and sulphuration of (1) (R=Bu^t or Pr^i).



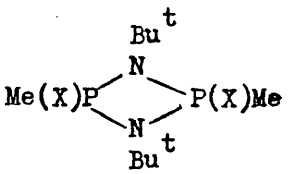
R=Bu^t or Pr^i

X=O or S

Oxothiocyclodiphosph(v)azanes could also be obtained by a related method.[17] Interestingly, the action of two molar equivalents of dimethyl sulphoxide on cis - $(ClPNBu^t)_2$ led to the formation of trans - $[Cl(O)PNBu^t]_2$ indicating stereospecific oxidation by a mechanism involving both retention and inversion of configuration.[62] t-Butylhydroperoxide has also been used[48] to oxidise cyclodiphosph(111)azanes. Oxidation by sulphur is now fairly commonplace,[20,22,34,38,48,51,63,64] and Scherer and Schnabl have also reported[48] the mono- (15) and di- (16) selenides and tellurides,



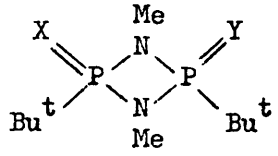
(15) (X=Se or Te)



(16) (X=Se or Te)

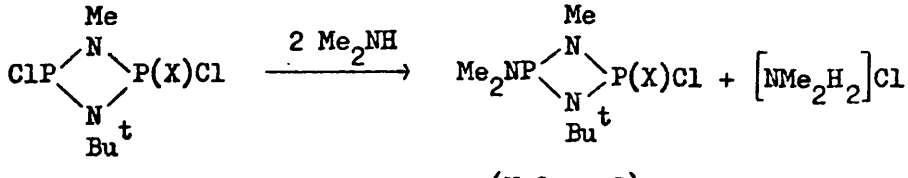
prepared by the action of the elemental chalcogen (one or two molar equivalents) on the corresponding cyclodiphosph(111)azane. In (15) it is worthwhile to note that oxidation has occurred exclusively at the phosphorus-methyl end of the molecule presumably because chlorine, being more electronegative than carbon, results in a less nucleophilic phosphorus. The one other report[65] of a reaction with tellurium is the preparation of the mono- and ditellurides (17).

The monotelluride is of interest in that it apparently shows both intra- and intermolecular exchange of tellurium on the n.m.r. time scale.

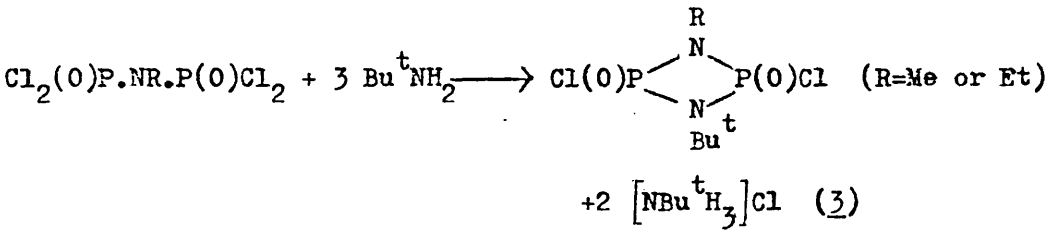


(17) (X=lone-pair, Y=Te)
(X=Y=Te)

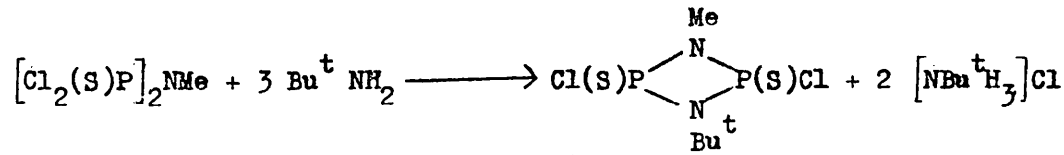
An alternative route to cyclodiphosphazanes containing one or two four co-ordinated phosphorus atoms is the reaction of nitrogen-bridged diphosphorus compounds with t-butylamine[20,22] (Scheme 2). Reaction (3) is similar to that discussed earlier between $(Cl_2P)_2NMe$ and t-butylamine except that the bisphosphinoyl compounds, $[Cl(O)P]_2NMe$, are less reactive and require slightly more forcing conditions. Reaction (4) is dissimilar to reaction (3) in that the yield of $Cl(S)\overline{P.NMe.P(S)Cl.NBu^t}$ is very low, the reaction mixture consisting mainly of starting material and unidentified products - a better route to the above 2,4-dithiocyclodiphosph(v)azane being the sulphuration of $ClP.NMe.PCl.NBu^t$.[20,22] Similarly, it was discovered[22] that the reaction of dichlorophosphinothioyl(dichlorophosphinoyl) methylamine, $Cl_2(O)P.NMe.P(S)Cl_2$, with three molar equivalents of t-butylamine gave a complex mixture of products, in this case with no trace of the expected cyclodiphosph(v)azane. In reaction (5), the presence of $Bu^tNH\overline{P.NMe.P(O)Cl.NBu^t}$ was detected by ^1H-$\{^{31}P\}$n.m.r. during the course of the reaction, though it was not isolated. However, in the slower reaction with the thio analogue (6) the reaction did not proceed beyond $Bu^tNH\overline{P.NMe.P(S)Cl.NBu^t}$. It is notable here that partial aminolysis has occurred exclusively at the phosphorus(III) centre. A similar situation was encountered when the reactions of the mixed oxidation state cyclodiphosphazanes, $Cl\overline{P.NMe.P(X)Cl.NBu^t}$ (X=O or S), with dimethylamine were studied.[22]



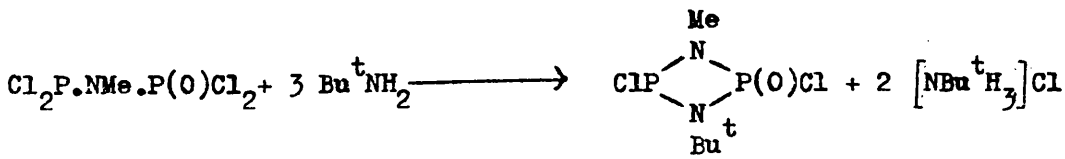
(X=O or S)



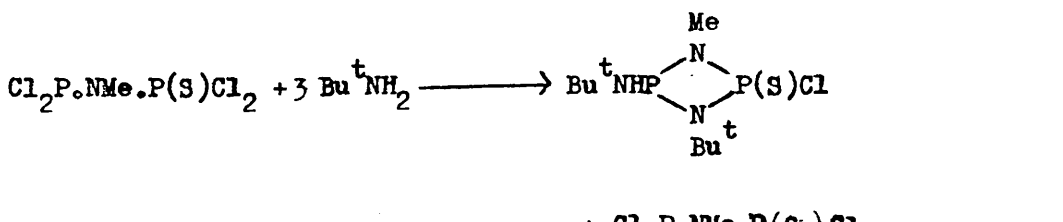
$$Cl_2(O)P.NR.P(O)Cl_2 + 3\ Bu^tNH_2 \longrightarrow Cl(O)P\langle N(R)P(O)Cl,\ N(Bu^t)\rangle + 2\ [NBu^tH_3]Cl \quad (R=Me \text{ or } Et) \quad (3)$$



$$[Cl_2(S)P]_2NMe + 3\ Bu^tNH_2 \longrightarrow Cl(S)P\langle N(Me)P(S)Cl,\ N(Bu^t)\rangle + 2\ [NBu^tH_3]Cl \quad (4)$$



$$Cl_2P.NMe.P(O)Cl_2 + 3\ Bu^tNH_2 \longrightarrow ClP\langle N(Me)P(O)Cl,\ N(Bu^t)\rangle + 2\ [NBu^tH_3]Cl \quad (5)$$



$$Cl_2P.NMe.P(S)Cl_2 + 3\ Bu^tNH_2 \longrightarrow Bu^tNHP\langle N(Me)P(S)Cl,\ N(Bu^t)\rangle + Cl_2P.NMe.P(S)Cl_2 \quad (6)$$

Scheme 2

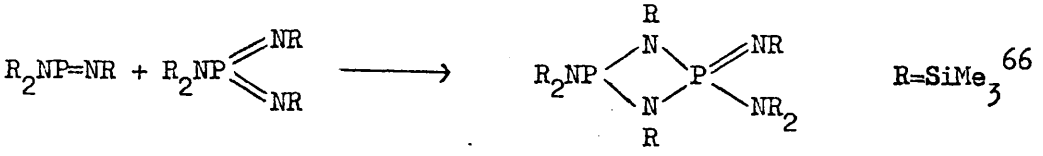
Recently, a number of other cyclodiphosphazanes containing at least one four co-ordinated phosphorus have been isolated, examples of which are shown in Scheme 3. These reactions are difficult to generalise, but essentially they involve the use of monomeric phosph(III)azenes or are quaternisation-type reactions.

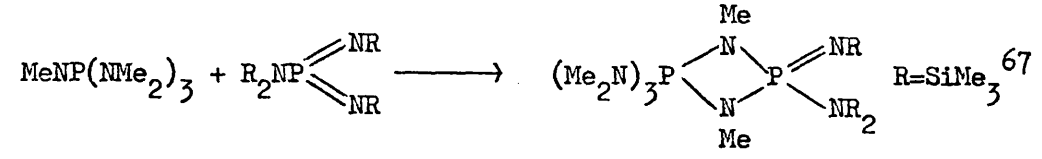
CYCLODIPHOSPH(V)AZANES (five co-ordinate phosphorus)

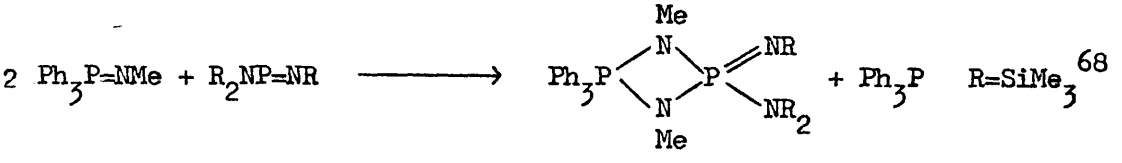
Phosphorus pentachloride readily reacts with primary aromatic[71-74] or alkyl[75,76] amines and their hydrochlorides to produce either cyclodiphosph(v)azanes with five co-ordinate phosphorus or phosphine imines, the monomeric form. Frequently there is little difference in the relative thermodynamic stabilities of the two forms and it has been found that aromatic amines of low basicity,[71] or highly branched alkyl amines[76] lead to the monomeric form, whereas other amines generally produce the dimer. In a number of cases, however, dimers may be reversibly converted to monomers in solution and on heating.[71,77]

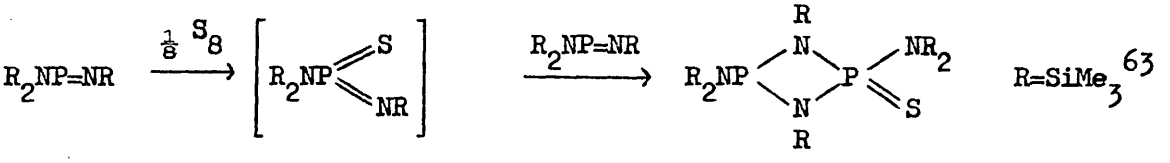
Tetrachloroalkylphosphoranes react with aryl amines or their hydrochlorides[78,79] and alkylammonium chlorides[77] in a similar fashion. Dichloro(triphenyl)phosphorane, Ph_3PCl_2,[80] and dichloro(triphenoxy)phosphorane, $(PhO)_3PCl_2$,[81] on reaction with primary aryl amines may also produce dimers. These and other reactions are summarised in Scheme 4.

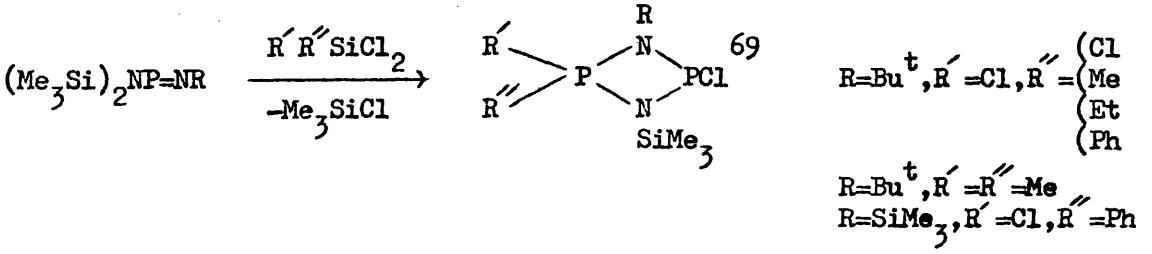
Fluorophosphoranes have also been extensively used in the preparation of these compounds. For example, phosphorus pentafluoride and primary alkyl or aryl amines (at times in the presence of tertiary amine) readily produce the 2,2,2,4,4,4-hexafluoro compounds, $(F_3PNR)_2$ (R=alkyl or aryl).[83]



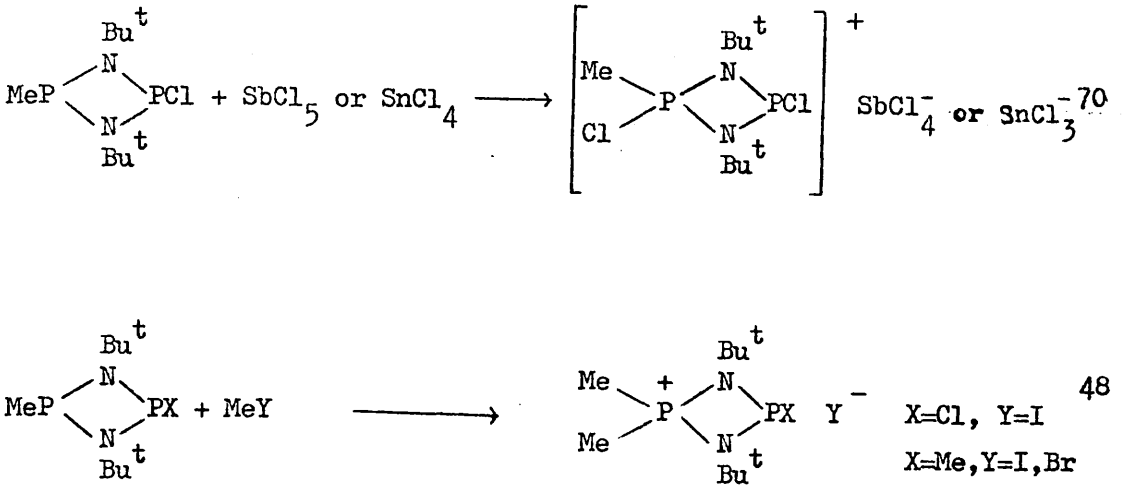






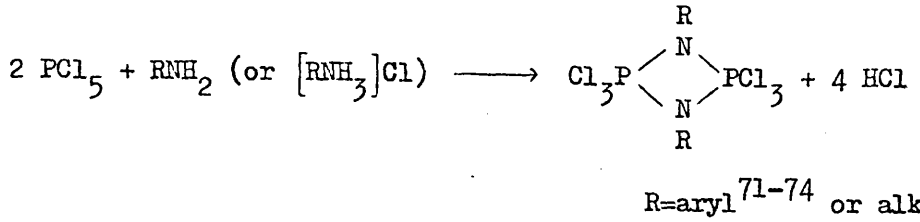


Scheme 3

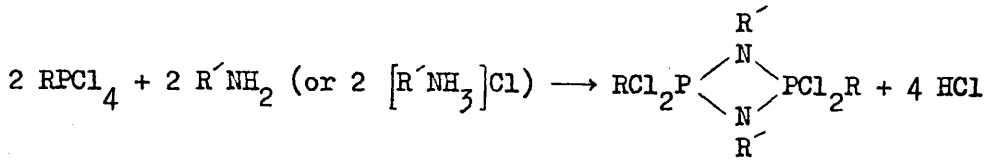


Scheme 3 (contd)

$(F_3PNR)_2$ (R=Me[84-88] or Ph[86-88]) may also be prepared through the action of phosphorus pentafluoride on $RN(SiMe_3)_2$ (R=Me or Ph). However, where N-substituted hexamethyldisilazanes have been found particularly useful is in preparing the 2,2,4,4-tetrafluoro compounds, $(RPF_2NR')_2$ (R,R'=alkyl or aryl), from the less reactive alkyl or aryl tetrafluorophosphoranes, RPF_4.[7,86-89] When the even less reactive dialkyl/aryl trifluorophosphoranes are involved, reactions with N-substituted hexamethyldisilazanes are very slow[88] and it is preferable to use the more reactive lithiated amine, $MeNLi_2$.[90] The preparation of a 2,2,4,4-tetrafluoro ring compound with different substituents on the ring nitrogens has also been reported.[91]

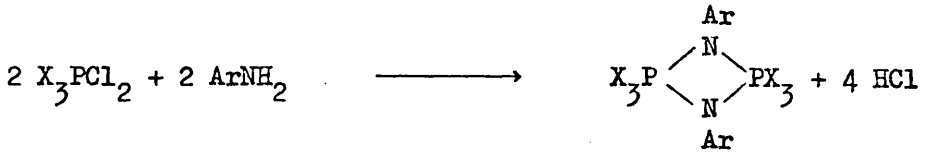


R=aryl[71-74] or alkyl[75,76]

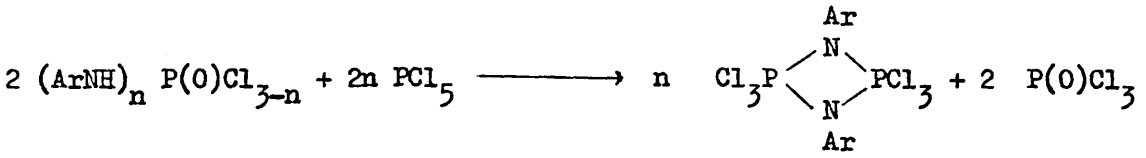


R=Me, R´=aryl[79]

R=Ph, R´=aryl[78] or alkyl[77]

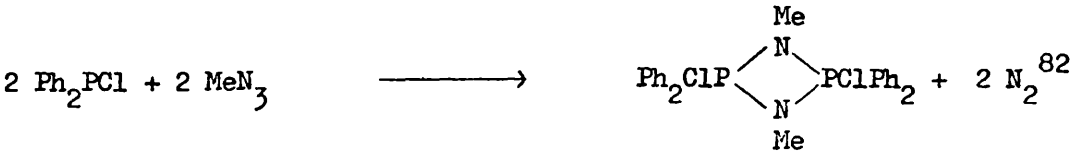


X=Ph[80] or OPh[81]



+ 2n HCl

n=1,2, or 3[7]



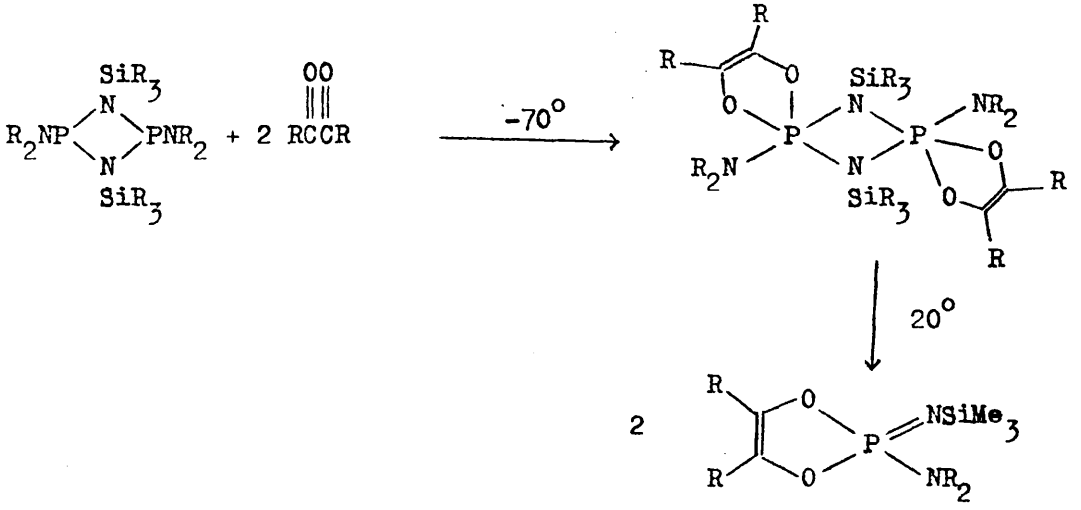
Scheme 4

$$2\ MePF_4 + MeN(SiMe_3)_2 + PhN(SiMe_3)_2 \longrightarrow MeF_2P\begin{smallmatrix}\diagup\ \text{Me}\ \diagdown\\ \diagdown\ \text{N}\ \diagup\\ \diagup\ \text{N}\ \diagdown\\ \diagdown\ \text{Ph}\ \diagup\end{smallmatrix}PF_2Me + 4\ Me_3SiF$$

A number of substitution reactions in which the four-membered ring is retained are now known. Antimony trifluoride fluorinates the hexachlorocyclodiphosph(v)azanes, $(Cl_3PNR)_2$, to the corresponding hexafluorocyclodiphosph(v)azanes, $(F_3PNR)_2$,[7,8] and on heating together a mixture of hexachloro and hexafluoro 1,3-dimethylcyclodiphosph(v)azanes a range of mixed chloro/fluoro-derivatives is obtained.[92] More recently, however, a number of methyl and methoxy-derivatives of $(F_3PNMe)_2$ (including the first known asymmetrically substituted derivatives) have been prepared using MeMgI or LiMe and LiOMe,[90,91] for example,

$$(F_3PNMe)_2 + 3\ MeLi \longrightarrow MeF_2P\begin{smallmatrix}\diagup\ \text{Me}\ \diagdown\\ \diagdown\ \text{N}\ \diagup\\ \diagup\ \text{N}\ \diagdown\\ \diagdown\ \text{Me}\ \diagup\end{smallmatrix}PFMe_2 + 3\ LiF.$$

Finally, several cyclodiphosph(v)azanes with five co-ordinated phosphorus have been isolated from cyclodiphosph(III)azanes using either benzil[53] or biacetyl.[64] In each case thermal decomposition to a monomeric species occurs and has been attributed[64] to the presence of bulky groups on nitrogen together with electron donor groups on phosphorus.



R=Me

STRUCTURAL FEATURES

A consequence of the fact that the geometry about phosphorus may be either pseudo-tetrahedral (three or four co-ordinate phosphorus) or trigonal-bipyramidal (five co-ordinate phosphorus) is that cyclodiphosphazanes can exist in one or both of two possible isomeric forms (assuming a near planar geometry about nitrogen), Figure 1.

(X=lone-pair, oxygen, sulphur etc.)

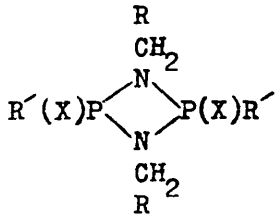
a

b

Figure 1

In many cases isomers have been detected, though frequently structural assignments have proved difficult without the aid of X-ray crystallography.

The first observation [58] of the existence of two geometrical isomers was made during the study by ^1H n.m.r. of 1,3-dimethyl-2,4-diphenyl-2,4-dithiocyclodiphosph(v)azane, $[Ph(S)PNMe]_2$, when two methyl proton triplets in a 10:1 ratio were found. Since then many isomeric mixtures have been discovered using n.m.r., though seldom have conclusive structural assignments been made using this method alone. An exception to this is where symmetrical compounds of the general type (18) have been studied, as the methylene protons in the trans isomer are diastereotopic (giving rise to an AB quartet of signals), whereas in the cis isomer they are magnetically equivalent, assuming free C-N bond rotation (Figure 2).



(18)

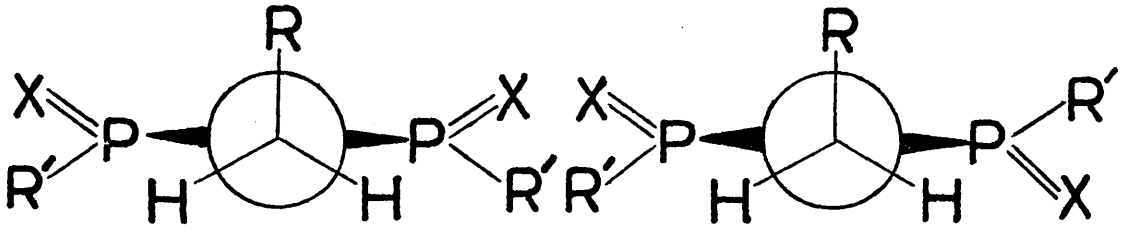


Figure 2

It has also been established [90,91,93] by n.m.r. that in five co-ordinate cyclodiphosph(v)azanes of the type, $(RF_2PNMe)_2$, concerted pseudorotation at each phosphorus can occur leading to gauche $\rightleftharpoons$ trans isomerisation. Frequently this isomerisation may

be slowed on the n.m.r. time scale allowing the observation of both isomers.[90,91,93] In compounds of the type, $(R_2FPNMe)_2$, interchange of analogous isomers may occur[94] and is likely to be a relatively high energy process as intermediates with at least one R-group axial must be involved, and so the pseudorotation exchange process in, for example, $(Ph_2FPNMe)_2$,[94] is slow enough at ambient temperatures on the n.m.r. time scale for both isomeric forms to be detected. Additionally, in the study of five co-ordinate cyclodiphosph(v)azanes, n.m.r has been particularly useful in determining whether a monomeric or dimeric species is present.[90,94]

Vibrational spectroscopy has been employed[95,96] in structural elucidation, for instance, in determining which isomer of $[Ph(S)PNEt]_2$[95] is cis and which is trans. The trans isomer, being centrosymmetric, showed complementary infrared and Raman spectra (no coincident bands), whereas for the cis isomer, ten coincident bands ($\pm 3\,cm^{-1}$) were found. This structural assignment method can probably be extended to other cyclodiphosphazanes, although there are drawbacks in that the method is restricted to symmetrically substituted cyclodiphosphazanes and not one but both isomers may have to be isolated to avoid ambiguous results. Other than this, vibrational spectroscopy has not played a major role in determining the structures of cyclodiphosphazanes.

There are two reports of the use of physical properties in distinguishing geometrical isomers. It was discovered[97] that the trans isomer is eluted first from a mixture of isomers in column

chromatography, and dipole moments have been used[98] with some success, employing the fact that the cis isomershould have a greater dipole moment than the trans isomer; however, inaccuracies both in the measurement and calculation of dipole moments restrict the latter method to cyclodiphosphazanes in which the cis isomer dipole moment is expected to be high.

Because many cyclodiphosphazanes are not amenable to definite structural assignment using the aforementioned techniques, the onus has fallen largely on X-ray crystallography. A number of crystal structures on these small ring compounds have been determined and selected data are shown in Table 1. In all cases the structures were determined by X-ray crystallography except that of $(F_3PNMe)_2$ which was derived from an electron diffraction study.[101] Earlier work on $(X_3PNMe)_2$ (X=F[114] or Cl[75]) employing infrared and Raman spectroscopy had predicted planar rings for both these compounds. In fact, all the compounds except the two cis isomers possess planer rings, and all the P...P and N...N distances across the ring are ca. 30% shorter than the sum of the Van der Waal's radii, implying some dependence of ring geometry on cross-ring interactions.[108]

In the cyclodiphosph(v)azanes containing five co-ordinate phosphorus a distorted trigonal-bipyramidal geometry is found at phosphorus with small N_{ax} ——P—— N_{eq} angles of ca. 80° necessitated by its inclusion in a four-membered ring. As the ring spans axial/equatorial sites, two different P-N bond lengths are found, the longer P-N bond, which approximates to the generally accepted P-N single bond length (1.77 Å), being axial. Sheldrick and co-workers noted [103,104] a correlation between the increase in P-N axial and equatorial bond lengths with decreasing electronegativity in the series $(RF_2PNMe)_2$ (R=F,[101] CCl_3,[103] C_6F_5,[104] Ph[102]). Furthermore, a direct relationship was found[89,93,104] between the electronegativity of R and the two-bonded phosphorus-phosphorus coupling constant, ^2J(PNP) (Table 2).

Table 1 Cyclodiphosphazanes, selected structural data [a]

Compound (ref)	P — N [b] Å	PNP	NPN	P...P Å	N...N Å
$(Cl_3PNMe)_2$ [99]	1.769(7);1.635(7)	99.5(4)°	80.5(4)°	2.599	2.202
[100]	1.776(10);1.629(10)	98.3(5)°	81.7(5)°	2.577	2.230
$(F_3PNMe)_2$ [101]	1.74 ;1.60	102°	78°	2.59	2.09
$(PhF_2PNMe)_2$ [102]	1.78(2); 1.64(2)	99.4°	80.6°	2.61	2.21
$[(Cl_3C)F_2PNMe]_2$ [103]	1.742(3) ;1.621(3)	100.1(2)°	79.9(2)°	2.579	2.159
$[(C_6F_5)F_2PNMe]_2$ [104]	1.750(4) ;1.631(4)	100.2(1)°	79.8(2)°	2.594	2.169
$(Ph_2FPNMe)_2$ [94]	1.780(1) ;1.652(3)	101.6(2)°	78.4(3)°	2.659	2.169
trans - $[(Me_3Si)_2NPNSiMe_3]_2$ [47]	1.727 endo 1.712 exo	97.5°	82.5°	2.59	2.28
cis - $(ClPNBu^t)_2$ [105,106]	1.689(4)	97.3(4)°	82.5(3)°	2.540	2.232
trans - $[Cl(O)PNBut]_2$ [62,107]	1.661(5)	94.5(2)°	85.5(2)°	2.439	2.255

Table 1 (cont'd)

Compound (ref)	P —— N [b] Å	P...P Å	N...N Å
trans - $[Ph(S)PNPh]_2$ [108]	1.695(4)	98.1(3)°	81.9(2)°	2.562	2.221
trans - $[Ph(S)PNMe]_2$ [97,109]	1.69(1)	96.0(3)°	84.0(3)°	2.50	2.26
trans - $[Ph(S)PNEt]_2$ [97,110]	1.686(6)	96.7(2)°	83.4(3)°	2.518	2.241
cis - $[Ph(S)PNEt]_2$ [97,111]	1.687(10)	95.2(5)°	84.2(5)°	2.491	2.261
trans - $[Cl(S)PNMe]_2$ [112]	1.67	96°	84°	2.48	2.23
trans - $(C_{15}H_{15}N_2PS)_2$ [113]	1.74(2); 1.80(2) (endo) 1.75(2) (exo)	91.0(2)°	89.0(2)°	2.53	2.48

a Standard deviations in parentheses.

b Endo or exo with respect to the cyclodiphosphazane ring.

Table 2

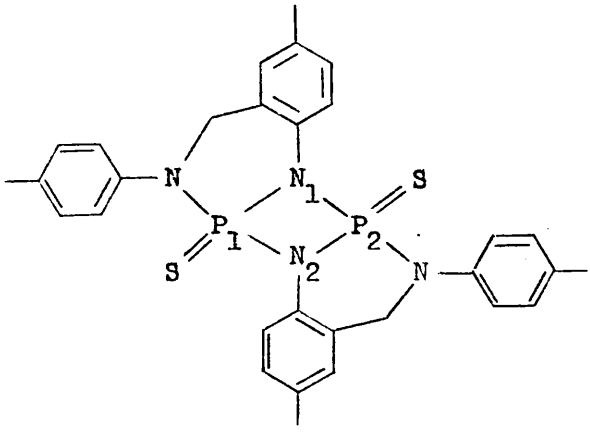
Variation of $^2J(PNP)$ with R^1, R^2, and the P...P intramolecular distance in the compounds $(R^1R^2FPNMe)_2$

R^1	R^2	$^2J(PNP)$ Hz	P...P Å
F	CCl_3	125	2.579
F	C_6F_5	111	2.594
F	Ph	80	2.61
Ph	Ph	28	2.659

As expected, replacement of a second fluorine by a phenyl substituent reduces the value of $^2J(PNP)$ in $(Ph_2FPNMe)_2$ to 28 Hz.[94] Concurrent with this trend is the observation[94] of the good correlation between P...P intramolecular distance and $^2J(PNP)$ which is as predicted on the basis of simple orbital overlap considerations (Table 2).

It is also of interest to note that in an earlier preparation of $(Ph_2FPNMe)_2$[86,88] only the monomer, $Ph_2FP{=}NMe$, was reported and its structure established by X-ray crystallography (P-N bond length, 1.641 Å), though this work has since proved unrepeatable.[94]

Cyclodiphosphazanes with three and four co-ordinate phosphorus, with the exception of trans-$(C_{15}H_{15}N_2PS)_2$, (19), all possess P-N bonds which are considerably shorter than the pure single bond length (1.77 Å).



	Å
$P_1—N_1, P_2—N_2$	1.74(2)
$P_1—N_2, P_2—N_1$	1.80(2)

(19)

The unusually long P-N distances in (19) of 1.74 and 1.80 Å have been explained by Cameron and co-workers[113] in terms of the non-planarity of the bonds to the ring-nitrogen atoms which are, therefore, largely sp^3 hybridised. The very long N...N interatomic distance of 2.48 Å within the ring is also in accordance with sp^3 hybridisation as this requires more space [117] than sp^2 hybridisation. What detracts from this explanation is that it is only in trans-$\left[Ph(S)PNEt\right]_2$[118] that an accurately planar (and hence close to sp^2 hybridised) phosphazane-nitrogen environment occurs; displacements of the nitrogen atoms of up to 0.28 Å[107] from the plane defined by adjacent phosphorus and carbon atoms being reported for the other compounds studied, so that planer co-ordination is, in fact, the exception rather than the rule for the ring-nitrogen atoms.

The slight non-planarity of the ring in the two cis isomers may be due to the steric interactions of the phosphorus substituents, although it has been suggested [105] that the non-planarity in cis-$(ClPNBu^t)_2$ may be the result of crystal packing forces. It is also interesting to note that oxidation of cis-$(ClPNBu^t)_2$ to trans-$\left[Cl(O)PNBu^t\right]_2$ reduces the P...P interatomic distance across the ring by a shortening of the P-N bond lengths and an increase in the $\hat{NPN}$ angle.

Finally, in trans-$[(Me_3Si)_2NPNSiMe_3]_2$ the two $\hat{PNSi}$ bond angles at the exocyclic nitrogen are 108.4 and 131.0°. This unexpectedly large difference is caused by the steric strain of the bulky trimethylsilyl-groups.[47] The larger angle results from one of the trimethylsilyl-groups on the exocyclic nitrogen being bent away from the trimethylsilyl-group bonded to the ring, the other trimethylsilyl-group being free from such an interaction as the amino-group bisects the plane of the ring.

PHOSPHORUS-NITROGEN BONDING

Phosphorus-nitorgen bonding has been a subject of considerable interest in recent years. In particular, controversy has arisen over the participation and importance of phosphorus 3d-orbitals, especially in π-bonding. The topic is still poorly understood, probably as a result of the number of orbitals which may be used and the varying extents in which they may be involved.

The formation of a formal single phosphorus-nitrogen σ-bond involving tervalent or (four co-ordinate) quinquevalent phosphorus can be described (using molecular orbital theory) as the combination of a phosphorus sp^3 hybrid orbital with a nitrogen sp^2 hybrid orbital. The use of an sp^2 hybridised nitrogen orbital (or one closely approaching sp^2 hybridisation) instead of an sp^3 hybridised orbital is substantiated by structural data on a variety of aminophosphorus compounds which show planar (or near planar) geometry about nitrogen[118,119] (Table 3).

In almost all the compounds studied the P-N bond length (generally between 1.65 and 1.70 Å) is considerably shorter than the generally accepted formal single P-N bond length of about 1.77 Å. The one notable exception is $P[N(CH_2)_2]_3$ in which the nitrogen atoms are constrained in three-membered rings. Here, the average valence angle at nitrogen is only 101° and the P-N bond length is longer than found in other

Table 3

Selected structural data for some aminophosphorus compounds

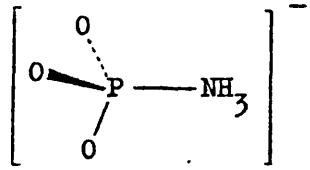
Compound	Sum of N bond angles	P-N bond length (Å)	Source
$P(NMe_2)_3$	352.5°	1.700(5)	e.d.[120]
$(Me_2N)_2PCl$	360°	1.730(5)	e.d.[119,121]
$(Me_2N)PCl_2$	360°	1.69(3)	e.d.[118,119]
$(Me_2N)P(O)Cl_2$	348°	1.67(4)	e.d.[118,119]
$P[N(CH_2)_2]_3$	303.5°	1.75(1)	e.d.[120]
Me_2NPF_2	360°	1.628(5)	X-ray[122]
Me_2NPF_2	348.4°	1.684(8)	e.d.[123]
Me_2NPF_2	360°	1.66	m.w.[124]
H_2NPF_2	345°	1.661(7)	e.d.[123]
H_2NPF_2	360°	1.650(4)	m.w.[125]
$(Cl_2P)_2NMe$	360°	1.664(10)	n.m.r.[126]
$(F_2P)_2NMe$	360°	1.680(6)	e.d.[127]
$Ph_2P.NMe.P(S)Ph_2$	353°	1.719(4) P^{III}	X-ray[128]
		1.680(4)	
$P_2(NMe)_6$	345°	1.68(3)	X-ray[129]
$P_2O_2(NMe)_6$	343°	1.66(3)	X-ray[130]
$P_4(NMe)_6S_4$	358°	1.66(3)	X-ray[131]
$P_4(NMe)_6S_4$	358°	1.656(14)	X-ray[132]
$P_4(NMe)_6O_4$	351°	1.667(20)	X-ray[132]
$P_4(NMe)_6MeI$	352°	1.71(3) P^{III}	X-ray[133]
		1.65(1)	
$P_4(NMe)_6$	356°	1.695(10)	X-ray[134]

aminophosphines, being 1.75 Å.[120] It is a general observation that while the valence angles at phosphorus become wider on passing from three co-ordinate (tervalent) phosphorus to four co-ordinate (quinquevalent) phosphorus, the P-N bond becomes slightly shorter (Tables 1 and 3), and this has been used to argue greater p-character in the P-N bonds of the former type of compound.[118,119]

The trigonal bipyramidal geometry about five co-ordinate phosphorus may be accounted for in terms of sp^3d hybridisation, although Hudson[135] has offered a description in terms of s and p-orbitals alone which may be preferable as the phosphorus 3d-orbitals may possess energies which are too great to participate in σ-bonding. Hudson's description comprises of an axial three centre, two electron bond using a phosphorus p-orbital, with three sp^2 hybrid orbitals bonding equatorially.

π-Bonding between phosphorus and nitrogen has been a subject of much debate and controversy. There is considerable evidence to suggest some degree of bond multiplicity, and this will be outlined below, but the actual nature of the π-bonding in many cases is still unknown.

Bond lengths themselves have been most extensively cited as evidence for P-N π-bonding: in cyclophosphazene rings[7] and in phosphine imines possessing four co-ordinate phosphorus,[118] bond lengths between 1.55 Å and 1.65 Å are generally found which may be compared with the P-N bond length of 1.77(2) Å in the anion (20) which has been considered as a good approximation to the pure P-N single bond length.[136,137] The shorter bonds have been thought to arise from overlap of the filled sp^2 hybridised nitrogen orbitals with the vacant phosphorus 3d-orbitals;



(20)

the P-N bonds in cyclophosphazene rings and phosphine imines thus closely resemble formal double bonds. Further evidence for this double bond character comes from infrared studies on phosphine imines for which the P=N stretching frequency has been assigned to the range 1240-1330 cm^{-1} [138,139] as against 650-850 cm^{-1}, the range assigned to the P-N single bond vibration by Corbridge.[140] The low barriers to rotation about P-N multiple bonds are said to provide more evidence of $\underline{(p\text{-}d)\pi}$ bonding.[138,139] This may be explained in terms of rotation of the P-N bond through 90°, whereupon overlap with a second phosphorus d-orbital may occur, thus lowering the electronic barrier to rotation. This is in contrast with, for example, carbon-nitrogen double bonds in which the participation of d-orbitals is not significant.[141] Furthermore, if $\underline{(p\text{-}d)\pi}$ bonding is prominent in P-N bonds, more electronegative substituents on phosphorus should contract and lower the energy of the 3d-orbitals,[142-144] increase the π-overlap, and so increase the bond order. This in turn should, and does, result in an increase in the P=N stretching frequency.[139]

These observations, while not proving conclusively the presence of $\underline{(p\text{-}d)\pi}$ bonding in what may be regarded as formal double bonds between four co-ordinate phosphorus and nitrogen, do preclude a zwitterionic description of the bond (Figure 3).

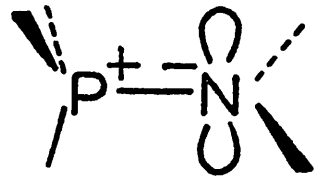
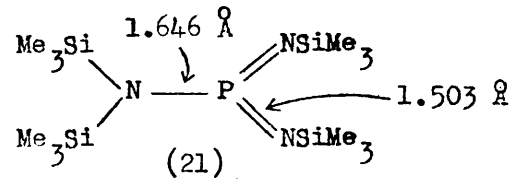


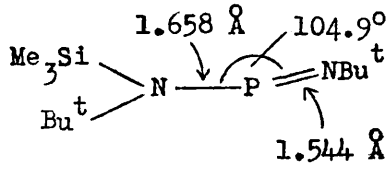
Figure 3

The only known structural study to date of a compound containing a formal double bond between three co-ordinate phosphorus and nitrogen is that of compound (21) [145] in which the phosphorus has a planar distribution of bonds, and the P=N bond length of 1.503 Å is at the lower limit of all known values for phosphorus-nitrogen bonds.[146]



(21)

It was proposed [145] that this is the result of planarity at phosphorus favouring very strong $(2p-3p)\pi$ bonding, which probably also helps to stabilise the co-ordinatively unsaturated phosphorus. Very short bond lengths of around 1.54 Å have been measured in the monophosphazenes (22)[147] and (23)[148]



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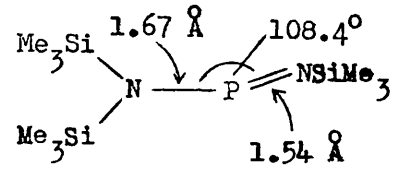


(23)

in which extensive $(2p-3p)\pi$ bonding has been argued in the P=N bond, especially in view of the $\hat{NPN}$ bond angles of 104.9° and 108.4° which imply considerable participation of the phosphorus p-orbitals.

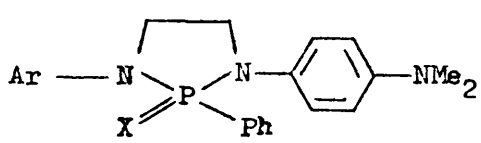
Many P-N formal single bonds have lengths between those discovered for formal double P-N bonds and the 1.77(2) Å found for the anion (20) (see Tables 1 and 3). In the past these have often been explained in terms of a small degree of $(p-d)\pi$ bonding. The evidence which has been presented on behalf of $(p-d)\pi$ bonding in these formal single P-N bonds is varied. Firstly, there is the aforementioned shortening of the bond length.

Secondly, as was found with P=N compounds (above), the bond length is decreased by electronegative substituents on phosphorus[118] and increased by the presence of π-donor substituents on nitrogen as expected if (p-d)π bonding is present.[142] Thirdly, planar geometry about nitrogen, which is found for many aminophosphorus compounds (Table 3), has been interpreted as evidence of (p-d)π bonding in P-N bonds as this geometry allows greater π-overlap. Mathis and co-workers[149] in an infrared study of a number of aminophosphines of the type, X_2P-NHR (R=alkyl) found that the hybridisation state of the nitrogen atom varies widely, depending on X. When the substituents, X, are electron-releasing (such as Bu^t) the valence bonds of the nitrogen atom are in a pyramidal configuration, whereas when the substituents, X, are strongly electronegative (such as Cl) the geometry about nitrogen is near planar. This they attributed to the enhanced (p-d)π bonding associated with electron-attracting substituents attached to phosphorus, though such results are perhaps open to question. In addition, both the coupling constants $^1J(\underline{NH})$ [150] and $^1J(\underline{PN})$[151] are thought to be sensitive to the geometry at nitrogen and the results interpreted as being consistent with (p-d)π bonding when nitrogen is planar, though the precise dependence of $^1J(\underline{PN})$ on geometry at nitrogen is disputed.[152]

While it is generally accepted that the geometry at nitrogen is an important consequence of the type of P-N bonding, reasons other than (p-d)π bonding have been proposed to explain why nitrogen adopts a trigonal planar geometry. One of the strongest arguments is that of Glidewell[153,154] who suggested that planarity at nitrogen could be due, at least in part, to steric interactions between substituents causing the bond angles to open out,

with the result that d-orbital participation then arises largely as a result of the more favourable geometry. In addition, ab initio theoretical calculations on the aminophosphine, H_2NPH_2, indicate that the near planarity at nitrogen when the molecule is in the ground state conformation originates from the electron-releasing inductive effect of the phosphorus,[155] though other workers have since disagreed with this.[156,157]

Final evidence in support of (p-d)π bonding comes from n.m.r studies, especially from measurements of torsional barriers about P-N single bonds. In a number of cases the magnitude of the barriers has been interpreted in terms of (p-d)π bonding.[158-162] Typical evidence[160] is the greater barrier found in $Ph(X)P(S)NPr^i_2$ when X=Cl as against X=Ph. Since the chlorine atom is more electronegative and supposedly a worse π-donor than the phenyl-group, the enhancement in barrier when chlorine is present has been attributed to a contribution from (p-d)π bonding.[160] On the other hand, whether (p-d)π bonding is present or not, there is good evidence to suggest it makes little contribution to rotational barriers in that phosphine imines, containing a P-N formal double bond, possess extremely low barriers to rotation (below 8 kcal mol^{-1}) possibly because of the availability of more than one phosphorus d-orbital for π-bonding.[138,139] Nitrogen inversion during rotation [163,164] and lone-pair-lone-pair repulsions [165] have been offered as alternative explanations for the substantial barriers about tervalent P-N single bonds. N.m.r. chemical shifts have also been used to explore the bonding between phosphorus and nitrogen; (p-d)π bonding being a possible explanation for the transmission of substituent effects on the chemical shift of the dimethylamino-group protons in compound (24).[166]



(24) (X=lone-pair or O)

Recently the importance in P-N bonding of the conformation of the P-N bond itself and the consequent non-bonded electron interactions between phosphorus and nitrogen have been realised, with the result that there has been increasing use of ultraviolet photoelectron spectroscopy (p.e.s.) in the study of phosphorus-nitrogen compounds, particularly aminophosphines.[167-170] It could be hoped that as the optimum condition for $\underline{(p\text{-}d)\pi}$ overlap is where the nitrogen and phosphorus lone-pairs are mutually orthogonal, p.e.s., in affording information on the conformations of the lone-pairs of electrons, may also reveal the degree to which $\underline{(p\text{-}d)\pi}$ bonding is present in the molecule. However, recent *ab initio* molecular orbital calculations have shown that molecules with adjacent electron-pairs or polar bonds exhibit a 'gauche effect'. In other words, a tendency to adopt that structure which has the maximum number of gauche interactions between the adjacent electron-pairs and/or polar bonds.[171] An example of this is the preferred conformation of biphosphine, P_2H_4, in which the dihedral angle between the two lone-pairs of electrons is 90-100° (Figure 4).[172-174] Hence, mutual

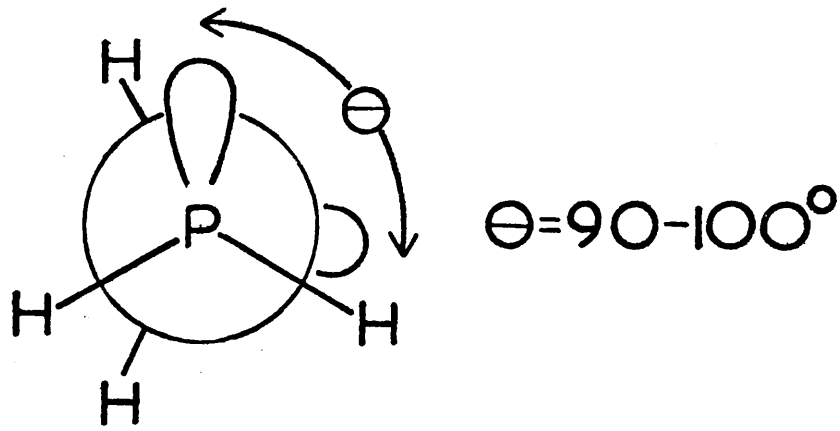


Figure 4

orthogonality of the lone-pairs of electrons in phosphorus-nitrogen compounds may not be a consequence of $\underline{(p\text{-}d)\pi}$ bonding but an expression of the 'gauche effect', though it should be remembered that this by no means precludes the presence of such bonding.

The main advantage of p.e.s. is that even in molecules with very low barriers to bond rotation the spectrum produced is that of the predominant conformation (or conformations) because of the rapid time scale of the ionisation process involved (Franck-Condon Principle). 'Time-averaged' spectra which detract from the use of n.m.r. in conformational studies are avoided. The main disadvantage of p.e.s. is that interpretation of the spectra is often complicated and ambiguous, even when dealing with relatively simple molecules. An example of the type of confusion which may exist is in the p.e.s. studies of tris(dimethylamino)phosphine, $(Me_2N)_3P$. An electron diffraction study[120] of this molecule had already suggested that all the nitrogen atoms should be considered to be sp^2 hybridised and the phosphorus atom sp^3 hybridised. A p.e.s. study of $(Me_2N)_3P$ was then undertaken by Cowley and co-workers[167] to determine the lone-pair interactions and conformations within the molecule. In short, to discover which of the four structural models in Figure 5 with three, two, one, or no lone-pairs mutually orthogonal was the more correct ($\underline{a}$,$\underline{b}$,$\underline{c}$,$\underline{d}$ respectively). By comparing the spectra of the aminophosphines, $(Me_2N)_nPF_{3-n}$ and $(Me_2N)_nPF_{5-n}$ (n=1,2 or 3) they concluded[167] that $(Me_2N)_3P$ must have two of the nitrogen lone-pairs interacting in a σ-fashion, while the third interacts in a π-manner with the phosphorus lone-pair (Figure 5$\underline{b}$). Later, however, Lappert and co-workers[168] criticised this interpretation and suggested that $(Me_2N)_3P$ has no nitrogen lone-pairs mutually orthogonal to the phosphorus lone-pair (Figure 5$\underline{d}$). This view, in turn, was attacked by

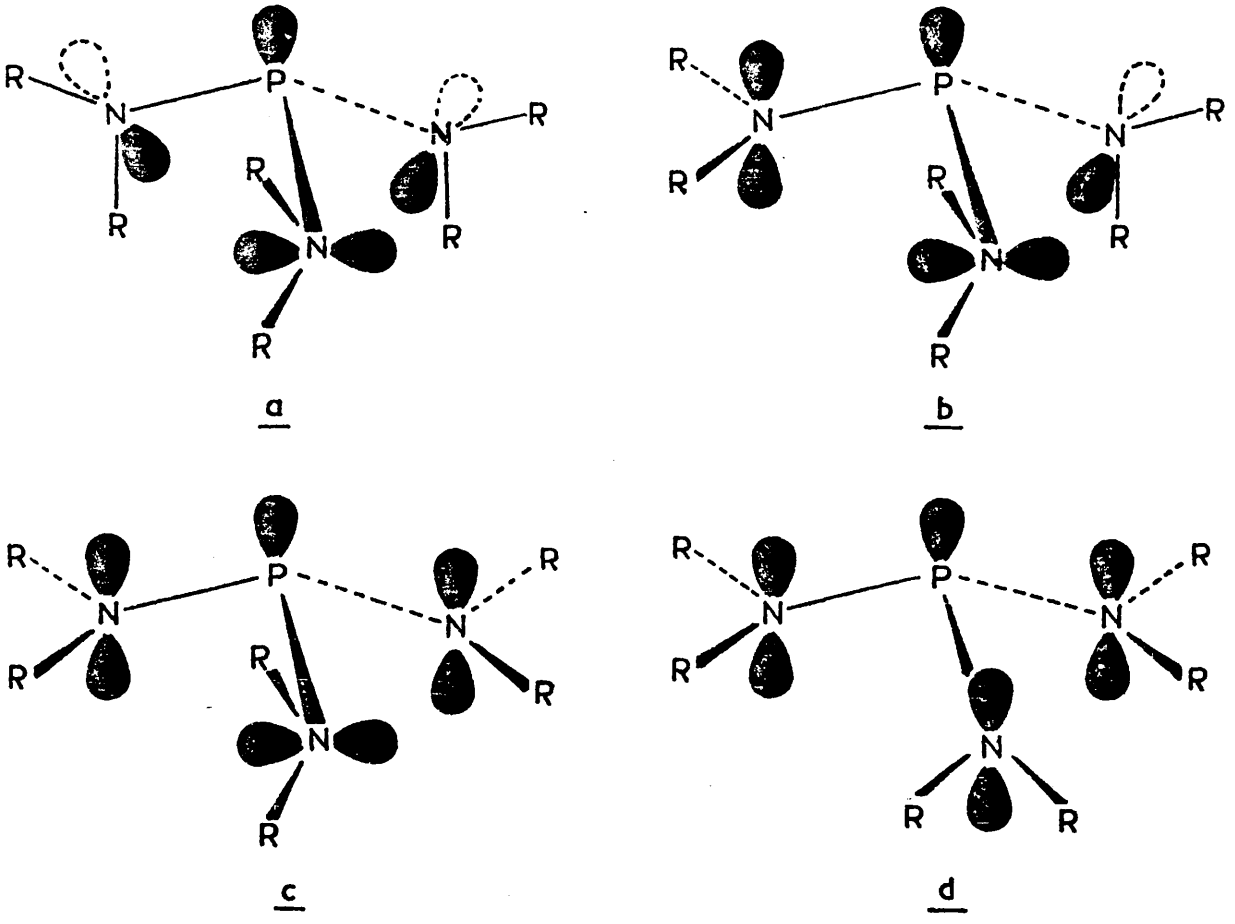


Figure 5 (R=Me)

Cowley and co-workers[169] who argued that the π-interaction between nitrogen lone-pairs (of 0.14 eV) as proposed by Lappert[168] was unreasonably small and the steric hindrance between the three dimethylamino-groups was too considerable for such a conformation to be preferred. Cowley's structure was later confirmed by other workers[170] but they disagreed with the original interpretation of the spectra. Such disputes are not restricted to phosphorus-nitrogen compounds either. Recent molecular orbital calculations[175] on the bicyclic phosphites, $P(OCH_2)_3CMe$ and $P(CH_2O)_3CMe$, while in good agreement with the p.e.s. data published

by Cowley and co-workers,[169] again radically disagreed with their interpretation. Almost simultaneously with this recent theoretical publication,[175] however, Cowley and co-workers revised [176] their interpretation of the p.e. spectra of acyclic phosphites such that it is in close agreement with the theoretical treatment, but they were highly critical of the approach used by Hargis and Worley[170] in their p.e.s. study of $(Me_2N)_3P$. Therefore, at present, while p.e.s. could prove to be a most valuable tool in giving an insight into the lone-pair-lone-pair interactions and conformations within phosphorus-nitrogen compounds, the results and conclusions drawn from such studies must be treated with a great deal of caution.

Another type of bonding interaction which may be of importance in many phosphorus-nitrogen compounds is that of so-called negative hyperconjugation. Hyperconjugation itself is an old idea[177] and is most readily described as an interaction between the best donor lone-pair or bond and the best acceptor bond (in other words, the bond with the lowest lying antibonding orbital). Negative hyperconjugation is an $n \longrightarrow \sigma^*$ interaction which is a function of the geometry of the interacting fragments and so displays strong directional preferences which in turn may be responsible for the relative stability of geometrical isomers. This type of bonding could be of particular significance in cyclodiphosphazanes which may exist in either <u>cis</u> or <u>trans</u> forms. A brief description of the effect of negative hyperconjugation is outlined below using the diimides, X_2N_2(X=H or F), as examples (Figure 6).[178,179] The molecule diimide, H_2N_2, may exist in <u>cis</u> and <u>trans</u> geometries for which the dominating

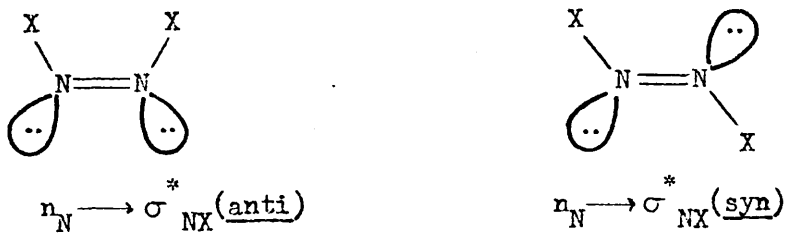


Figure 7 (X=H or F)

stabilising interactions which are dependent on conformation are the negative hyperconjugative $n \longrightarrow \sigma^*$ interactions. $\sigma \longrightarrow \sigma^*$ interactions depend on geometry too, but, since the energy gap separating n and σ^* orbitals is generally much smaller than that separating σ and σ^* orbitals, this will not be considered here. The orientation affording maximal $n \longrightarrow \sigma^*$ interaction is anti and not syn,[178,179] and so H_2N_2 will be expected to exist in the sterically crowded cis geometry, provided the $n \longrightarrow \sigma^*$ interaction is strong enough to overcome this adverse steric effect. In fact, the trans isomer is found to be more stable than the cis isomer[180,181] and so geometrical isomerism in N_2H_2 is dominated by steric effects. If, however, the protons are replaced by the more electronegative fluorine atoms, the $n \longrightarrow \sigma^*$ interaction should be increased, and is indeed now strong enough to overcome the adverse steric effects; the cis isomer being found experimentally to be more stable than the trans.[182] A further consequence of this hyperconjunction is that, as in the case of N_2F_2 where it is the dominant factor, one would expect the cis fluorines to be more negative than the fluorines in the trans isomer, since charge transfer from n_N to σ^*_{N-F} is greater in the cis isomer. However, this is a rather simplistic view as electrostatic and non-bonded interactions have been ignored. The important point is that deviations from steric control may occur whenever strong $n \rightarrow \sigma^*$ interactions obtain, and this could be one reason why, for example, $(ClPNBu^t)_2$ exists in the cis rather than the trans form (Figure 7).[105,106]

Certainly negative hyperconjugation has been a useful (though not necessarily unique) explanation for a number of chemical phenonoma including: the barriers to inversion in sulphenylaziridines,[183] the 10^6-10^8 fold rate increase in the hydrolysis of cyclic over acyclic

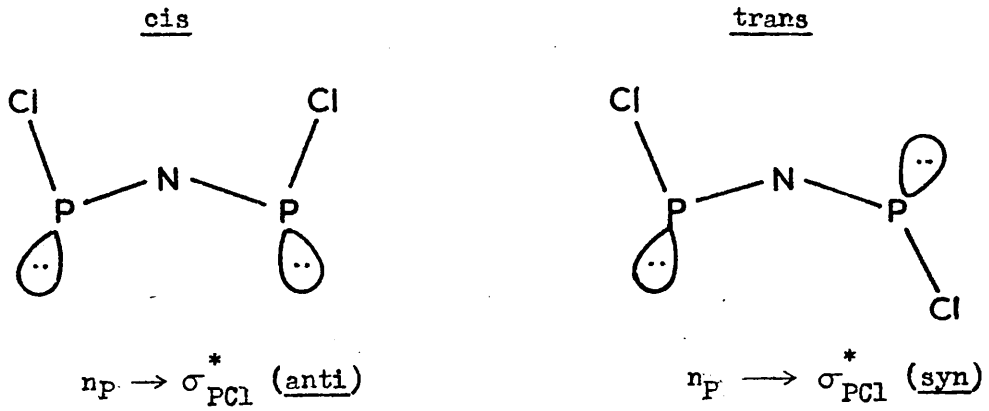
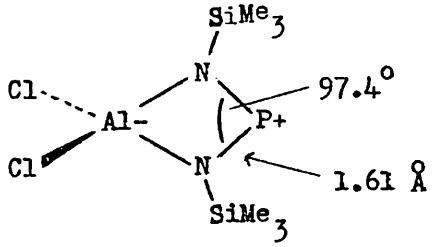


Figure 7: a view of $(ClPNBu^t)_2$ through the plane of the ring (t-butyl-groups omitted)

phosphates,[184,185] the conformational properties of 1,3,2-dioxaphosphorinanes[186] and phosphates,[184] and the sensitivity of $^1J(PN)$ to both electronegativity and conformation [151] [which may also be explained in terms of (p-d) π bonding as discussed earlier].

Finally, before leaving the topic of P-N bonding, the novel compounds (25) and (26) are of some interest. The ring compound (25), which is



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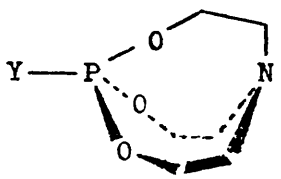


(26)

unusual in that it possesses a two co-ordinate cationic phosphorus, has a short formal single P-N bond length of 1.61 Å and this and the $\hat{NPN}$ angle of 97.4° have been used to postulate the presence of $\underline{(2p-3p)\pi}$ bonding.[187] In the cyclic phosphatrane (26) a well-developed transannular P ⟵ N bond is formed when the phosphorus lone-pair is strongly polarised by a positively charged Lewis acid (such as $Y=H^+$ or Ph_3C^+), while no P-N interaction is apparent with less polarising neutral substituents.[188] In the latter case, X-ray crystallographic evidence[189] suggests the phosphorus is tetrahedral and the nitrogen nearly planar, whereas in the former case the phosphorus is five co-ordinate and trigonal-bipyramidal with an axial P-N bond length of 1.986 Å in the fluoroborate salt of (26) ($Y=H^+$).[190]

One may conclude that the complete nature of P-N bonding is still not well understood. $\underline{(p-d)\pi}$ Bonding may be of significance in some cases, but its importance as a general phenonomen is now certainly open to question. Factors such as the geometry at nitrogen and the non-bonded interactions between nitrogen and phosphorus lone-pairs, which are both subject to outside influences such as the electronic and substituent effects of substituent groups, have to be considered. The situation is further complicated in that many of the effects discussed above are complementary, and consequently experimentally indistinguishable. Thus care must be exercised when drawing conclusions especially from earlier work. What is certain about the P-N bond is that it is not a singular entity; it may vary greatly from one molecule to another, and because its nature should be explicable in one class of compound does not necessarily mean that such an explanation should hold for all phosphorus-nitrogen compounds.

PHOSPHORUS-NITROGEN BOND TORSIONAL BARRIERS

The first report[191] of the detection of restricted rotation about a formal single P-N bond using variable-temperature n.m.r. techniques was that of Simonnin and co-workers in 1967 who discovered coalescence of the methyl-proton signals of $Ph(Cl)PNMe_2$ at -52°C. Cowley, Dewar, and Jackson[192] also claimed the first measurement of a P-N bond rotational barrier from their work on the same compound, but their manuscript (also preceded by reference 193) did not appear till a year later. Nowadays, the measurement of rotational barriers about P-N bonds by variable-temperature n.m.r. is well-established,[22,158-161,191-201] though barriers involving P(III)-N bonds have generally been found more accessible by this technique than those about P(V)-N bonds.

In many cases the ^1H n.m.r. effect, on complete ^{31}P spin decoupling, comprises of two uncoupled singlets which coalesce with increasing temperature eventually to produce one sharp signal. Under such conditions, the approximation that the rate constant at the coalescence temperature, $K_c=(\pi/\sqrt{2})\Delta\nu$ [$\Delta\nu$=separation of the two singlets (in Hz) in the absence of exchange] is valid,[202] and so the free energy of activation, ΔG^*_{Tc}, may be calculated from the Eyring Equation (assuming a transmission coefficient of unity):

$$K_c=\frac{K_B T_c}{h}\, e^{-\Delta G^*/RT_c} \quad \text{from which it may be derived that,}$$

$$\Delta G^*_{Tc} = T_c \left[45.63 + 4.58 \log_{10}(T_c/\Delta\nu)\right] \text{cal mol}^{-1}$$

where, K_B = Boltzmann's constant

T_c = coalescence temperature (K)

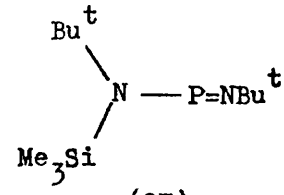
h = Planck's constant

R = gas constant

In fact ^{31}P decoupling facilities do not appear to be widely available. Under these circumstances, or when the rate process involves a number of sites and cannot be determined accurately with a simple analytical equation like above, then computer bandshape analysis has to be used to obtain the exchange rate.[203-205]

There are, in fact, a number of dynamic processes which could give rise to variable-temperature ^{1}H n.m.r. effects of the above type. These are: inversion at phosphorus, inversion at nitrogen, and substituent dissociation and recombination. It is wise to consider evidence which discounts these processes before discussing factors which may influence P-N torsional barriers. Cowley and co-workers[159] studied the chiral aminophosphine, $Ph(Cl)PNPr^{i}_{2}$, and discovered that above the coalescence temperature the i-propyl methyl-groups were still chemically non-equivalent, which would not have been the case had there been pyramidal inversion at phosphorus. Furthermore, variable-temperature n.m.r. experiments on dimethylamino-substituted cyclodiphosphazanes[22] did not result in any isomerisation at, or above, the coalescence temperature, indicating again that the phosphorus is configurationally stable. In fact, barriers about P(III)-N bonds are generally too low to be attributed to inversion at phosphorus.[206,207] On the other hand, the barrier to inversion at nitrogen is generally too low to be measured by dynamic n.m.r.[159] and where such barriers have been measured[207,208] the nitrogen has never been bonded to phosphorus. In addition, it is found that increasing the bulk of the R-group in the aminophosphines, $Ph(Cl)PNR_2$, increases the barrier for the dynamic process.[159,193,198] If nitrogen inversion was the cause of the exchange process then increasing the bulk of the R-group would increase the steric congestion in the pyramidal ground state and so lower the inversion barrier. Goldwhite and

co-workers[198] discovered that there was no effect, within experimental error, of solvent polarity or solute concentration on the barriers found for $XCH_2(Cl)PNMe_2$ (X=H or Cl). Hence the observed process is an intramolecular change in which there is no significant charge separation between the ground and transition states. In other words, the barrier does not arise from substituent dissociation and recombination. However, it is worthwhile to point out that substituent exchange which can be slowed down on the n.m.r. time scale may give rise to n.m.r. effects of the type described above. For example, on monitoring the t-butyl signal in the ^1H n.m.r. spectrum of the monophosphazene (27), two doublets are observed at -30^oC ($\Delta\nu$ =6.0Hz) which coalesce at 0^oC and form a single doublet at room temperature. This is the result of the trimethylsilyl-group fluctuating between the two nitrogen atoms above coalescence (ΔG^*_{Tc} = 14.5 kcal mol^{-1}). Nevertheless, there is now general agreement that the dynamic n.m.r. process generally encountered in the study of aminophosphines arises from hindered rotation about the P-N bond.



(27)

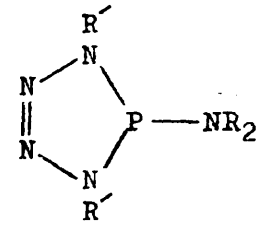
Attempts at identifying the factors comprising P-N rotational barriers have had mixed success. That there is a steric dependence both on the nitrogen and phosphorus substituents is certain. For instance, on decreasing the size of the nitrogen substituent in Cl_2PNR_2 from Bu^t [199] to Me,[159] ΔG^* drops from 17.5 to 8.4 kcal mol^{-1}, and lower barriers are found in $Cl(R)PNMe_2$ relative to $Cl(R)PNPr^i_2$ (R=Me,[198,200] or Ph [159,200]). The barrier increases marginally (0.4 kcal mol^{-1}) with increasing size of the

phosphorus substituent in the series $Cl(R)PNPr^{i}_{2}$ (R=Me or Bu^{t}),[200] but unexpectedly decreases with increasing size of the phosphorus substituent in the series $Cl(R)PNMe_2$ (R=Me,Ph, or Bu^{t}).[198,200] The reason for this inverse steric effect is not readily apparent, though it has been suggested[200] that in $Cl(Bu^{t})PNMe_2$ the low barrier may arise from a ground state which is more hindered than the transition state. A similar explanation has been proposed by Cowley and co-workers from their studies on H_2NPH_2.[163] It has also been found[198] that fluoroaminophosphines, $F(R)PNR'_2$ (R=Me or Ph,R' =alkyl) have lower barriers (by ca. 2 kcal mol^{-1}) than the corresponding chloroaminophosphines.

Study of dialkylaminocyclodiphosph(III)azanes by variable-temperature n.m.r. shows[22] they exhibit hindered rotation about the (exocyclic) P-N bonds too. The barriers to rotation are largely determined by steric effects as is illustrated by the decrease in ΔG^{*}_{Tc} from 11.4 to ca. 9.5 kcal mol^{-1} for $Me_2\overline{NP.NR.PNMe_2.NBu^{t}}$, R=$Bu^{t}$ and Me respectively. A similar dependence of P-N torsional barrier on the steric bulk of the ring-nitrogen substituents was found[22] for the monodimethylamino-derivatives, $Me_2\overline{NP.NR.PCl.NBu^{t}}$ (R=Me or Bu^{t}) where the ring with the less sterically demanding methyl-group attached had a smaller barrier by around 2.4 kcal $mol.^{-1}$ The most dramatic differences in torsional barrier were between geometrical isomers where, for example, cis and trans isomers of $Me_2\overline{NP.NMe.P(O)Cl.NBu^{t}}$ and $Me_2\overline{NP.NBu^{t}.PNMe_2.NMe}$ showed differences in barriers of around 4 and 3 kcal mol^{-1} respectively. Unfortunately, as geometrical assignments for these compounds were only tentative, the reasons for this were unclear. Cross-ring interactions between the dimethylamino-groups in the cis isomers could destabilise the normally preferred conformations of these groups, which lie in, or close to, the plane bisecting the ring, and so lower the barrier.

On the other hand, on a steric basis alone, such cross-ring interactions might result in a higher barrier in the cis isomers. Indeed, those isomers with the higher barriers possessed tentatively assigned cis structures.[22] A further feature which arose from the variable-temperature $^{1}H-\{^{31}P\}$ n.m.r. experiments on dialkylaminocyclodiphosph(III)azanes was the temperature dependence of the phosphorus chemical shifts: upfield shifts, on lowering the temperature, of the order of 5×10^{-2} p.p.m. per ^{o}C being discovered.[22] These are generally greater than those found for acyclic aminophosphines.[209] It was also found[22] that those compounds with relatively high torsional barriers about the exocyclic P-N bond(s) have the greatest dependence of phosphorus chemical shift with temperature. A possible reason for this effect is that the dialkylamino-group spends a greater proportion of time in a preferred conformation at low temperature in which the strength of the exocyclic P-N bond is increased through (p-d)π bonding.[22] However, as yet the effect of changes in P-N bond strength on ^{31}P chemical shift is little understood. Hindered rotation has also been observed[47] about the exocyclic P-N bond in trans- $[(Me_3Si)_2NPNSiMe_3]_2$. The extremely high barrier in the latter compound ($\Delta G^{*}_{Tc} > 27$ Kcal mol^{-1}) is the largest yet reported about a formal single P-N bond, and is almost certainly the result of the extreme steric hindrance of the trimethylsilyl-groups.

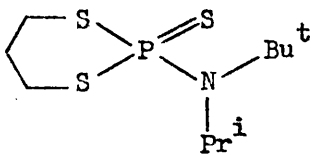
Hindered rotation about the exocyclic P-N bond has also been noted[210,211] in the novel compound (28) and has been attributed to a steric interaction between the di-i-propylamino-group and the t-butyl-groups bound to the ring.



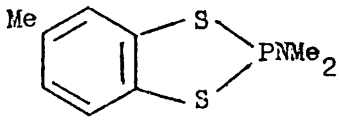
(28) (R=Pr^{i}, R =Bu^{t})

So far the factors which have been considered in influencing the P-N torsional barrier have been mainly steric in origin. It appears certain that electronic effects are often important, but the nature and magnitude of such effects are still open to question. The origin of the P-N rotational barrier was originally postulated[191] to be a result of lone-pair-lone-pair repulsions between the nitrogen and phosphorus atoms and of $\underline{(p\text{-}d)\pi}$ bonding. Cowley and co-workers[192] rejected explanations in terms of $\underline{(p\text{-}d)\pi}$ bonding since it had earlier been shown that π-bonding does not lead to hindered P-N bond rotation in phosphonitrilic chlorides.[212] Goldwhite and Rowsell[158] later presented strong evidence in support of $\underline{(p\text{-}d)\pi}$ bonding, but recently the results of photoelectron spectroscopy on the series of aminophosphines, $PCl_{2-n}(CF_3)_n(NMe_2)$ (n=0,1 or 2) have been used to indicate the barrier arises from steric effects and lone-pair-lone-pair repulsion effects rather than $\underline{(p\text{-}d)\pi}$ bonding.[165] However, the interpretation of the photoelectron spectra has since been disputed by other workers.[168] In addition to this, theoretical studies on the aminophosphine, H_2NPH_2,[163,164] have been used to deduce that the P-N torsional barrier is not a pure rotational barrier at all, but a hybrid process involving both rotation and pyramidal inversion at nitrogen, with phosphorus d-orbitals having no significant role in the bonding. This appears to explain why increasing the steric bulk at phosphorus decreases the barrier[198,200] since larger groups on phosphorus promote the pyramidality at nitrogen which is predicted[163] in the transition state. However, as there are no experimental data on H_2NPH_2 this theory remains unjustified, especially as other workers have proposed a different geometry about nitrogen in the ground state configuration[157] and that the method[164] of restraining $\hat{HNH}$ such that it equals $\hat{HNP}$ is erroneous.

Some evidence for the involvement of lone-pair-lone-pair interactions is the fact that barriers about P(V)-N bonds at four co-ordinated phosphorus usually tend to be much lower than those about P(III)-N bonds. For example, barriers in compounds of the type, $Cl(R)P(X)NR'_2$ (R=Me or Ph, R'=Me or Pr^i), tend to be 2-3 kcal mol^{-1} lower when X=S as against X=lone-pair.[200] However, it is also possible that tervalent phosphorus, possessing a lone-pair of electrons, introduces more conformational dependence into the bond rotation than quinquevalent phosphorus. Evidence against repulsion with the nitrogen lone-pair is that in the dithiaphosphorinane, (29), the barrier about the P(S)-N bond is greater than that about the P-N bond in the analogous three co-ordinate species.[201]



(29)

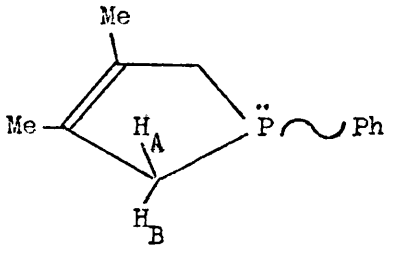


(30)

Finally, the incorporation of phosphorus into a five-membered ring, such as in compound (30), has been shown [213] to result in an increase in the barrier to P-N bond rotation compared with the acyclic compound, $(EtS)_2PNMe_2$. The reasons for this are probably related to those which determine the higher barriers discovered in dialkylaminocyclodiphosph(III)azanes.[22]

Hence, the factors which influence P-N torsional barriers are still not fully understood: steric effects certainly exist, as do electronic effects but whether the latter arise through vicinal lone-pair repulsion and/or π-bonding in the P-N bond, or some different mechanism, is still a matter of controversy.

Variable-temperature n.m.r. has also been used to provide information on the stereochemical dependence of a number of coupling constants involving tervalent phosphorus, especially in non-rigid, acyclic phosphines. Gagnaire and co-workers[214] in their studies of the 3,4-dimethyl-1-phenylphosphacyclopentene (31) discovered two $^2J(\underline{P}C\underline{H})$ coupling constants of different magnitude and sign which they attributed to the lone-pair orientation of the phosphorus atom. Since then there has been considerable interest[215-228]



(31)

$^2J(\underline{P}C\underline{H}_A)=\pm 25$ Hz

$^2J(\underline{P}C\underline{H}_B)=\mp 6$ Hz

in two and three-bond phosphorus-proton and phosphorus-carbon coupling constants: in all cases it being found that the coupling constants were strongly dependent on the dihedral angle, Θ, subtended by the bond and the lone-pair on phosphorus (Figure 8).

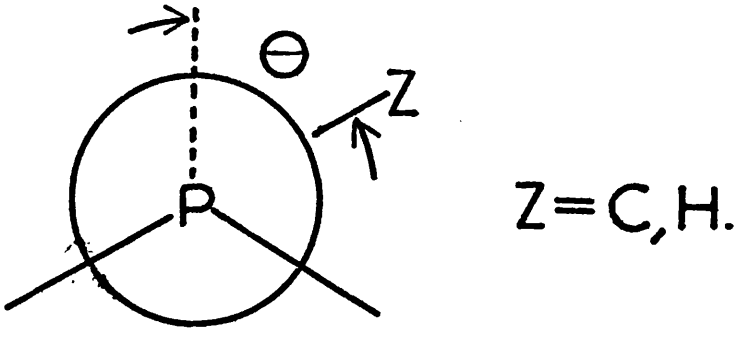


Figure 8

The angular dependence of these coupling constants along with leading references, is summarised in Table 4. Generally when the dihedral angle is 0° the coupling constant is large and positive - almost certainly the result of a 'through-space' interaction -[228,229] whereas a smaller coupling constant (either positive or negative) is associated with 180° angles. $^{3}J(\underline{P}O\underline{C}H)$ is also dependent on the orientation of the phosphorus lone-pair,

Table 4

Angular dependence of coupling constants

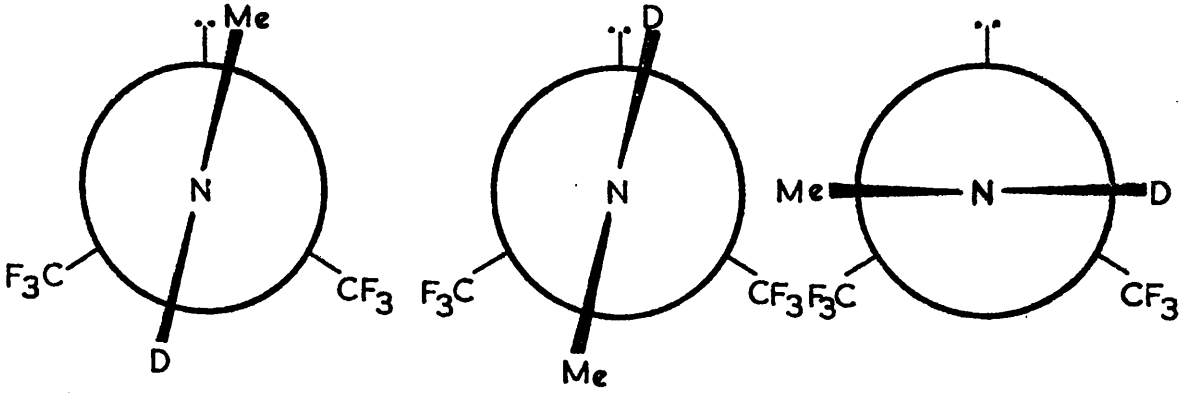
Coupling Constant	Dihedral Angle 0°	Dihedral Angle 180°	Reference(s)
$^{2}J(\underline{P}C\underline{H})$	ca. +20 Hz	0 Hz[a]	214,216-219
$^{2}J(\underline{P}C\underline{C})$	35±5 Hz	0±3 Hz	220-223
$^{2}J(\underline{P}N\underline{C})$	ca. +50 Hz	ca. -10 Hz	224,225
$^{2}J(\underline{P}O\underline{C})$	ca. +18 Hz	0±3 Hz	226
$^{3}J(\underline{P}C\underline{C}H)$	ca. +20 Hz	3±2 Hz	191,227
$^{3}J(\underline{P}N\underline{C}H)$	+18±3 Hz	3±2 Hz	22,159,198,225
$^{3}J(\underline{P}N\underline{C}\underline{C})$	23 Hz	3±3 Hz	228

a A minimum, corresponding to a small negative coupling constant, was obtained at 120°.

although no correlation between this and Θ has yet been made, as only the dihedral angle between the phosphorus lone-pair and the O-C bond has been considered.[230,231]

There have been a number of reports of quinquevalent phosphorus -proton or -carbon coupling constants being stereochemically dependent [$^{3}J(\underline{P}C\underline{C}H)$,[232] $^{3}J(\underline{P}O\underline{C}H)$,[230] $^{3}J(\underline{P}N\underline{C}C)$,[228] $^{3}J(\underline{P}O\underline{C}C)$,[233-235], $^{3}J(\underline{P}O\underline{C}H)$,[236] and $^{3}J(\underline{P}C\underline{C}C)$[237]] although because the effect of lone-pair orientation is now absent, the range of values which these coupling constants adopt is not usually as extreme as that found when phosphorus is in the tervalent oxidation state. Indeed some coupling constants involving phosphorus(V) have been shown to have very little conformational dependence, unlike their phosphorus(III) counterparts.[201,221,227,228]

As well as being of theoretical interest,[215,218] the stereochemical dependence of two and three-bond phosphorus-proton and phosphorus-carbon couplings is of use in determining the ground state conformation, in solution, of non-rigid molecules such as aminophosphines. For example, the low-temperature ^{1}H n.m.r. spectrum of the methylaminobis(trifluoromethyl)-phosphine, $MeND.P(CF_3)_2$, indicates the presence of two unequally populated rotamers which, as a result of steric considerations and the magnitudes of the $^{3}J(\underline{P}N\underline{C}H)$ coupling constants, are assigned as rotamer a (80%) and rotamer b (20%), but not rotamer c (Figure 9).[194]



a — major rotamer, $^{3}J(\underline{P}N\underline{C}H)$ 13.9 Hz

b — minor rotamer, $^{3}J(\underline{P}N\underline{C}H)$ ca. 4 Hz

c — rotamer not observed

Figure 9

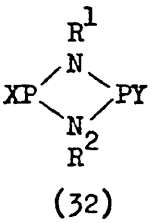
Finally, several two and three-bond couplings between phosphorus and nuclei other than carbon or hydrogen have also been shown to be stereochemically dependent. Of particular note are $^{2}J(\underline{P}\underline{C}\underline{F})$,[218] $^{3}J(\underline{P}\underline{C}\underline{C}\underline{F})$,[218] $^{2}J(\underline{P}\underline{N}\underline{S}\underline{i})$,[225] and $^{2}J(\underline{P}\underline{N}\underline{P})$.[51,238]

CHAPTER 2

AMINOCYCLODIPHOSPH(111)AZANES

INTRODUCTION

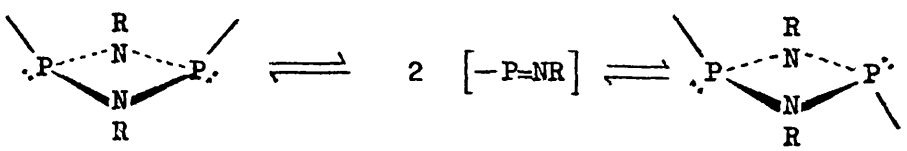
Cyclodiphosph(III)azanes (32) are phosphorus-nitrogen four-membered rings, the first of which, (32) (R^1=R^2=Ph, X=Y=Cl), was reported[6] towards the end of the last century, although it has not been until recently that a detailed study of the chemistry of these compounds has been undertaken.[7,8,15,20,22,36-38,50] Some of these compounds display geometrical isomerism (Figure 1 a), presumably through the different mutual orientations of the exocyclic phosphorus substituents in a ring containing planar, or near planar, nitrogen atoms.[106] These isomers are characterised by exceptionally large differences (65-90 p.p.m.) in ^{31}P chemical shift.[22,34,50] In some cases isomerisation has been observed, and in compounds of the type (32) (R^1=Bu^t, R^2=alkyl, X=Y=amino) this has always been from the isomer with the 'low-field' phosphorus shift (δ_P ca. 190 p.p.m.) to that with the 'high-field' shift (δ_P ca. 100 p.p.m.).[22] The actual mechanism of isomerisation is unknown. It may be via,



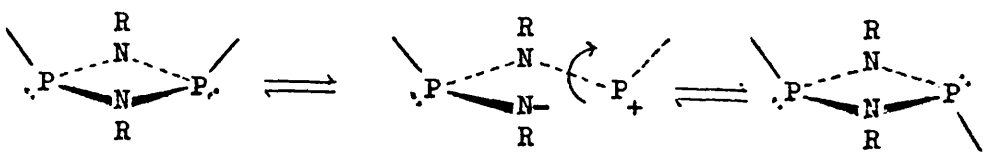
(32)

i) phosphorus inversion

ii) a monophosph(III)azene intermediate,



or iii) a ring-opening mechanism,



The first case is unlikely as the barriers to phosphorus inversion are generally quite high, especially when the phosphorus atom forms part of a small strained ring system.[239] The last two mechanisms are reasonable possibilities. A number of monophosph(III)azenes have now been isolated and are characterised by extremely low-field ^{31}P chemical shifts (ca. 300 p.p.m.).[36,45] Such shifts have never been observed during the isomerisation of cyclodiphosph(III)azanes, so if the monomer is formed it must have a very short lifetime. On the other hand, there are recent reports of the dimerisation of monophosph(III)azenes to the four-membered ring species.[36,47] The ring-opening mechanism too is quite feasible, but again there is no direct evidence for this.

In dialkylaminocyclodiphosph(III)azanes torsional barriers of considerable magnitude about the exocyclic P-N bonds have been measured.[22] Furthermore, substantial differences in ΔG^{*}_{Tc} for pairs of isomers have been noted[22]; for example, the difference in barrier between cis and trans - (32) (R^1=Me, R^2=Bu^t, X=Y=NMe_2) is ca. 3 kcal $mol.^{-1}$ Thus, as dialkylaminocyclodiphosph(III)azanes possess rotational barriers well within the range measurable by variable-temperature n.m.r. (5-25 kcal mol^{-1}), systematic changes in the groups R^1,R^2,X, and Y in (32) may well provide interesting information about the torsional process. The one major drawback is that, to date, no definite assignment of the geometrical isomers has been made, although on the basis of n.m.r. evidence, Bulloch[22] tentatively assigned cis structures to the isomers of (32) (R^1=Bu^t,R^2=alkyl,X=Y=NMe_2) with 'low-field' phosphorus shifts.

Thus it is of interest to extend the range of alkylaminocyclodiphosph-(111)azanes known and reinvestigate some of the work already done in order to,

a) discover which isomer is cis and which is trans,

b) separate individual cis and trans isomers in order to study the effects of geometrical isomerism on chemical and physical properties,

c) extend present knowledge on the aminolysis reactions of compounds of the type $RN(PCl_2)_2$ and $(ClPNR)_2$,

d) extend present knowledge on the chemistry of alkylaminocyclodiphosph(111)azanes, and,

e) produce series of compounds of interest for a study by variable-temperature n.m.r. (particularly with a view to measuring P-N torsional barriers).

The domain of this chapter is principally the synthesis and physical properties of alkylaminocyclodiphosph(111)azanes, points d) and e) (above) being dealt with in subsequent chapters (3 and 5).

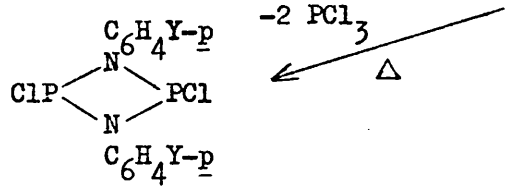
RESULTS

(1) The preparation of N-arylcyclodiphosph(111)azanes

The preparation of N-arylcyclodiphosph(111)azanes (34) (Y=H,Cl,Me, or OMe) by the reaction of arylamine hydrochlorides with phosphorus trichloride in refluxing sym-tetrachloroethane has recently been described[15]:

$$2\ [N(C_6H_4Y\text{-}\underline{p})H_3]\,Cl + 4\ PCl_3 \xrightarrow{-6\ HCl} 2\ (C_6H_4Y\text{-}\underline{p})N(PCl_2)_2$$

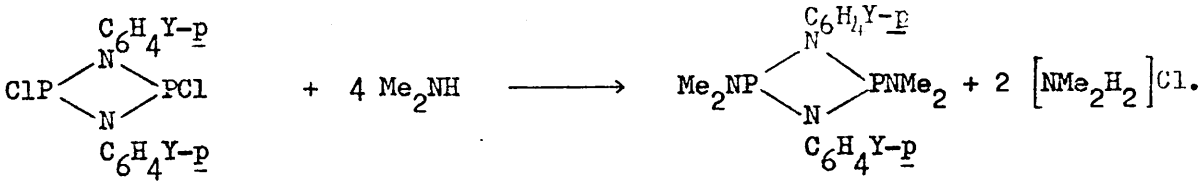
(33)



(34) (Y=H,Cl,Me, or OMe)

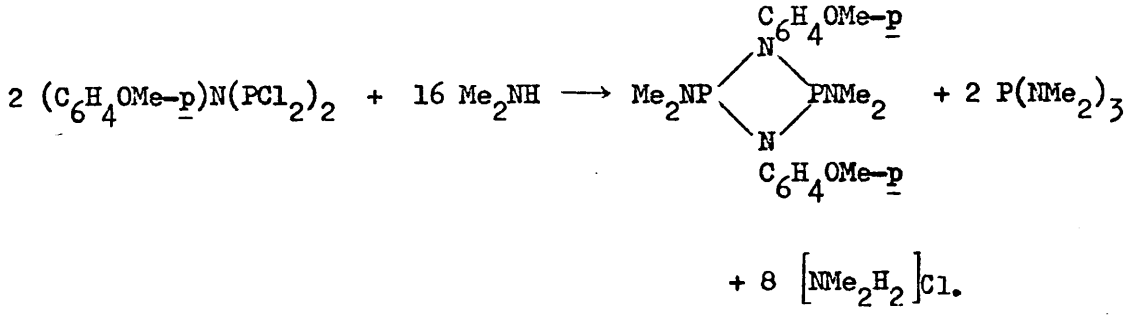
The bis(dichlorophosphino)amines (33) (Y=H,Cl,Me, or OMe) were isolated in high yield only if the temperature during work up was kept at or below 30°C, whereas a temperature of 100-150°C led to thermal elimination of phosphorus trichloride and formation of the dimer (34).[15] These preparations were found to be repeatable only when Y=H or Cl, but not when Y=Me or OMe. When Y=Me, the cyclodiphosph(111)azane was only obtained by heating the intermediate bis(dichlorophosphino)amine under reduced pressure (0.1 mmHg) for several hours at 145°C. When Y=OMe, there was no thermal elimination of phosphorus trichloride even under such extreme conditions.

Dimethylaminolysis of the chlorocyclodiphosph(111)azanes (34) (Y=H,Cl, or Me) readily gave the bis(dimethylamino)-derivatives (35) (Y=H,Cl, or Me):



(35) (Y=H, Cl or Me)

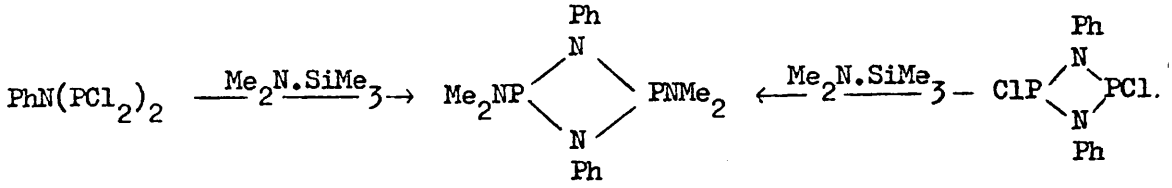
The p-methoxyphenyl-derivative was obtained by the dimethylaminolysis of the bis(dichlorophosphino)amine, $(C_6H_4OMe\text{-}p)N(PCl_2)_2$,



Mass spectroscopy, and in the case of $(Me_2NPNPh)_2$, molecular weight determination by osmometry in benzene solution showed that the products were dimers.

The various routes by which dimethylaminocyclodiphosph(III)azanes might be formed in this reaction could not be distinguished. Careful examination of the products of the reaction of $PhN(PCl_2)_2$ with four molar equivalents of dimethylamine by ^1H n.m.r. spectroscopy showed that the cyclisation step is extremely facile, for only $ClP.NPh.PNMe_2.NPh$ [also prepared by the reaction of (34) (Y=H) with two molar equivalents of dimethylamine], Me_2NPCl_2 and $(Me_2N)_2PCl$ could be detected.

Only the N-phenyl-derivative, $(Me_2NPNPh)_2$, has been previously reported,[15] and this apparently as one isomer,



In three out of four cases (Y=H,Cl, or OMe) a mixture of isomers was found initially. As was found[22] for (32) (R^1=Bu^t;R^2=Me,Et, or Bu^t;X=Y=NMe$_2$) these isomers showed very large differences in ^{31}P chemical shifts. In all three cases, on standing in solution for several weeks, isomerisation occurred to the isomer with the 'low-field' ^{31}P chemical shift, in contrast to the N-alkyl-derivatives where the isomers with the 'high-field' shifts were favoured (Table 5).

Table 5

^{31}P chemical shifts and isomer ratios of $(Me_2NPNC_6H_4Y\text{-}p)_2$.

Y	δ_P[a] p.p.m.	Isomer Ratio[b] Initially	After several weeks
H	101.0	1	0
	166.5	1	1
Cl	100.8	1	0
	166.1	1	1
Me	166.8	1	1
OMe	101.5	1	0
	168.9	10	1

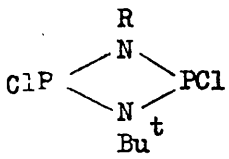
[a] Downfield shifts are positive;relative to external 85% H_3PO_4.

[b] In benzene solution at ambient temperatures.

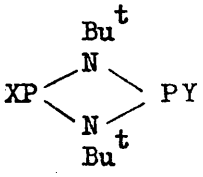
Diethylaminolysis of (34) (Y=H) readily afforded one isomer of $(Et_2NPNPh)_2$ and this had a 'low-field' ^{31}P chemical shift (δ_P 161.2 p.p.m.). This is again in marked contrast to the N-alkyl-derivatives, for which the single isomer of $(Et_2NPNBu^t)_2$ had a 'high-field' shift (δ_P 91.3 p.p.m.).

(2) The reaction of cis- $(ClPNBu^t)_2$ with amines

Although it had been reported [25] that dimethylaminolysis of (3) (R=Bu^t) led only to complicated mixtures, it was later found [22] that (36) (X=Y=NMe_2) was the sole product of reaction with excess amine. The reaction is straightforward therefore,

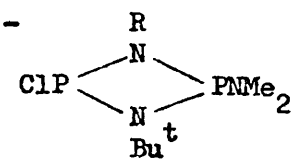


(3)



(36)

except that a mixture of geometrical isomers is found with ^{31}P chemical shifts of 95 and 184 p.p.m. Similar results were found when (3) (R=Me or Et) was treated with four, or more, molar equivalents of dimethylamine. Isomerisation of these 2,4-bis(dimethylamino)cyclodiphosph(III)azanes was found to occur; in each case isomerisation resulting in an increased proportion of the isomer with the 'high-field' ^{31}P signal ($\delta_P \sim 100$ p.p.m.). Qualitative observations showed[22] that the rate of isomerisation increases with increasing bulk of the ring-nitrogen substituents; isomerisation of $Me_2NP.NMe.PNMe_2.NBu^t$ only being apparent after standing for several weeks at ambient temperatures, whereas isomerisation of $(Me_2NPNBu^t)_2$ occured within a few days. Similar reactions with two molar equivalents of dimethylamine on (3) (R=Me or Bu^t) gave the mono(dimethylamino)-derivatives (37) (R=Me or Bu^t) which differed from the bis(dimethylamino)-derivatives in that only one isomer was formed in each case.[22]

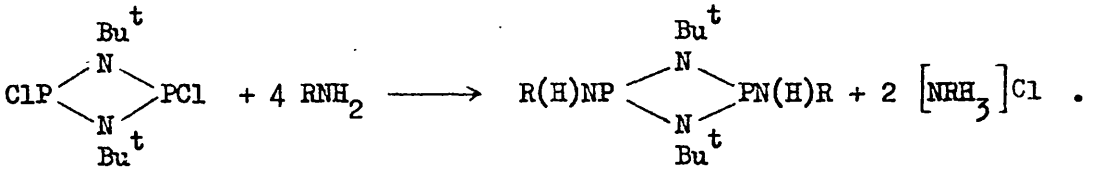


(37)

Reaction of (34) ($R=Bu^t$) with excess diethylamine afforded $(Et_2NPNBu^t)_2$ in one isomeric form only and this with a 'high-field' ^{31}P chemical shift.

The reactions of <u>cis</u>-$(ClPNBu^t)_2$ with a variety of other amines were investigated.

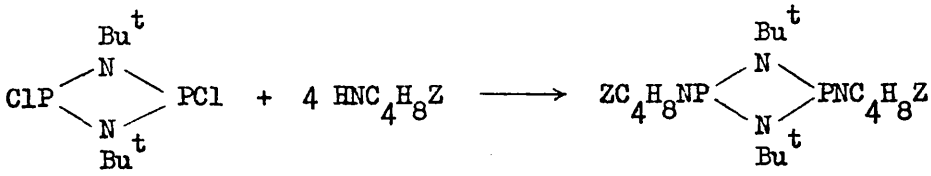
(a) <u>Reactions with primary amines</u>:- The reaction of <u>cis</u>-$(ClPNBu^t)_2$ with four molar equivalents of methylamine, ethylamine, and t-butylamine readily afforded the bis(alkylamino)-derivatives (36) ($X=Y=MeNH, EtNH$, or Bu^tNH),



$R=Me, Et$, or Bu^t

In only one case was a mixture of isomers produced, (36) ($X=Y=MeNH$), isomerisation occurring very rapidly (<u>ca.</u> 0.5 h at 33°C) to the isomer with the 'high-field' ^{31}P chemical shift. The preparation of (36) ($X=Y=Bu^tNH$) has been reported [19] before, and a minor product was found which may have been the less stable isomer. This was not detected in the present work, the t-butylamino-derivative, like the ethylamino-derivative, existing in only the one form, that with the 'high-field' ^{31}P chemical shift. Hereafter, until a definite structural assignment is made, isomers will be termed 'low' or 'high-field' depending on the phosphorus chemical shift.

(b) Reactions with cyclic amines:- The products of the reactions of cis-$(ClPNBu^t)_2$ with the secondary cyclic amines, pyrrolidine, piperidine, and morpholine were examined:

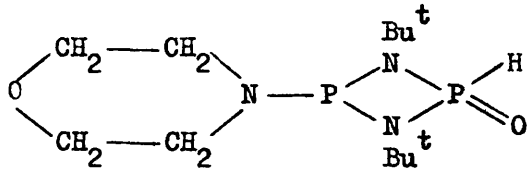


Z=nothing (pyrrolidine),
CH_2(piperidine), or
O (morpholine)

+

$2\left[NC_4H_8ZH_2\right]Cl.$

Pyrrolidine and piperidine gave very low yields (< 10%) of the 'low-field' isomer. On the other hand, with morpholine no 'low-field' isomer could be detected (n.m.r.). However, the reaction with morpholine did give a small quantity of unidentified material (δ_{PNCH_2} 75.5 p.p.m.), which increased markedly in proportion on heating in benzene. Mass spectroscopic evidence, in particular, suggested compound (38) was obtained, evidently by water-induced cleavage of an exocyclic P-N bond.



(38)

(c) Reactions with other secondary amines:- The reaction of cis-$(ClPNBu^t)_2$ with dimethylamine[22] has already been discussed. However, when this was repeated it was found for the first time that a thermodynamically unstable cyclodiphosph(III)azane could be isolated; the kinetically favoured, higher melting isomer of (36) (X=Y=NMe_2) being separated by repeated fractional crystallisation from pentane. In the solid state, no isomerisation of this

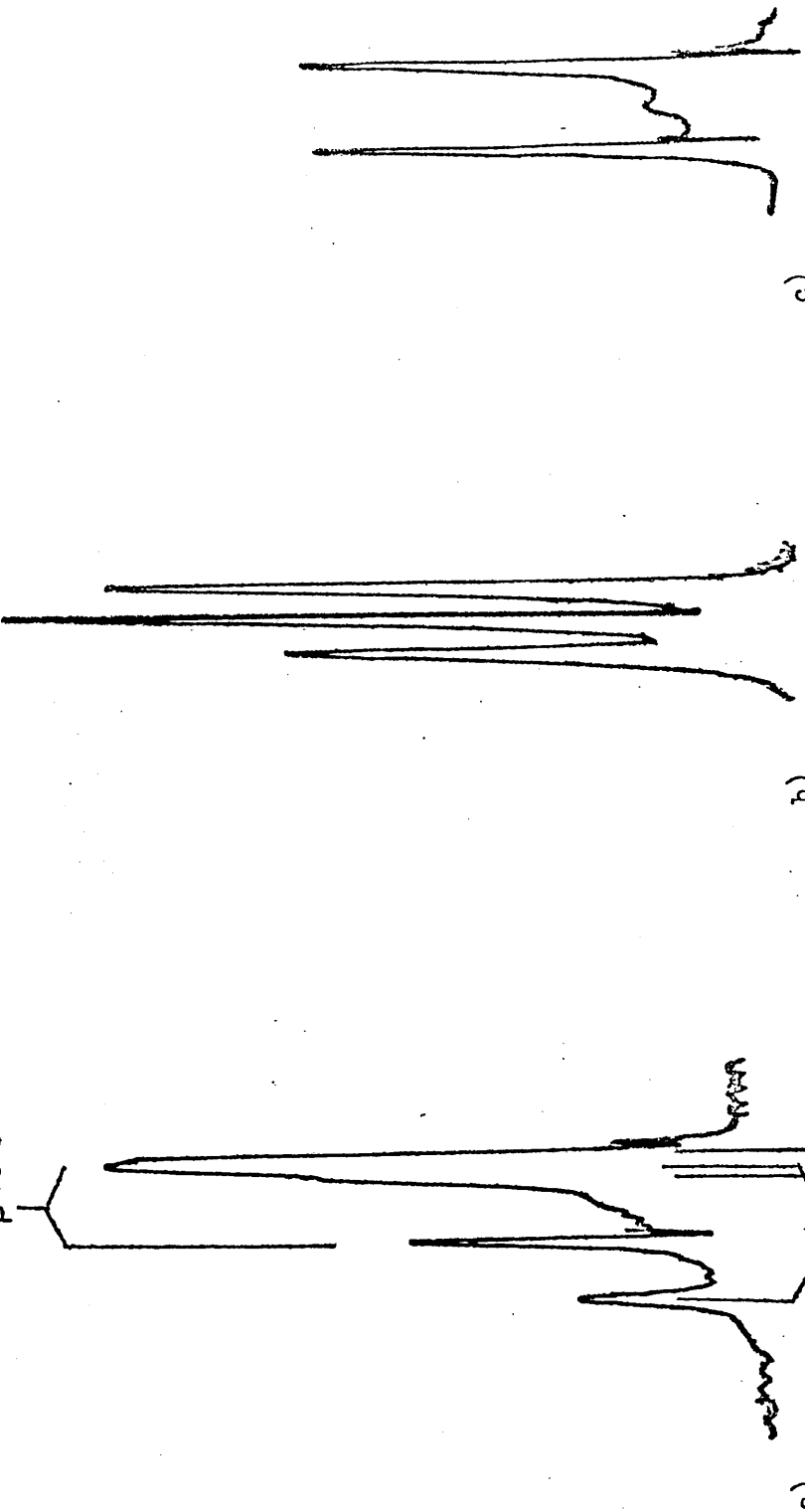
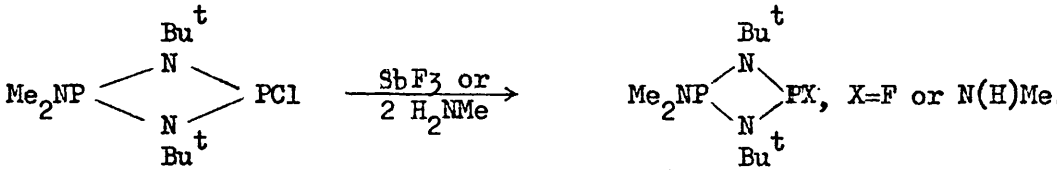


Figure 10. Partial ^{1}H n.m.r. spectrum of $(Me_2NPNBu^{t})_2$, showing N-methyl signals only.

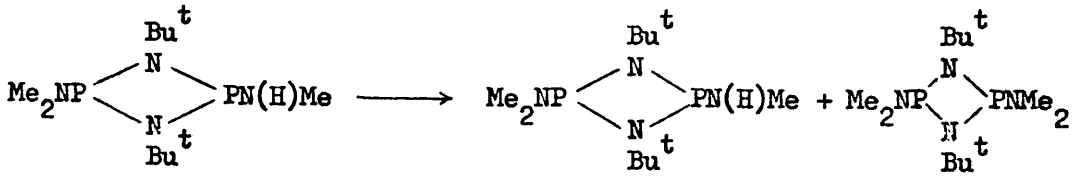
a) Initial product b) $^{1}H-\{^{31}P\}$ spectrum c) product on heating.

isomer could be detected after three months, in contrast to its solution properties. Earlier confusion[35] about the products of this reaction possibly arose from the complexity of the ^1H n.m.r. spectrum (Figure 10) which initially shows six signals in the $\underline{NMe}_2$ region. Four of these signals belong to the kinetically favoured isomer which exhibits restricted rotation about the exocyclic P-N bonds at ambient temperatures on the n.m.r. time scale (see Chapter 5).

The reaction of $\underline{cis}$-$(ClPNBu^t)_2$ with two molar equivalents of dimethylamine to produce (37) ($R=Bu^t$) was also repeated. Again only one isomer, with an intermediate ^{31}P chemical shift ($\delta_{\underline{P}NMe_2}$ 131.5 p.p.m.) relative to the other N-t-butyl-derivatives, was observed. This compound could be readily fluorinated using antimony trifluoride, or reacted with methylamine to produce a mixed amino-derivative:

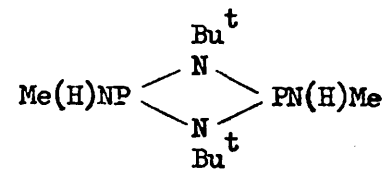


$Me(H)NP.NBu^t.PNMe_2.NBu^t$ was initially spectroscopically identified as the 'low-field' isomer, but on standing this produced a mixture of products all of which were 'high-field' isomers (relative proportions in parentheses),



$\underline{cis}$ or $\underline{trans}$ (6) (1)

+

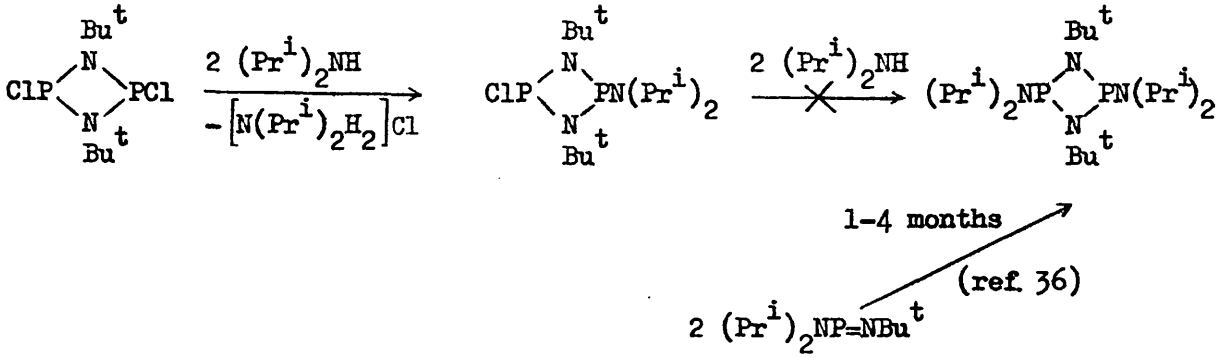


(1)

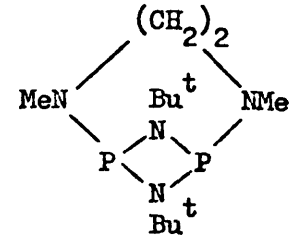
all $\underline{trans}$ or $\underline{cis}$.

The components of this isomerisation/exchange process were identified by ^{31}P n.m.r. (^{1}H n.m.r. data were too complex to establish this). No evidence was found to suggest whether the exchange process occurs by simple interchange of amino-groups with the ring remaining intact, or by the intervention of monomeric phosph(111)azenes, $Me_2NP{=}NBu^t$ and $MeNH.P{=}NBu^t$. A further surprising feature was that the 'high-field' isomer of (36) $\left[X{=}Me_2N,\ Y{=}N(H)Me\right]$ gave only one ^{31}P n.m.r. signal.

As it has been established[45] that bulky nitrogen substituents stabilise monomeric phosph(111)azenes, it was hoped that one route to such compounds might be via the cleavage of sterically congested cyclodiphosph(111)azanes. Hence, cis-$(ClPNBu^t)_2$ was reacted with four molar equivalents of di-isopropylamine. However, only the mono(di-isopropylamino)-derivative was produced, even under extremely forcing conditions. Interestingly, it was recently reported[36] that the monophosph(111)azene, $(Pr^i)_2NP{=}NBu^t$, produced by heating $(Pr^i)_2N.PCl.N(SiMe_3)Bu^t$ with elimination of Me_3SiCl, slowly dimerises at ambient temperatures to the bis(di-isopropylamino)-compound.



On treatment of cis-$(ClPNBu^t)_2$ with N,N´-dimethylethylenediamine, $Me(H)N(CH_2)_2N(H)Me$, the new crystalline bicyclic compound, (39), was formed. Yields were low due to other, presumably polymeric, materials being formed, but were found to be higher when the diamine, rather than triethylamine, was used as hydrogen chloride acceptor. No cage compound of this type was isolated on treating



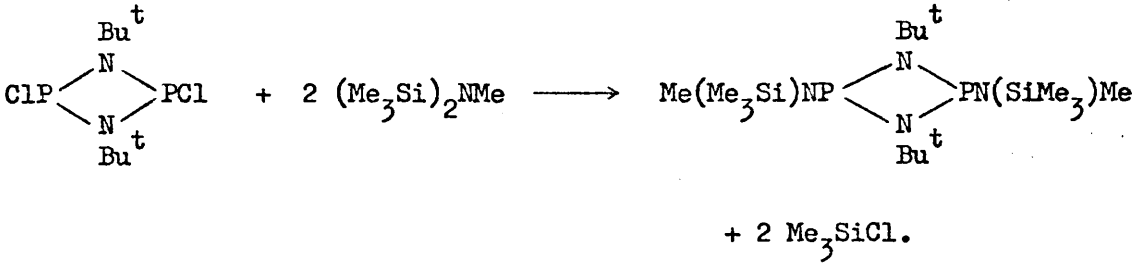
(39)

cis-$(ClPNBu^t)_2$ with N,N′-dimethyltrimethylenediamine.

(d) cis-$(ClPNBu^t)_2$ with N,N′-dimethyltrimethylenediamine.

equ (d) Aminolysis of cis-$(ClPNBu^t)_2$ with heptamethyldisilazane:- Two molar

pro equivalents of heptamethyldisilazane slowly reacted with cis-$(ClPNBu^t)_2$ to produce the single 'high-field' isomer of (36) (X=Y=$MeNSiMe_3$),



+ 2 Me_3SiCl.

This compound has also been recently reported[36] as the result of the slow dimerisation of $Me(Me_3Si)NP{=}NBu^t$, though it was not fully characterised.

(3) Physical properties of alkylaminocyclodiphosph(111)azanes

One of the most striking features which became evident from the synthesis of the above alkylaminocyclodiphosph(111)azanes was the marked influence of geometrical isomerism on the physical and chemical properties of these compounds. Differences between isomers such as chemical reactivity and exocyclic P-N torsional barriers will be dealt with in separate chapters (3 and 5 respectively). Here, the emphasis will be on physical properties, especially those used to determine whether the 'low' or 'high-field' isomer is cis or trans as without such a structural determination many future conclusions become exceedingly tenuous. As the only pair of alkylaminocyclodiphosph(111)azane isomers which have been separated is that of $(Me_2NPNBu^t)_2$, most of the studies are on this compound.

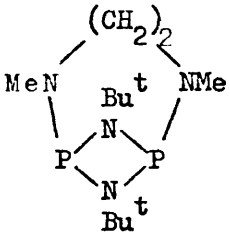
(a) Relative basicity measurements:- A convenient method of measuring relative base strengths is to compare the strength of the hydrogen bond formed between the base [in this case the cyclodiphosph(111)azane] and a reference acid. The extent of the interaction can be determined spectroscopically in one of two ways: by infrared spectroscopy [240,241] or nuclear magnetic resonance.[242,243] Deuteriochloroform is used as the

reference acid in infrared spectroscopy because the C-D stretch at 2252.3 cm^{-1} (liquid phase)[244] is free from other absorptions and it is useful in that it has only one site to which the base will complex. Chloroform itself is a convenient receptor acid in n.m.r.; the shift of the complexed proton being measured at infinite dilution in hexane relative to the free chloroform peak. Both methods indicated the 'low-field' isomer of $(Me_2NPNBu^t)_2$ to be the more basic (Table 6). Results for other alkylaminocyclodiphosph(111)azanes are also shown,[245] and generally they have similar basicities to $(Me_2NPNBu^t)_2$(δ_P 95.0 p.p.m.) and on this basis all 'high-field' isomers have the same geometrical configuration.

(b) Vibrational spectroscopy:- The i.r. spectra of alkylaminocyclodiphosph-(111)azanes tend to be complex, the most diagnostic band being the strong asymmetrical P-N vibration of the P-N-P group which usually occurs in the range 845-935 cm^{-1} [16,96,246-248] though the exact assignment of this vibration is still regarded as a matter of some uncertainty.[249] It can be seen (Table 6) that the cage compound (39) possesses a considerably smaller P-N-P stretching frequency than either of the two $(Me_2NPNBu^t)_2$ isomers, implying weaker P-N bonds in the ring possibly as a result of the cage being strained. $(Me_3SiNMe.PNBu^t)_2$ shows the smallest frequency (837 cm^{-1}), probably on account of the considerable steric interactions imposed by the bulky amino-groups. The isomeric forms of $(Me_2NPNBu^t)_2$ provide quite distinct i.r. spectra; that of the 'high-field' isomer being far more complex (see, for example, those bands quoted in Table 7). On a purely qualitative basis, this suggests this isomer is cis, as the trans isomer, being centrosymmetric, should have fewer i.r. active absorptions.

Table 6

Relative basicities and ν(P-N-P) asym. of alkylaminocyclodiphosph(III)azanes

Compound	δ_P [a]	$\Delta\nu$/cm^{-1} [b]	$\Delta\nu$/Hz [c]	ν(P-N-P)asym./cm^{-1} [d]
$(Me_2NPNBu^t)_2$	95.0	22	21	872,862
$(Me_2NPNBu^t)_2$	184.7	42	42	880
$(MeNH.PNBu^t)_2$	98.1	32	24.5	882
$(EtNH.PNBu^t)_2$	94.7	34	23.5	900,892
$(C_4H_8NPNBu^t)_2$	76.7	25	16	873
$(C_5H_{10}NPNBu^t)_2$	91.9	28	22	865,852
$(Me_3SiNMe.PNBu^t)_2$	89.9	[e]	[e]	837
	155.0	[e]	[e]	846

[a] Downfield shifts positive; relative to external 85% H_3PO_4.

[b] I.r. shift of ν(C-D) for $CDCl_3$ (0.04 M)/compound (1 M) mixture in hexane, relative to pure $CDCl_3$.

[c] ^1H n.m.r. chemical shift (60 MHz) of $CHCl_3$, 0.02 M in hexane relative to the same solution with compound added (0.5 M).

[d] In nujol.

[e] Not measured.

Table 7

Comparison of the i.r. [a] and Raman [b] active bands of $(Me_2NPNBu^t)_2$ in the range 600–900 cm^{-1}

'high-field' isomer		'low-field' isomer	
i.r./cm^{-1}	Raman/cm^{-1}	i.r./cm^{-1}	Raman/cm^{-1}
646	645		616
659		662	665
688	687		
792	798	797	810
862			
872		880	
897	(902)		

[a] In nujol. [b] Solid state.

It was hoped that a definite structural assignment could be made by comparing the i.r. and Raman spectra of both isomers of $(Me_2NPNBu^t)_2$, as the trans isomer should have i.r. and Raman spectra which show no coincidences. This technique had been successfully employed in distinguishing the isomeric forms of $[PhP(S)NEt]_2$.[95] Unfortunately, in this case the results were slightly ambiguous. However, the 'high-field' isomer possessed a greater number of coincidences within the 600–900 cm^{-1} range which should encompass all the ring vibrations[249] (Table 7), thus favouring a cis assignment to this form.

(c) Photoelectron spectroscopy:- The photoelectron spectra of both the cis and trans isomers of $(Me_2NPNBu^t)_2$ and the 'high-field' isomer of the dipiperidino-derivative $(C_5H_{10}NPNBu^t)_2$, were recorded. In all the spectra there is a broad mound above about 11 eV that is due to σ-bonding levels and from which no features can be reliably isolated. Table 8 (p.81) shows the groups of bands found below 11 eV, which are the result of nitrogen-phosphorus nonbonded electron-pair interactions which are difficult to assign in these complex systems.[169,170] What is clear is that the two dimethylamino-derivatives possess quite different spectra, and further, that as the spectrum of $(C_5H_{10}NPNBu^t)_2$ is almost identical to that of the 'high-field' $(Me_2NPNBu^t)_2$ isomer, it appears likely that the orbital pattern and geometry in both these isomers are very similar. The photoelectron spectra also reveal that the lowest energy bands are ca. 0.5 eV lower in binding energy in the 'low-field' relative to the 'high-field' isomers. This is consistent with the increased basicity of this isomer.

(d) Dipole moments:- Dipole moments have been used to distinguish cis and trans cyclodiphosph(v)azanes with some success[98] though the method has never been applied to the P(III) species. The dipole moments of the 'high-field' isomer of $(C_5H_{10}NPNBu^t)_2$ and both isomeric forms of $(Me_2NPNBu^t)_2$ were measured by dielectric constant and refractive index measurements on solutions of the compounds in benzene using the Debye theory.[250] The 'low-field' isomer of $(Me_2NPNBu^t)_2$ had a dipole moment of zero D implying it is centrosymmetric, ie. trans. Both the 'high-field' isomers of $(Me_2NPNBu^t)_2$ and $(C_5H_{10}NPNBu^t)_2$ had substantial dipole moments of 2.2 and 2.8 D respectively, implying cis structures. $(ClPNBu^t)_2$, of known cis configuration, had a dipole moment of 3.3 D.

Table 8

Compound		Photoelectron spectrum eV
$(Me_2NPNBu^t)_2$	('low-field' isomer)	7.1,7.5,8.5,10.0
$(Me_2NPNBu^t)_2$	('high-field' isomer)	7.5,8.2,8.8
$(C_5H_{10}NPNBu^t)_2$	('high-field' isomer)	7.5,8.3,8.7

(e) X-ray diffraction:- While dipole moments and, to a lesser extent, vibrational spectroscopy point to the 'high-field' isomers of the compounds studied as being cis, the evidence is not entirely conclusive. Why, for example, should $(Et_2NPNBu^t)_2$ exist exclusively as the cis isomer, with no evidence at all for the trans form which one would expect on steric grounds? In particular, it had recently been established that the 'high-field' isomer of $(MeOPNPh)_2$ possesses a trans structure.[251] In view of the need for a definite structural assignment to the above compounds, an X-ray analysis of the highly crystalline and relatively stable dipiperidino-derivative (δ_P 91.9 p.p.m.) was undertaken.[252] This revealed almost exactly C_2 molecular symmetry and that the piperidine rings are mutually cis with respect to the P_2N_2 ring (Figure 11). The cis configuration leads to cross-ring steric interactions between the piperidino-substituents [C(9)...C(14)=3.64 Å] which are relieved partly by opening of the P(1)-N(3)-C(9) and P(2)-N(4)-C(14) angles [respectively, 126.4(2) and 125.8(2)° compared with 118.2(2) and 118.6(2)° for P(1)-N(3)-C(13) and P(2)-N(4)-C(18)] and partly by twisting of the co-ordination planes of N(3) and N(4) so that they make dihedral angles of 100° with the

mean P_2N_2 ring plane. The sum of the angles at N(3) and N(4) is 357.6° in comparison with the 346.4° found for N(1) and N(2). Pronounced puckering of the ring is found; successive atoms lying ± 0.138 Å from the

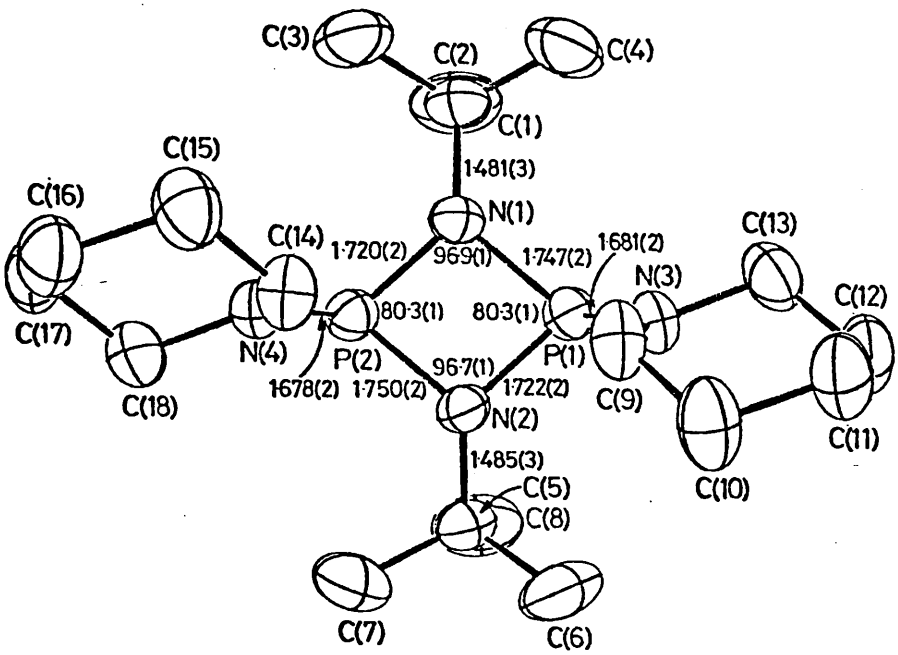
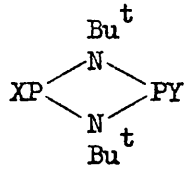


Figure 11 X-ray analysis data for cis-$(C_5H_{10}NPNBu^t)_2$ (reproduced by courtesy of the Chemical Society).

mean ring plane [cf. ± 0.045 Å in cis-$(ClPNBu^t)_2$[106] and the planer rings found in trans-cyclodiphosph(v)azanes[47,251]]. The P...P and N...N intramolecular distances are 2.59 and 2.24 Å respectively. Other novel features of the ring are that the P-N bond lengths are the longest yet observed for P(III)-N bonds, and they alternate in length significantly (Figure 11).

DISCUSSION

The presence of geometrical isomers in a variety of N-aryl and N-alkylcyclodiphosph(III)azanes has now been established. The crystal structure of $(C_5H_{10}NPNBu^t)_2$ (δ_P 91.9 p.p.m.) proves that this isomer has a cis structure, a result supported by dipole moment measurements and vibrational spectroscopy. The latter two methods, along with relative basicity measurements, photoelectron spectroscopy and trends in the exocyclic P-N torsional barriers and $^2J(PNP)$ coupling constants (Chapter 5) indicate that all 'high-field' isomers of (36) (X,Y=amino) are cis. Although evidence is weaker concerning the analogous N-aryl-derivatives, the magnitude of the torsional barriers about the P-NMe_2 bonds in both isomeric forms (Chapter 5) indicates again a cis structure for the 'high-field' isomer.

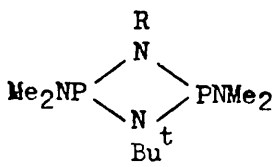


(36)

The fact that thermodynamically favoured cis isomers are produced on heating the trans isomers of (36) (X,Y= amino) is interesting in view of the adverse cross-ring steric effects in the former isomers. It is possible that these are overcome by a negative hyperconjugative ($n_P \rightarrow \sigma^*_{P-N}$) interaction, similar to that which determines the relative stabilities of azo-compounds.[178, 179] Twisting of the cyclodiphosph(III)azane ring in cis-$(C_5H_{10}NPNBu^t)_2$ may be to reduce destabilising interactions between the nitrogen and phosphorus lone-pairs as well as reducing steric interactions, although the latter could well be the dominant interactions here as trans-cyclodiphosph(III)azanes have planar rings.[47,251] Another puzzling point is why increasing the size of the amino-group in compounds (36) (X=Y) from NMe_2 to NEt_2 and $MeNSiMe_3$ or from MeNH to EtNH and Bu^tNH should result in no observation of the trans isomer. One might naively expect, again from steric considerations, that increasing the size of the amino-group

should decrease the stability of the cis relative to the trans structure, with a concomitant increase in the amount of trans isomer observed. One possible explanation is that the rate of isomerisation increases with the size of the amino-group. This could be true, especially if isomerisation is via the monomeric phosph(111)azenes, $XP{=}NBu^t$, which are known to be stabilised by bulky nitrogen substituents.[45] No evidence was obtained during isomerisation for the formation of monophosph(111)azenes which are best characterised by their low-field ^{31}P chemical shifts ($\delta P \sim 300$ p.p.m.) This argument also loses credence in that large amino-groups, while perhaps encouraging the formation of stabilised monomers, may consequently discourage their dimerisation back to the four-membered ring. The slow dimerisation over a period of years of $Me_3SiNMe.P{=}NBu^t$ to (36) ($X{=}Y{=}Me_3SiNMe$) is a case in point.[36] A ready answer to this problem is not forthcoming except that it probably involves a subtle interplay of electronic and steric effects which are not well understood. The N-aryl-derivatives behave as might be expected on steric grounds; a 1:1 mixture of isomers of $(Me_2NPNPh)_2$ is initially formed, whereas only the trans isomer of $(Et_2NPNPh)_2$ is observed.

An important difference between the compounds (11) (R=Me,Et, or Bu^t) and (35) (Y=H,Cl,Me, or OMe) is that



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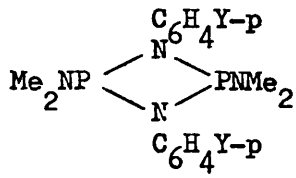


(35)

in the former cis isomers are thermodynamically favoured, whereas in the latter trans isomers are the more stable. It was found[22] that the stability of the trans isomer with respect to isomerisation in (11) (R=Me,Et, or Bu^t) increases with decreasing size of the alkyl-group. The sterically less

demanding aryl-groups in compounds (35) may well be one reason why trans isomers are favoured here. Further evidence of this is that mixtures of isomeric aminocyclodiphosph(III)azanes (40) can be obtained by heating the acyclic diphosphinoamines, $(Me_2N)_2P.NR.P(NMe_2)_2$ (R=Me or Et), in sealed tubes,[253]

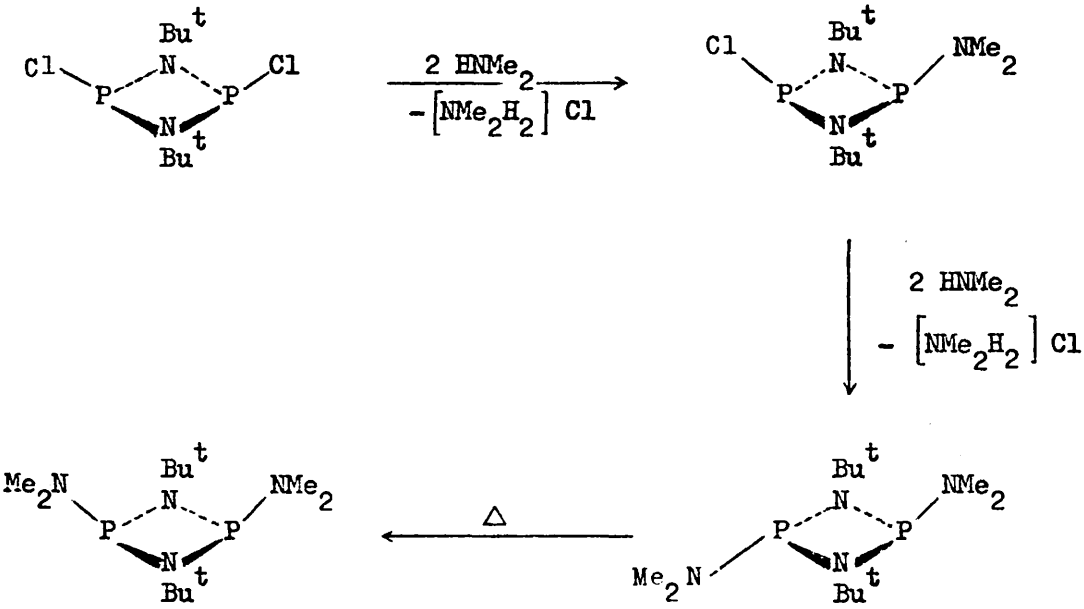
$$2\ (Me_2N)_2P.NR.P(NMe_2)_2 \longrightarrow Me_2NP\begin{<}{R \atop N}\end{>}PNMe_2 + 2\ (Me_2N)_3P.$$

(40) (R=Me or Et)

Both (40) (R=Me and Et) were obtained as 1:1 mixtures of isomers, but crystallisation of the methyl compound converted it almost exclusively to the trans form.[253] In addition, Zeiss and co-workers recently discovered[38] that in compounds of the type $(XPNSiMe_3)_2$ $[X=NMe_2, N(CH_2)_4$ or $N(CH_2)_5]$ the trans isomer is again favoured. This might arise from the long N-Si bond reducing the steric interactions associated with the bulky trimethylsilyl-groups.

Since dimethylaminolysis of cis-$(ClPNBu^t)_2$ initially produces almost exclusively trans-$(Me_2NPNBu^t)_2$ under low-temperature work up conditions (traces of the other isomer are assumed to arise through isomerisation during the reaction time), the reaction is probably a two step procedure involving both retention and inversion of configuration at phosphorus. This is in contrast to the inversion of configuration at phosphorus found on nucleophilic displacement of chlorine by amino-groups in phosphetans[254] but similar to the oxidation of cis-$(ClPNBu^t)_2$ by dimethyl sulphoxide to trans-$[Cl(O)PNBu^t]_2$.[62] Assignment of configuration to the monodimethylamino-derivative, $Me_2NP.NBu^t.PCl.NBu^t$, is made slightly

difficult as only one isomer with an intermediate $\underline{P}NMe_2$ chemical shift (δ_P 131.5 p.p.m.) is formed. The $^2J(\underline{P}N\underline{P})$ coupling constant of +32.5 Hz, however, is a good indication that this compound is cis (Chapter 5). This being the case, the nucleophilic displacement of the first chlorine atom must be with retention of configuration (assuming no rapid isomerisation has occurred); displacement of the second occurring with inversion of configuration at phosphorus.



Since the thermodynamically unstable cis-$(Me_2NPNPh)_2$ is produced in the dimethylaminolysis of $(ClPNPh)_2$ this could imply a different, or less stereospecific, mechanism operates here, but as the geometric configuration of $(ClPNPh)_2$ is unknown, it is unwise to infer too much from this.

Basicity measurements (Table 6) reveal the trans-derivatives of (36) (X=Y=amino) are more basic than the cis. Reasons for this are unclear as the hydrogen-bonding could occur at one of three sites in the cyclodiphosph(III)azane ring, viz. the phosphorus or the endo- or exocyclic nitrogen atoms. However, these results do parallel those obtained by

photoelectron spectroscopy (Table 8) which reveal that the lowest energy bands are ca. 0.5 eV lower in energy in the trans relative to the cis isomers, which is consistent with greater phosphorus-nitrogen nonbonded electron-pair interactions in the former isomer. I.r. spectroscopy (Table 6) indicates that in a given pair of alkylaminocyclodiphosph(III)-azane isomers the cis isomer has the smaller asymmetric P-N ring vibrational energy. This is as expected where strong steric interactions obtain, causing puckering of the ring and long endocyclic P-N bond lengths [1.721(2) and 1.749(2) Å in cis - $(C_5H_{10}NPNBu^t)_2$]. On the other hand, were a substantial $np \rightarrow \sigma^*_{P-N}$ bonding interaction present, one might have expected the endocyclic P-N bonds in the cis isomer to be the stronger, associated with a ν(P-N-P)asym. at higher frequency than is found.

The crystal structure of cis-$(C_5H_{10}NPNBu^t)_2$ showed the piperidino-groups lie close to the mirror plane passing through the phosphorus atoms and bisecting the P_2N_2 ring. By making use of the conformational dependence of $^3J(\underline{P}NC\underline{H})$[22,159,198,225] and $^2J(\underline{P}N\underline{C})$[224,225] it is found that a similar conformation holds for the cis isomers, $(Me_3SiNMe.PNBu^t)_2$, $Me_2\overline{NP.NBu^t.PX.NBu^t}$ (X=F or Cl), $(Pr^i)_2\overline{NP.NBu^t.PCl.NBu^t}$, and trans-$(Me_2NPNBu^t)_2$ (Tables 10 and 11). For example, the relatively small couplings to the N-methyl protons and carbon atom of ca. 4.8 and 3.6 Hz respectively in cis-$(Me_3SiNMe.PNBu^t)_2$ and the quite large $^4J(\underline{P}NSiC\underline{H})$ and $^3J(\underline{P}NSi\underline{C})$ couplings (ca. 2.1 and 11.7 Hz respectively) imply[225] a conformation in which the plane containing the amino-group is approximately perpendicular to the plane of the cyclodiphosph(III)azane ring with the N-methyl-group trans to the phosphorus lone-pair (Figure 12).

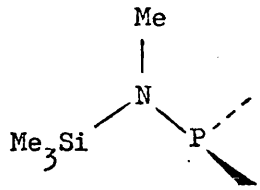


Figure 12. The preferred conformation of the trimethylsilyl(methyl)amino-group in cis-$(Me_3SiNMe.PNBu^t)_2$

Similar conformations hold for the other compounds and these agree with the conformations found by Bulloch[22] for cis-(11) (R=Me or Bu^t). The cage compound, (39), which is restrained to a conformation in which the N-methyl and N-methylene-groups are mutually cis and trans respectively to the phosphorus lone-pair, also illustrates the angular dependence of $^3J(PNCH)$ and $^2J(PNC)$ (Tables 10 and 11).

It is still very difficult to explain the large ^{31}P chemical shift differences found between pairs of isomers. Bulloch[22] proposed that this may be related to conformational changes about the exocyclic groups. However, the X-ray analysis of cis-$(C_5H_{10}NPNBu^t)_2$ and the ^1H and ^{13}C n.m.r. data as discussed above for cis and trans-dialkylaminocyclodiphosph(111)-azanes indicate that in both geometrical forms the preferred conformation is roughly the same; in every case being one in which the dialkylamino-group lies in, or close to, the mirror plane passing through the phosphorus atoms which bisects the ring. Perhaps it is the rotamer populations which affect the ^{31}P chemical shifts. In trans isomers the dialkylamino-group may spend most of its time in the preferred conformation, whereas in the cis isomer, although the preferred conformation is the same, the populations of other rotamers may be increased as a result of the enhanced steric interactions of the cis configuration. There may be an element of truth in this for in the sterically rigid cage molecule, (39), which must be cis, a quite 'low-field' ^{31}P chemical shift (155.0 p.p.m.) is observed. Another effect which might be considered is conformational changes

within the ring itself and that ring puckering, as found in the cis isomers, in some way causes an upfield shift. This is unlikely to be significant, though, as the cage compound, (39), probably possesses a fairly puckered ring [ν(P-N-P)asym., 846 cm^{-1}], as does cis-$(ClPNBu^t)_2$[106] (δ_P 207.3 p.p.m.). Whatever it is that causes these dramatic changes in the ^{31}P chemical shift, it would appear to be intrinsically involved with the exocyclic nitrogen atom and the presence of a lone-pair on each phosphorus atom [alkylaminocyclodiphosph(v)azanes and their mixed oxidation state analogues generally have ^{31}P chemical shifts which differ between isomers by less than 20 p.p.m., eg. ref. 38].

EXPERIMENTAL

Methods used in the purification and drying of solvents and reagents can be found in Appendix A. Instruments used in the recording of i.r., Raman, photoelectron, n.m.r. (Tables 9, 10 and 11) and mass (Table 12) spectroscopic data, plus the source of microanalyses (Table 12) along with instruments used in the measurement of dipole moments and collection of X-ray diffraction data can be found in Appendix B. The compounds, $(ClPNBu^t)_2$,[17] cis-$(Me_2NPNBu^t)_2$,[22] $(Et_2NPNBu^t)_2$,[22] $(Bu^tNH.PNBu^t)_2$,[19] $Me_2NP(NBu^t).PCl.NBu^t$,[22] $(Me_3Si)_2NMe$,[255] $(Cl_2P)_2NC_6H_4Y$-p (Y=H,Cl,Me or OMe),[15] and $(ClPNC_6H_4Y$-p$)_2$ (Y=H,Cl or OMe)[15] were prepared by slightly modified literature methods. Other preparative details are outlined below.

2,4-Bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane:- Dimethylamine (5.6 g, 120 mmol) was added to a stirred suspension of 2,4-dichloro-1,3-diphenylcyclodiphosph(III)azane (9.9 g, 31 mmol) in methylene chloride (20 cm^3) at -78°C. The solution was stirred (0.5 h), brought to ambient temperature, and diethyl ether (30 cm^3) was added. The precipitate was removed and evaporation of the solvent left a white solid. Recrystallisation

from methylene chloride–light petroleum (b.p. 40–60°C) (1:2) gave 2,4-bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (crude yield 5.6 g, 54%) as colourless, moisture-sensitive needles, m.p. 125–127°C (lit.,[15] 188,206–208°C?).

1,3-Bis-(4-chlorophenyl)-2,4-bis(dimethylamino)cyclodiphosph(III)azane:- Dimethylamine (2.4 g, 53 mmol) and 2,4-dichloro-1,3-bis-(4-chlorophenyl)-cyclodiphosph(III)azane (5.0 g, 13 mmol) in methylene chloride (30 cm^3) at -78°C on similar treatment to the above, gave the compound (4.5 g, 86%) as colourless prisms, m.p. 117–118°C.

2,4-Bis(dimethylamino)-1,3-bis-(4-methylphenyl)cyclodiphosph(III)azane:- Dimethylamine (3.6 g, 80 mmol) and 2,4-dichloro-1,3-bis-(4-methylphenyl)-cyclodiphosph(III)azane (6.9 g, 20 mmol) in diethyl ether (30 cm^3) at -78°C on similar treatment to the above, gave the compound (6.2 g, 86%) as colourless needles, m.p. 111–113°C.

1,3-Bis-(4-methoxyphenyl)-2,4-bis(dimethylamino)cyclodiphosph(III)azane:- Dimethylamine (11.3 g, 251 mmol) and bis(dichlorophosphino)-(4-methoxyphenyl)-amine (10.0 g, 31 mmol) in diethyl ether (30 cm^3) at -78°C on similar treatment to the above and with careful removal of tris(dimethylamino)-phosphine, gave the compound (7.8 g, 65%) as colourless needles, m.p. 112°C.

2,4-Bis(diethylamino)-1,3-diphenylcyclodiphosph(III)azane:- Diethylamine (8.8 g, 121 mmol) and 2,4-dichloro-1,3-diphenylcyclodiphosph(III)azane (9.5 g, 30 mmol) in methylene chloride (20 cm^3) at 20°C on similar treatment to the above, gave the compound (6.8 g, 58%) as colourless plates, m.p. 104–105°C.

2-Chloro-4-dimethylamino-1,3-diphenylcyclodiphosph(III)azane:- Dimethylamine (2.9 g, 64 mmol) and 2,4-dichloro-1,3-diphenylcyclodiphosph-(III)azane (10.1 g, 32 mmol) in a mixture of methylene chloride (10 cm^3) and diethyl ether (30 cm^3) at -78° C on similar treatment to the above, gave the compound (9.2 g, 89%) as colourless needles, m.p. 84°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)cyclodiphosph(111)azane:- 1,3-Di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (10.9 g, 40 mmol) was mixed with dimethylamine (7.2 g, 160 mmol) in diethyl ether (500 cm^3) at -78°C. The solution was brought to ambient temperatures and stirred (1 h). The dimethylamine hydrochloride was removed by filtration and the solvent carefully evaporated under reduced pressure at or below room temperature. The white solid produced (10.8 g, 92%) was shown (^1H n.m.r.) to consist of a (9:1) (trans:cis) mixture of isomers. Repeated recrystallisation of this solid from pentane gave the compound (4.3 g, 37%) as colourless crystals, m.p. 114-116°C. Distillation under reduced pressure of the oily residues gave the cis isomer (5.2 g, 45%) as a clear viscous liquid, b.p. 85-90°C (0.1 mmHg), which crystallised on standing, m.p. 38-40°C.

Attempted preparation of 1,3-di-t-butyl-2-methylamino-4-dimethylaminocyclodiphosph(111)azane:- To a rapidly stirred solution of 1,3-di-t-butyl-2-chloro-4-dimethylaminocyclodiphosph(111)azane (4.45 g, 15.7 mmol) in diethyl ether (100 cm^3) at ambient temperatures was slowly bubbled an excess of (0.97 g, 31.4 mmol) methylamine. Removal of the methylamine hydrochloride and solvent left a colourless oil which was shown by ^1H n.m.r. to consist of a 1:1 mixture of isomers. Isomerisation to the cis isomer was complete after ca. 1 h at 33°C (0.1 M solution in deuteriochloroform). Vacuum distillation of the oil gave a clear colourless liquid (3.0 g), b.p. 62-65 °C (0.06 mmHg), which analysed for the compound (Table 12), but was shown (^{31}P n.m.r.) to consist of a mixture of the compound, 1,3-di-t-butyl-2,4-bis(dimethylamino)cyclodiphosph(111)azane, and 1,3-di-t-butyl-2,4,-bis(methylamino)cyclodiphosph(111)azane (all cis isomers) in a 6:1:1 ratio respectively.

1,3-Di-t-butyl-2-fluoro-4-dimethylaminocyclodiphosph(111)azane:- 1,3-di-t-butyl-2-chloro-4-dimethylaminocyclodiphosph(111)azane (2.97 g, 10.5 mmol) in pentane (20 cm^3) was stirred with anhydrous antimony trifluoride (3.46 g, 19.3 mmol) at ambient temperatures for 12 h. The dark coloured solid and the solvent were removed to leave a colourless oil which was purified by distillation under reduced pressure to give the compound (1.4 g, 50%), b.p. 62°C (1.2 mmHg).

1,3-Di-t-butyl-2-chloro-4-di-isopropylaminocyclodiphosph(111)azane:- 1,3 -di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (3.5 g, 12.7 mmol) in benzene (40 cm^3) was mixed with di-isopropylamine (7.7 g, 76.2 mmol) and sealed in a thick-walled glass tube. The tube was heated (18 h) at 130°C. Di-isopropylamine hydrochloride (1.6 g, 11.6 mmol) was removed and the filtrate was evaporated to dryness. The residue was extracted with hot light petroleum (25 cm^3, b.p. 40-60°C) to give a white solid, which on crystallisation from benzene gave the compound (3.6 g, 86%), m.p. 162°C. There was no evidence to suggest the formation of any 1,3-di-t-butyl-2,4-bis(di-isopropylamino)cyclodiphosph(111)azane. A further experiment in which the above mono(di-isopropylamino)-derivative was heated with excess di-isopropylamine in a sealed tube at 175°C for 11 d led to extensive decomposition of the starting material.

1,3 -Di-t-butyl-2,4-bis [(trimethylsilyl)(methyl)amino] cyclodiphosph(111)-azane:- Heptamethyldisilazane (5.95 g, 34.0 mmol) and 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (4.67 g, 17.0 mmol) were refluxed with rapid stirring in benzene (20 cm^3) for 7 d. Removal of the solvent and trimethylchlorosilane left a light brown solid which on crystallisation from pentane gave the compound (2.1 g, 30%), m.p. 123-124°C.

1,3-Di-t-butyl-2,4-bis(methylamino)cyclodiphosph(111)azane:- To a rapidly stirred solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (6.3 g, 23 mmol) in diethyl ether (150 cm^3) at 20°C was slowly bubbled an excess of (2.9 g, 94 mmol) methylamine. Removal of the methylamine hydrochloride and solvent left a white solid which ^1H n.m.r. showed to consist of a 3:2 (cis:trans) mixture of isomers. Isomerisation to the cis isomer was rapid (ca. 20 min at 33°C in deuteriochloroform solution). The solid was melted and distilled under reduced pressure to give the compound (3.9 g, 64%), a colourless oil, b.p. 88°C (0.01 mmHg) which crystallised on standing, m.p. 39-42°C.

1,3-Di-t-butyl-2,4-bis(ethylamino)cyclodiphosph(111)azane:- Ethylamine (2.6 g, 58 mmol) in diethyl ether (20 cm^3) was mixed with 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (4.0 g, 14.5 mmol) in diethyl ether (100 cm^3) at -78°C. The reaction mixture was brought to ambient temperatures after 0.5 h and the ethylamine hydrochloride and solvent removed to produce a white solid which was readily crystallised from light petroleum (b.p. 40-60°C) yielding the compound (3.2 g, 76%) as colourless crystals, m.p. 91°C. ^1H n.m.r. indicated the presence of one isomer (cis) both during and after work up.

1,3-Di-t-butyl-2,4-dipiperidinocyclodiphosph(111)azane:- To a rapidly stirred solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (6.0 g, 21.8 mmol) in diethyl ether (300 cm^3) at 0°C was slowly added dropwise a solution of piperidine (7.4 g, 87.1 mmol) in diethyl ether (100 cm^3). The mixture was allowed to warm to ambient temperatures and on work up produced a white solid (cis:trans ca. 20:1) which on crystallisation from light petroleum (b.p. 40-60°C) afforded the pure compound (4.1 g, 50%) (cis:trans, 1:0) as colourless crystals, m.p. 97-98°C.

1,3-Di-t-butyl-2,4-dipyrrolidinocyclodiphosph(111)azane:- As above, 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (2.95 g, 10.7 mmol) in diethyl ether (150 cm^3) was mixed with pyrrolidine (3.04 g, 42.8 mmol) in diethyl ether (50 cm^3) at 0°C. After warming to ambient temperatures, the solution was filtered and the solvent removed yielding a white solid (cis:trans ca. 10:1) which on crystallisation from light petroleum (b.p. 40-60°C) afforded the pure compound (2.2 g, 60%) (cis:trans, 1:0) as white plates (colourless in solution), m.p. 107-108°C.

1,3-Di-t-butyl-2,4-dimorpholinocyclodiphosph(111)azane:- 1,3-Di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (5.10 g, 18.5 mmol) in light petroleum (100 cm^3, b.p. 40-60°C) was mixed with a solution of morpholine (3.22 g, 37.0 mmol) and triethylamine (3.74 g, 37.0 mmol) in light petroleum (50 cm^3, b.p. 40-60°C) at 0°C. The mixture was allowed to come to ambient temperatures, stirred for 0.5 h, and the solvent and triethylamine hydrochloride removed to yield a white solid (6.0 g) which $^1H\{^{31}P\}$ n.m.r. showed to consist mainly of a 1:1 mixture of products (δ_P 75.5 and 94.8 p.p.m.) Crystallisation of the crude product from pentane afforded the pure compound (0.6 g, 9%) (δ_P 94.8 p.p.m.) as colourless needles, m.p. 155-157°C. On heating in benzene solution (75°C for 5 d), the compound was almost quantitively converted to the impurity [$\delta_{P(111)}$ 75.5 p.p.m.] which was tentatively identified by mass spectroscopy as 1,3,-di-t-butyl-2-morpholino-4-oxocyclodiphosphazane; found $^m/_e$ 307, calc. $^m/_e$ 307.

7,8,-Di-t-butyl-2,5-dimethyl-2,5,7,8-tetraaza-1,6-diphospha(111)bicyclo-[4.1.1]octane:- A solution of N,N´-dimethylethylenediamine (2.75 g, 31.2 mmol) in diethyl ether (30 cm^3) was slowly added with stirring at ambient temperatures to a solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)-

azane (4.30 g, 15.6 mmol) in diethyl ether (120 cm^3). The precipitate and solvent were removed to leave a colourless oil which was purified by distillation under reduced pressure to give the compound (0.90 g, 20%), b.p. 73°C (0.1 mmHg). The distillation residue, a very viscous intractable oil, appeared to consist (^1H n.m.r.) solely of polymeric material. Yields of the compound were dramatically reduced (< 5%) when triethylamine was used as hydrogen chloride acceptor.

No bicyclic compound of the above type was isolated in a similar reaction of N,N′-dimethyltrimethylenediamine with 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(III)azane.

Table 9

Phosphorus chemical shifts of $(Cl_2P)_2NR$ and $(ClPNR)_2$ (R=alkyl or aryl) [a]

Compound	δ_P [b] p.p.m.
$(Cl_2P)_2NMe$	160.8
$(Cl_2P)_2NEt$	162.5
$(Cl_2P)_2NBu^t$	169.1
$(Cl_2P)_2NPh$	155.3
$(Cl_2P)_2NC_6H_4Cl$-p	155.0
$(Cl_2P)_2NC_6H_4Me$-p	157.3 [c]
$(Cl_2P)_2NC_6H_4OMe$-p	157.7
$(ClPNEt)_2$	227.3
$(ClPNBu^t)_2$	207.3
$(ClPNPh)_2$	202.5
$(ClPNC_6H_4Cl$-p$)_2$	202.4
$(ClPNC_6H_4Me$-p$)_2$	203.2

[a] At ambient temperatures in $CDCl_3$ solutions unless stated otherwise.

[b] Downfield shifts are positive; relative to external 85% H_3PO_4.

[c] PCl_3 solution.

Table 10

Phosphorus - 31 and ^{1}H n.m.r. data for aminocyclodiphosph(III)azanes [a]

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{PNCH} p.p.m.	$^{3}J(PNCH)$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCCH)$ Hz
cis-$(Me_2NPNPh)_2$	101.0	>0 [d]	2.87	8.7		
trans-$(Me_2NPNPh)_2$	166.5	<0 [d]	2.78	8.4		
cis-$(Me_2NPNC_6H_4Cl\text{-}p)_2$	100.8	[e]	2.88	8.5		
trans-$(Me_2NPNC_6H_4Cl\text{-}p)_2$	166.1	[e]	2.83	8.5		
trans-$(Me_2NPNC_6H_4Me\text{-}p)_2$	166.8	[e]	2.86	8.5		
cis-$(Me_2NPNC_6H_4OMe\text{-}p)_2$	101.5	[e]	2.88	8.9		
trans-$(Me_2NPNC_6H_4OMe\text{-}p)_2$	168.9	[e]	2.83	8.6		
trans-$(Et_2NPNPh)_2$	162.2	[e]	3.28	8.0	1.05(Et)	<0.5(Et)

Table 10 cont'd

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{PNCH} p.p.m.	$^{3}J(PNCH)$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCCH)$ Hz
cis-$Me_2NP.NPh.PCl.NPh$	136.3	e	2.91	9.0		
	178.6(P**Cl**)					
cis-$(Me_2NPNBu^t)_2$	95.0	+14 ± 5 [d]	2.66	8.0	1.17	<0.3
trans-$(Me_2NPNBu^t)_2$	184.7	-10 ± 5 [d]	2.74 [f]	12.2	1.13	0.8
			2.63	3.2		
cis-$(Et_2NPNBu^t)_2$	91.3	e	3.17	8.0	1.20	<0.3
					1.05(Et)	<0.5(Et)
cis-$Me_2NP.NBu^t.P(NHMe).NBu^t$	99.2	g	2.57	8.0	1.19	ca. 0.3

Table 10 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
trans-$Me_2NP(NBu^t).P(NHMe).NBu^t$	170.7	10 ± 2	e	e	1.13	ca.0.6
	184.3($PNMe_2$)		e			
cis-$Me_2NP(NBu^t).PF.NBu^t$	116.3[i]	+ 14.0	2.70 [f,j]	13.7 [j]	1.24	0.5
	145.9(PF)		2.55	2.8		0.3(PF)
cis-$Me_2NP(NBu^t).PCl.NBu^t$	131.5	+ 32.5	2.80 [f]	12.6	1.29	0.5
	186.6(PCl)		2.80	4.1		0.7(PCl)
cis-$Pr^i_2NP(NBu^t).PCl.NBu^t$	114.5	30 ± 2	4.30 [f,k]	ca. 15	1.37	0.6(both)

Table 10 cont'd

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{PNCH} p.p.m.	$^{3}J(PNCH)$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCCH)$ Hz
	184.0(PCl)		3.08	2.5	0.94 $[CH(CH_3)_2]$ [f]	<0.3
					1.20	<0.5
cis-$(Me_3SiNMe.PNBu^t)_2$	89.9	e,l	2.67	4.8	1.24	ca. 0.3
					0.19($SiMe_3$)	2.1 [m]
cis-$(MeNH.PNBu^t)_2$	98.1	e	2.61	10.3	1.26	ca. 0.3
trans-$(MeNH.PNBu^t)_2$	172.4	e	e	e	1.22	ca. 0.8
cis-$(EtNH.PNBu^t)_2$	94.7	e	2.98	6.4	1.26	ca. 0.5
					1.10(Et)	0(Et)

Table 10 cont'd

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{PNCH} p.p.m.	$^{3}J(PNCH)$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCCH)$ Hz
cis-$(Bu^tNH.PNBu^t)_2$	89.4	e	2.75(NH) [n]	9.8(NH) [n]	1.27	0.4
					1.25($NHBu^t$)	1.2($NHBu^t$)
cis-$(C_5H_{10}NPNBu^t)_2$	91.9	e	3.13	5.0 ± 1 [o]	1.20	ca. 0.3
trans-$(C_5H_{10}NPNBu^t)_2$	182.3	e	e	e	1.15	0.9
cis-$(C_4H_8NPNBu^t)_2$	76.7	e	3.26	e	1.21	ca 0.3
trans-$(C_4H_8NPNBu^t)_2$	165.1	e	e	e	1.14	0.9
cis-$(OC_4H_8NPNBu^t)_2$	94.8	e	3.17	e	1.24	ca. 0.3

Table 10 cont'd

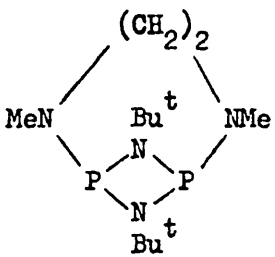
Compound	^{31}P		^{1}H				
	δ_P [b] p.p.m.	$^{2}J(\underline{P}N\underline{P})$ Hz	$\delta_{PNC\underline{H}}$ p.p.m.	$^{3}J(\underline{P}NC\underline{H})$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCC\underline{H})$ Hz
	155.0	[e]	3.61 [p] 3.12 2.69(N<u>Me</u>)	 5.6 13.8	1.19	0.5

Table 10 cont'd

a At ambient temperatures in $CDCl_3$ solution (no reaction), except where otherwise stated.

b Downfield shifts are positive; relative to external 85% H_3PO_4.

c More correctly, $|^3J(\underline{P}N\underline{C}H) + {}^5J(\underline{P}N\underline{P}N\underline{C}H)|$ for symmetrical aminocyclodiphosph(lll)azanes

d From $^1H-\{^{31}P\}$ INDOR experiments (see Chapter 5).

e Not measured.

f Restricted rotation about exocyclic P-N bond.

g One signal only.

h Signal broad.

i Fluorine-19 n.m.r. data; $\delta_{\underline{F}}$ -17.8 p.p.m. (upfield, relative to external CCl_3F); $^1J(\underline{P}\underline{F})$ -1,149 ± 1 Hz; $^3J(\underline{P}N\underline{P}\underline{F})$ -14.9 ± 0.5 Hz

j Chlorobenzene solution at -15°C.

k Chlorobenzene solution.

l Signal broad, line half-width ca.12 Hz; $^2J(\underline{P}N\underline{S}i) < 50$ Hz.

m $|^4J(\underline{P}NSi\underline{C}H) + {}^6J(\underline{P}NPNSi\underline{C}H)|$.

n At -55°C.

o Measured by $^1H-\{^1H\}$ double-resonance.

p $\delta_{PNCC\underline{H}}$.

Table 11

Carbon -13 n.m.r. data [a]

Compound	$\delta_{PN(endo)C}$ p.p.m.	$^2J(PNC)$ Hz	$\delta_{PN(endo)CC}$ p.p.m.	$^3J(PNCC)$ Hz	$\delta_{PN(exo)C}$ p.p.m.	$^2J(PNC)$ [b] Hz	$\delta_{PN(exo)CC}$ p.p.m.	$^3J(PNCC)$ [c] Hz
cis-$(ClPNBu^t)_2$	54.2	6.75	30.3	6.25				
cis-$Me_2NP(NBu^t).PCl.NBu^t$	52.3	9.0	30.6	6.3	38.3 [d]	±49.4		
					35.1	∓10.1		
cis-$(Me_2NPNBu^t)_2$	50.6	14.0	30.6	6.5	35.4	20.2		
trans-$(Me_2NPNBu^t)_2$	49.8	6.1	30.2	5.8	37.2 [d]	±49.3		
					33.6	∓ 6.2		
cis-$(Et_2NPNBu^t)_2$	51.5	15.0	30.8	6.9	ca. 38 [e]	[e]	15.0	0
					38.4 [f]	21.5		
cis-$(Me_3SiNMe.PNBu^t)_2$	51.7	14.8	30.7	6.6	25.5	3.6	0.3 [g]	11.7 [h]

Table 11 cont'd

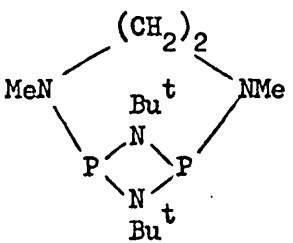
Compound	$\delta_{PN(endo)C}$ p.p.m.	$^2J(PNC)$ Hz	$\delta_{PN(endo)CC}$ p.p.m.	$^3J(PNCC)$ Hz	$\delta_{PN(exo)C}$ p.p.m.	$^2J(PNC)$[b] Hz	$\delta_{PN(exo)CC}$ p.p.m.	$^3J(PNCC)$[c] Hz
cis-$(MeNH.PNBu^t)_2$	50.8	13.5	30.9	6.5	25.1	10.3		
cis-$(EtNH.PNBu^t)_2$	51.2	13.55	31.0	6.75	34.0	11.8	18.5[i]	3.3
cis-$(C_5H_{10}NPNBu^t)_2$	50.8	14.4	31.0	6.5	44.8	18.4	27.0	>0
cis-$(C_4H_8NPNBu^t)_2$	50.6	14.2	30.6	6.5	44.9	15.2	26.3	3.2
	49.9	11.95	30.3	6.1	38.0	37.6[i]		
					52.3(NCH_2)	8.1		

Table 11 cont'd

a At ambient temperatures in $CDCl_3$ solution, except where stated otherwise.

b More correctly, $|^2J(\underline{P}N\underline{C}) + {}^4J(\underline{P}NP\underline{N}\underline{C})|$ for symmetrical aminocyclodiphosph(111)azanes.

c More correctly, $|^3J(\underline{P}N\underline{C}\underline{C}) + {}^5J(\underline{P}NP\underline{N}\underline{C}\underline{C})|$ for symmetrical aminocyclodiphosph(111)azanes.

d Restricted rotation about exocyclic P-N bond.

e Coalescence of signals at ambient temperatures; coupling constant not measurable.

f Measured at 60°C.

g $\delta_{PN(exo)Si\underline{C}}$.

h $|^3J(\underline{P}NSi\underline{C}) + {}^5J(\underline{P}NP\underline{N}Si\underline{C})|$.

i $\delta_{PN(exo)C\underline{C}\underline{C}}$, 25.5 p.p.m.; $^4J(\underline{P}NC\underline{C}\underline{C})$, 0 Hz.

j $|^2J(\underline{P}N\underline{C}) + {}^4J(\underline{P}NP\underline{N}\underline{C})|$ = 40.9 Hz, if $^2J(\underline{P}N\underline{C})$ and $^4J(\underline{P}NP\underline{N}\underline{C})$ of opposite sign.

Table 12

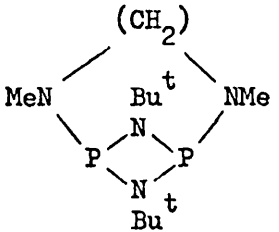
Analytical data [a]

Compound	Found C	Found H	Found N	Found m/e [b]	Calc. C	Calc. H	Calc. N	Calc. m/e
trans-$(Me_2NPNPh)_2$	58.1	6.5	16.6	332	57.8	6.6	16.9	332
trans-$(Me_2NPNC_6H_4Cl\text{-}p)_2$	48.1	4.9	14.1	400(427)	47.9	5.0	14.0	400 (401)
trans-$(Me_2NPNC_6H_4Me\text{-}p)_2$	59.1	7.1	15.7	360	60.0	7.2	15.6	360
trans-$(Me_2NPNC_6H_4OMe\text{-}p)_2$	55.1	6.7	14.3	392	55.1	6.6	14.3	392
trans-$(Et_2NPNPh)_2$	61.7	7.6	14.85	388	61.9	7.7	14.4	388
cis-$Me_2NP.NPh.PCl.NPh$	52.1	5.1	13.45	323	51.9	4.9	13.0	323
trans-$(Me_2NPNBu^t)_2$	49.4	10.3	19.0	292	49.3	10.3	19.2	292
cis-$(Me_2NPNBu^t)_2$	49.4	10.7	19.0	292(291)	49.3	10.3	19.2	292
cis-$Me_2NP.NBu^t.P(NHMe).NBu^t$ [c]	47.5	10.2	20.0	278	47.5	10.1	20.1	278

Table 12 cont'd

Compound	Found				Calc.			
	C	H	N	m/e [b]	C	H	N	m/e
cis-$Me_2NP.NBu^t.PF.NBu^t$	44.6	9.0	15.45	267	44.9	9.0	15.7	267
cis-$Pr^i_2NP.NBu^t.PCl.NBu^t$	49.2	9.9	12.3	339	49.5	9.4	12.4	339
cis-$(Me_3SiNMe.PNBu^t)_2$	46.9	10.3	13.9	408	47.1	10.3	13.7	408
cis-$(MeNH.PNBu^t)_2$	45.2	9.85	21.0	264	45.45	9.85	21.2	264
cis-$(EtNH.PNBu^t)_2$	49.3	10.3	19.0	292	49.3	10.3	19.2	292
cis-$(Bu^tNH.PNBu^t)_2$	55.3	11.1	16.4	348	55.2	10.9	16.1	348
cis-$(C_5H_{10}NPNBu^t)_2$	58.1	10.3	15.2	372	58.1	10.2	15.05	372
cis-$(C_4H_8NPNBu^t)_2$	56.0	9.85	16.2	344	55.8	9.9	16.3	344
cis-$(OC_4H_8NPNBu^t)_2$	50.9	9.3	14.7	376	51.1	9.0	14.9	376

Table 12 cont'd

Compound	Found C	Found H	Found N	Found m/e[b]	Calc. C	Calc. H	Calc. N	Calc. m/e
	49.3	9.8	19.5	290	49.7	9.7	19.3	290

[a] Elemental analyses figures are given in %.

[b] m/e for ^{35}Cl - containing species. Values in parentheses are molecular weights obtained by osmometry in benzene solution.

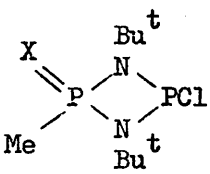
[c] Mixture with cis-$(Me_2NPNBu^t)_2$ and cis-$(MeNH.PNBu^t)_2$ (see text).

CHAPTER 3

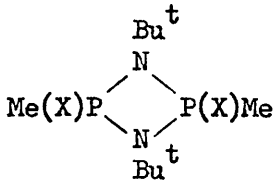
PRODUCTS OF THE OXIDATION OF AMINOCYCLODIPHOSPH(111)AZANES

INTRODUCTION

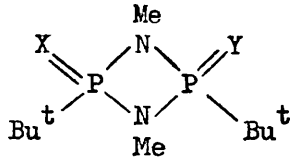
The controlled oxidation and sulphuration of cyclodiphosph(111)azanes was first reported[17] in 1973. This was the formation of $\overline{ClP.NR.P(X)Cl.NR}$ and $[Cl(X)PNR]_2$ (R=Pr^i or Bu^t, X=O or S) from the action of one or two molar equivalents, respectively, of dimethyl sulphoxide or sulphur on $(ClPNR)_2$ (R=Pr^i or Bu^t). More recently, oxidation has been effected by t-butylhydroperoxide [48] and elemental oxygen,[38] whereas sulphuration by elemental sulphur has remained the most convenient route to the mono- and dithiocyclodiphosphazanes.[20,22,34,38,48,51,63,64] There are no reports to date on the action of selenium or tellurium on alkylaminocyclodiphosph(111)azanes, though very recently the compounds (15), (16), and (17) have been isolated.[48,65]



(15) (X=Se or Te)



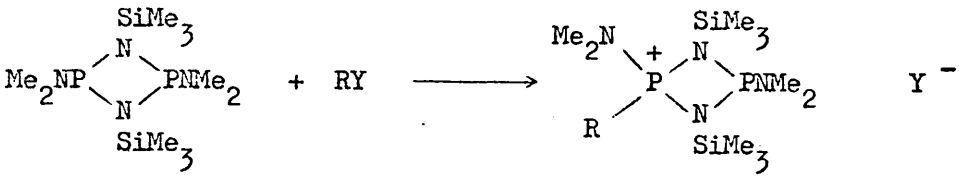
(16) (X=Se or Te)



(17) (X=lone-pair, Y=Te; X=Y=Te)

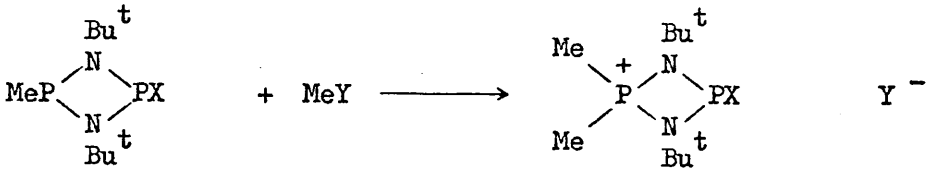
The aminolysis of 2,4-dichlorocyclodiphosph(v)azanes, $[Cl(X)PNR]_2$ (X=O or S), provides an alternative route to aminocyclodiphosph(v)azanes.[7,8] Interestingly, Bulloch[22] found that treatment of the mixed oxidation state cyclodiphosphazanes, $\overline{ClP.NMe.P(X)Cl.NBu^t}$, with two molar equivalents of dimethylamine resulted in partial dimethylaminolysis exclusively at the phosphorus(111) centre, producing $Me_2\overline{NP.NMe.P(X)Cl.NBu^t}$ (X=O or S).

Quaternisation of cyclodiphosph(111)azanes has been achieved using methyl iodide, [38,48] methyl bromide,[48] or ethyl bromide[38] - for example,



R=Me, Y=I
R=Et, Y=Br

38



X=Cl, Y=I
X=Me, Y=I,Br

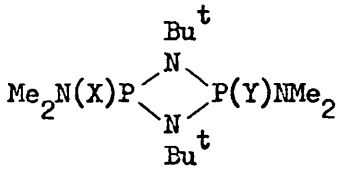
48

Scherer and Schnabl have also reported[48] the adduct, $\overline{\text{MeP.NBu}^t\text{.P}^+\text{.NBu}^t}$ $AlCl_4^-$ (in which phosphorus is still formally in the +3 oxidation state), formed on treatment of $\overline{\text{MeP.NBu}^t\text{.PCl.NBu}^t}$ with aluminium trichloride. Finally, several transition metal complexes have been prepared [39,40] using cyclodiphosph(III)azanes as ligands.

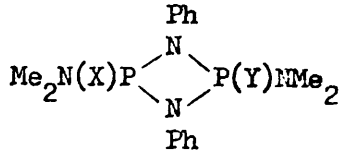
To date, apart from the very recent report[36] of Zeiss and co-workers, the oxidation of alkylaminocyclodiphosph(III)azanes has received little attention. It was therefore of interest to examine in detail the oxidation products of some of the alkylaminocyclodiphosph(III)azanes discussed in Chapter 2.

RESULTS AND DISCUSSION

An initial attempt to prepare (41) (X=Y=O or S) by dimethylaminolysis of $\left[\text{Cl(X)PNBu}^t\right]_2$ (X=O or S) was unsuccessful at ambient temperatures. However, $\text{Me}_2\text{N(S)}\overline{\text{P.NBu}^t\text{.P(S)Cl.NBu}^t}$ was formed in very low yield and identified by mass spectroscopy as a result of heating excess dimethylamine and $\left[\text{Cl(S)PNBu}^t\right]_2$ in a sealed tube at 85°C for 16 h.



(41)



(42)

On heating a mixture of dimethyl sulphoxide and cis-$(Me_2NPNBu^t)_2$ or trans-$(Me_2NPNPh)_2$ in benzene at 70-80 °C for 24 h no reaction occurred. Both cis and trans-(41) (X=Y=O) were eventually prepared using t-butylhydroperoxide as an oxidising agent. In contrast to the reaction with dimethyl sulphoxide, treatment of cis or trans - $(Me_2NPNBu^t)_2$ with one or two molar equivalents of sulphur or selenium results in a smooth, stereospecific, stepwise addition of the chalcogen, affording (41) (X=S or Se, Y=lone-pair) and (41) (X=Y=S or Se) respectively (Figure 13).

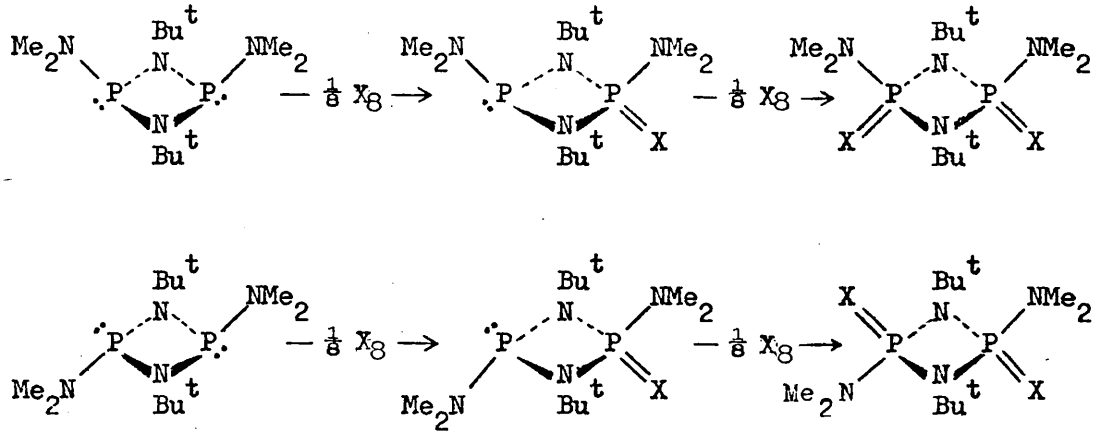
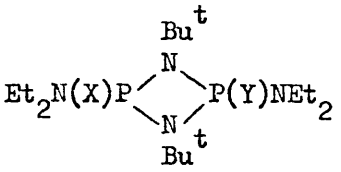


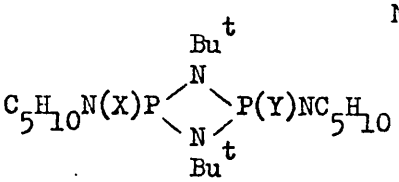
Figure 13 (X=S or Se)

Notably, the mixed oxidation state cyclodiphosphazanes are less reactive towards sulphur or selenium than the cyclodiphosph(111)azanes, presumably because the electron deficient P(V) atom affects the activity of the P(111) atom in the mono-oxidised product.

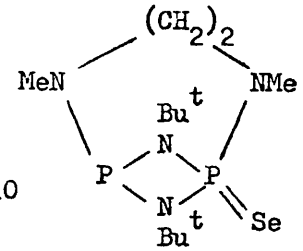
Corresponding reactions with elemental sulphur on trans-$(Me_2NPNPh)_2$ and cis-$(Et_2NPNBu^t)_2$ and with elemental selenium on cis-$(Et_2NPNBu^t)_2$ cis-$(C_5H_{10}NPNBu^t)_2$, and the cage compound, (39), readily afforded again the mono- and disulphides, (42) and (43) (X=S, Y=lone-pair or S), the mono- and diselenides (43) and (44) (X=Se, Y=lone-pair or Se), and compound (45).



(43)



(44)



(45)

That retention rather than inversion of configuration at phosphorus occurs (as indicated in Figure 13) is shown by assigning structures to the above compounds.

Structures

i) Variable-temperature ^{1}H n.m.r. measurements of torsional barriers about the exocyclic P-N bonds where pairs of isomers are available show that in all cases the isomer with the lower barrier(s) arises from the alkylaminocyclodiphosph(111)azane with the lower barrier, implying retention of the (cis) configuration (Chapter 5). Also, the ^{31}P(111) chemical shifts found in the mixed oxidation state cyclodiphosphazanes which are to 'high-field' (Table 15) arise from the cis-cyclodiphosph(111)azanes which have 'high-field' ^{31}P chemical shifts. Similar arguments hold in turn for the trans isomers. It is of interest that the ^{31}P chemical shift differences between isomeric forms of mixed oxidation state alkylaminocyclodiphosphazanes and alkylaminocyclodiphosph(v)azanes is considerably smaller (generally $\leqslant$ 25 p.p.m.; Table 15) than that found for the tervalent analogues (60–95 p.p.m.; Table 10).

ii) Vibrational spectroscopy too is of some, though limited, value in assigning structures. The asymmetric P-N vibration of the P-N-P group in cis-$(Me_2NPNBu^t)_2$ occurs at lower vibrational energy than that for trans-$(Me_2NPNBu^t)_2$ (Table 13). In every case the isomer of (41) arising from cis-$(Me_2NPNBu^t)_2$ shows an asymmetric P-N vibration in the i.r. spectrum at lower energy than that for the analogous isomer arising from

Table 13

ν(P-N-P)asym. in compounds of the type $Me_2N(X)P.NBu^t.P(Y)NMe_2.NBu^t$.[a]

X	Y	cis ν(P-N-P)asym./cm^{-1}	trans ν(P-N-P)asym./cm^{-1}
lone-pair	lone-pair	872,862	880
Te	lone-pair	-	884
Se	lone-pair	879	890
S	lone-pair	884	897
Se	Se	898	904
S	S	905	912
O	O	919	930

[a] All spectra run as nujol mulls.

trans-$(Me_2NPNBu^t)_2$, favouring (though by no means conclusively) retention of configuration (Table 13). Inspection of Table 13 also shows that $\nu(P\text{-}N\text{-}P)_{asym.}$ is at higher energy in the cyclodiphosph(v)azanes than in the mixed oxidation state species and also that on passing from chalcogens of lower electronegativity to ones of higher electronegativity in both types of compound increases the vibrational energy of the aforementioned group. If withdrawal of electron density by the chalcogen results in increased P-N π-overlap and so strengthening of the P-N bonds then this is the trend expected. I.r. and Raman comparisons of cis and trans-cyclodiphosph(v)azanes, as for the cyclodiphosph(III)azanes (Chapter 2), were again slightly ambiguous, both cis and trans isomers showing coincidences. In each case the isomer of (41) (X=Y=O,S, or Se) arising from cis-$(Me_2NPNBu^t)_2$ possessed a greater number of coincidences within the 600-950 cm^{-1} range (which should include all the ring vibrations)

than the other isomer, implying cis and trans forms respectively (Table 14). The lower symmetry of the mixed oxidation state cyclodiphosphazanes precludes such a structural assignment by this method.

Table 14

Comparison of the i.r.[a] and Raman[b] active bands of cis and trans-$[Me_2N(S)PNBu^t]_2$ in the range 600-950 cm^{-1}

cis-$[Me_2N(S)PNBu^t]_2$		trans-$[Me_2N(S)PNBu^t]_2$	
i.r./cm^{-1}	Raman/cm^{-1}	i.r./cm^{-1}	Raman/cm^{-1}
626	620	622	
728	727	738	724
743	740	742	
762	758	767	763
818		816	
823	826		877
905	927	912	925
934	935	932	933

[a] In nujol. [b] Solid state.

iii) Chemical Reactions: it was recently shown that on mixing equimolar solutions of the tertiary phosphine diselenide, $Ph_2P(Se)CH_2P(Se)Ph_2$, with the tertiary phosphine, $Ph_2PCH_2PPh_2$, a quantitive reaction occurred immediately, producing $Ph_2P(Se)CH_2PPh_2$.[256] Similarly, it was found by

$^1H-\{^{31}P\}$ n.m.r. that rapid equilibration (< 2 min) via intermolecular selenium exchange to $Me_2N(Se)\overline{P.NBu^t.PNMe_2.NBu^t}$ occurs on mixing equimolar solutions of $(Me_2NPNBu^t)_2$ and $[Me_2N(Se)PNBu^t]_2$. Furthermore, this affords an elegant route to the determination of the geometric forms of the mono- and diselenide isomers. It was found that on mixing cis-$(Me_2NPNBu^t)_2$ with its diselenide, only one isomeric form of the monoselenide was produced. Addition of the other diselenide [prepared from trans-$(Me_2NPNBu^t)_2$] afforded a 1:1 mixture of the monoselenide isomers. The former result implies that both compounds are of the same configuration (cis), the latter, opposite configurations. It would also appear reasonable to assume that the monoselenide produced on mixing cis-$(Me_2NPNBu^t)_2$ and cis-$[Me_2N(Se)PNBu^t]_2$ must be cis too, and as this is the same isomer as afforded by the reaction of cis-$(Me_2NPNBu^t)_2$ with one molar equivalent of elemental selenium then the latter reaction would appear to involve retention of configuration at phosphorus (Figure 14).

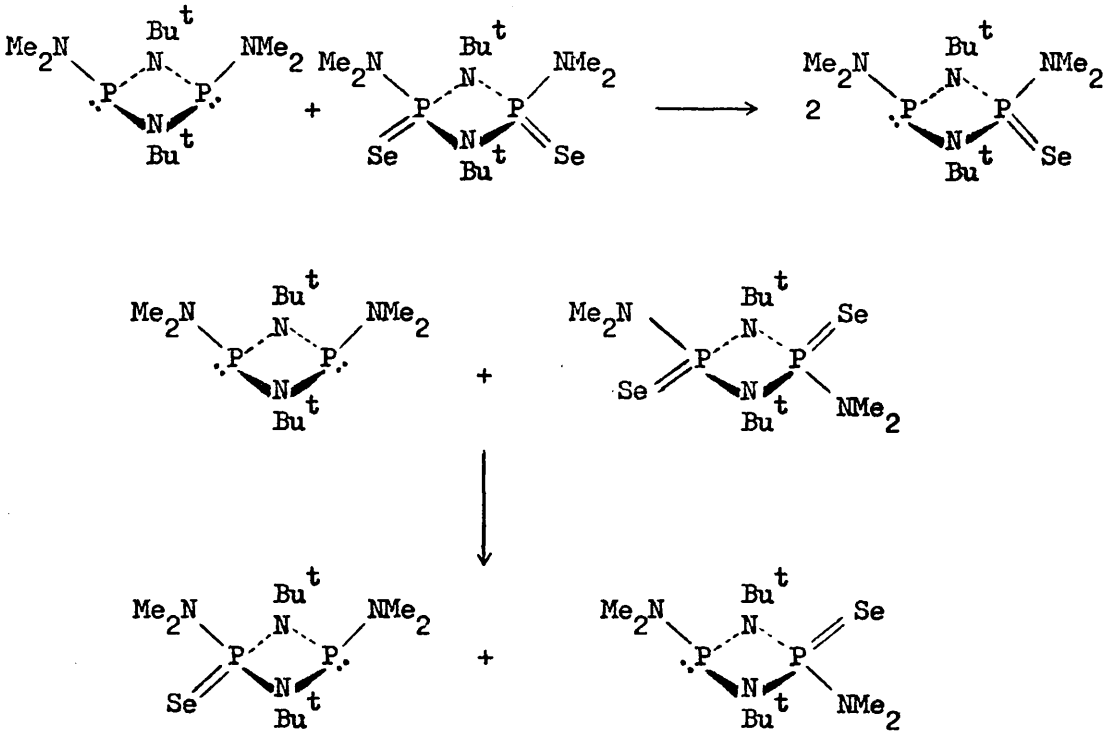
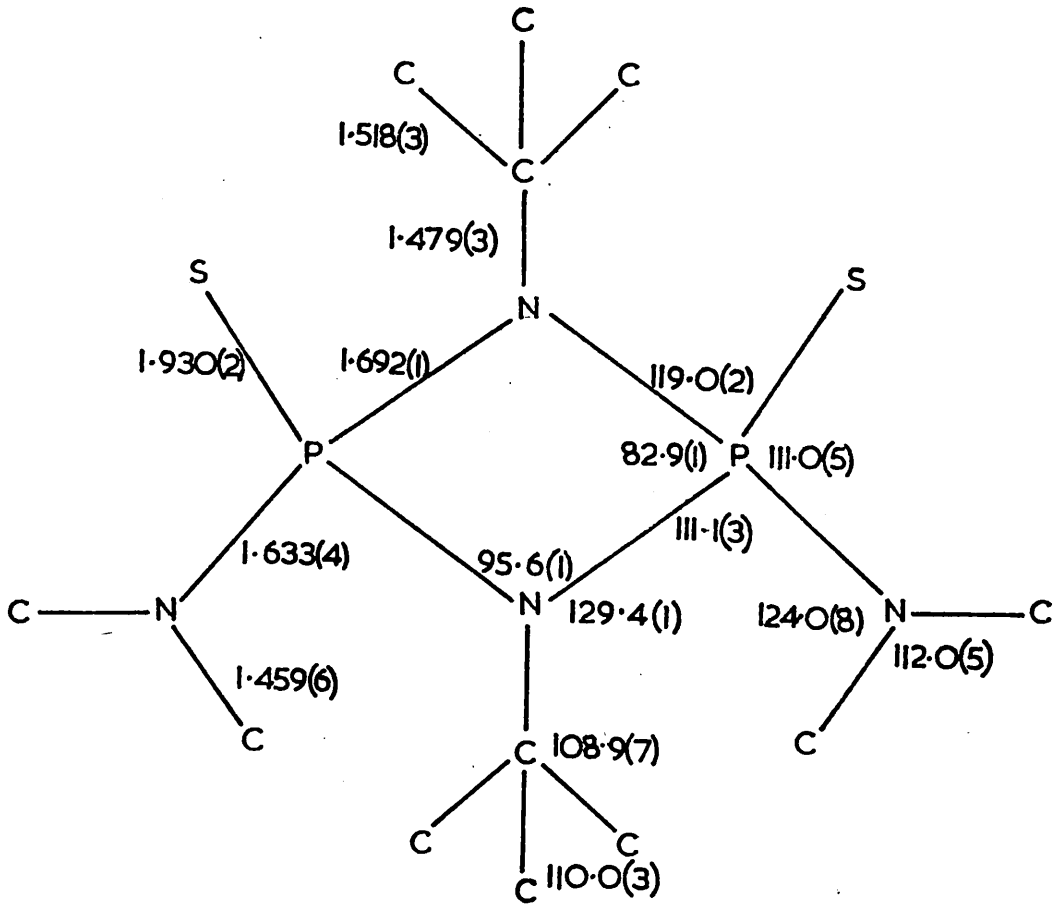


Figure 14.

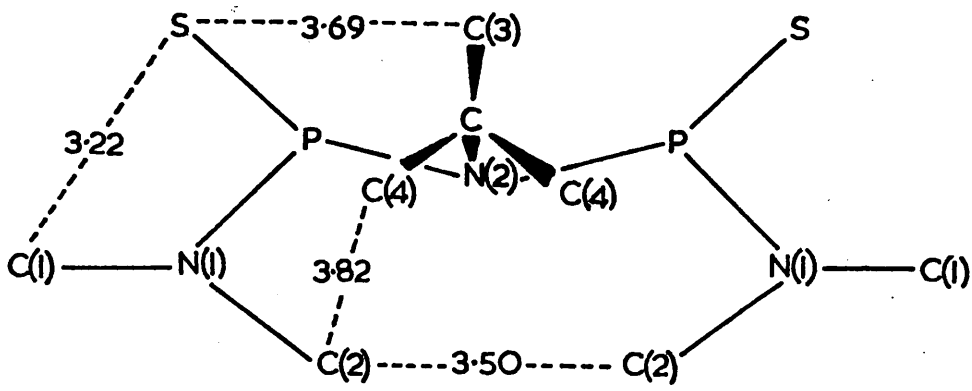
iv) X-Ray diffraction: a study of (41) (X=Y=S), produced by treatment of cis-$(Me_2NPNBu^t)_2$ with two molar equivalents of elemental sulphur, was undertaken.[257] This established that the symmetry is close to C_{2V} with dimethylamino-groups mutually cis with respect to the ring (Figure 15 a). The greatest distortation from C_{2V} symmetry arises mainly from twisting of the dimethylamino-groups about the P-N bonds by ca. 4^o from the plane passing through the phosphorus atoms and normal to the mean P_2N_2 ring plane. This is almost certainly a consequence of intramolecular crowding, as is the non-planarity of the P_2N_2 ring in which there is a torsion angle about the P-N ring bond of 13^o, somewhat larger than the 8^o found in cis-$\left[Ph(S)PNEt\right]_2$, the only other structurally characterised cis-dithiocyclodiphosph(v)azane.[97,111] Steric congestion is also shown by the number of close intramolecular contacts (Figure 15 b). The dimethylamino PNC_2 units are flat, whereas the co-ordination of the endocyclic nitrogen atoms is appreciably pyramidal, each nitrogen atom lying 0.21 Å from the plane defined by adjacent phosphorus and carbon atoms.

The other isomer of (41) (X=Y=S) was shown[257] by oscillation and Weissenberg photographs to have crystallographic C_i symmetry which is consistent only with a trans configuration.

Points i)-iv) above establish that the stepwise addition of elemental sulphur or selenium to alkylaminocyclodiphosph(III)azanes proceeds with retention of configuration at phosphorus. This is consistent with the addition of elemental sulphur [258-260] or selenium[261] to optically active tertiary phosphines which proceeds with retention of



a)



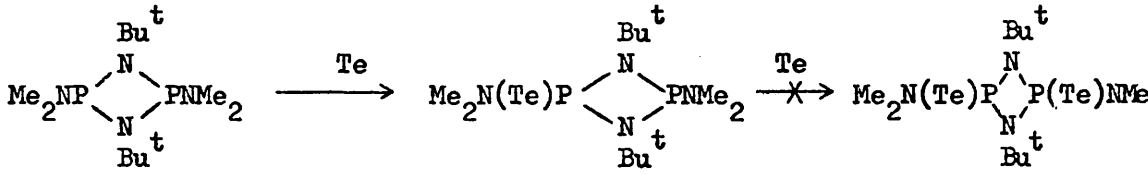
b)

Figure 15 a) A diagrammatic representation of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)-2,4-dithiocyclodiphosph(v)azane showing selected bond lengths (Å) and angles (°).

b) The same molecule, projected on to the SPN(2)PS plane (one Bu^t-group is overlapped) showing intramolecular contacts (Å).

configuration. By comparison of the vibrational spectra of cis and trans-(41) (X=Y=S or Se) with those of (41) (X=Y=O) it was confirmed that cis and trans-$(Me_2NPNBu^t)_2$, on treatment with t-butylhydroperoxide (which is assumed to effect oxidation with retention of configuration at phosphorus [262]), yield cis and trans- $[Me_2N(O)PNBu^t]_2$ respectively.

In contrast to the action of selenium on cis or trans-$(Me_2NPNBu^t)_2$, tellurium produced only the one monotelluride, trans-(41) (X=Te,Y=lone-pair). No ditelluride could be obtained.



cis or trans — trans

The ambient temperature ^1H n.m.r. spectrum of the dimethylamino-protons of this monotelluride consisted of a single, slightly broadened doublet which could be collapsed to a singlet at either of two separate ^{31}P decoupling frequencies (Figure 16). This is attributed to tellurium atom exchange at an intermediate rate on the n.m.r. time scale. The spin-lattice relaxation times for the ^{31}P nuclei must be greater than the

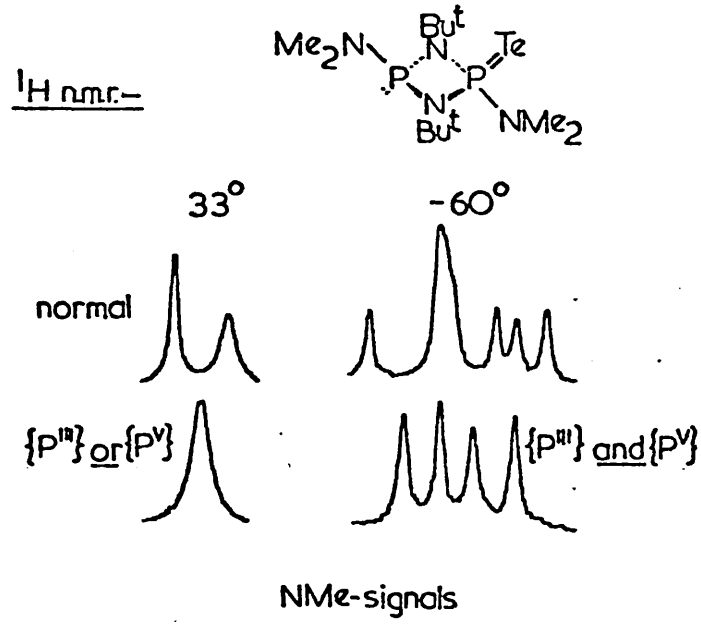
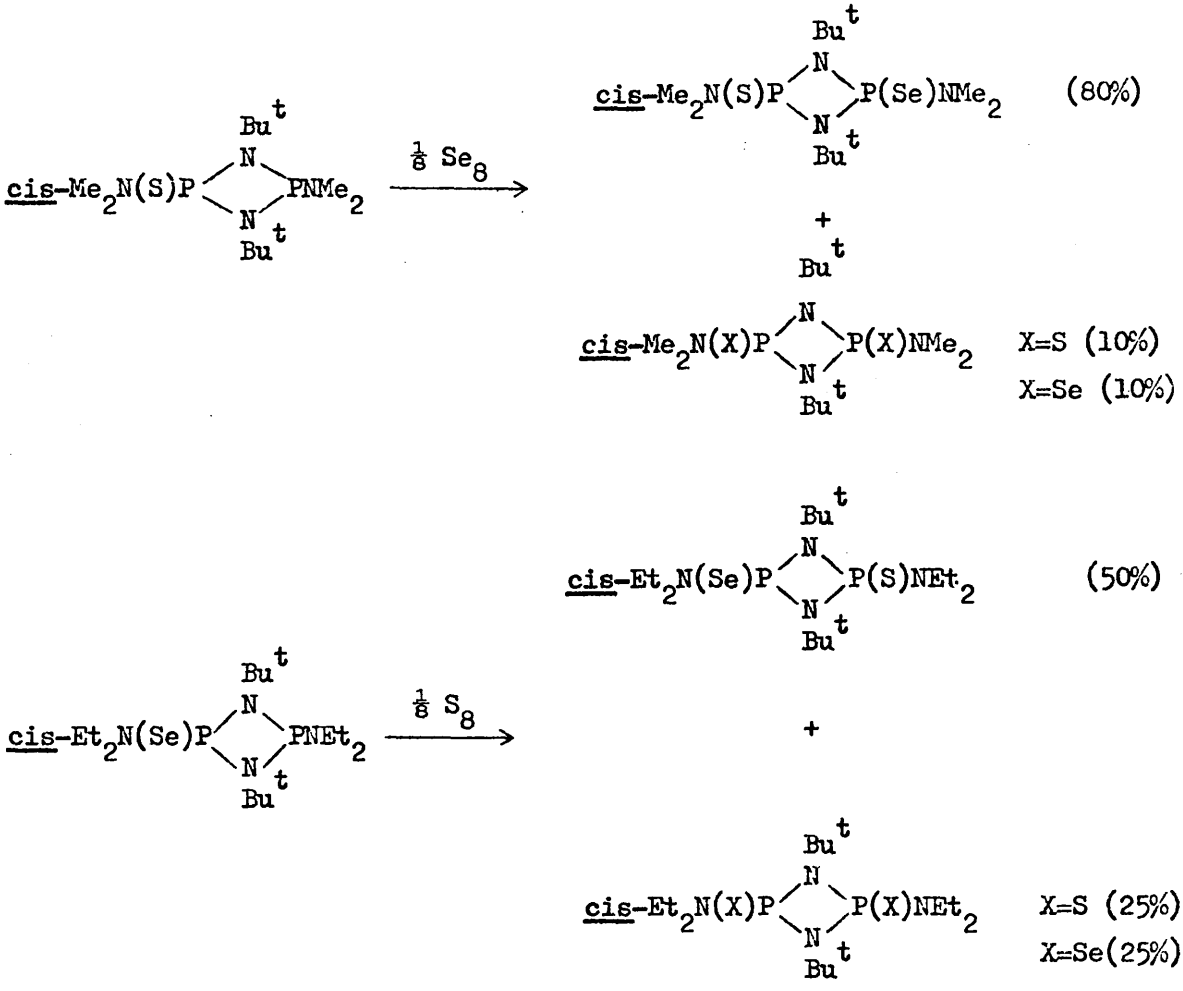


Figure 16.

exchange lifetime to allow complete $^{1}H-\{^{31}P\}$ spin decoupling by irradiation at either of the two ^{31}P signals though there is no precedence for spin relaxation effects of this type. The study of this exchange process by low-temperature n.m.r. was complicated by the slowing of rotation about both exocyclic P-N bonds so that at -60°C the dimethylamino-proton signals consisted of four doublets (Figure 16) as a result of both slow tellurium exchange and restricted rotation (Chapter 5). That the tellurium exchange is at least partly intermolecular was suggested by the concentration dependence of this process. Rapid exchange of tellurium has been observed in tertiary phosphine/tertiary phosphine telluride mixtures [263,264] and also in cis-$Bu^{t}(Te)\overline{P.NMe.PBu^{t}.NMe}$.[65] The latter compound is interesting in that the cis form [produced from cis-$(Bu^{t}PNMe)_{2}$] is stable and that the ditelluride, cis-$[Bu^{t}(Te)PNMe]_{2}$, may also be synthesised.[65]

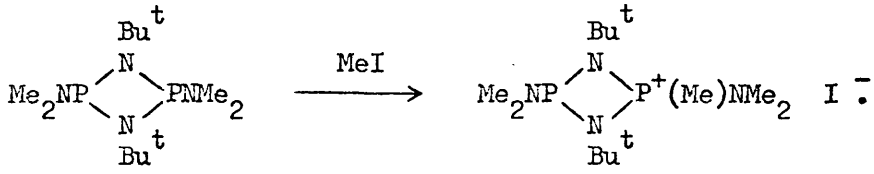
Tellurium is clearly much more mobile than selenium or sulphur in these systems as neither the cis nor the trans isomers of (41) (X=S or Se, Y=lone-pair) exhibited chalcogen exchange on the n.m.r. time-scale, even at ca. 140°C. At ca. 160°C, however, the phosphorus-selenium bond does become labile, the cis isomer isomerising completely to the trans form. It would therefore appear that it is the lability of the phosphorus-tellurium bond which precludes the formation of more than one isomer of (41) (X=Te, Y=lone-pair). No isomerisation of the monosulphides was detected. Attempted syntheses of the chalcogen-derivatives, (41) and (43) (X=S, Y=Se) from cis-(41) (X=S, Y=lone-pair) and cis-(43) (X=Se, Y=lone-pair) were hampered by 'scrambling' of the chalcogen atoms, producing in each case mixtures of the sulphide-selenide, disulphide, and diselenide species (approximate percentages in parentheses),



In the latter reaction, cis-$Et_2N(Se)\overline{P.NBu^t.P(S)NEt_2.NBu^t}$ could not be isolated from the mixture of products.

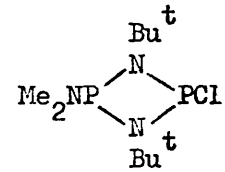
A slightly different situation obtained on addition of one molar equivalent of sulphur to trans-(41) (X=Te, Y=lone-pair), tellurium being displaced and trans-(41) (X=S, Y=lone-pair) being produced along with trans-(41) (X=Y=S). Unreacted monotelluride could not be observed in the ^1H n.m.r. spectrum owing to the complexity of the signals and broadening effects in the dimethylamino-proton region arising from hindered rotation about the $P(S)NMe_2$ bond in the monosulphide. This provides an alternative route to the trans-monosulphide as the trans-monotelluride may be made from the thermodynamically stable cis-$(Me_2NPNBu^t)_2$.

Cis or trans-$(Me_2NPNBu^t)_2$ may be readily quaternised using methyl iodide,



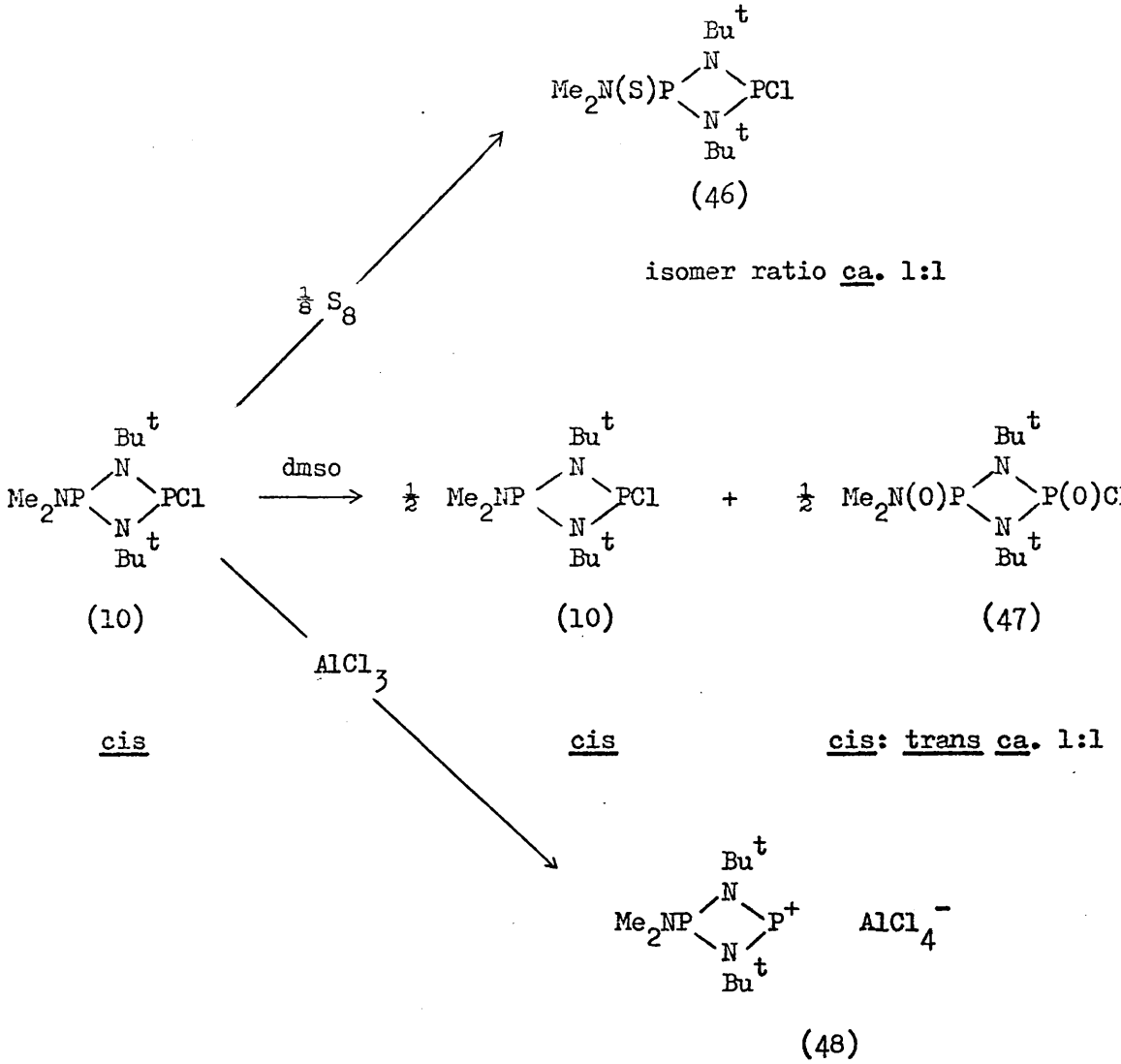
The higher barriers to rotation about the exocyclic P-N bonds (Chapter 5) and the 'low field' ^{31}P chemical shifts (Table 15) found in the product from the trans isomer indicate retention of configuration at phosphorus. No diquaternised products were obtained on further addition of methyl iodide.

The reactions of compound (10) with one molar equivalent of sulphur, dimethyl sulphoxide, and aluminium trichloride were also investigated (Scheme 5).



(10)

Sulphuration occurs exclusively at the P — NMe_2 end of the molecule producing compound (46) though surprisingly, unlike the reactions of $(R_2NPNBu^t)_2$ (R=Me or Et) with sulphur, the reaction is less stereospecific, a 1:1 mixture of isomers being produced. The reaction with one molar equivalent of dimethyl sulphoxide is even more surprising. As cis-$(ClPNBu^t)_2$ was readily oxidised by dimethyl sulphoxide,[17] yet cis-$(Me_2NPNBu^t)_2$ was not, mono-oxidation at the P-Cl centre might have been expected. Instead a 1:1 mixture of dioxide isomers, (47), plus starting material is produced. Therefore, the reactions of dimethyl sulphoxide with cyclodiphosph(III)azanes are not



Scheme 5.

straightforward. A possible explanation for this is that reactions of phosphines with dimethyl sulphoxide may proceed by one of two distinct types of mechanism as proposed by Shaw and co-workers[265]: either nucleophilic attack by phosphorus on sulphur as in the case of tris(dimethylamino)phosphine which is a strong electron donor and poor acceptor (Figure 17a) or one in which there is electrophilic attack by phosphorus on oxygen, as with phosphorus trichloride which has negligible donor but strong acceptor properties (Figure 17b).

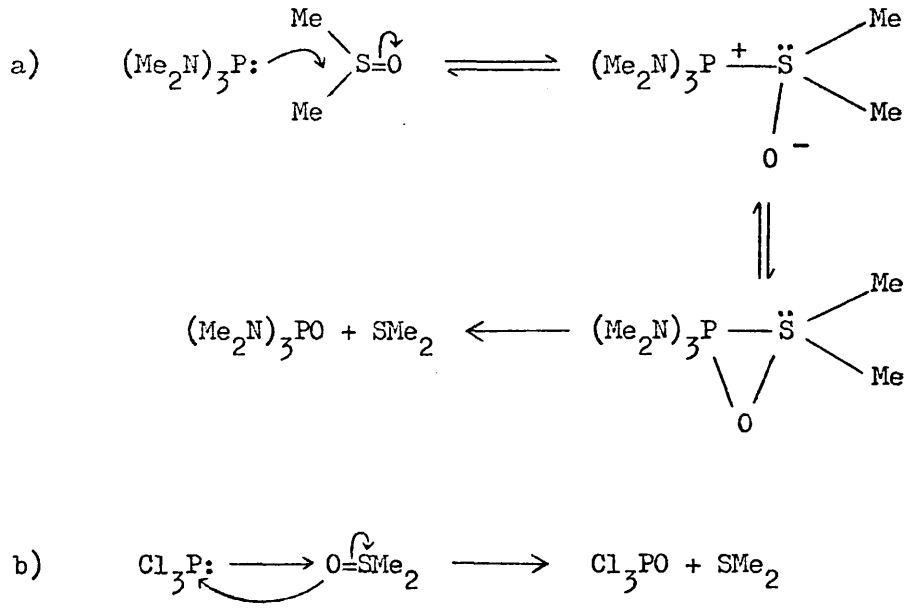


Figure 17.

It may be the case, therefore, that $(ClPNBu^t)_2$, being a good acceptor, is readily susceptible to nucleophilic attack by the oxygen atom of dimethyl sulphoxide whereas the bis(dimethylamino)-derivatives, being worse acceptors, and also perhaps not good enough electron donors, react very slowly or not at all. Interpretation of the reaction of $Me_2N\overline{P.NBu^t.PCl.NBu^t}$ with one molar equivalent of dimethyl sulphoxide is difficult. Apparently, the mono-oxidised form must react more rapidly than the starting material, but whether oxidation occurs initially at the P-Cl or P-NMe_2 end of the molecule is unknown. The adduct, (48), was readily prepared in a similar fashion to the methyl analogue, $Me\overline{P.NBu^t.P^+.NBu^t}\ AlCl_4^-$, [48] though a pure sample was not isolated owing to its extreme air and moisture sensitivity.

Finally, it is significant that reactions of a 1:1 mixture of isomers of $(Me_2NPNBu^t)_2$ (total one molar equivalent) with sulphur, selenium, or methyl iodide (0.5 molar equivalent) result in the formation of the <u>trans</u> mono-oxidation products, (41) (X=S, Se, or 'MeI'; Y=lone-pair), from the <u>trans</u> isomer leaving the <u>cis</u> isomer unchanged. Such dramatic differences in chemical reactivity resulting from

geometrical isomerism in inorganic ring systems are unique. For example, in cyclophosph(v)azenes small differences in reactivity could only be indirectly inferred from observed reaction patterns.[266] What causes these differences in reactivity is not clear but the results do parallel the higher basicity of trans-$(Me_2NPNBu^t)_2$ relative to cis-$(Me_2NPNBu^t)_2$ and the fact that the lowest energy bands in the photoelectron spectra are ca. 0.5 eV lower in energy in the trans isomer (Chapter 2). Both these observations are in accordance with a mechanism involving nucleophilic attack by phosphorus on sulphur, selenium, or the carbon atom in methyl iodide. As cross-ring $n_P \longrightarrow \sigma^*_{P-N}$ bonding interactions (if significant) will be greater in the cis isomer [178,179] and so reduce the nucleophilicity of the phosphorus atoms in this isomer, then perhaps the observed reactivity pattern is a manifestation of this. Similarly, it was found on adding elemental sulphur or selenium (0.5 molar equivalent) to a 1:1 mixture of cis and trans-(41) (X=S or Se, Y=lone-pair) that the trans isomer again reacted more rapidly. However, in this instance the difference in reactivity between the isomers (as followed by ^1H n.m.r.) was not so marked, some of the cis isomer reacting before complete removal of the elemental chalcogen.

EXPERIMENTAL

Solvents were dried by conventional means. Commercially obtained reagents were purified as described in Appendix A. The compounds, cis-$(Me_2NPNBu^t)_2$,[22] $(Et_2NPNBu^t)_2$,[22] $Me_2NP(NBu^t)PCl(NBu^t)$,[22] trans-$[Cl(O)PNBu^t]_2$,[62] and $[Cl(S)PNBu^t]_2$[253] were prepared using literature methods. Other cyclodiphosphazanes were obtained as described in Chapter 2. Information on the instruments used in the measurement of n.m.r. (Table 15), i.r., Raman and mass (Table 16) spectroscopic data, the collection of X-ray diffraction data, and the source of microanalyses (Table 16) can be found in Appendix B. Other preparative details are summarised below.

Attempted preparations of 1,3-di-t-butyl-2,4-bis(dimethylamino)-2,4-dioxocyclodiphosph(v)azane:- 1,3-Di-t-butyl-2,4-dichloro-2,4-dioxocyclodiphosph(v)azane (0.6 g, 2 mmol) was mixed with dimethylamine (0.4 g, 9 mmol) in methylene chloride (35 cm^3) at -10°C. The solution was brought to ambient temperatures and stirred (3 h). Examination of the reaction mixture by ^1H n.m.r. indicated that no reaction had taken place. In a further experiment, dimethyl sulphoxide (0.83 g, 10.6 mmol) was added to a solution of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)cyclodiphosph(III)azane (1.55 g, 5.3 mmol) in benzene (60 cm^3) at room temperature. The mixture was refluxed (24 h) whereupon examination by ^1H n.m.r. indicated no reaction to have occurred.

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2,4-dioxocyclodiphosph(v)-azane:- To a solution of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)-cyclodiphosph(III)azane (5.2 g, 18 mmol) in benzene (35 cm^3) at 0°C was carefully added dropwise a solution of t-butylhydroperoxide (3.3 g, 37 mmol) in benzene (20 cm^3). After the mixture was allowed to reflux and return to ambient temperatures, the solvent and t-butanol were removed affording a light yellow solid which was washed with cold pentane (30 cm^3) and crystallised from methylene chloride-light petroleum (b.p. 40-60°C) (1:4) to give the compound (2.6 g, 44%) as white air-stable needles, m.p. 194-196°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2,4-dioxocyclodiphosph(v)-azane was prepared similarly from 1,3-di-t-butyl-2-trans-4-bis(dimethylamino)cyclodiphosph(III)azane and crystallised from methylene chloride - light petroleum (b.p. 40-60°C) (1:4) yielding the compound (53%) as colourless needles (which become white on exposure to air), m.p. 205°C.

Attempted preparations of 1,3-di-t-butyl-2,4-bis(dimethylamino)-2,4-dithiocyclodiphosph(v)azane:- Dimethylamine (1.6 g, 36 mmol) was mixed with 1,3-di-t-butyl-2,4-dichloro-2,4-dithiocyclodiphosph(v)azane (2.9 g, 8.6 mmol) in diethyl ether (60 cm^3) at -78°C. The solution was allowed to warm to ambient temperatures and stirred (3 h). Examination of the product by ^1H n.m.r. showed that no reaction had occurred. A further experiment in which the above dithiocyclodiphosph(v)-azane (2.7 g, 8.0 mmol) was heated with excess dimethylamine (ca. 20 g) in a sealed tube at 85°C for 16 h provided evidence after work up for the starting material and traces of 1,3-di-t-butyl-2-chloro-4-dimethylamino-2,4-dithiocyclodiphosph(v)azane, identified by mass spectroscopy; found $^m/e$ 347, calc. $^m/e$ 347 (^{35}Cl).

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2,4-dithiocyclodiphosph(v)-azane:- To 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)cyclodiphosph-(111)azane (3.2 g, 11 mmol) in benzene (60 cm^3) at ambient temperature was added flowers of sulphur (0.7 g, 22 mmol). After an initial mild exothermic reaction the mixture was stirred at 60°C for 4 h by which time all the sulphur had dissolved. Concentration of the benzene solution afforded the pure compound (2.9 g, 73%) as colourless octahedral crystals, m.p. 255-256°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2,4-dithiocyclodiphosph(v)-azane:- 1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)cyclodiphosph(111)-azane (1:1 g, 3.8 mmol) and flowers of sulphur (0.24 g, 7.6 mmol) in benzene (30 cm^3), on similar treatment to the above gave the compound (0.9 g, 66%) as colourless needles, m.p. 214°C.

Cis and trans-1,3-di-t-butyl-2,4-bis(dimethylamino)-2,4-diseleno-cyclodiphosph(v)azanes:- To a 1:1 mixture of cis and trans-1,3-di-t-butyl-2,4-bis(dimethylamino)cyclodiphosph(III)azanes (6.25 g, 21.4 mmol) in benzene (50 cm^3) at ambient temperature was added finely powdered elemental selenium (3.38 g, 42.8 mmol). The mixture was refluxed (2 d), traces of unreacted selenium and the solvent were removed, and the off-white residue crystallised from methylene chloride affording the compound (7.4 g, 77%) as colourless crystals. The cis and trans forms were separated by fractional crystallisation from benzene (the trans isomer being the less soluble); cis isomer, m.p. 253-255°C; trans isomer, m.p. 264°C.

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2-thiocyclodiphosphazane:- To a rapidly stirred solution of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)cyclodiphosph(III)azane (6.5 g, 22 mmol) in benzene (80 cm^3) at ambient temperature was added flowers of sulphur (0.71 g, 22 mmol). After 6 h the solvent was removed and the white solid residue crystallised from a pentane-methylene chloride mixture (10:1) to yield the compound (3.6 g, 50%) as colourless needles, m.p. 73-75°C.

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2-selenocyclodiphosphazane:- The compound was prepared using a similar method to the above; white needles (54%), m.p. 102-104°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2-thiocyclodiphosphazane:- To a mixture of cis and trans (1:4 respectively) 1,3-di-t-butyl-2-4-bis(dimethylamino)cyclodiphosph(III)azanes (6.20 g, 21.2 mmol) in benzene (50 cm^3) at ambient temperature was added flowers of sulphur (0.544 g, 17.0 mmol). A mildly exothermic reaction occurred and the mixture was stirred (1 h). Removal of the solvent left an oily white solid which was carefully washed with cold pentane (ca. 2 cm^3) and then crystallised from light petroleum (b.p. 40-60°C)-pentane (1:1) to yield the pure compound (3.3 g, 59% based on sulphur) as white needles, m.p. 127-129°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2-selenocyclodiphosphazane:- The compound, was prepared using a similar method to the above; white needles (69%), m.p. 126-127°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2-tellurocyclodiphosphazane:- (1) To a solution of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)-cyclodiphosph(III)azane (3.30 g, 11.3 mmol) in benzene (10 cm^3) at ambient temperature was added finely ground tellurium (1.44 g, 11.3 mmol). There appeared to be no immediate reaction, but the tellurium dissolved after reflux (4 h) and the solution turned green. Removal of the solvent and crystallisation of the residue from a light petroleum (b.p. 40-60°C)-methylene chloride (4:1) mixture afforded the pure compound (1.40 g, 29%) as pale yellow crystals, m.p. 120°C (decomp.). The compound is stable on exposure to light and air but slowly decomposes when left in solution for extended periods.
(2) To a solution of 1,3-di-t-butyl-2-trans-4-bis(dimethylamino)-cyclodiphosph(III)azane (4.5 g, 15 mmol) in benzene (15 cm^3) at ambient temperature was added finely ground tellurium (1.2 g, 9 mmol). The solution immediately turned green, was stirred (2 h), and on removal of the solvent and after work up afforded the compound (2.3 g, 60%).

On refluxing the compound with an equimolar amount of tellurium in benzene for 3 d there was no evidence (^1H n.m.r.) of a ditelluride species.

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2-seleno-4-thiocyclocyclodiphosph(v)azane:- To 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)-2-thiocyclodiphosphazane (6.7 g, 21 mmol) in benzene (100 cm^3) at ambient temperature was added powdered selenium (1.7 g, 21 mmol). The mixture was refluxed (24 h) and studied by ^1H n.m.r. This showed it to consist of a ca. 8:1:1 mixture of the compound and the analogous 2-cis-4-dithio

and 2-cis-4-diselenocyclodiphosph(v)azanes respectively. The mixture was separated after work up by careful crystallisation from light petroleum (b.p. 40-60°C)-methylene chloride (3:1) yielding the compound (3.9 g, 46%) as colourless crystals, m.p. 236°C.

Attempted preparation of 1,3-di-t-butyl-2,4-bis(dimethylamino)-2-telluro-4-thiocyclodiphosph(v)azane:- Flowers of sulphur (0.102 g, 3.20 mmol) were added at ambient temperatures to a solution of 1,3-di-t-butyl-2-trans-4-bis(dimethylamino)-2-tellurocyclodiphosphazane (1.345 g, 3.20 mmol) in benzene (15 cm^3). The solution immediately appeared black due to deposition of elemental tellurium. On refluxing (60 h) there was no evidence for the recombination of tellurium, ^1H n.m.r. indicating the solution to consist mainly of the cis-2-thio and 2-cis-4-dithio-derivatives in a ca. 6:1 ratio respectively. Signals from the starting material (if present) may be obscured by those of the other species in solution.

1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-2-methylcyclodiphosph-azanium iodide:- 1,3-Di-t-butyl-2-cis-4-bis(dimethylamino)-cyclodiphosph(111)azane (4.47 g, 15.3 mmol) and methyl iodide (8.5 g, 60 mmol) were mixed in benzene (25 cm^3) at ambient temperature. The mixture warmed slightly and was stirred (6 h) during which time a white flocculent precipate appeared. This was removed by filtration and crystallised from benzene to yield the compound (4.00 g, 60%) as white needles, m.p. 132-134°C.

1,3-Di-t-butyl-2-trans-4-bis(dimethylamino)-2-methylcyclodiphosph-azanium iodide:- To a mixture of cis and trans (1:3 respectively) 1,3-di-t-butyl-2,4-bis(dimethylamino)cyclodiphosph(111)azanes (1.20 g, 4.11 mmol) in benzene (5 cm^3) at ambient temperature was added methyl iodide (0.44 g, 3.10 mmol). Almost immediately there was a vigorous exothermic reaction and the production of a copious white precipitate. This was filtered and washed with benzene (3 x 10 cm^3) to yield the pure

compound (1.16 g, 86% based on methyl iodide), m.p. 150-153°C. Crystallisation proved difficult owing to the very poor solubility of the compound in most common organic solvents. Study of the filtrate by ^{1}H n.m.r. indicated it to consist almost entirely of 1,3-di-t-butyl-2-cis-4-bis(dimethylamino)cyclodiphosph(III)azane.

Attempted preparation of 2,4-bis(dimethylamino)-2,4-dioxo-1,3-diphenylcyclodiphosph(V)azane:- Dimethyl sulphoxide (0.2 g, 2.6 mmol) was added to a solution of 2-trans-4-bis(dimethylamino)-1,3-diphenyl-cyclodiphosph(III)azane (0.6 g, 1.8 mmol) in benzene (5 cm^3). The mixture was refluxed (24 h) and studied by ^{1}H n.m.r. which indicated no reaction had taken place.

2-Trans-4-bis(dimethylamino)-1,3-diphenyl-2,4-dithiocyclodiphosph(V)-azane:- Flowers of sulphur (0.48 g, 15 mmol) were added to a solution of 2-trans-4-bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (2.5 g, 7.5 mmol) in benzene (100 cm^3) at ambient temperature. After reflux (6 h) the solution became cloudy. The mixture was allowed to cool and the solvent removed, affording the pure compound (2.7 g, 92%) as a fine white powder, m.p. 302-305°C, only sparingly soluble in most common organic solvents.

2-Trans-4-bis(dimethylamino)-1,3-diphenyl-2-thiocyclodiphosphazane:- 2-Trans-4-bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (2.57 g, 7.74 mmol) in benzene (100 cm^3) was mixed with flowers of sulphur (0.25 g, 7.8 mmol) at ambient temperature. The mixture was refluxed (2 h) and after work up and crystallisation from benzene afforded the compound (1.90 g, 68%) as white crystals, m.p. 219°C.

1,3-Di-t-butyl-2-cis-4-bis(diethylamino)-2,4-dithiocyclodiphosph(V)-azane:- To 1,3-di-t-butyl-2-cis-4-bis(diethylamino)cyclodiphosph(III)-azane (4.68 g, 13.45 mmol) in benzene (60 cm^3) was added flowers of sulphur (0.86 g, 26.9 mmol). The mixture warmed slightly, was stirred at ambient temperature (0.5 h) and refluxed (2 h).

Removal of the solvent and crystallisation of the residue from light petroleum (b.p. 40-60°C) afforded the pure compound (3.85 g, 69%) as white needles, m.p. 169°C.

1,3-Di-t-butyl-2-cis-4-bis(diethylamino)-2,4-diselenocyclodiphosph(v)-azane was prepared similarly; colourless needles (59%), m.p. 219-221°C.

1,3-Di-t-butyl-2-cis-4-bis(diethylamino)-2-thiocyclodiphosphazane:- As above, flowers of sulphur (0.69 g, 21.6 mmol) and 1,3-di-t-butyl-2-cis-4-bis(diethylamino)cyclodiphosph(111)azane (7.5 g, 21.6 mmol) were mixed with rapid stirring (0.5 h) at ambient temperature in benzene solution (60 cm^3). Removal of the solvent left a brownish low melting point solid. This was washed with cold pentane (1 cm^3) and crystallised from pentane giving the compound (3.82 g, 47%) as colourless needles, m.p. 93-95°C.

1,3-Di-t-butyl-2-cis-4-bis(diethylamino)-2-selenocyclodiphosphazane was prepared similarly in refluxing benzene (2 h); colourless needles (79%), m.p. 101-102°C.

Attempted preparation of 1,3-di-t-butyl-2-cis-4-bis(diethylamino)-2-seleno-4-thiocyclodiphosph(v)azane:- Flowers of sulphur (0.41 g, 12.8 mmol) were added at ambient temperature to a solution of 1,3-di-t-butyl-2-cis-4-bis(diethylamino)-2-selenocyclodiphosphazane (5.5 g, 12.9 mmol) in benzene (60 cm^3). The mixture was stirred (0.5 h) at 60°C. Removal of the solvent and work up yielded a white solid (5.6 g) which was shown by ^{31}P n.m.r. to consist of a 2:1:1 mixture of the compound and the 2-cis-4-dithio and 2-cis-4-diseleno analogues respectively. Isolation of the compound by fractional crystallisation from a variety of solvents, solvent mixtures and by thin layer chromatography proved impossible, the components of the mixture being too physically and chemically similar for separation by such techniques.

1,3-Di-t-butyl-2-cis-4-dipiperidino-2,4-diselenocyclodiphosph(v)azane:- To a solution of 1,3-di-t-butyl-2-cis-4-dipiperidinocyclodiphosph(111)-azane (1.559 g, 4.185 mmol) in benzene (25 cm^3) at ambient temperature was added finely powdered elemental selenium (0.661 g, 8.370 mmol). The mixture was refluxed with rapid stirring (1 h), allowed to cool to ambient temperature, the solvent removed and the white solid residue crystallised from methylene chloride and pentane (1:1) to give the compound (1.1 g, 50%) as colourless prisms, m.p. 214-215°C.

1,3-Di-t-butyl-2-cis-4-dipiperidino-2-selenocyclodiphosphazane:- Similarly, a solution of 1,3-di-t-butyl-2-cis-4-dipiperidinocyclodiphosph(111)azane (1.476 g, 3.968 mmol) and elemental selenium (0.313 g, 3.968 mmol) in benzene (50 cm^3) was refluxed (1 h). After work up, crystallisation from pentane afforded the compound (1.4 g, 78%), colourless crystals, m.p. 110°C.

7,8-Di-t-butyl-2,5-dimethyl-2,5,7,8-tetraaza-1-seleno-1,6-diphospha-bicyclo[4.1.1]octane:- Finely powdered selenium (2.0 g, 25 mmol) was added at ambient temperature to a solution of 7,8-di-t-butyl-2,5-dimethyl-2,5,7,8-tetraaza-1,6-diphospha(111)bicyclo[4.1.1]octane (7.2 g, 25 mmol) in methylene chloride (10 cm^3). An exothermic reaction occurred and the solution came to reflux. After stirring (0.5 h), the reaction had gone to completion (^1H n.m.r.). Traces of unreacted selenium were removed by filtration and the solvent evaporated leaving a cloudy oil which was crystallised from pentane and methylene chloride (1:1) and recrystallised from pentane to yield the compound (2.9 g, 32%) as colourless needles, m.p. 80-82°C.

1,3-Di-t-butyl-2-chloro-4-dimethylamino-4-thiocyclodiphosphazane:- Flowers of sulphur (0.64 g, 20 mmol) were added at ambient temperature to a solution of 1,3-di-t-butyl-2-chloro-4-dimethylaminocyclodiphosph-(111)azane (5.6 g, 20 mmol) in benzene (100 cm^3). The solution was

heated (3 h) with rapid stirring at 70°C. Removal of the solvent left a colourless oil which was purified by distillation under reduced pressure to give the compound (1.5 g, 24%), b.p. 98-100°C (0.02 mmHg). Examination of the product by $^{1}H-\{^{31}P\}$ and ^{31}P n.m.r. indicated a 1:1 mixture of isomers to be present both before and after purification.

1,3-Di-t-butyl-2-chloro-4-dimethylamino-2,4-dioxocyclodiphosph(v)azane:- To a stirred solution of 1,3-di-t-butyl-2-chloro-4-dimethylamino-cyclodiphosph(111)azane (3.43 g, 12.1 mmol) in methylene chloride (50 cm^3) at -78°C was slowly added dimethyl sulphoxide (0.94 g, 12.1 mmol) in methylene chloride (30 cm^3). The solution was allowed to warm to ambient temperatures after which time the methylene chloride and dimethyl sulphide were removed under reduced pressure and collected in a trap held at -78°C. The oily residue was shown by $^{1}H-\{^{31}P\}$ n.m.r. to consist of a 1:1 mixture of the compound and starting material. Partial purification was effected by distillation under reduced pressure, yielding 1,3-di-t-butyl-2-chloro-4-dimethylaminocyclodiphosph(111)azane (1.36 g, 40% recovery), b.p. 70-80°C (0.1 mmHg) [lit.[22] 55-65°C (0.03 mmHg)]. The distillation residue now consisted mainly of the compound, which $^{1}H-\{^{31}P\}$ n.m.r. showed to be a 1:1 mixture of isomers both before and after distillation.

1,3-Di-t-butyl-2-dimethylamino-4-yliumcyclodiphosphazane-tetrachloroaluminate:- To a stirred solution of 1,3-di-t-butyl-2-chloro-4-dimethylaminocyclodiphosph(111)azane (0.82 g, 2.9 mmol) in methylene chloride (1 cm^3) was added anhydrous aluminium trichloride (0.53 g, 4.0 mmol). The solution became warm, turned green and was stirred (0.5 h). Excess aluminium trichloride was carefully removed by filtration. A pure sample was not obtained, but the integrated ^{1}H and $^{31}P-\{^{1}H\}$ spectra are consistent with that expected for the compound.

Table 15

Phosphorus -31 and ^{1}H n.m.r. data [a]

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{PNCH} p.p.m.	$^{3}J(PNCH)$ [c] Hz	δ_{Bu^t} p.p.m.	$^{4}J(PNCCH)$ Hz
cis-$[Me_2N(S)PNBu^t]_2$	44.8	+ 41.2 ± 3 [d]	2.93	11.8	1.44	0.5
trans-$[Me_2N(S)PNBu^t]_2$	53.8	+ 20.2 ± 2 [d]	2.92	12.0	1.38	0.5
cis- $[Me_2N(Se)PNBu^t]_2$	39.8	33.1 [e]	2.92	12.8	1.47	0.6
trans-$[Me_2N(Se)PNBu^t]_2$	48.9	6.2 [e]	3.01	12.8	1.46	0.6
cis- $[Me_2N(O)PNBu^t]_2$	4.0	+ 55 ± 5 [f]	2.72	10.5	1.30	0.4
trans-$[Me_2N(O)PNBu^t]_2$	1.6	+ 45 ± 10 [f]	2.78 [g]	10.5	1.31	0.5
cis-$Me_2NP.NBu^t.P(S)NMe_2.NBu^t$	91.4 (P^{III})	11.2	2.64 (P^{III})	9.0	1.30	<0.5
	49.0		2.90	11.6		ca. 0.5

Table 15 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
trans-$Me_2NP(NBu^t).P(S)NMe_2.NBu^t$	103.6 (P^{III})[h]	11.2	2.72 (P^{III})[i]	3.4	1.23	1.1
			2.57 (P^{III})	14.3		
	68.9		ca. 2.65 [g]	[j]		0.6
cis-$Me_2NP(NBu^t).P(Se)NMe_2.NBu^t$	90.0 (P^{III})	9.4	2.68	8.3 ± 0.5 [g]	1.36	⩽0.3
	36.2		2.99	12.0		⩽0.5
trans-$Me_2NP(NBu^t).P(Se)NMe_2.NBu^t$	111.7 (P^{III})	10.1	2.78 (P^{III})[h,i]	3.0	1.23	1.0
			2.56 (P^{III})	13.9		
	61.0		ca. 2.65 [g]	[j]		0.5

Table 15 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
trans-$Me_2N\overline{P.NBu^t.P(Te)NMe_2.NBu^t}$	127.7 (P^{III}) [k]	[k,j]	2.83 [k]	10.3 [k]	1.29	0.75
	16.7		2.83	10.3		0.75
cis-$Me_2N(S)\overline{P.NBu^t.P(Se)NMe_2.NBu^t}$	48.5(S)	36.7	2.94 (S)	12.3	1.50	ca. 0.4
	40.5 (Se)		2.97 (Se)	12.8		ca. 0.4
cis-$Me_2N\overline{P.NBu^t.P^+(Me)NMe_2.NBu^t}$ I^-	86.1 (P^{III})	5.2	2.82 (P^{III})[i]	15.7	1.35	<0.3 (P^{III})
			2.66 (P^{III})	3.3		ca. 0.3 (P^+)
	30.3		3.02	11.3	2.38 [l]	14.8 [m]
trans-$Me_2N\overline{P.NBu^t.P^+(Me)NMe_2.NBu^t}$ I^-	123.5 (P^{III})	6.0	2.83 (P^{III})[i]	14.6	1.31	<0.5
			2.68 (P^{III})	3.7		

Table 15 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δBu^t p.p.m.	^1H $^4J(PNCCH)$ Hz
	51.5		3.07 [i]	10.0 ± 1		⩽0.5
			2.78	9.4 ± 0.5	2.69 [l]	13.6 [m]
trans-$[Me_2N(S)PNPh]_2$	49.7	j	3.06	13.2		
trans-$Me_2NP.NPh.P(S)NMe_2.NPh$	99.5 (P^{III})	j	2.88 (P^{III})	9.1		
	64.5		2.87	12.0		
cis-$[Et_2N(S)PNBu^t]_2$	47.8	j	3.40	14.0	1.47	ca. 0.4
					1.15 (Et)	7.2 [n]
cis-$[Et_2N(Se)PNBu^t]_2$	38.2	29.5	3.41	14.4	1.51	ca. 0.4
					1.15 (Et)	7.3 [n]

Table 15 cont'd

Compound	^{31}P δ_P [b]	^{31}P $^2J(PNP)$	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
cis-$Et_2NP(NBu^t).P(S)NEt_2.NBu^t$	87.4 (P^{III})	j	3.07 [g]	j	1.40	<0.4
					1.12 (Et)	6.7 [n]
	47.0 (P^V)		3.44	13 ± 2	1.40	ca. 0.4
					1.17 (Et)	6.5 [n]
cis-$Et_2NP(NBu^t).P(Se)NEt_2.NBu^t$	87.2 (P^{III})	8.0	3.01 [g]	j	1.41	<0.4
					1.12 (Et)	6.8 [n]
	34.7		3.38	13 ± 2	1.41	ca. 0.4
					1.16 (Et)	6.6 [n]
cis-$Et_2N(S)P(NBu^t).P(Se)NEt_2.NBu^t$	47.4(S)	33.6	ca. 3.4	j	1.49	ca. 0.4

Table 15 cont'd

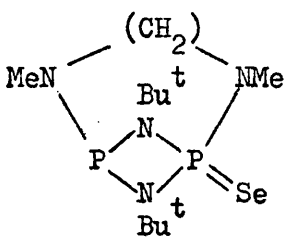
Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
					1.15 (Et)	7.2 [n]
	38.6 (Se)		ca. 3.4	j	1.15 (Et)	7.2 [n]
cis-$[C_5H_{10}N(Se)PNBu^t]_2$	39.0	17.2	3.47	j	1.55	$\leqslant$0.3
cis-$C_5H_{10}NP.NBu^t.P(Se)NC_5H_{10}.NBu^t$	86.6 (P^{III})	7.2	3.03	j	1.39	<0.3
	35.6		3.44	j		ca. 0.3
	97.5 (P^{III})	20.6	2.69 (NMe)	13.8	1.36	$\leqslant$0.6
			ca. 3.15	j		
	66.1		3.00 (NMe)	13.1		$\leqslant$0.4
			ca. 3.25	j		

Table 15 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(\underline{P}NP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(\underline{P}NC\underline{H})$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(\underline{P}NCC\underline{H})$ Hz
$ClP(NBu^t).P(S)NMe_2.NBu^t$	150.2 (PCl)	22.6			1.38	<0.4
	77.2		ca. 2.9 [i]	12 ± 1		⩽0.4
			2.51	10.7 ± 0.5		
	155.8 (PCl)	30.9			1.38	<0.4
	63.3		2.88	12.1		⩽0.4
$Cl(O)P(NBu^t).P(O)NMe_2.NBu^t$	0.3	55.9	2.74	11.9	1.41	⩽0.5
	-1.6 (PCl)					⩽0.5
	-2.5	59.5	2.80 [i]	10 ± 1	1.41	⩽0.5
			2.72	11.5 ± 1		

Table 15 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{PNCH} p.p.m.	^1H $^3J(PNCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
$Me_2\overline{NP.NBu^t.P^+.NBu^t}$ $AlCl_4^-$	-5.3 ($\underline{P}Cl$)					$\leqslant 0.5$
	331.5 ($\underline{P}^+$)	58 ± 5	2.84 [i]	15.1	1.43	1.2
	124.3		2.46	3.7		0.7

Table 15 cont'd

[a] For $CDCl_3$ or CH_2Cl_2 solutions at ca. 33°C unless stated otherwise.

[b] Downfield ^{31}P chemical shifts are positive, relative to external 85% H_3PO_4.

[c] More correctly, $|^3J(PNCH) + {}^5J(PNPNCH)|$ for symmetrical cyclodiphosph(v)azanes.

[d] Obtained by $^1H-\{^{31}P\}$ INDOR.

[e] Obtained by observing the ^{77}Se satellites in the $^{31}P-\{^1H\}$ n.m.r. spectrum.

[f] Obtained by $^1H-\{^{31}P\}$ double-resonance.

[g] Signal broadened as a result of slow rotation about the exocyclic P-N bond.

[h] In C_6H_5Cl solution.

[i] Two N-methyl signals due to restricted rotation at 33°C.

[j] Not measured.

[k] Signals broadened due to tellurium exchange.

[l] δ_{PCH}.

[m] $^2J(PCH)$.

[n] $^3J(HCCH)$.

Table 16

Analytical data [a]

Compound	Found				Calc.			
	C	H	N	m/e	C	H	N	m/e [b]
cis-$[Me_2N(S)PNBu^t]_2$	40.4	8.45	15.35	356	40.45	8.4	15.7	356
trans-$[Me_2N(S)PNBu^t]_2$	40.5	8.3	15.7	356	40.45	8.4	15.7	356
cis-$[Me_2N(Se)PNBu^t]_2$	32.1	6.7	12.5	452	32.0	6.7	12.4	452
trans-$[Me_2N(Se)PNBu^t]_2$	32.25	6.6	12.5	452	32.0	6.7	12.4	452
cis-$[Me_2N(O)PNBu^t]_2$	44.4	9.2	17.5	324	44.4	9.3	17.3	324
trans-$[Me_2N(O)PNBu^t]_2$	44.65	9.0	17.2	324	44.4	9.3	17.3	324
cis-$Me_2N\overline{P.NBu^t.P(S)NMe_2.NBu^t}$	44.7	9.0	17.5	324	44.4	9.3	17.3	324

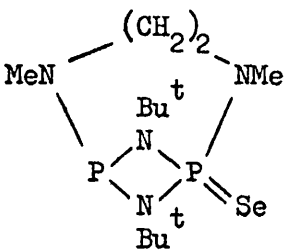
Table 16 cont'd

Compound	Found C	Found H	Found N	Found m/e	Calc. C	Calc. H	Calc. N	Calc. m/e [b]
trans-$Me_2NP.NBu^t.P(S)NMe_2.NBu^t$	44.5	9.3	17.3	324	44.4	9.3	17.3	324
cis-$Me_2NP.NBu^t.P(Se)NMe_2.NBu^t$	38.6	8.1	14.7	372	38.8	8.1	15.1	372
trans-$Me_2NP.NBu^t.P(Se)NMe_2.NBu^t$	39.1	7.9	14.75	372	38.8	8.1	15.1	372
trans-$Me_2NP.NBu^t.P(Te)NMe_2.NBu^t$	34.5	7.3	13.2	422	34.3	7.15	13.35	422
cis-$Me_2N(S)P.NBu^t.P(Se)NMe_2.NBu^t$	36.0	7.15	13.5	404	35.7	7.4	13.9	404
cis-$Me_2NP.NBu^t.P^+(Me)NMe_2.NBu^t\ I^-$	36.4	7.9	12.7		35.9	7.6	12.9	
trans-$Me_2NP.NBu^t.P^+(Me)NMe_2.NBu^t\ I^-$	35.1	7.7	12.9		35.9	7.6	12.9	

Table 16 cont'd

Compound	Found				Calc.			
	C	H	N	m/e	C	H	N	m/e [b]
trans-$[Me_2N(S)PNPh]_2$	48.4	5.35	14.1	396	48.5	5.55	14.1	396
trans-$Me_2N\overline{P.NPh.P(S)NMe_2.NPh}$	52.5	6.1	15.5	364	52.75	6.0	15.4	364
cis-$[Et_2N(S)PNBu^t]_2$	46.3	9.1	13.5	412	46.6	9.2	13.6	412
cis-$[Et_2N(Se)PNBu^t]_2$	37.7	7.5	11.5	508	37.9	7.5	11.1	508
cis-$Et_2N\overline{P.NBu^t.P(S)NEt_2.NBu^t}$	50.4	10.2	14.7	380	50.5	10.0	14.7	380
cis-$Et_2N\overline{P.NBu^t.P(Se)NEt_2.NBu^t}$	44.7	8.8	13.4	428	45.0	8.9	13.1	428
cis-$Et_2N(S)\overline{P.NBu^t.P(Se)NEt_2.NBu^t}$				460				460
cis-$[C_5H_{10}N(Se)PNBu^t]_2$	40.6	7.2	10.6	532	40.75	7.2	10.6	532

Table 16 cont'd

Compound	Found C	Found H	Found N	Found m/e	Calc. C	Calc. H	Calc. N	Calc. m/e [b]
cis-$C_5H_{10}NP.NBu^t.P(Se)NC_5H_{10}.NBu^t$	47.6	8.6	12.8	452	47.9	8.4	12.4	452
	39.0	7.85	15.2	370	39.0	7.6	15.2	370
$ClP.NBu^t.P(S)NMe_2.NBu^t$ [c]	38.1	7.75	13.6	315	38.0	7.6	13.3	315
$Cl(O)P.NBu^t.P(O)NMe_2.NBu^t$				315				315

[a] Elemental analyses figures are given in %.

[b] For ions containing ^{35}Cl, ^{80}Se, or ^{130}Te where appropriate.

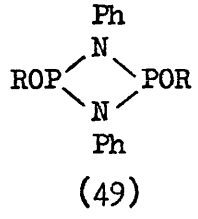
[c] 1:1 Mixture of isomers analysed.

CHAPTER 4

ALKOXYCYCLODIPHOSPHAZANES

INTRODUCTION

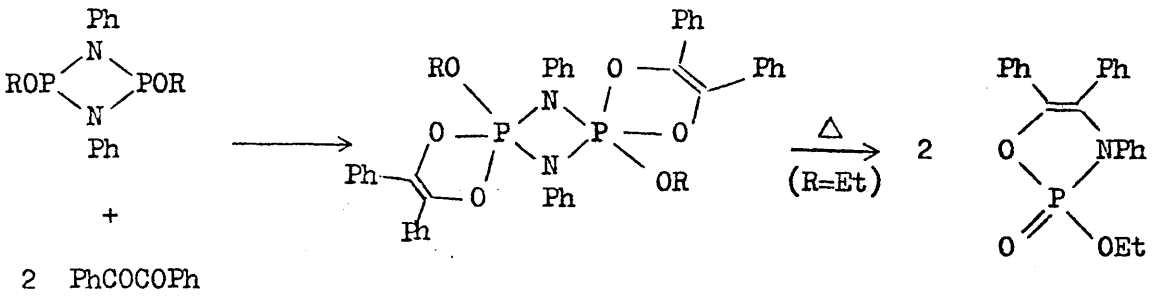
Until the very recent reports of Kawashima and Inamoto (1976)[53] and Zeiss and Weis (1977)[50] there had been little detailed work on alkoxycyclodiphosphazanes. An earlier report[52] that treatment of the dichloroalkylphosphine, $EtOPCl_2$, with aniline led to the monophosph(III)azene, EtOP=NPh, was refuted,[50,53] the product being shown to exist as a dimer, (49) (R=Et), which could also be prepared through the action of ethanol on $(ClPNPh)_2$ using triethylamine as hydrogen chloride acceptor.[50] Cis and trans isomers, which display large differences in phosphorus chemical shift (ca. 50 p.p.m.), were reported[50,53] for (49) (R=Me or Et). An X-ray diffraction study [251] of (49) (R=Me) (δ_P 142.0 p.p.m.) showed this isomer exists in the trans form and it is assumed [50] that all compounds of type (49) with 'high-field' ^{31}P chemical shifts exist as trans isomers. Isomerisation was observed in (49) (R=Me or Et) from the cis to the trans forms which is similar in direction to that proposed for $(Me_2NPNC_6H_4Y\text{-}p)_2$ (Y=H,Cl, or MeO) (Chapter 2), but an important difference is that the trans isomers in the latter compounds were assigned the 'low-field' ^{31}P chemical shifts. The compounds, (49) (R=Bu^{t}O; trans isomer only), MeOP.NPh.POEt.NPh (two isomers) and ROP.NPh.PCl.NPh (R=Me or Et; trans isomers only) were also prepared.[50] McFarlane and Colquhoun reported [51] the preparation of $(MeOPNBu^t)_2$ from treatment of $(ClPNBu^t)_2$ with methanol, though only the thermodynamically more stable isomer (δ_P 133.8 p.p.m.) was isolated. No structural assignment was made.



(49)

Few oxidation reactions of alkoxycyclodiphosph(III)azanes have been reported. In refluxing benzene, or acetonitrile at room temperature, treatment of (49) (R=Me or Et) with benzil gives a cyclodiphosph(v)azane

with five co-ordinate phosphorus, (50), which in the case of (50) (R=Et), decomposes in refluxing o-dichlorobenzene to the compound (51).[53]



(50) (R=Me or Et) (51)

Addition of two molar equivalents of sulphur to the thermodynamically stable form of $(MeOPNBu^t)_2$ readily gave $[MeO(S)PNBu^t]_2$, the monosulphide, $MeO(S)\overline{P.NBu^t.POMe.NBu^t}$, being observed by ^1H-$\{^{31}P\}$ n.m.r. during the course of the reaction.[51]

It was therefore of interest to study the reactions of $(ClPNBu^t)_2$ with alcohols in order to,

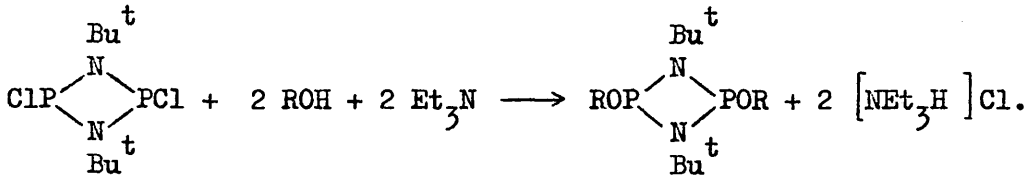
i) extend our present knowledge of the chemistry of alkoxycyclodiphosph(lll)azanes

ii) for the first time undertake a systematic study of the oxidation reactions of these compounds (with sulphur, selenium, and methyl iodide) and,

iii) compare and contrast the properties of all these compounds with those of the related alkylamino-derivatives (Chapters 2 and 3).

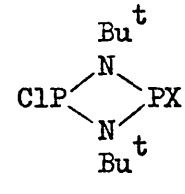
RESULTS

The reactions of $(ClPNBu^t)_2$ with primary alcohols in the presence of triethylamine as hydrogen chloride acceptor gave the 2,4-dialkoxycyclodiphosph(lll)azanes, (52), in good yield:



(52) (R=Me,Et or CF_3CH_2)

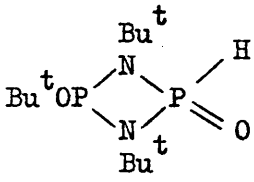
When R=Me or Et goemetrical isomers with a difference in ^{31}P chemical shift of around 70 p.p.m. were obtained initially in roughly equimolar proportions. When R=CF_3CH_2 the isomer with the 'low-field' ^{31}P chemical shift was found in relatively low yield and not isolated, although the other isomer was readily obtained. In the former two cases the mixture of isomers was purified by vacuum distillation; the distillate containing an increased proportion of the isomer with the 'high-field' ^{31}P chemical shift (isomers will hereafter be termed 'low' or 'high-field' depending on their ^{31}P chemical shift until a definite structural assignment is made). On standing, both (52) (R=Me and Et) deposited crystals which on repeated recrystallisation from pentane afforded the pure 'low-field' isomers. Prolonged heating resulted in isomerisation to the pure 'high-field' isomers. The monomethoxy-derivative, (53) (X=OMe) was obtained in good yield from an analogous reaction with one molar equivalent of methanol.



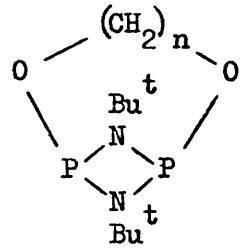
(53)

The di-t-butoxy-derivative, (52) (R=Bu^t), identified by i.r. and n.m.r. spectroscopy, could not be isolated in a pure state owing to what is assumed to be butene elimination, the product of which, (54), could be isolated. Butene elimination has been observed for acyclic t-butylphosphites.[267] The reaction of $(ClPNBu^t)_2$ with one molar

equivalent of t-butanol gave a mixture of (53) (X=Bu^tO), (54), and starting material in a 2:1:1 ratio respectively.



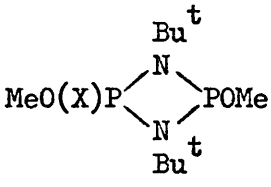
(54)



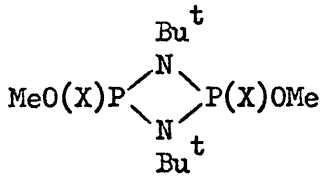
(55)

The new cage compounds (55) (n=2 or 3) which must have a mutual cis-orientation of oxygen atoms were prepared in somewhat low yield by the reaction of $(ClPNBu^t)_2$ with 1,2-ethylene and 1,3-propylene diols in the presence of triethylamine. Appreciable amounts of other, presumably polymeric, materials were also formed. Compounds (55) could be purified by distillation or sublimation under reduced pressure as the 'polymeric materials' were considerably less volatile. Unfortunately, yields of (55) were further reduced by heating during purification.

The oxidation reactions of <u>cis</u> and <u>trans</u>-(52) (R=Me) with elemental sulphur and with selenium were also investigated. The reactions were stereospecific, and both isomers of the mono-(56) (X=S or Se, Y=lone-pair) and di-(57) (X=S or Se) oxidised forms were obtained in each case.



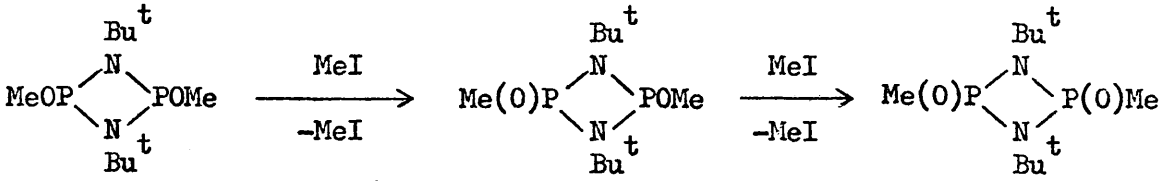
(56)



(57)

No tellurides could be isolated, even from extended reactions with elemental tellurium.

Reactions of cis and trans-(52) (R=Me) with methyl iodide did not result in a quaternary salt, but an Arbuzov-type rearrangement to give both isomeric forms of (58) and (59), the latter only being formed after extended reaction periods.



(58) (59)

The same products, (58) and (59), could also be produced under more forcing conditions by heating the 'high-field ' isomer of (52) (R=Me) in vacuo at 130°C [the 'low-field' isomer of (52) (R=Me) isomerises under such conditions].

Reaction of a 1:1 mixture of cis and trans (52) (R=Me) (total one molar equivalent) with sulphur, selenium, or methyl iodide (total 0.5 molar equivalent) resulted solely in the mono-oxidation product of the 'low-field' isomer in each case, indicating the lower reactivity of the 'high-field' isomer. There was little or no difference in the relative rates of oxidation of (56) (X=S or Se) and (58) with sulphur, selenium, and methyl iodide respectively.

DISCUSSION

As with the alkylaminocyclodiphosph(111)azanes (Chapter 2) and their oxidation products (Chapter 3) it is of primary importance to establish which isomer is cis and which is trans. Indeed, this problem may be solved in part by realising the many chemical similarities between the compounds discussed here and those examined earlier.

The presence of a four-membered ring rather than a phosph(III)azene monomer is clearly indicated in a number of ways:-

i) The ^{1}H and ^{13}C n.m.r. signals from the bridging N-t-butyl-group in (52) (R=Me, Et, or CF_3CH_2) show triplet structure because of equal coupling to two equivalent phosphorus nuclei (Tables 21 and 22).

ii) The mass spectra indicate a dimeric, rather than a monomeric, species is present (Table 23).

iii) Monomeric phosph(III)azenes are generally characterised by exceptionally low-field ^{31}P chemical shifts (generally >300 p.p.m.)[36,45] for which there was no evidence here (Table 21).

The reactions of $(ClPNBu^t)_2$ with alcohols and amines (Chapter 2) are closely related. Both result in a 'low-field' isomer which on standing (in solution) slowly reverts to the thermodynamically favoured 'high-field' isomer, which has a cis structure in the amino-derivatives. By contrast, in the alkoxy-derivatives, $(ROPNPh)_2$ (R=alkyl), the 'high-field' isomer has a trans arrangement of alkoxy-groups[50,251] and so there is no ready correlation with the compounds reported here. It was hoped that the synthesis of the caged derivatives (55) with cis structures would provide a clear indication of the ^{31}P chemical shift to be expected for a cis isomer. Unfortunately, compound (55) (n=2) has a ^{31}P chemical shift intermediate between that of (52) (R=Me or Et), but the analogous trimethylene compound, (55) (n=3),has a shift similar to those of the 'high-field' isomers. These somewhat inconclusive results only tentatively suggest that the 'high-field' isomers have cis structures, though they do indicate a strong dependence of the ^{31}P chemical shift on the phosphorus substituents.

The dipole moments of the 'high' and 'low-field' isomers of (52) (R=Me) were measured in benzene solution and found to be 2.1 and 1.5 Debye units respectively. Again these results are ambiguous, though again they weakly favour a cis assignment of structure to the thermodynamically favoured 'high-field' isomer.

An examination of the i.r. and Raman spectra of both isomeric forms of (52) (R=Me) did not reveal which isomer is centrosymmetric. However, there did appear to be more coincidences between the i.r. and Raman bands in the 'high-field' isomer (selected i.r. and Raman data are shown in Table 17). It was noted (Chapter 2) that

Table 17

Comparison of the i.r. and Raman active bands of $(MeOPNBu^t)_2$ in the range 600-950 $cm.^{-1}$

'high-field' isomer		'low-field' isomer	
i.r./cm^{-1} [a]	Raman/cm^{-1} [b]	i.r./cm^{-1} [c]	Raman/cm^{-1} [d]
	613		615
	633		
648	650		
	668		
704	707	699	
731	736	733	
799	813	800	811
878			
897	916	892	914
928	928	928	928

[a] Liquid film.

[b] Liquid.

[c] Nujol mull.

[d] Solid.

alkylaminocyclodiphosph(lll)azanes have a strong asymmetric P-N ring vibration in the range 845-935 cm^{-1}. The same is true of the alkoxycyclodiphosph(lll)azanes studied here, but in this case the 'high-field' isomers have a band at greater vibrational energy than the 'low-field' isomers (Table 18) which is opposite to that found in

Table 18

ν(P-N-P)asym. in compounds of the type, $RO(X)P(NBu^t)P(Y)OR.NBu^t$

R	X	Y	ν(P-N-P)asym./cm^{-1} 'high-field' isomer (cis)	'low-field' isomer (trans)
Me	l.p.[a]	l.p.	897[b]	890[c]
Et	l.p.	l.p.	890[b]	882[c]
CF_3CH_2	l.p.	l.p.	905[b]	
Bu^t	l.p.	l.p.	873[b]	
Me	S	l.p.	903[b]	902[b]
Me	Se	l.p.	899[b]	895[b]
Me	S	S	922[c]	921[c]
Me	Se	Se	916[c]	914[c]

[a] l.p.=lone-pair. [b] Liquid film. [c] In nujol.

$(Me_2NPNBu^t)_2$, for example, (Table 6). If the 'high-field' alkoxycyclodiphosph(lll)azane isomers are indeed cis then their

relatively large ν(P-N-P)asym. vibrational energies are possibly the consequence of a strong $n_P \longrightarrow \sigma^*_{P-O}$ interaction which should be stronger than that found in alkylaminocyclodiphosph(III)azanes ($n_P \longrightarrow \sigma^*_{P-N}$) owing to the greater electronegativity of oxygen. The asymmetric P-N ring vibration in the cage compounds (55) (n=2 or 3) occurs at 860 and 900 cm^{-1} respectively. This band is, therefore, at considerably lower energy in (55) (n=2) and this is probably the reflection of a considerable strain imposed on the four-membered ring by the dimethylene bridge.

The above results do not show clearly which isomer is cis and which is trans and such a definitive assignment will probably have to await a crystal structure determination. The assignment that the thermodynamically favoured 'high-field' isomers have cis structures is favoured here. This is contrary to the assignment applied to the compounds, $(ROPNPh)_2$ (R=alkyl),[50] but an important factor here is the similarity in properties with those of the amino-derivatives (Chapter 2). Though little difference in basicity was noted[245] between the two isomeric forms of (52) (R=Me), the 'low-field' isomer had bands of considerably lower energy in the photoelectron spectra (Table 19). The 'low-field' isomer of (52) (R=Me) was also the more reactive towards sulphur, selenium, and methyl iodide and possessed a negative P...P coupling constant (Chapter 5). In these respects, the 'low' and 'high-field' isomers of (52) (R=Me) closely parallel the 'low' (trans) and 'high-field' (cis) isomers of $(Me_2NPNBu^t)_2$ and, accordingly, similar structures are proposed.

Table 19

The photoelectron spectra of $(MeOPNBu^t)_2$.

Isomer	eV
'high-field'	8.4, 10.1
'low-field'	7.7, 8.3, 10.1

(bands observed below 11 eV only)

This structural assignment again raises the intriguing question of why cyclodiphosph(III)azanes tend to form cis structures despite adverse steric effects. This has yet to be explained, and the problem is highlighted by the observation of only one (cis) isomeric form of (52) ($R=Bu^t$) whereas both isomers of (52) (R=Me) are found. The only explanation at present is the somewhat speculative one that in some way bulky alkoxy- (like amino-) groups facilitate the isomerisation process.

An attempt was made to discover the preferred conformations of the alkoxy-groups in both cis and trans- alkoxycyclodiphosph(III)azanes. It was anticipated that these would be reflected in the relative signs and magnitudes of $^2J(POC)$[226] and $^3J(POCH)$.[215] It is predicted that the preferred conformation of the alkoxy-group will be that in which the number of gauche interactions between nonbonded electrons on phosphorus and oxygen is maximised (unless steric effects are dominant).[171] This will be either conformation A or B (Figure 18), the former being found in the crystal structure of trans- $(MeOPNPh)_2$.[251]

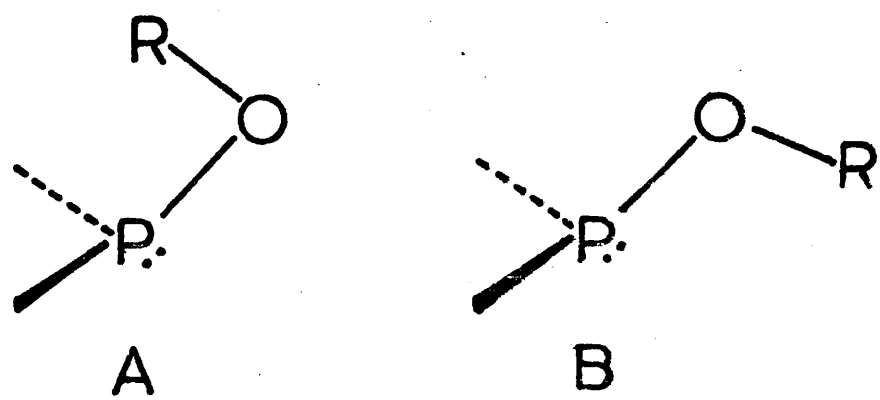


Figure 18.

$^2J(POC)$ should be small (sign unknown) in A and relatively large and positive in B. The ^{13}C n.m.r. spectra of (52) (R=Me, Et, and CF_3CH_2) generally consist of a 'triplet' (assuming ^1H and ^{19}F

decoupling) in the POC region due to inequivalence of the phosphorus nuclei.[268] The spacing of the outer components of this 'triplet' is $|^2J(POC) + {}^4J(PNPOC)|$. As $^4J(PNPOC)$ is small [it is 1.3 Hz in (53) (X=OMe)] this spacing is a close approximation to $^2J(POC)$. The situation is more complicated in the cage compounds, (55) (n=2 or 3) as spin coupling may also be transmitted via P-O-C-C (n=2) and P-O-C-C-C (n=3); similarly, deceptively simple proton 'triplets' in the ^1H n.m.r. spectra of these cage compounds may be affected by coupling over P-O-C-C-H and P-O-C-C-C-H bonds respectively. In (55) (n=2) a series of $^{13}C-\{^1H\}$ double-resonance experiments established that $^2J(POC) + {}^3J(POCC) + {}^4J(PNPOC)$ (4.5 Hz) is opposite in sign to $^3J(POCH) + {}^4J(POCCH) + {}^5J(PNPOCH)$ (9.1 Hz). The latter combination will be positive as four and five bond couplings are small and $^3J(POCH)$ is assumed to be positive.[215] Given that $^4J(PNPOC)$ is likely to be small (<2 Hz) and $^3J(POCC)$ is likely to be positive [it is 2.1 Hz in (55) (n=3)], then this compound possesses the first known negative $^2J(P^{III}OC)$ coupling, although it cannot be measured accurately.

Inspection of Table 22 shows striking differences in $|^2J(POC) + {}^4J(PNPOC)|$ when *cis* and *trans* isomers of (52) (R=Me, Et and CF_3CH_2) are compared. In the *cis* isomer this coupling is always larger and this may be interpreted in terms of greater population of conformers analogous to B (Figure 18) which perhaps is to be expected owing to the greater cross-ring steric interactions implicit in A. The small negative coupling attributed to $^2J(POC)$ in (55) (n=2) is consistent with this assignment, but the reason why the analogous coupling, $^2J(POC) + {}^4J(POCCC) + {}^4J(PNPOC)$, is 8.4 Hz in (55) (n=3) is not clear. Further, $^{13}C-\{^1H\}$ double-resonance experiments

indicate the latter coupling to be the same sign as $^{3}J(\underline{POCH})$ + $^{5}J(\underline{POCCCH})$ + $^{5}J(\underline{PNPOCH})$ which is probably positive. It would appear, therefore, that $^{2}J(\underline{POC})$ may be extremely sensitive to slight changes in conformation when the alkoxy-group spends most of its time in a conformation similar to A, and indeed, even in the cis isomers in which conformation B is important, the dominant conformer may still be that of A.

Comparing $|^{3}J(\underline{POCH}) + {}^{5}J(\underline{PNPOCH})|$ obtained from the ^{1}H spectra of both isomers of (52) (R=Me and Et) shows that this coupling is again slightly smaller in both trans isomers, but the results obtained for (55) (n=2 and 3) do not indicate that the proton couplings have a marked stereochemical dependence (Table 21).

The conformational dependence of the couplings discussed above is considerably less when bonding is to phosphorus(v) as inspection of Tables 21 and 22 shows.

The coupling constants, $^{2}J(\underline{P}^{III}\underline{NC})$ (quaternary carbon) and $^{4}J(\underline{P}^{III}\underline{NCCH})$, depend on the isomer examined and vary in the same way as the amino-derivatives (Tables 21 and 22 and 10 and 11 respectively). $^{2}J(\underline{P}^{III}\underline{NC})$ is always larger (>10 Hz) in the cis isomers relative to the trans isomers (<7 Hz) whereas $^{4}J(\underline{P}^{III}\underline{NCCH})$ is greater in the trans isomers. The dichloro-derivative, cis-$(ClPNBu^{t})_{2}$, is an enigma in that $^{2}J(\underline{PNC})$ is only 6.8 Hz (Table 11) and $^{4}J(\underline{PNCCH})$is 1.0 Hz.[17]

The oxidation of cis and trans-(52) (R=Me) by sulphur, selenium, or methyl iodide is likely to occur by nucleophilic attack of phosphorus on the chalcogen or the carbon atom in methyl iodide. That treatment of the aforementioned alkoxycyclodiphosph(III)azanes with sulphur or selenium results in retention of configuration at phosphorus is shown in several ways:-

i) The ^{31}P chemical shifts of cis isomers of $[Me_2N(X)PNBu^t]_2$ and $Me_2NP(NBu^t).P(X)NMe_2.NBu^t$ (X=S or Se) are upfield of the shifts for the analogous trans isomers (Chapter 3). Assigning structures on this basis to the sulphides and selenides from cis and trans-(52) (R=Me) implies retention of configuration at phosphorus (Table 21).

ii) As was found when mixing equimolar amounts of cis-$(Me_2NPNBu^t)_2$ with cis or trans- $[Me_2N(Se)PNBu^t]_2$, cis- (52) (R=Me) and its diselenide resulted in one monoselenide [the same isomer as that found on treating cis- (52) (R=Me) with one molar equivalent of selenium] whereas addition of the other diselenide resulted in a 1:1 mixture of monoselenide isomers (Figure 19).

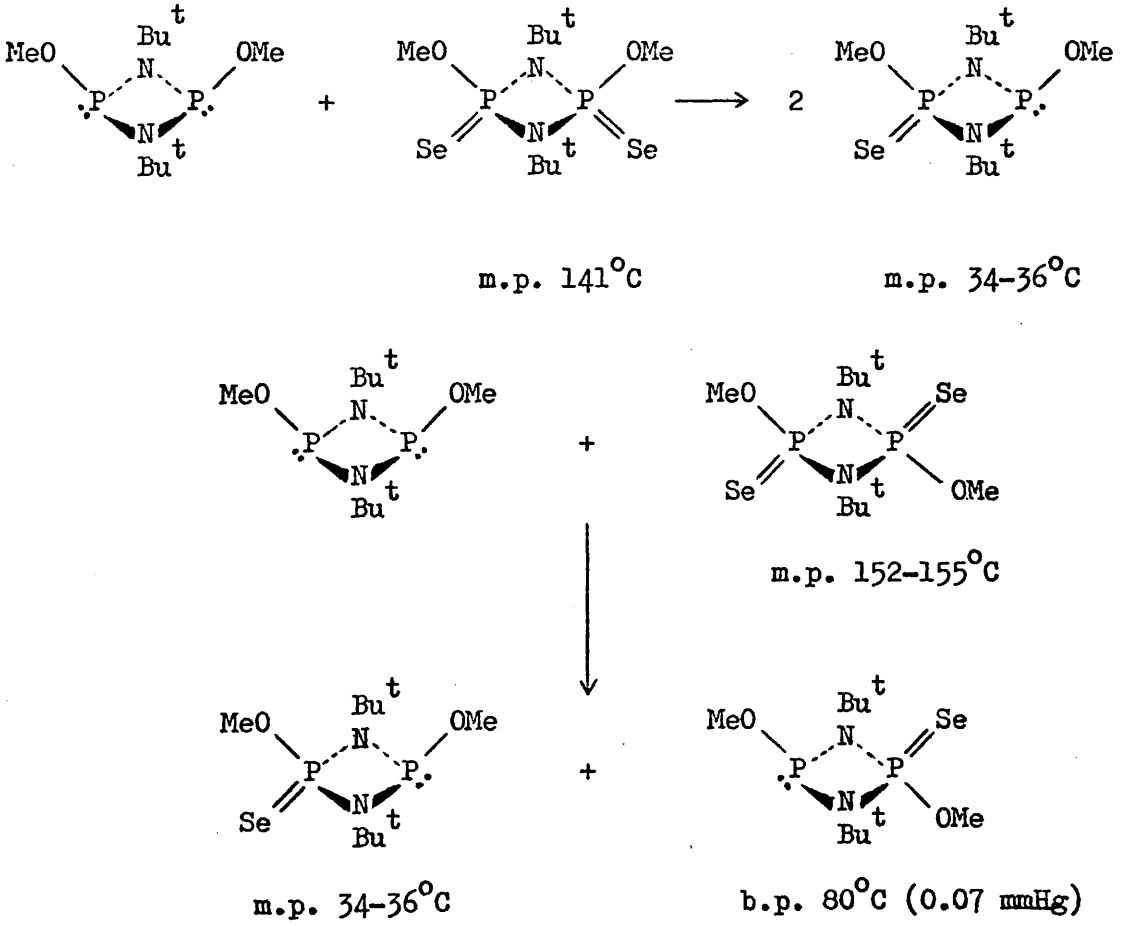


Figure 19.

iii) The ^{77}Se chemical shifts of *cis* isomers of $[Me_2N(Se)PNBu^t]_2$ and $Me_2N\overline{P.NBu^t.P(Se)NMe_2.NBu^t}$ are well upfield (35-100 p.p.m.) of the shifts for the analogous *trans* isomers (Chapter 5, Table 26). Assignment of structure on this basis to (56) and (57) (X=Se) also implies retention of configuration at phosphorus as the *cis* and *trans* mono- (56) and diselenides, (57), arise from *cis* and *trans*-(52) (R=Me) respectively.

Spin couplings, $^1J(PSe)$,[269] in the range 890-960 Hz indicate that the P(Se)(OMe) rather than the P(O)SeMe group is present (Table 20). However, on heating either of the isomeric forms of (57) (X=Se) with methyl iodide, sequential rearrangement of the P(Se)OMe groups to P(O)SeMe was observed by ^{31}P n.m.r. [$^1J(PSe)$ *ca.* 500 Hz] (Table 20).

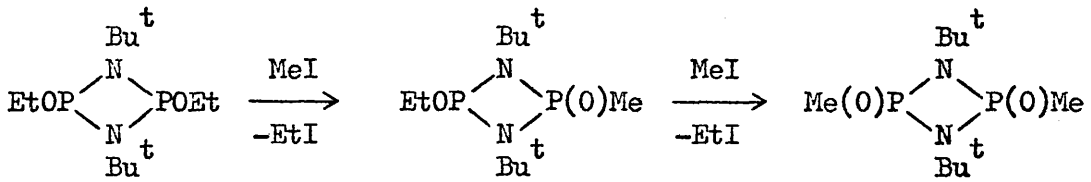
Table 20

Compound	δ_P [a] p.p.m.	$^1J(PSe)$ Hz	δ_P [a] p.p.m.	$^1J(PSe)$ Hz
cis-$MeO\overline{P.NBu^t.P(Se)OMe.NBu^t}$	53.8	891.9	96.2	
trans-$MeO\overline{P.NBu^t.P(Se)OMe.NBu^t}$	72.3	893.5	119.3	
cis-$[MeO(Se)PNBu^t]_2$	46.4	954.5		
$MeO(Se)\overline{P.NBu^t.P(O)SeMe.NBu^t}$	46.5	955.5	9.4	511.8
$[MeSe(O)PNBu^t]_2$			5.2	493.2
trans-$[MeO(Se)PNBu^t]_2$	53.0	952.7		
$MeO(Se)\overline{P.NBu^t.P(O)SeMe.NBu^t}$	51.4	957.9	13.2	516.5
$[MeSe(O)PNBu^t]_2$			10.9	532.8

[a] Shifts are downfield, relative to 85% (external) H_3PO_4.

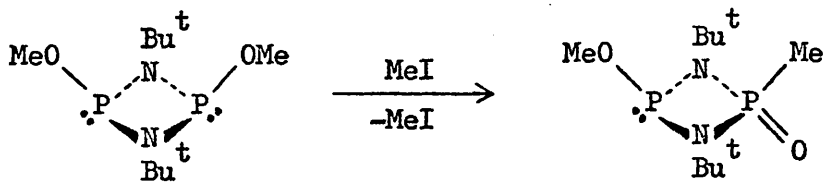
It is interesting to note that cis and trans isomers of (56) and (57) (X=S or Se) cannot be distinguished by their ν(P-N-P)asym. vibrational energies (Table 18) unlike their bis(dimethylamino)-counterparts (Chapter 3, Table 13). Nevertheless, it is again found that consecutive addition of sulphur or selenium to the cyclodiphosph(111)azane raises the energy of the ν(P-N-P)asym. vibration and that this vibration is at higher energy in the sulphides compared with the analogous selenides.

In the oxidation of (52) (R=Me) by methyl iodide it was established that the alkyl- group bonded to phosphorus as a result of the Arbuzov rearrangement arises from the methyl iodide (and not the alkoxy-group). This was shown by the reaction of methyl iodide on cis-(52) (R=Et) in which compounds (60) and (59) were the sole products as shown by $^{1}H-\{^{31}P\}$ n.m.r.

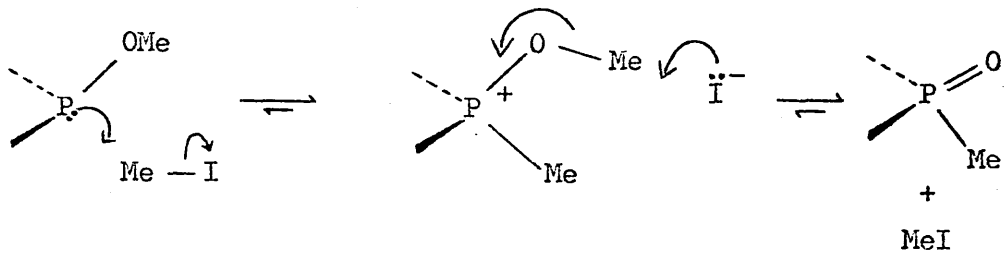


cis (60) cis-(59)

The compound, (58), produced by the action of methyl iodide on cis-(52) (R=Me) would appear to have a mutual cis arrangement of methoxy and methyl-groups as the $^{31}P(111)$ chemical shift of this compound is to high-field of the other isomer (Table 21).



The above structural assignment suggests overall inversion of configuration at phosphorus, though whether inversion occurs at the first or second stage of the mechanism proposed (below) is unknown.



The thermodynamic instability of trans-(52) (R=Me) is paralleled by its enhanced nucleophilic reactivity relative to the cis isomer. Trans-$(Me_2NPNBu^t)_2$ behaved similarly (Chapter 3). This difference would not appear to be steric in origin: a conclusion supported by the fact that the lowest energy bands in the photoelectron spectra of (52) (R=Me) are ca. 0.5 eV lower in binding energy in the trans relative to the cis isomer. (Table 19). These bands are likely to arise from interactions between nitrogen (or less likely, oxygen) and phosphorus lone-pair orbitals[169] but a thorough investigation into the bonding in geometrical isomers of (52) (R=Me) will be needed to provide further insight into the reasons for their reactivity (and stability) differences.

EXPERIMENTAL

Methods used in the purification of solvents and reagents can be found in Appendix A. Instruments used in the recording of i.r., Raman, photoelectron, n.m.r. (Tables 21 and 22) and mass (Table 23) spectroscopic data along with those used in the measurement of dipole moments plus the source of microanalyses (Table 23) can be found in Appendix B. The compound, $(ClPNBu^t)_2$,[17] was prepared as in literature. Other preparative details are briefly outlined below.

1,3-Di-t-butyl-2-cis-4 (and 2-trans-4)-dimethoxycyclodiphosph(III)azanes:- Methanol (1.2 g, 37 mmol) and triethylamine (3.7 g, 36 mmol) were added dropwise to a stirred solution of 1,3-di-t-butyl-2,4-dichloro-cyclodiphosph(III)azane (5.0 g, 18 mmol) in light petroleum (b.p. 40-60°C; 150 cm^3) held at 0°C. On completion of the addition, the mixture was refluxed (0.5 h), the triethylamine hydrochloride removed by filtration, and the solvent evaporated from the filtrate. The oily residue was distilled under reduced pressure [b.p. 75-80°C (0.2 mmHg)] and left to stand (72 h) at ambient temperatures. During this time a crystalline solid was formed which was removed and recrystallised from pentane to give the trans-compound (0.9 g, 16%) as colourless needles, m.p. 56-60°C. The oily product was heated at 100°C (10 h) and redistilled to give the cis-compound (3.1 g, 64%), a colourless oil b.p. 66°C (0.1 mmHg). The yield of the cis isomer could be increased to ca. 80% by heating (24 h) the initial distillate at 120°C.

1,3-Di-t-butyl-2-cis-4(and 2-trans-4)-diethoxycyclodiphosph(III)azanes:- These were prepared similarly:
cis isomer (55%), colourless oil, b.p. 86-90°C (0.1 mmHg);
trans isomer (20%), colourless crystals, m.p. 56-60°C.

1,3-Di-t-butyl-2-cis-4-trifluoroethoxycyclodiphosph(III)azane:- Trifluoroethanol (4.32 g, 43.2 mmol) and triethylamine (4.36 g, 43.2 mmol) were added dropwise to a stirred solution of 1,3,-di-t-butyl-2,4-dichloro-cyclodiphosph(III)azane (5.93 g, 21.6 mmol) in diethyl ether (150 cm^3) at 20°C. The resulting mixture was stirred (0.5 h) and on work up afforded a cloudy oil which was shown by ^1H-$\{^{31}P\}$ and ^{19}F n.m.r. to be the 1,3-di-t-butyl-2,4-trifluoroethoxycyclodiphosph(III)azanes

(cis: trans ca. 4:1). The trans isomer did not crystallise from the oil on standing (7 d) at ambient temperatures. Distillation of the crude product under reduced pressure altered the cis: trans isomer ratio to ca. 10:1 respectively and the distillate on standing (ca. 1 month) gave the compound (5.65 g, 65%), a colourless oil, b.p. 58-60°C (0.04 mmHg).

2-Trans-4-di-t-butoxy-1,3-di-t-butylcyclodiphosph(111)azane:-
t-Butanol (2.47 g, 33.4 mmol) and triethylamine (3.37 g, 33.4 mmol) were slowly added to a stirred solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(111)azane (4.60 g, 16.7 mmol) in light petroleum (b.p. 60-80°C; 120 cm^3) at 20°C. On completion of the addition, the mixture was refluxed (3 h) and after work up gave a colourless oil which was identified by $^1H-\{^{31}P\}$ n.m.r. as the compound. Purfication of this oil by distillation under reduced pressure proved impossible owing to decomposition to 2-t-butoxy-1,3-di-t-butyl-4-hydro-4-oxocyclodiphosphazane. Decomposition to the latter compound also occurred on standing at ambient temperatures (14 d). 2-t-Butoxy-1,3-di-t-butyl-4-hydro-4-oxocyclodiphosphazane was readily crystallised from light petroleum (b.p. 40-60°C), colourless needles (65%), m.p. 114-116°C.

1,3-Di-t-butyl-2-chloro-cis-4-methoxycyclodiphosph(111)azane:-
Methanol (0.49 g, 15.3 mmol) and triethylamine (1.62 g, 16.0 mmol) were added to a stirred solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph-(111)azane (4.21 g, 15.3 mmol) in light petroleum (b.p. 40-60°C; 100 cm^3) at 20°C. The resultant mixture was stirred (0.5 h) and after work up yielded the compound (3.31 g, 80%), a colourless oil, b.p. 60-62°C (0.03 mmHg).

2-t-Butoxy-1,3-di-t-butyl-4-chlorocyclodiphosph(III)azane:- t-Butanol (1.38 g, 18.7 mmol) and triethylamine (1.89 g, 18.7 mmol) were added to a stirred solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(III)azane (5.15 g, 18.7 mmol) in light petroleum (b.p. 40-60°C; 150 cm^3) at 20°C. On completion of the addition, the mixture was refluxed (2 h). Work up gave a slightly cloudy oil which was shown by ^{31}P n.m.r. to consist of the compound, the 2,4-dichloro-, and the 2,4-di-t-butoxy-derivatives in a ca. 2:1:1 ratio respectively. On standing, the latter compound was quantitively converted to 2-t-butoxy-1,3-di-t-butyl-4-hydro-4-oxocyclodiphosphazane (see above).

7,8-Di-t-butyl-2,5-dioxa-7,8-diaza-1,6-diphospha(III)bicyclo[4.1.1]-octane:- 1,2-Ethylene diol (0.7 g, 11 mmol) and triethylamine (2.4 g, 24 mmol) in chloroform (30 cm^3) was added slowly to a solution of 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(III)azane (3.2 g, 12 mmol) in light petroleum (b.p. 40-60°C; 200 cm^3) at 0°C. On warming to ambient temperatures, the solution was stirred (0.5 h). Work up afforded the compound which was separated from other, presumably polymeric, materials by two vacuum sublimations [ca. 50°C (0.1 mmHg)]; colourless needles (0.7 g, 23%), m.p. 65-67°C.

8,9-Di-t-butyl-2,6-dioxa-8,9-diaza-1,7-diphospha(III)bicyclo [5.1.1]-nonane:- This was prepared similarly to the above and recrystallised from pentane; white needles (20%), m.p. 182°C.

1,3-Di-t-butyl-2-cis-4-dimethoxy-2,4-dithiocyclodiphosph(v)azane:- 1,3-Di-t-butyl-2-cis-4-dimethoxycyclodiphosph(III)azane (1.04 g, 3.91 mmol) and sulphur (0.25 g, 7.82 mmol) were heated (6 h) under reflux in toluene (6 cm^3). The solvent was evaporated and the residue crystallised from a light petroleum (b.p. 40-60°C) - methylene chloride mixture (3:1) to give the compound (0.96 g, 74%), white needles, m.p. 159-160°C (lit.[51] m.p. 124°C).

1,3-Di-t-butyl-2-trans-4-dimethoxy-2,4-dithiocyclodiphosph(v)azane:- This was prepared similarly from 1,3-di-t-butyl-2-trans-4-dimethoxycyclodiphosph(III)azane; white needles (56%), m.p. 152-154°C.

1,3-Di-t-butyl-2-cis-4-dimethoxy-2,4-diselenocyclodiphosph(v)azane:- This, too, was prepared similarly; white needles (41%), m.p. 141°C. The compound slowly degrades to a red solid if kept at ambient temperatures.

1,3-Di-t-butyl-2-trans-4-dimethoxy-2,4-diselenocyclodiphosph(v)azane:- This was prepared similarly from 1,3-di-t-butyl-2-trans-4-dimethoxycyclodiphosph(III)azane; white needles (which slowly turn pink if kept at ca. 20°C) (61%), m.p. 152-155°C.

1,3-Di-t-butyl-2-cis-4-dimethoxy-2-thiocyclodiphosphazane:- 1,3-Di-t-butyl-2-cis-4-dimethoxycyclodiphosph(III)azane (1.84 g, 6.91 mmol) and sulphur (0.221 g, 6.91 mmol) were stirred (0.5 h) together in benzene (10 cm^3) at ambient temperatures. The benzene was evaporated and the residue distilled under reduced pressure to give the compound (1.32 g, 64%), a colourless oil, b.p. 54°C (0.02 mmHg).

1,3-Di-t-butyl-2-trans-4-dimethoxy-2-thiocyclodiphosphazane:- This was obtained similarly from 1,3-di-t-butyl-2-trans-4-dimethoxycyclodiphosph(III)azane; colourless oil (88%), b.p. 60°C (0.03 mmHg).

1,3-Di-t-butyl-2-cis-4(and 2-trans-4)-dimethoxy-2-selenocyclodiphosphazanes:- These were again obtained similarly to the above, using one molar equivalent of selenium instead of elemental sulphur: cis isomer (63%), a colourless oil, b.p. 72-76°C (0.07 mmHg) which crystallised on standing, m.p. 34-36°C;

trans isomer (83%), colourless oil, b.p. 80°C (0.07 mmHg).

Attempted preparation of 1,3-di-t-butyl-2,4-dimethoxy-2-telluro-cyclodiphosphazane:- 1,3-di-t-butyl-2-cis-4-dimethoxycyclodiphosph(111)azane (0.227 g, 0.854 mmol) and finely ground tellurium (0.109 g, 0.854 mmol) were heated together (72 h) in benzene (0.5 cm^3) at 80°C. Study of the mixture by ^1H n.m.r. showed that no reaction had occurred.

1,3-Di-t-butyl-2-cis-4-dimethyl-2,4-dioxocyclodiphosph(v)azane:-
(1) To a rapidly stirred solution of 1,3-di-t-butyl-2-cis-4-dimethoxycyclodiphosph(111)azane (2.27 g, 8.53 mmol) in benzene (10 cm^3) at 20°C was added methyl iodide (2.42 g, 17.06 mmol). The mixture was refluxed (24 h), the solvent and methyl iodide were removed, and the white residue crystallised from a light petroleum (b.p. 40-60°C)-methylene chloride mixture (1:1) to yield the compound (1.86 g, 82%), colourless needles (turning white on exposure to air), m.p. 160°C.
(2) 1,3-Di-t-butyl-2-cis-4-dimethoxycyclodiphosph(111)azane (0.5 g, 2 mmol) was placed in an evacuated, sealed, n.m.r.-tube and heated (130°C). The reaction was followed spectroscopically and after 16 h complete rearrangement to the compound had occurred.
(3) 1,3-Di-t-butyl-2-cis-4-diethoxycyclodiphosph(111)azane (0.2 g, 0.7 mmol) and methyl iodide (0.2 g, 1.4 mmol) were mixed at 20°C in deuteriochloroform (0.5 cm^3) in a sealed tube. On heating at 90°C (0.5 h) the products were identified by n.m.r. as solely consisting of the compound and ethyl iodide.

1,3-Di-t-butyl-2-trans-4-dimethyl-2,4-dioxocyclodiphosph(v)azane:-
This was prepared similarly to method (1) above from 1,3-di-t-butyl-2-trans-4-dimethoxycyclodiphosph(111)azane: colourless crystals (78%), m.p. 230-232°C.

1,3-Di-t-butyl-2-methoxy-4-methyl-4-oxocyclodiphosphazane:-
1,3-Di-t-butyl-2-cis-4-dimethoxycyclodiphosph(III)azane (1.19 g, 4.48 mmol) and methyl iodide (0.64 g, 4.51 mmol) were mixed in methylene chloride (10 cm^3) at 20°C. After stirring (6 h), the solvent and methyl iodide were removed under reduced pressure leaving a white solid which was crystallised from pentane giving the compound (0.78 g, 65%) as colourless prisms, m.p. 97-98°C.

A second isomer of the compound was obtained in a similar fashion from 1,3-di-t-butyl-2-trans-4-dimethoxycyclodiphosph(III)azane [stirring time (0.5 h)]: colourless oil (88%), b.p. 64°C (0.05 mmHg).

1,3-Di-t-butyl-2-ethoxy-4-methyl-4-oxocyclodiphosphazane:-
1,3-Di-t-butyl-2-cis-4-diethoxycyclodiphosph(III)azane (0.2 g, 0.7 mmol) and methyl iodide (0.1 g, 0.7 mmol) were mixed at 20°C in deuteriochloroform. Examination of the products by $^1H-\{^{31}P\}$ n.m.r. (0.1 after mixing) indicated quantitative conversion to the compound and ethyl iodide.

The relative rates of reactions of isomeric forms of $(MeOPNBu^t)_2$ with sulphur, selenium, or methyl iodide (all in benzene solution) were carried out monitoring the progress of the reaction by ^1H n.m.r. spectroscopy. $^1H-\{^{31}P\}$ experiments were also used to confirm the nature of the products. Reactions of isomers of $MeOP\overline{.NBu^t.P(X)OMe.NBu^t}$ (X=S or Se) and $MeOP\overline{.NBu^t.P(O)Me.NBu^t}$ with sulphur, selenium, and methyl iodide respectively were also carried out on an n.m.r.-tube scale, as were the reactions of cis-$(MeOPNBu^t)_2$ with equimolar amounts of cis or trans-$[MeO(Se)PNBu^t]_2$ and the reactions of cis or trans-$[MeO(Se)PNBu^t]_2$ with methyl iodide.

Table 21

Phosphorus -31 and ^{1}H n.m.r. data [a]

Compound	^{31}P		^{1}H			
	δ_P [b] p.p.m.	$^{2}J(PNP)$ Hz	δ_{POCH} p.p.m.	$^{3}J(POCH)$ [c] Hz	δ Bu^t p.p.m.	$^{4}J(PNCCH)$ Hz
cis-(MeOPNBu^t)$_2$	133.7	15.9	3.48	10.1	1.29	<0.5
trans-(MeOPNBu^t)$_2$	202.4	9.5	3.65	9.0	1.24	0.7
cis-(EtOPNBu^t)$_2$	131.4	d	3.92	7.6	1.29	<0.5
trans-(EtOPNBu^t)$_2$	209.7	d	3.98	7.0	1.24	0.8
cis-(CF$_3$CH$_2$OPNBu^t)$_2$ [e]	143.3	17.5 ± 1	4.17	6.5	1.30	<0.5
trans-(CF$_3$CH$_2$OPNBu^t)$_2$ [f]	222.9	d	4.23	ca. 6.5	1.23	0.9
cis-(Bu^{t}OPNBu^t)$_2$	129.6	d	1.45 [g]	<0.4 [h]	1.34	0.4
cis-MeOP.NBu^t.PCl.NBu^t	188.0 (PCl)	39.2			1.38	0.8 (PCl)

Table 21 cont'd

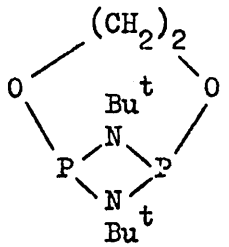
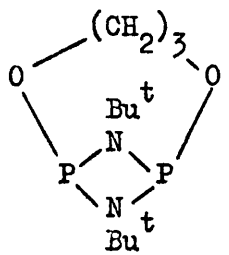
Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{POCH} p.p.m.	^1H $^3J(POCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
cis-$Bu^tOP(NBu^t)PCl(NBu^t)$	137.8		3.75	8.1		0.6
	191.8 (PCl)	49.7			1.37	[d]
	163.8		1.46 [g]	[d],[h]		[d]
	177.5	[d],[i]	4.17	9.1	1.26	0.6
	135.4	[d]	3.97	6.6	1.29	<0.3
			1.87 [j]	0 [h]		6.9 [k]

Table 21 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{POCH} p.p.m.	^1H $^3J(POCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
cis-$[MeO(S)PNBu^t]_2$	51.6	28.5	3.81	16.0	1.51	0.4
trans-$[MeO(S)PNBu^t]_2$	56.6	20.8	3.93	16.2	1.52	0.4
cis-$[MeO(Se)PNBu^t]_2$	46.4	8.0	3.78	16.8	1.54	0.5
trans-$[MeO(Se)PNBu^t]_2$	53.0	2.1	3.87	16.7	1.55	0.5
cis-$MeOP(NBu^t).P(S)OMe.NBu^t$	94.2 (P^{III})	14.7	3.45	9.3	1.37	ca. 0.3
	60.2		3.77	15.0		0.6
trans-$MeOP(NBu^t).P(S)OMe.NBu^t$	110.0 (P^{III})	12.6	3.59	8.7	1.35	0.9
	75.7		3.71	15.5		0.5
cis-$MeOP(NBu^t).P(Se)OMe.NBu^t$	96.2 (P^{III})	17.3	3.46	8.8	1.39	<0.3
	53.8		3.75	15.7		ca. 0.4

Table 21 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{POCH} p.p.m.	^1H $^3J(POCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
trans-$MeOP(NBu^t).P(Se)OMe.NBu^t$	119.3 (P^{III})	11.1	3.65	8.6	1.37	0.9
	72.3		3.73	16.0		0.5
cis-$[Me(O)PNBu^t]_2$	18.9	10.5	1.83 [l]	17.0 [m]	1.51	0.5
trans-$[Me(O)PNBu^t]_2$	24.5	[d]	2.05 [l]	16.8 [m]	1.49	0.6
$MeOP(NBu^t).P(O)Me.NBu^t$ (m.p. 97-98°C)	89.0 (P^{III})	8.6	3.54	9.3	1.41	ca. 0.5
	22.1		1.77 [l]	16.4 [n]		ca. 0.3
$MeOP(NBu^t).P(O)Me.NBu^t$ [b.p. 64°C (0.05 mmHg)]	131.4 (P^{III})	<0.2	3.57	10.0	1.38	ca. 0.5
	38.0		1.85 [l]	15.6 [n]		<0.3
$Bu^tOP(NBu^t).P(O)H.NBu^t$	105.1 (P^{III})	12.1	1.47 [g]	1.1 [h]	1.39	0.9
	-3.2		7.38 [o]	590 ± 1 [p]		ca. 0.5
				2.4 [q]		

Table 21 cont'd

Compound	^{31}P δ_P [b] p.p.m.	^{31}P $^2J(PNP)$ Hz	^1H δ_{POCH} p.p.m.	^1H $^3J(POCH)$ [c] Hz	^1H δ_{Bu^t} p.p.m.	^1H $^4J(PNCCH)$ Hz
$EtOP(NBu^t).P(O)Me.NBu^t$	89.3 (P^{III})	[d]	3.94	6.7	1.37	$\leqslant 0.5$
	22.2		1.74 [l]	15.7 [n]		$\leqslant 0.5$

[a] All n.m.r. data for $CDCl_3$ solutions.

[b] Downfield ^{31}P chemical shifts are positive; relative to external H_3PO_4.

[c] More correctly, $|{}^3J(POCH) + {}^5J(PNPOCH)|$ for symmetrical alkoxycyclodiphosphazanes.

[d] Not measured.

[e] Fluorine n.m.r. data (upfield shifts are negative; relative to external CCl_3F): δ_F -75.5 p.p.m., $^4J(POCCF)$ 2.8 Hz, $^3J(FCCH)$ 8.6 Hz.

[f] Fluorine n.m.r. data: δ_F -74.6 p.p.m., $^4J(POCCF)$ 2 ± 1 Hz, $^3J(FCCH)$ 8.6 Hz.

[g] δOBu^t.

[h] $^4J(POCCH)$.

Table 21 cont'd

i Same sign as $^{3}J(POCH) + {}^{4}J(POCCH) + {}^{5}J(PNPOCH)$.

j δ_{POCCH}.

k $^{3}J(HCCH)$.

l δ_{PCH}.

m $\left|{}^{2}J(PCH) + {}^{4}J(PNPCH)\right|$.

n $^{2}J(PCH)$.

o δ_{PH}.

p $^{1}J(PH)$.

q $^{3}J(PNPH)$.

Table 22

Carbon -13 n.m.r. data [a]

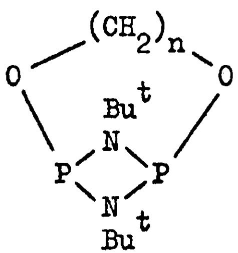
Compound	δ PNC p.p.m.	^2J(PNC) Hz	δ PNCC p.p.m.	^3J(PNCC) Hz	δ POC p.p.m.	^2J(POC) [b] Hz	δ POCC p.p.m.	^3J(POCC) [c] Hz
cis-$(MeOPNBu^t)_2$	51.1	12.1	31.1	6.0	48.6	7.5		
trans-$(MeOPNBu^t)_2$	50.9	6.0	30.2	5.4	48.1	2.9		
cis-$(EtOPNBu^t)_2$	51.2	12.5	31.1	6.1	57.5	7.9	17.2	1.9
trans-$(EtOPNBu^t)_2$	51.0	6.1	30.5	5.5	56.9	0	16.4	2.1
cis-$(CF_3CH_2OPNBu^t)_2$	52.0	11.8	31.0	6.1	60.0	8.3 [d]	124.5	<1.2 [e]
cis-$MeOP.NBu^t.PCl.NBu^t$	52.9	9.8 (av.)	30.7	5.7,6.5	51.2	10.3 [f]		
 n=2	51.1	10.5	30.3	5.7	66.8	4.5 [g]		
n=3	51.0	12.2	31.1	6.2	60.5	8.4	33.0	2.1

Table 22 cont'd

Compound	δ_{PNC} p.p.m.	$^2J(PNC)$ Hz	δ_{PNCC} p.p.m.	$^3J(PNCC)$ Hz	δ_{POC} p.p.m.	$^2J(POC)$ [b] Hz	δ_{POCC} p.p.m.	$^3J(POCC)$ [c] Hz
cis-$[MeO(S)PNBu^t]_2$	56.2	0	29.5	4.45	55.1	7.6		
trans-$[MeO(S)PNBu^t]_2$	56.8	0	30.2	4.65	55.6	8.9		
cis-$[MeO(Se)PNBu^t]_2$	56.7	0.6	29.4	4.45	55.7	8.3		
cis-$MeOP(NBu^t).P(S)OMe.NBu^t$	53.1	10.8 (P^{III})	30.3	4.95 (av.)	47.5	5.6 (P^{III})		
		0			54.6	6.9		
cis-$[Me(O)PNBu^t]_2$	55.0	0	30.9	4.3	19.1 [h]	113.7 [i]		
						5.2 [j]		
trans-$[Me(O)PNBu^t]_2$	54.6	0	30.8	4.0	21.0	111.9 [i]		
						4.8 [j]		
$MeOP(NBu^t).P(O)Me.NBu^t$ [k]	52.3	8.9 (P^{III})	31.0	4.5 (av.)	46.9	9.0	21.0 [h]	102.3 [i]
		1.2				0.5 [l]		0 [j]

Table 22 cont'd

Compound	δ_{PNC} p.p.m.	$^{2}J(PNC)$ Hz	δ_{PNCC} p.p.m.	$^{3}J(PNCC)$ Hz	δ_{POC} p.p.m.	$^{2}J(POC)$ [b] Hz	δ_{POCC} p.p.m.	$^{3}J(POCC)$ [c] Hz
$MeO\overline{P.NBu^{t}.P(O)Me.NBu^{t}}$ [m]	52.7	10.3 (P^{III})	30.8	4.9 (av)	48.0	3.9	21.7	99.6 [i]
		0				0.7 [l]		5.1 [j]
$Bu^{t}O\overline{P.NBu^{t}.P(O)H.NBu^{t}}$	52.4	7.3 (P^{III})	31.5	5.4 (av)	31.6	8.7	78.7	[n]
		0				0 [l]		

[a] In $CDCl_3$ solution.

[b] More correctly, $|^{2}J(POC) + {}^{4}J(PNPOC)|$ for symmetrical alkoxycyclodiphosphazanes.

[c] More correctly, $|^{3}J(POCC) + {}^{5}J(PNPOCC)|$ for symmetrical alkoxycyclodiphosphazanes.

[d] $^{2}J(FCC)=35.8$ Hz.

[e] $^{1}J(FC)=277.3$ Hz.

[f] $^{4}J(PNPOC)=1.3$ Hz.

[g] Opposite sign to $^{3}J(POCH) + {}^{4}J(POCCH) + {}^{5}J(PNPOCH)$ as shown by $^{13}C-\{^{1}H\}$ experiments.

h δ_{PC}.

i $^{1}J(PC)$ [Approximately 1st order spectrum for the symmetrical alkoxycyclodiphosph(v)azanes as this coupling is large with respect to $^{2}J(PNP)$].

j $^{3}J(PNPC)$.

k mp. 97-98°C.

l $^{4}J(PNPOC)$.

m b.p. 64°C (0.05 mmHg).

n Not measured.

Table 23

Analytical data [a]

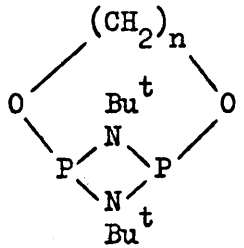
COMPOUND	Found C	Found H	Found N	Found m/e	Calc. C	Calc. H	Calc. N	Calc. m/e [b]
cis-$(MeOPNBu^t)_2$	45.15	9.0	10.55	266	45.1	9.0	10.5	266
trans-$(MeOPNBu^t)_2$	45.0	8.8	10.4	266	45.1	9.0	10.5	266
cis-$(EtOPNBu^t)_2$	48.75	9.75	9.6	294	49.0	9.5	9.5	294
trans-$(EtOPNBu^t)_2$	49.1	9.8	10.0	294	49.0	9.5	9.5	294
cis-$(CF_3CH_2OPNBu^t)_2$	36.2	5.6	7.2	402	35.8	5.5	7.0	402
cis-MeOP.NBu^t.PCl.NBu^t	40.1	8.1	10.7	270	39.9	7.8	10.35	270
 n=2	42.25	8.5	10.5	264	45.45	8.3	10.6	264
n=3	47.3	8.55	10.4	278	47.5	8.6	10.1	278

Table 23 cont'd

Compound	Found C	Found H	Found N	Found $^{m}/_{e}$	Calc. C	Calc. H	Calc. N	Calc. $^{m}/_{e}$ [b]
cis-$[MeO(S)PNBu^{t}]_2$	36.2	7.0	8.6	330	36.4	7.3	8.5	330
trans-$[MeO(S)PNBu^{t}]_2$	36.1	7.4	8.1	330	36.4	7.3	8.5	330
cis-$[MeO(Se)PNBu^{t}]_2$	28.6	5.8	6.4	426	28.3	5.7	6.6	426
trans-$[MeO(Se)PNBu^{t}]_2$	29.1	5.9	6.7	426	28.3	5.7	6.6	426
cis-$MeOP(NBu^{t})P(S)OMe(NBu^{t})$	40.0	8.3	9.2	298	40.3	8.05	9.4	298
trans-$MeOP(NBu^{t})P(S)OMe(NBu^{t})$	40.0	8.05	9.4	298	40.3	8.05	9.4	298
cis-$MeOP(NBu^{t})P(Se)OMe(NBu^{t})$	35.1	7.4	8.3	346	34.8	7.0	8.1	346
trans-$MeOP(NBu^{t})P(Se)OMe(NBu^{t})$	34.6	7.2	7.7	346	34.8	7.0	8.1	346
cis-$[Me(O)PNBu^{t}]_2$	44.7	9.1	10.5	266	45.1	9.0	10.5	266
trans-$[Me(O)PNBu^{t}]_2$	45.0	8.8	10.4	266	45.1	9.0	10.5	266
$MeOP(NBu^{t})P(O)Me(NBu^{t})$ [c]	45.0	8.5	10.4	266	45.1	9.0	10.5	266
$MeOP(NBu^{t})P(O)Me(NBu^{t})$ [d]	45.0	9.3	10.3	266	45.1	9.0	10.5	266
$Bu^{t}OP(NBu^{t})P(O)H(NBu^{t})$	48.9	9.5	9.8	294	49.0	9.5	9.5	294

Table 23 cont'd

[a] Elemental analyses figures are given in %.

[b] For ions containing ^{35}Cl or ^{80}Se where appropriate.

[c] m.p. 97-98°C.

[d] b.p. 64°C (0.05 mm Hg).

CHAPTER 5

N.M.R. STUDIES ON CYCLODIPHOSPHAZANES

A The Sign and Magnitude of $^2J(PNP)$

INTRODUCTION

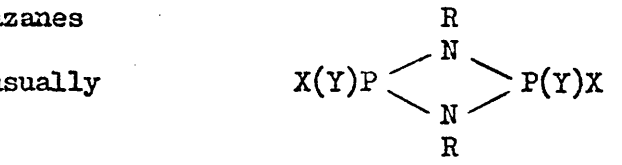
The study of spin-spin coupling constants not involving protons is of considerable interest because of the possibility of several coupling mechanisms being of importance and because, where the known ranges of these couplings tend to be large, they are therefore more sensitive to alterations in the chemical environment (such as substituents and stereochemistry).[270]

The coupling constant, $^2J(PNP)$, covers a wide range (*ca.* -35 to 665 Hz). Despite the fact that a considerable number of such couplings have been measured, very little is known about the factors which affect this coupling. This is largely for two reasons: firstly, because many of the species studied have not been amenable to sign determination, and secondly, because it has been recently shown [51,238] that the magnitude of this coupling (when it involves two tervalent phosphorus atoms) is strongly influenced by the conformation which the P-N bonds adopt in solution. This last point clouds other issues which might be considered, such as the electronegativity of the phosphorus and/or nitrogen substituents. On increase of the co-ordination number at phosphorus, $^2J(PNP)$ decreases greatly [51] and indeed in all phosphorus(v) compounds containing the P-N-P unit, $^2J(PNP)$ is typically <100 Hz. [22,94,271-275] Studies of substituent effects on $^2J(PNP)$ in cyclophosphazenes have pointed to the importance of substituent electronegativity.[271,276]

The isolation of a number of cyclodiphosphazanes (Chapters 2-4) provides an opportunity to systematically study the effects of substitution and co-ordination number at phosphorus on $^2J(PNP)$ without large changes in the mutual conformations of the two phosphorus atoms. The fact that many of these compounds are symmetrical with magnetically inequivalent phosphorus atoms provides an advantage in that the sign of $^2J(PNP)$ is frequently obtainable by double-resonance methods as is

briefly outlined below.

The ^{1}H n.m.r. signals arising from the X-groups of symmetrical cyclodiphosphazanes of the general type (61) usually consist of a deceptively simple triplet (assuming fast rotation about the P-X bond), the central line being a broad (often unresolved) multiplet. An example is shown in Figure 20. These spectra are examples of the $X_3AA'X_3'$ [277],



(61) { R=Bu^t or aryl; X=Me$_2$N or MeO; Y=lone-pair, O, S or Se. }

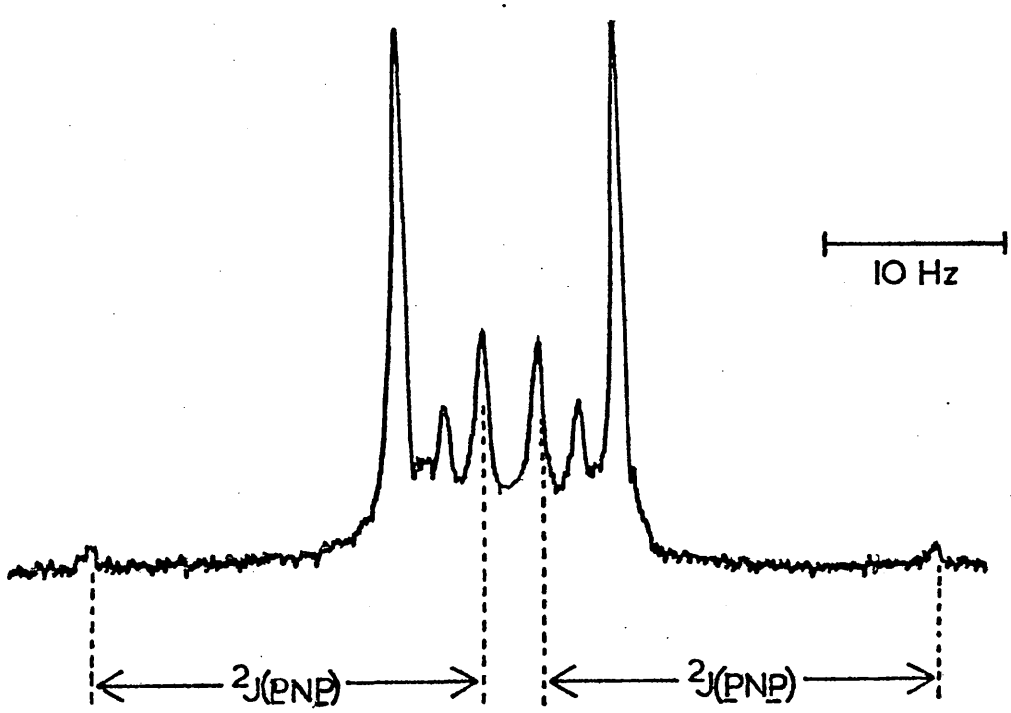


Figure 20. ^{1}H n.m.r. spectrum, O-methyl region, of cis-$[MeO(S)PNBu^t]_2$ $[|^2J(PNP)| = 28.5$ Hz$]$.

^{278}(X=OMe) and $X_6AA'X'_6$ ^{279} (X=Me_2N) spin systems (ignoring coupling to the aryl or t-butyl protons). Harris ^{268} developed formulae to describe the general $X_nAA'X'_n$ case, subject to three conditions:-

i) $J(XX')=0$

ii) Only nuclei of spin quantum number $I=\frac{1}{2}$ considered

iii) The chemical shift between the A and X nuclei is large compared with the coupling constant.

These limitations are adhered to in the compounds discussed here, where A=P and X=H. When the coupling constant, $^2J(PP')$, is small with respect to $\underline{L}$ $\left[\underline{L}=|J(P...H)-J(P'...H)|\right]$ then weak 'outer' lines may be visible in the proton spectrum and these can be used to obtain the magnitude of $^2J(PP')$ by spectral analysis ^{268} (Figure 20). The relative sign of $^2J(PP')$ may be obtained by $^1H-\{^{31}P\}$ double-resonance experiments. These take advantage of the connection between the components of the $\underline{N}$ doublet $\left[\underline{N}=|J(P...H)+J(P'...H)|\right]$ in the ^1H spectrum and a multiplet in the ^{31}P spectrum which is separated from the main ^{31}P signal by (approximately) $^2J(PP')$. The connection between this multiplet and the components of the $\underline{N}$ doublet determines the sign of $^2J(PP')$ relative to $J(P...H)+J(P'...H)$.^{280,281} The position of this group of outer lines may be determined either by conventional $^1H-\{^{31}P\}$ double-resonance or, more accurately, by recording the $^1H-\{^{31}P\}$ INDOR spectra. An alternative method of finding the relative sign of $^2J(\underline{PNP})$ exists in compounds of the type, (61) (R=Bu^t), where coupling to the t-butyl protons is easily resolved. $^1H-\{^{31}P\}$ double-resonance experiments in this case allow the signs of $^2J(\underline{PNP}')$ and $^4J(\underline{PNCCH})$ to be compared.^{51}

In the symmetrical cyclodiphosph(v)azanes, (61) (Y=Se), $^2J(\underline{PNP})$ may be obtained by direct observation of the ^{31}P n.m.r. spectrum as the spin system for molecules containing ^{77}Se is of the $AA'X$ type

(ignoring couplings to the protons). ^{77}Se, the only naturally occurring magnetic isotope of selenium, possesses a spin quantum number $I=\frac{1}{2}$ (natural abundance 7.6%) and so the selenium satellites in the phosphorus spectrum consist of an eight line pattern, the three couplings being J(PSe), J(P´Se), and J(PP´) (Figure 21).

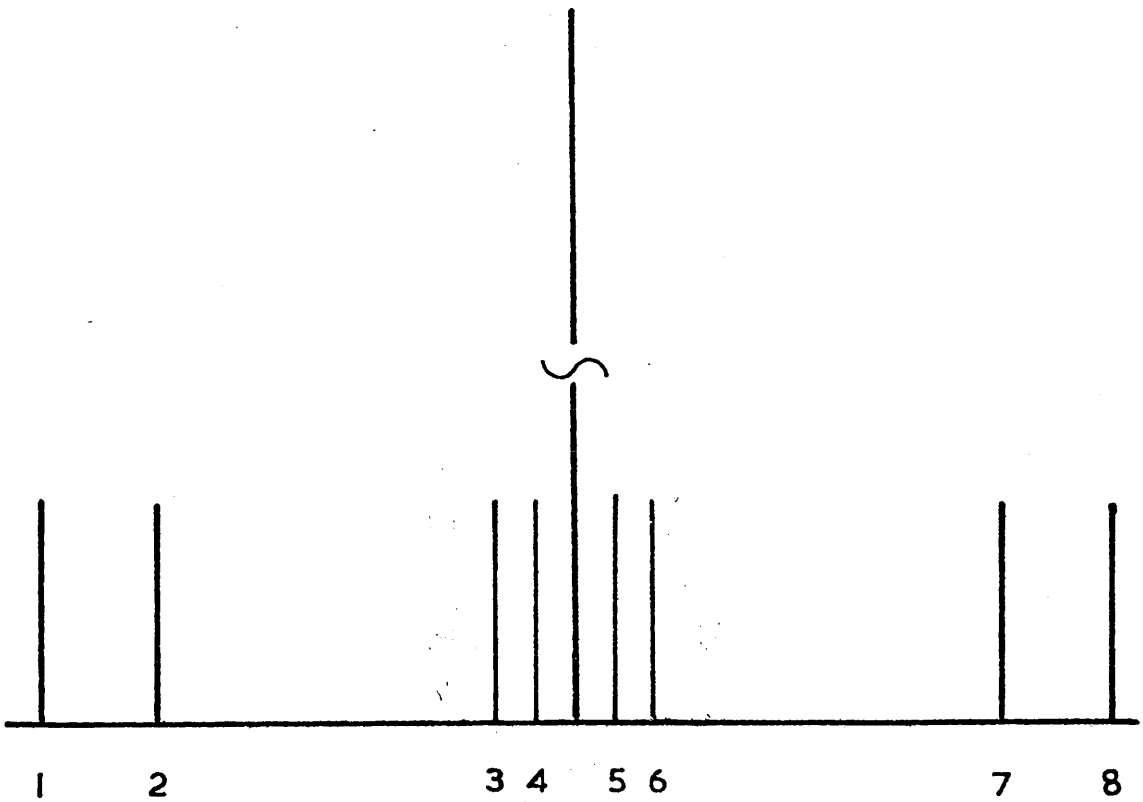


Figure 21: A diagrammatic representation of the A spectrum of an AA´X spin system, assuming $J(AX) > J(AA´) > J(A´X)$, ($A=^{31}P$, $X=^{77}Se$). The separation between lines,

1 and 7 = 2 and 8 = J(PSe)

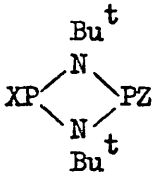
1 and 2 = 3 and 5 = 4 and 6 = 7 and 8 = J(PP´)

3 and 4 = 5 and 6 = J(P´Se)

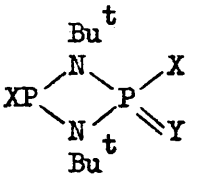
The sign of $^{2}J(\underline{PNP})$ relative to $^{3}J(\underline{PNPSe})$ may be obtained by heteronuclear $^{31}P-\{^{1}H, ^{77}Se\}$ triple-resonance, employing selective irradiation of the ^{77}Se resonant frequencies and observing the two 'outer' pairs of selenium satellites. No measurements have been reported

to date of $^{3}J(\underline{PNPSe})$. However, $^{1}J(\underline{PSe})$ is both substantial[269] and always negative.[282] The sign of $^{3}J(\underline{PNPSe})$ relative to $^{1}J(\underline{PSe})$ may be determined by homonuclear $^{31}P-\{^{1}H, ^{31}P\}$ triple-resonance, selectively irradiating at the phosphorus resonant frequencies. When the 'inner' two pairs of selenium satellites are clearly resolvable, $^{31}P-\{^{1}H, ^{77}Se\}$ triple-resonance allows the signs of $^{1}J(\underline{PSe})$ and $^{2}J(\underline{PNP})$ to be compared.

In asymmetric cyclodiphosphazanes of types (62) and



(62)



(63)

(63), $|^{2}J(\underline{PNP})|$ is readily obtained by direct observation of ^{31}P spectrum. As above, there are a number of ways of determining the sign of $^{2}J(\underline{PNP})$, and these often depend on the nature of X,Y, or Z:-

i) If there is resolvable coupling to the t-butyl protons, $^{2}J(\underline{PNP})$ may be compared in sign with $^{4}J(\underline{PNCCH})$ by $^{1}H-\{^{31}P\}$ double-resonance.

ii) If there is a long-range coupling from phosphorus to X or Z, then the sign of $^{2}J(\underline{PNP})$ may be compared with that of the analogous short-range coupling. This is especially useful if X or Z=F as $^{3}J(\underline{PNPF})$ is usually quite large, facilitating $^{19}F-\{^{31}P\}$ double-resonance experiments,[283,284] and the sign of $^{1}J(\underline{PF})$ is known to be negative. When X or Z=alkoxy or amino, $^{5}J(\underline{P...H})$ may be zero or too small for this technique to be viable.

(iii) In compounds (63) (Y=Se), as above, heteronuclear $^{31}P-\{^{1}H, ^{77}Se\}$ triple-resonance will permit comparison of the signs of $^{2}J(\underline{P}N\underline{P})$ and $^{3}J(\underline{P}NP\underline{Se})$. $^{3}J(\underline{P}NP\underline{Se})$ usually has to be measured by triple-resonance as broadening of the phosphorus(111) signal obscures the selenium satellites. This broadening also precludes a sign comparison between $^{1}J(\underline{P}Se)$ and $^{2}J(\underline{P}N\underline{P})$ in compounds of this type

RESULTS AND DISCUSSION

The sign and magnitude of $^{2}J(\underline{P}N\underline{P})$ for the compounds studied, including the method of sign determination are shown in Table 25. One compound in particular, $(FPNBu^{t})_{2}$, deserves special mention as this illustrates a spin system, $XAA'X'$ (ignoring proton couplings), in which the condition [268] of $J(XX')=0$ is not met. Accordingly, analysis of this spectrum has yet to be discussed. Nixon and Wilkins[27] originally examined the ^{19}F n.m.r. spectrum of $(FPNBu^{t})_{2}$ and the results here are similar to those originally obtained except that $^{19}F-\{^{31}P\}$ double-resonance experiments have now been used to establish the signs of $^{2}J(\underline{P}N\underline{P})$ and $^{4}J(\underline{F}PNP\underline{F})$ relative to $^{1}J(\underline{P}F)$ and $^{3}J(\underline{P}NP\underline{F})$. The energy level diagram for this $XAA'X'$ spin system indicates [285] that each component of the intense N doublet in the ^{19}F spectrum is connected with the N doublet and two of the transitions (5 and 7 or 6 and 8) in the ^{31}P spectrum (the numbering of transitions is taken from reference 285). The connection between the two spectra was obtained by $^{19}F-\{^{31}P\}$ double-resonance as outlined in Figure 22. This distinguished the two pairs of couplings, $^{2}J(\underline{P}N\underline{P}) + {}^{4}J(\underline{F}PNP\underline{F})$, (125.5 Hz), and $^{1}J(\underline{P}F) + {}^{3}J(\underline{F}PNP\underline{F})$, (1158.5 Hz), and established that they are opposite in sign. As $^{1}J(\underline{P}F)$ is large and negative[283,284] then $^{2}J(\underline{P}N\underline{P})$ and $^{4}J(\underline{F}PNP\underline{F})$ (30.7 and 94.8 Hz) are both positive, but they are not distinguished. An assignment of 92.5 Hz to $^{2}J(\underline{P}N\underline{P})$ was originally made [27] for this compound. This is now disputed on two counts. Firstly, inspection of Table 25 shows that changes in

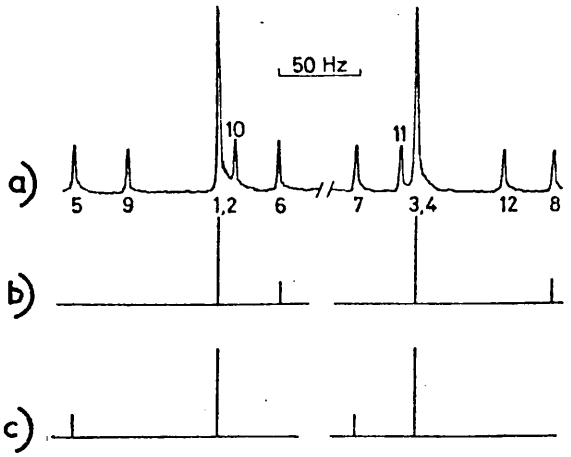


Figure 22: a) ^{19}F n.m.r. spectrum of $(FPNBu^t)_2$;
b) ^{31}P transitions detected by monitoring transitions 1,2 in a) (diagrammatic); c) as in b), now monitoring transitions 3,4.

$^2J(\underline{PNP})$ in cyclodiphosph(III)azanes appear to be dominated by electronegativity effects. This being the case, 30.7 Hz represents the best progression from other symmetric cyclodiphosph(III)azanes. Against this, it should be noted that $^2J(\underline{PNP})$ in $\overline{FP.NBu^t.PCl.NBu^t}$ is +49.6 Hz and so perhaps the larger coupling to the difluoride might be the correct assignment. However, comparison of the values of $^2J(\underline{PNP})$ for $Me_2\overline{NP.NBu^t.PX.NBu^t}$ [X=F (+14.0 Hz) and X=Cl (+32.5 Hz)] indicates that a chlorine, rather than a fluorine, substituent gives the larger P...P coupling. Secondly, Table 24 shows that in compounds of the type, $\overline{FP.NBu^t.PX.NBu^t}$ (X=F, Cl, or NMe_2), there is a close parallel between $^2J(\underline{PNP})$ and $^3J(\underline{PNPF})$, but only when $^2J(\underline{PNP})$ is 30.7 Hz in $(FPNBu^t)_2$.

Table 24

Comparison of ^{19}F n.m.r. data with $^{2}J(PNP)$ in compounds, $FP(NBu^{t})PX(NBu^{t})$ [a]

X	δ_F [b] p.p.m.	$^{1}J(PF)$ Hz	$^{3}J(PNPF)$ Hz	$^{2}J(PNP)$ Hz
NMe_2	-17.8	-1149±1	-14.9±0.5	+14.0±0.5
F	-21.9	-1181±1	+22.5±1	+30.7±1 [c]
Cl	-26.5	-1189±1	+59.0±1	+49.6±0.5

[a] In $CDCl_3$ solution at *ca.* 33°C.

[b] Upfield (negative) relative to external CCl_3F.

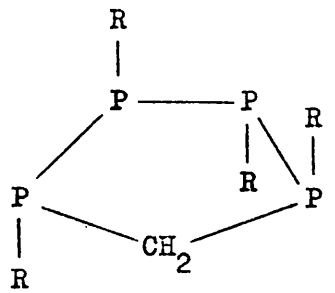
[c] $^{4}J(FPNPF)$=94.8±1 Hz.

One drawback is that this assumes the compounds in Table 24 are all isostructural (*cis*) and totally unambiguous evidence for this is lacking. The value of 94.2 Hz which is now assigned to $^{4}J(FPNPF)$ is very large, especially when compared with the same parameter in diphosphinoamines, $F_2P.NR.PF_2$ (R=H,[286] alkyl,[287,288] or aryl[287]) where it is less than 11.7 Hz, or the values of $^{4}J(FPNPF)$ in the complexes, $[ML_4]$ [M=Ni or Pt, L=$FPOC_6H_4O$ or $PF(OPh)_2$],[289] where it is less than 8.4 Hz. One possible explanation for this anomalously high value is that $^{4}J(FPNPF)$ has a sizeable 'through-space' contribution and that $(FPNBu^{t})_2$ must therefore have a *cis* arrangement of fluorine atoms. This is supported by the fact that the analogous dichloride, $(ClPNBu^{t})_2$, has a *cis* structure,[106] but on the other hand the Cl...Cl nonbonded distance is 4.10 Å [106] and the view has been expressed that at distances of greater than 2.5 Å, F...F 'through-space' coupling effects will be small.[290]

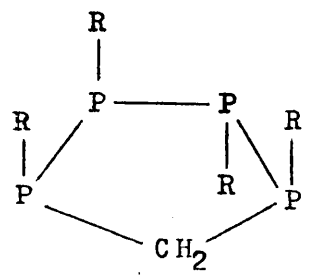
Inspection of Table 25 shows that there is a much smaller range of values of $^2J(\underline{PNP})$ in cyclodiphosph(III)azanes than that found in the acyclic diphosphinoamines [51,238,287] and this is reflected in the reduced conformational mobility of the ring relative to these acyclic systems.[51,238] $^2J(\underline{PNP})$ generally becomes more positive on substitution at phosphorus by more electronegative groups; its magnitude usually increasing in the series, $Me < Me_2N < MeO < F < Cl$, when compounds of like structure are compared. The major exceptions are the positive P...P coupling found in $\underline{cis}$-$(Me_2NPNPh)_2$, compared with the negative value found in $\underline{cis}$-$(MeOPNPh)_2$ (see below), and the somewhat large (if positive) value of 33.0 Hz found[48] for $\underline{cis}$-$MeP.NBu^t.PCl.NBu^t$. The extreme example of this electronegativity effect is found in the adduct $Me_2NP.NBu^t.P^+.NBu^t\ AlCl_4^-$, in which the $=P^+$ atom can be regarded as being bonded to a substituent of very high electronegativity and in which the most positive P...P coupling of all (+58 Hz) is found. $|^2J(\underline{PNP})|$ is 36.0 Hz in $MeP.NBu^t.P^+.NBu^t\ AlCl_4^-$.[48]

All four pairs of geometrical isomers, $(XPNR)_2$ (X=Me_2N or MeO, R=Bu^t or Ph), have P...P couplings of opposite sign and in all but one case, $[(MeOPNPh)_2]$, it is the $\underline{trans}$ isomer which possesses the negative coupling. There is no ready explanation for this anomalous result, though it may be noted that both $\underline{cis}$-$(MeOPNPh)_2$[50,53] and $\underline{trans}$-$(Me_2NPNPh)_2$, which have P...P couplings of the same (negative) sign are the thermodynamically favoured isomers. Reasons for the difference in sign on comparing cyclodiphosph(III)azane isomers are not clear, though this may be related to the marked difference found in the nonbonded electron-pair interactions which have been indicated by photoelectron spectroscopy (Chapters 2 and 4). A similar dependence of $^2J(PP)$ on the relative configuration of the substituents on phosphorus was observed in studies of the cyclomonocarbaphosphanes, (64)-(66), in which negative P...P couplings were found between

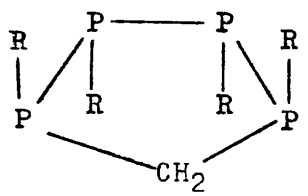
phosphorus atoms with trans substituents and more positive couplings were found when the substituents on phosphorus are cis.[291,292]



(64) (R=alkyl or aryl)



(65) (R=Me)



(66) (R=Me)

Oxidation of one phosphorus atom to produce mixed oxidation state cyclodiphosphazanes in some cases results in remarkably little change in the P...P coupling (Table 25). For example, the values of ^2J(PNP) for cis and trans-$(Me_2NPNBu^t)_2$ and cis and trans-$Me_2NP(NBu^t).P(Se)NMe_2.NBu^t$ respectively, are the same within experimental error. Unfortunately, the sign of ^2J(PNP) in cis and trans-$Me_2NP(NBu^t).P(S)NMe_2.NBu^t$ was not obtained as coupling to the t-butyl protons was not resolvable and there was no long-range coupling to phosphorus from either set of N-methyl protons. The mono-oxidation products of the methoxy-derivatives, $MeOP(NBu^t).P(X)OMe.NBu^t$ (X=S or Se), provided quite different results. When X=Se, the cis isomer had a more negative P...P coupling (-17.3 Hz) than the trans isomer, though again the P...P coupling in the trans isomer (-11.1 Hz) was almost identical to that of trans-$(MeOPNBu^t)_2$ (-9.5 Hz).

The sign of $^2J(\underline{PNP})$ was unobtainable for cis-MeOP.NBu^t.P(S)OMe.NBu^t, but the value of -17.6 Hz for the P...P coupling in the trans isomer closely resembles that for trans-MeOP.NBu^t.P(Se)OMe.NBu^t. The final enigma is that while $^2J(\underline{PNP})$ is positive (+7.2 Hz) in cis-C_5H_{10}NP.NBu^t.P(Se)NC_5H_{10}.NBu^t (as it is in the analogous dimethylamino-derivatives), the P...P coupling in the cage compound, (45), is negative (-20.6 Hz).

The above results may be compared with those found by Bulloch[22] for ClP.NMe.P(X)Cl.NBu^t [X=O (two isomers), $^2J(\underline{PNP})$=-12.0 and -36.3 Hz; X=S (two isomers), $^2J(\underline{PNP})$=-6.0 and -36.3 Hz] and Me_2NP.NMe.P(X)Cl.NBu^t [X=O, $^2J(\underline{PNP})$=-8±2 Hz; X=S (two isomers), $^2J(\underline{PNP})$=-12 ± 2 and -10 ± 4 Hz] in which all the P...P couplings are negative and seem little affected whether oxygen or sulphur is attached to phosphorus (no structural assignments were made to these compounds). This is in contrast to a report[273] that in compounds of the type, $(RO)_2P(X).NMe.P(OR)_2$ (R=Bu^{t}O or EtO), $|^2J(\underline{PNP})|$ depends on the nature of X (X=O, S, or Se), and increases according to the series, O <S <Se.

At present no discernible trend in $^2J(\underline{PNP})$ is obvious in the above mixed oxidation state cyclodiphosphazanes. It is probably suffice to state that $^2J(\underline{PNP})$ is small and may be either positive or negative. It may be affected by singly bonded substituents to phosphorus as more negative P...P couplings are found in the chloro-derivatives,[22] but whether oxygen, sulphur, or selenium is bonded seems to have little effect.

Inspection of the P...P couplings found in cyclodiphosph(v)azanes (Table 25) shows that three general points can be made:-

i) All the P...P couplings are positive as is generally found for compounds containing the P(V)-N-P(V) skeleton (cf. ref. 272).

ii) Replacement of dimethylamino-groups by the more electronegative methoxy-groups results in a less positive P...P coupling.

iii) The size of the P...P couplings increases in the order, Se<S<O. This is somewhat surprising as studies of compounds of the type, $[R_2P(X)]_2O$ (R=alkyl; X=O or S),[293] and bis(phosphinoyl)- and bis(phosphinothioyl)amines[272] showed that $^2J(PP)$ did not differ greatly whether oxygen or sulphur was attached to phosphorus.

The $^{31}P-\{^1H, ^{77}Se\}$ triple-resonance experiments used in determining the sign of $^2J(PNP)$ relative to $^nJ(PSe)$ also permit the calculation of the ^{77}Se chemical shifts on the basis that $\Xi(^{77}Se)$ for Me_2Se is 19,071,520 Hz,[294] (Table 26). The ^{77}Se chemical shifts are clearly dependent on the isomer studied: in every case, for a given pair of isomers, that which is cis has a higher field ^{77}Se shift by ca. 35-120 p.p.m. The reason for these ^{77}Se chemical shift differences is not clear, but it has been shown[294] that the resonance hybrid, $P^+ — Se^-$ is important, especially when π-bonding substituents are attached to phosphorus, and further that such a hybrid moves the ^{77}Se shift to higher field.[294] If the conclusions in ref. 294 are correct, it would appear that there is more $P^+ — Se^-$ character in the phosphorus-selenium bond in the cis cyclodiphosphazanes. Finally, it is apparent that $^1J(PSe)$ becomes more negative on replacing the dimethylamino by the more electronegative methoxy-group. This is consistent with the observations of McFarlane and Rycroft[294] though opposite to the trend found for a number of other one bond couplings,[295] notably $^1J(PH)$,[296] $^1J(CH)$,[297] and $^1J(CF)$.[298]

EXPERIMENTAL

Instruments used in the recording of ^{1}H, ^{19}F and ^{31}P n.m.r. spectra and double and triple-resonance experiments are described in Appendix B. The compounds, $(FPNBu^{t})_{2}$,[27] $(MePNBu^{t})_{2}$,[48] $(MeOPNPh)_{2}$,[53] $Me_{2}NP.NBu^{t}.PCl.NBu^{t}$,[22] $[Me_{2}N(O)PNPh]_{2}$,[56] and $[Me_{2}N(O)PNCH_{2}Ph]_{2}$[56] were prepared by literature methods. The other compounds were prepared as outlined in Chapters 2-4 except for 1,3-di-t-butyl-2-chloro-4-fluorocyclodiphosph(III)azane which was obtained by heating 1,3-di-t-butyl-2,4-dichloro- and 2,4-difluorocyclodiphosph(III)azanes together at ca. 100°C for 24 h after which time the proportions of the three compounds were ca. 2:1:1 respectively. ^{1}H and ^{31}P n.m.r. data for the compound ($CDCl_{3}$ solution): $\delta_{P(Cl)}$ 197.1, $\delta_{P(F)}$ 180.3, $^{2}J(PNP)$, +49.6 Hz; $\delta_{Bu^{t}}$ 1.40, $^{4}J(PNCCH)$ 0.9 Hz (both) [all positive shifts (in p.p.m.) downfield; ^{31}P shifts relative to 85% (external) $H_{3}PO_{4}$].

Table 25

The sign and magnitude of $^{2}J(PNP)$ in cyclodiphosphazanes

Compound	$^{2}J(PNP)$ Hz	$^{n}J(P...X)$ [a] Hz	Method of sign determination
cis-$(FPNBu^{t})_2$	+30.7 ± 1 [b]	$^{1}J(PF)$, -1,181 ± 1 [b]	c
cis-$(MeOPNBu^{t})_2$	+15.9 ± 0.5	$^{3}J(POCH) + {}^{5}J(PNPOCH)$, + 10.1	d
trans-$(MeOPNBu^{t})_2$	-9.5 ± 0.5	$^{3}J(POCH) + {}^{5}J(PNPOCH)$, + 9.0	d
cis-$(Me_2NPNBu^{t})_2$	+14 ± 5	$^{3}J(PNCH) + {}^{5}J(PNPNCH)$, + 8.0	d
trans-$(Me_2NPNBu^{t})_2$	-10 ± 5	$^{3}J(PNCH) + {}^{5}J(PNPNCH)$, + 12.2	d
cis-$(MePNBu^{t})_2$	+8.5	$^{2}J(PCH) + {}^{4}J(PNPCH)$, + 6.4	d
cis-$(MeOPNPh)_2$	<0 [e] (11.75 [f])	$^{3}J(POCH) + {}^{5}J(PNPOCH)$, + 9.3	d
trans-$(MeOPNPh)_2$	>0 [e]	$^{3}J(POCH) + {}^{5}J(PNPOCH)$, + 10.2	d
cis-$(Me_2NPNPh)_2$	>0 [e]	$^{3}J(PNCH) + {}^{5}J(PNPNCH)$, + 8.7	d

Table 25 cont'd

Compound	$^{2}J(\underline{P}N\underline{P})$ Hz	$^{n}J(\underline{P}...\underline{X})$ [a] Hz	Method of sign determination
trans-$(Me_2NPNPh)_2$	<0 [e]	$^{3}J(\underline{P}NC\underline{H})$ + $^{5}J(\underline{P}NPNC\underline{H})$, + 8.4	d
cis-$FP(NBu^t)(PCl)NBu^t$	+49.6 ± 0.5	$^{1}J(\underline{P}F)$, -1,189 ± 1	c
cis-$MeOP(NBu^t)(PCl)NBu^t$	+39.2 ± 0.5	$^{3}J(\underline{P}OC\underline{H})$,+ 8.1 [g]	h
		$^{4}J(\underline{P}NCC\underline{H})$, + 0.8 ($\underline{P}Cl$)	h
		$^{4}J(\underline{P}NCC\underline{H})$, + 0.6	h
cis-$Me_2NP(NBu^t)(PCl)NBu^t$	+32.5 ± 0.5	$^{4}J(\underline{P}NCC\underline{H})$, + 0.7 ($\underline{P}Cl$)	h
		$^{4}J(\underline{P}NCC\underline{H})$, + 0.5	h
cis-$MeP(NBu^t)(PCl)NBu^t$	33.0 [i]		
cis-$FP(NBu^t)(PNMe_2)NBu^t$	+14.0 ± 0.5	$^{1}J(\underline{P}F)$, -1,149 ± 1	c
$Me_2NP(NBu^t)(P^+)NBu^t$ $AlCl_4^-$	+58 ± 5	$^{4}J(\underline{P}NCC\underline{H})$, + 1.2 ($\underline{P}^+$)	h
		$^{4}J(\underline{P}NCC\underline{H})$, + 0.7	h
cis-$MeOP(NBu^t)(P(S)OMe)NBu^t$	14.7		
trans-$MeOP(NBu^t)(P(S)OMe)NBu^t$	-12.6	$^{4}J(\underline{P}NCC\underline{H})$, + 0.9 ($\underline{P}^{III}$)	h

Table 25 cont'd

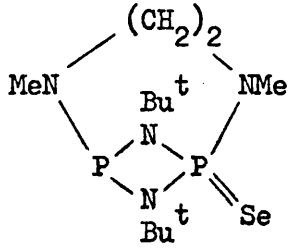
Compound	$^{2}J(\underline{P}N\underline{P})$ Hz	$^{n}J(\underline{P}...\underline{X})$ [a] Hz	Method of sign determination
<u>cis</u>-MeO$\overline{P.NBu^{t}.P(Se)OMe.NBu^{t}}$	-17.3	$^{3}J(\underline{P}N\underline{P}Se)$, + 2 ± 1	j
<u>trans</u>-MeO$\overline{P.NBu^{t}.P(Se)OMe.NBu^{t}}$	-11.1	$^{3}J(\underline{P}N\underline{P}Se)$, - 18 ± 1	j
<u>cis</u>-$Me_2N\overline{P.NBu^{t}.P(S)NMe_2.NBu^{t}}$	11.2		
<u>trans</u>-$Me_2N\overline{P.NBu^{t}.P(S)NMe_2.NBu^{t}}$	11.2		
<u>cis</u>-$Me_2N\overline{P.NBu^{t}.P(Se)NMe_2.NBu^{t}}$	+ 9.4	$^{3}J(\underline{P}N\underline{P}Se)$, + 2 ± 1	j
<u>trans</u>-$Me_2N\overline{P.NBu^{t}.P(Se)NMe_2.NBu^{t}}$	-10.1	$^{3}J(\underline{P}N\underline{P}Se)$, - 14 ± 1	j
<u>cis</u>-$C_5H_{10}N\overline{P.NBu^{t}.P(Se)NC_5H_{10}.NBu^{t}}$	+ 7.2	$^{3}J(\underline{P}N\underline{P}Se)$, + 2 ± 1	j
	-20.6	$^{3}J(\underline{P}N\underline{P}Se)$, - 10 ± 1	j

Table 25 cont'd

Compound	$^{2}J(\underline{P}N\underline{P})$ Hz	$^{n}J(\underline{P}\ldots\underline{X})$ [a] Hz	Method of sign determination
cis-$[MeO(S)PNBu^{t}]_2$	28.5 ± 0.5 (+27.4 ± 0.5 [k])	$^{3}J(\underline{POCH}) + {}^{5}J(\underline{PNPOCH})$, [k] + 16.0	h, k
trans-$[MeO(S)PNBu^{t}]_2$	20.8 ± 0.5		
cis-$[MeO(Se)PNBu^{t}]_2$	+ 8.0	$^{3}J(\underline{PNPSe})$, - 6.0; $^{1}J(\underline{PSe})$, - 954.5	j
trans-$[MeO(Se)PNBu^{t}]_2$	+ 2.1	$^{3}J(\underline{PNPSe})$, -14.2; $^{1}J(\underline{PSe})$, - 952.7	j
cis-$[Me_2N(O)PNBu^{t}]_2$	+55 ± 5	$^{3}J(\underline{PNCH}) + {}^{5}J(\underline{PNPNCH})$,+10.5	h
trans-$[Me_2N(O)PNBu^{t}]_2$	+45 ± 10	$^{3}J(\underline{PNCH}) + {}^{5}J(\underline{PNPNCH})$,+10.5	h
cis-$[Me_2N(S)PNBu^{t}]_2$	+41.2 ± 3	$^{3}J(\underline{PNCH}) + {}^{5}J(\underline{PNPNCH})$, + 11.8	d
trans-$[Me_2N(S)PNBu^{t}]_2$	+20.2 ± 2	$^{3}J(\underline{PNCH}) + {}^{5}J(\underline{PNPNCH})$, + 12.0	d
cis-$[Me_2N(Se)PNBu^{t}]_2$	+33.1	$^{3}J(\underline{PNPSe})$, + 2.0; $^{1}J(\underline{PSe})$, - 883.9	j
trans-$[Me_2N(Se)PNBu^{t}]_2$	+ 6.2	$^{3}J(\underline{PNPSe})$, - 11.5; $^{1}J(\underline{PSe})$, - 876.2	j

Table 25 cont'd

Compound	$^{2}J(\underline{P}N\underline{P})$ Hz	$^{n}J(\underline{P}...\underline{X})$ [a] Hz	Method of sign determination
cis-$[C_5H_{10}N(Se)PNBu^t]_2$	+ 17.2	$^{3}J(\underline{P}NP\underline{Se})$, + 1.1; $^{1}J(\underline{P}\underline{Se})$, - 879.5	i
cis-$Me_2N(S)\overline{P.NBu^t.P(Se)NMe_2}.NBu^t$	36.7		
$[Me_2N(O)PNPh]_2$	+ 55 ± 5	$^{3}J(\underline{P}NC\underline{H})$ + $^{5}J(\underline{P}NPNC\underline{H})$, + 11.1	d
$[Me_2N(O)PNCH_2Ph]_2$	+ 30 ± 10	$^{3}J(\underline{P}NC\underline{H})$ + $^{5}J(\underline{P}NPNC\underline{H})$, + 11.1	d

[a] Coupling constant(s) relative to which the sign of $^{2}J(\underline{P}N\underline{P})$ has been determined.

[b] More correctly, the signs of $^{2}J(\underline{P}N\underline{P})$ + $^{4}(\underline{F}PNP\underline{F})$ and $^{1}J(\underline{P}\underline{F})$ + $^{3}J(\underline{P}NP\underline{F})$ are compared. Ref 27 gives $^{2}J(\underline{P}N\underline{P})$ = 92.5 Hz.

[c] Sign obtained by $^{19}F-\{^{31}P\}$ double-resonance.

[d] Sign obtained by $^{1}H-\{^{31}P\}$ INDOR experiments.

[e] $|\,^{2}J(\underline{P}N\underline{P})\,| < 30$ Hz. Overlap of signals from the two isomers precludes definite measurement of $^{2}J(\underline{P}N\underline{P})$.

[f] From ref. 50.

[g] $^{5}J(\underline{P}NPOC\underline{H})$ = - 0.3 Hz.

h Sign obtained by $^{1}H-\{^{31}P\}$ double-resonance.

i Ref. 48

j Sign obtained by $^{31}P-\{^{1}H, ^{77}Se\}$ triple-resonance.

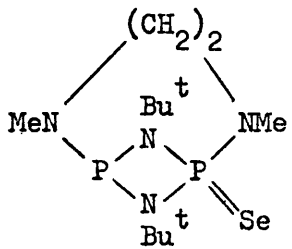
k From ref. 51.

Table 26

^{77}Se n.m.r. data [a]

Compound	^{1}J(PSe) Hz	^{3}J(PNPSe) Hz	Ξ (^{77}Se) [b] Hz	δ (^{77}Se) [c] p.p.m.
cis-MeOP.NBu^{t}.P(Se)OMe.NBu^{t}	-891.9	+2 ± 1	19,068,217	-173.2
trans-MeOP.NBu^{t}.P(Se)OMe.NBu^{t}	-893.5	-18 ± 1	19,070,544	-51.2
cis-[MeO(Se)PNBu^{t}]$_2$	-954.5	-6.0	19,067,514	-210.0
trans-[MeO(Se)PNBu^{t}]$_2$	-952.7	-14.2	19,068,882	-138.3
cis-Me$_2$NP.NBu^{t}.P(Se)NMe$_2$.NBu^{t}	-812.4	-2 ± 1	19,068,861	-139.4
trans-Me$_2$NP.NBu^{t}.P(Se)NMe$_2$.NBu^{t}	-829.8	-14 ± 1	19,070,744	-40.7
cis-[Me$_2$N(Se)PNBu^{t}]$_2$	-883.9	+2.0	19,068,127	-177.9
trans-[Me$_2$N(Se)PNBu^{t}]$_2$	-876.2	-11.5	19,068,773	-144.0
cis-C$_5$H$_{10}$NP.NBu^{t}.P(Se)NC$_5$H$_{10}$.NBu^{t}	-810.8	+2±1	19,068,720	-146.8

Table 26 cont'd

Compound	$^{1}J(\underline{P}Se)$ Hz	$^{3}J(\underline{PNP}Se)$ Hz	Ξ (^{77}Se) [b] Hz	δ (^{77}Se) [c] p.p.m.
<u>cis</u>-$[C_5H_{10}N(Se)PNBu^t]_2$	-879.5	+1.1	19,068,079	-180.4
	-847.5	-10 ± 1	19,068,566	-154.9

[a] In $CDCl_3$ solution.

[b] Ξ (^{77}Se) is the resonant frequency of ^{77}Se in a magnetic field where the protons of Me_4Si resonate at exactly 100 MHz.

[c] Downfield shifts are positive, relative to external Me_2Se. Ξ (^{77}Se in Me_2Se) = 19,071,520 Hz.

B P-N Torsional Barriers in Dialkylaminocyclodiphosphazanes.

The measurement of torisional barriers about P-N bonds by variable-temperature n.m.r. is now commonplace,[22,47,158-161,191-201] the free energy of activation at the coalescence temperature, ΔG^*_{Tc}, being calculated using the relationship (below) which is valid when

$$\Delta G^*_{Tc} = Tc\left[45.63 + 4.58 \log_{10}(Tc/\Delta\nu)\right] \text{ cal mol}^{-1}$$

where, Tc = the coalescence temperature (K)

$\Delta\nu$ = the chemical shift separation of the two uncoupled singlets (in Hz).

observing the coalescence of two equal-intensity singlets with temperature.[202] (A detailed discussion of the n.m.r. effect is contained in Chapter 1).

On examining the low-temperature ^1H n.m.r. spectra of the dimethylamino-substituted cyclodiphosphazanes, $ClP(NR)P(NMe_2)NBu^t$, $Me_2NP(NR)P(NMe_2)NBu^t$ (R=Me or Bu^t), and $Me_2NP(NMe)P(X)Cl(NBu^t)$ (X=O or S), it was found[22] in each case that the methyl protons of the dimethylamino-group were non-equivalent. The dynamic process giving rise to this effect was attributed[22] to hindered rotation about the exocyclic P-N bond(s), the first time it had been reported in relation to a cyclodiphosphazane ring. A list of the barriers measured[22] is shown in Table 27. Most of the dialkylaminocyclodiphosphazanes reported in Chapters 2 and 3 exhibited a similar effect. The torsional barriers and variable-temperature n.m.r. data are shown in Tables 28 and 29. Examples of variable-temperature ^1H and ^{13}C n.m.r. spectra are shown in Figures 23 and 24 respectively. Errors in ΔG^*_{Tc} (usually

Table 27

Compound	Tc (K)	ΔG^*_{Tc} (kcal mol^{-1})[a]
$ClP(NMe)PNMe_2NBu^t$	280	14.5
$ClP(NBu^t)PNMe_2NBu^t$	319	16.9
$Me_2NP(NMe)PNMe_2NBu^t$	239	12.5 [b]
	ca. 193	ca. 9.5
$(Me_2NPNBu^t)_2$	216	11.5
$Me_2NP(NMe)P(O)ClNBu^t$	297	15.5 [b]
	ca. 213	ca. 11.5
$Me_2NP(NMe)P(S)ClNBu^t$	301	16.2 [b]
	ca. 223	ca. 12

[a] All barriers taken from ref. 22.

[b] Major isomer.

ca. 0.3 kcal mol^{-1}) arise mainly from temperature measurements: calibration was by the method involving measurements of the shifts of methanol or ethylene glycol signals. Measurements of ΔG^*_{Tc} about the exocyclic P-N bonds in cis-$(Me_2NPNBu^t)_2$ and cis-$Me_2NP(NBu^t)PClNBu^t$ gave values (of 11.4 and 16.9 kcal mol^{-1} respectively) in excellent agreement with those found earlier[22] (Table 27).

At first sight it does not appear valid to compare rotational barriers found in different compounds as ΔG^*_{Tc} almost certainly has been measured at different coalescence temperatures, and from the relationship,

$$\Delta G^* = \Delta H^* - T\Delta S^*,$$

where, ΔH^* = enthalpy change,

and ΔS^* = entropy change,

it is seen that ΔG^*_{Tc} is

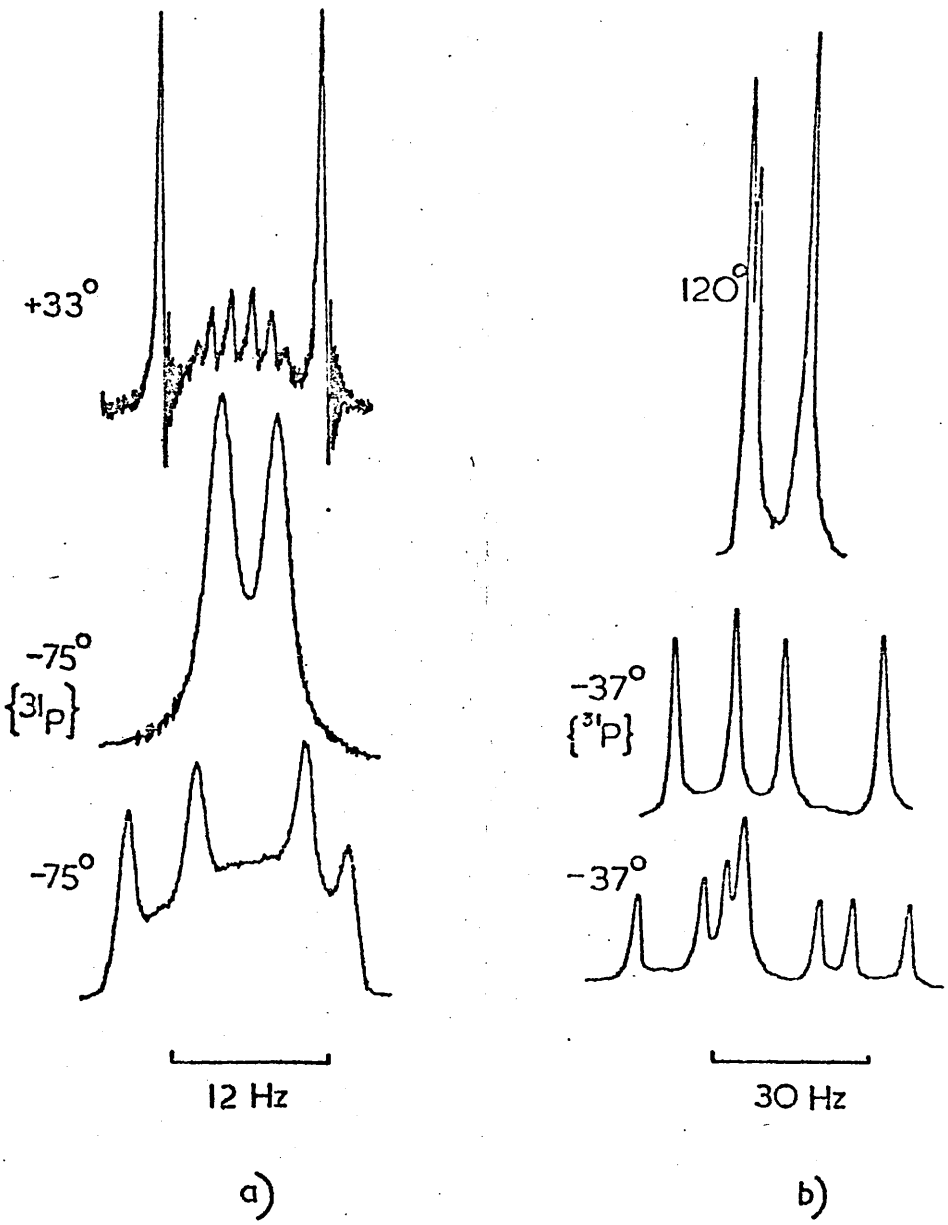


Figure 23: Variable-temperature ^{1}H n.m.r. spectra ($\underline{NMe_2}$ region) of a) <u>cis</u>-$\left[Me_2N(S)PNBu^t\right]_2$ b) <u>trans</u>-$Me_2N\overline{P.NBu^t.P(S)}NMe_2.NBu^t$.

temperature-dependent. However, as the dynamic process (of rotation about a P-N bond) is always the same, differences in entropy effects between compounds should be minimal and comparisons of ΔG^*_{Tc} valid.

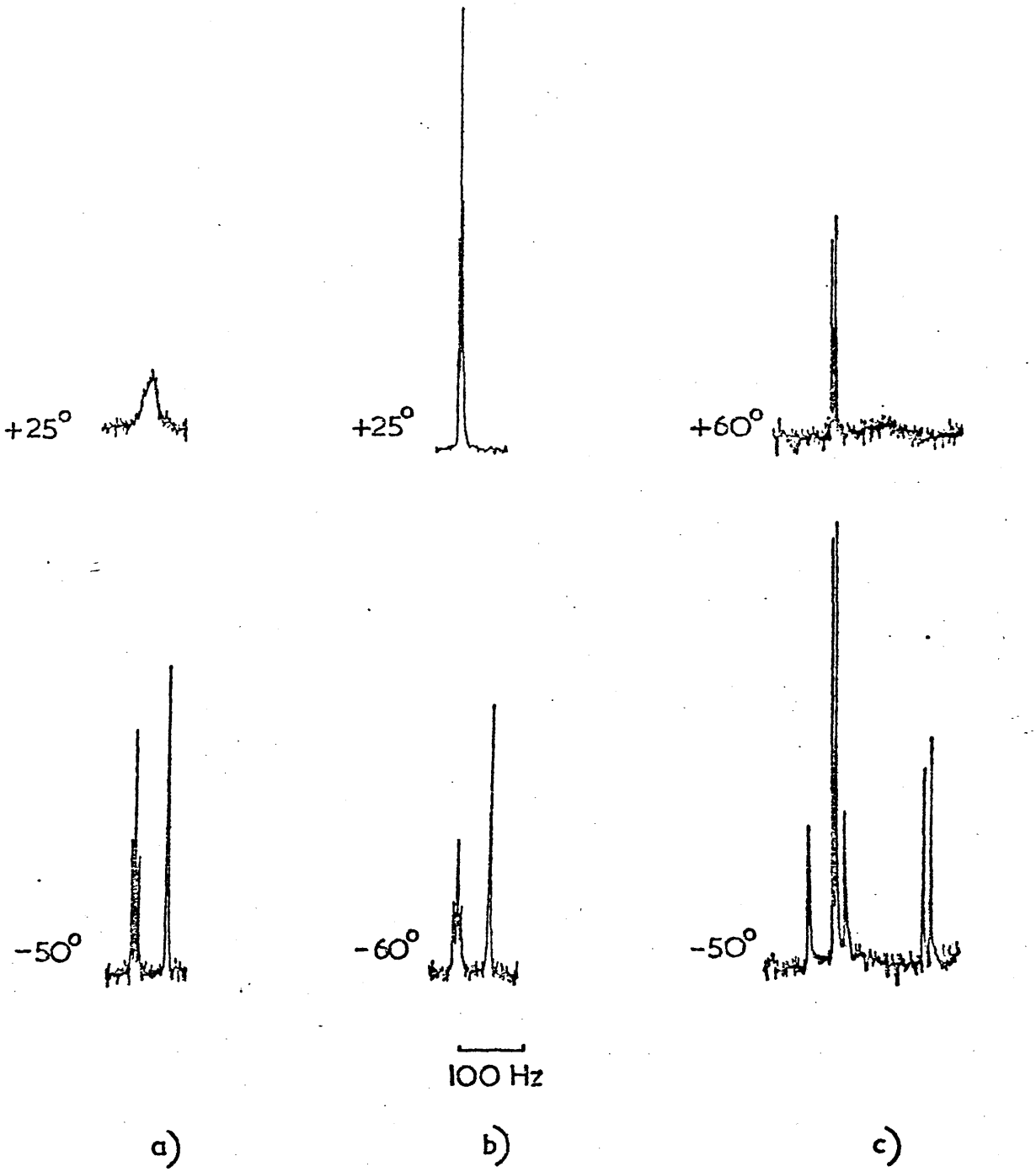


Figure 24: Variable-temperature ^{13}C n.m.r. spectra ($\underline{NMe}_2$) region of a) $\underline{trans}$-$[Me_2N(S)PNBu^t]_2$ b) $\underline{cis}$-$[Me_2N(S)PNBu^t]_2$ c) $\underline{cis}$-$Me_2NP(NBu^t).P(S)NMe_2.NBu^t$.

Before discussing the barriers in detail, the preferred conformation of the exocyclic dialkylamino-groups will be determined.

The low-temperature $^3J(\underline{P}^{III}NC\underline{H})$ (Table 28) and $^2J(\underline{P}^{III}N\underline{C})$ (Table 29) coupling constants clearly demonstrate that the preferred conformation

of the dimethylamino-group is one in which the methyl-groups lie in, or close to, the plane passing through the two phosphorus atoms and perpendicular to the cyclodiphosphazane ring (Figure 25).

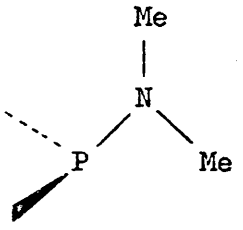


Figure 25

This is similar to the preferred conformations of the trimethylsilylamino-group in cis-$(Me_3SiNMe.PNBu^t)_2$ (Chapter 2, Figure 12) and the piperidino-groups in cis-$(C_5H_{10}NPNBu^t)_2$ (Chapter 2, Figure 11). The methyl-group cis to the phosphorus lone-pair has relatively large $^3J(\underline{PNCH})$[22,159,198,225] and $^2J(\underline{PNC})$[224,225] couplings, whereas the methyl-group trans to the phosphorus lone-pair has relatively small $^3J(\underline{PNCH})$ and $^2J(\underline{PNC})$ couplings, the latter being negative (Table 29). The same conformation is true of the ethyl-groups in trans-$(Et_2NPNPh)_2$ and cis-$(Et_2NPNBu^t)_2$ as inspection of Tables 28 and 29, respectively, shows. The X-ray diffraction study of cis-$[Me_2N(S)PNBu^t]_2$ established[257] a similar conformation to that in Figure 25 for the dimethylamino-groups. However, the low-temperature couplings, $^3J(\underline{P^{V}NCH})$, show little conformational dependence (13.7 and 10.0 Hz), assuming the same conformation holds in solution. A similar observation has been made by Martin and Robert.[201] On the other hand, $^2J(\underline{P^{V}NC})$ does, for the first time, exhibit an obvious conformational dependence, though considerably less than that found for $^2J(\underline{P^{III}NC})$ (Figure 24). By analogy with the low-temperature couplings in the ^1H n.m.r. spectrum for cis-$[Me_2N(S)PNBu^t]_2$ it is assumed that the preferred conformation of the dialkylamino-group attached to four co-ordinate phosphorus in the cyclodiphosphazanes in Table 28 is like that in Figure 25.

An attempt to discover which of the two low-temperature $^{3}J(\underline{P}^{V}NCH)$ couplings in $[Me_2N(O)PNBu^t]_2$ is associated with the methyl-group *cis* to the oxygen atom was made using the lanthanide shift reagent, $Eu(fod)_3$. The use of shift reagents is now widespread in n.m.r. spectroscopy.[299,300] Complexation of $[Me_2N(O)PNBu^t]_2$ by $Eu(fod)_3$ should occur at the oxygen atom and so it was hoped that a larger downfield shift would be shown by the methyl-group *cis* to the oxygen atom in the *cis* isomer. Ambiguity might exist in the results for *trans*-$[Me_2N(O)PNBu^t]_2$ as the methyl-group *trans* to the oxygen atom would also be adjacent to the oxygen atom on the other side of the ring. Complexation readily occurred: large downfield shifts of the N-methyl and t-butyl-groups (up to *ca.* 4 p.p.m.) and large upfield shifts of the phosphorus signals (up to *ca.* 100 p.p.m.) being recorded with additions of up to two molar equivalents of the shift reagent, indicating complexation at both ends of the molecule. Unfortunately, extreme broadening effects arising from the presence of europium(III) and the slow rate of exchange between the complexed and uncomplexed species at low temperature rendered the two N-methyl signals indistinguishable.

The various factors which influence the P-N torsional barriers in cyclidiphosphazanes include:

i) *Structure*:- One of the most striking features of Table 28 is the considerable difference in rotational barriers when pairs of isomers are considered. In $(Me_2NPNBu^t)_2$, for example, this difference is as large as 6.2 kcal mol^{-1} although in the dioxidised compounds, $[Me_2N(X)PNBu^t]_2$ (X=O, S, or Se) it is smaller (*ca.* 2-4 kcal mol^{-1}). In all cases where structural assignments are known it is, surprisingly, the *trans* isomer which has the greater barrier. This is contrary to what might at first be expected on steric grounds as cross-ring

interactions between the dimethylamino-groups in the cis isomers should increase the barrier. On the other hand, the preferred conformation is one in which steric interactions are minimised in the trans isomers. Thus the destabilisation in this conformation, brought about by cross-ring interactions in the cis isomers, might lower the barrier. This would appear to be the case, and is a conclusion supported by the observation that the difference in barrier between isomers in $[Me_2N(X)PNBu^t]_2$ (X=O,S, or Se) is less, as expected, since in both isomeric forms there is a moeity cis to the dimethylamino-group. Finally, it is noteworthy that the relatively low barrier associated with cis-$(C_5H_{10}NPNBu^t)_2$ (structure determined by X-ray analysis) is a further indication that the structural assignment to cis-$(Me_2NPNBu^t)_2$ is correct.

The above shows that when studying other effects on P-N rotational barriers it is imperative that cyclodiphosphazanes of like structure are compared.

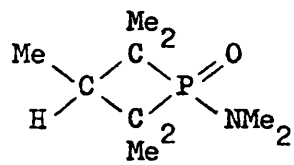
ii) Electronic effects:- Little is understood about the influence electronic effects exert on P-N bond rotation. In particular, there have been a number of arguments presented both for [158,191] and against [163-165,192] the contribution of (p-d)π bonding to P-N rotational barriers. A problem which is frequently encountered is that of maintaining constant steric interactions about the P-N bond whilst varying the substituents on the phosphorus and nitrogen atoms to induce different 'electronic effects.' This difficulty should be overcome by varying only the para-substituent, Y in compounds of the type, $(Me_2NPNC_6H_4Y\text{-}p)_2$ (Y=H, Cl, Me or OMe). However, in the above compounds the barriers are all equal within experimental error (12.5-12.7 kcal mol^{-1}).

The barrier of 20.2 kcal mol^{-1} found in the adduct, $Me_2NP.NBu^t.P^+NBu^t\ AlCl_4^-$, is the largest yet measured about a P-NMe_2 bond. This is probably because, consistent with the ideas proposed in i) above, removal of the chlorine atom from <u>cis</u>-$Me_2NP.NBu^t.PCl.NBu^t$ should stabilise the preferred conformation of the dimethylamino-group and so increase the barrier as observed. While this proposition might be termed an 'electronic effect' in that the preferred conformation of the dimethylamino-group is one in which the number of gauche interactions[171] between the phosphorus and nitrogen lone-pairs is maximised, there is no evidence in Table 28 to suggest that P-N torsional barriers are dominated by classical electronic effects such as <u>(p-d)π</u> bonding (if it exists) or the electronegativity of the substituents on phosphorus or nitrogen.

iii) <u>The effect of size of the group on phosphorus</u>:-
Increasing the size of the dialkylamino-group attached to phosphorus results in a slight increase in barrier as evidenced by comparing the barriers found in <u>trans</u>-$(R_2NPNPh)_2$ and <u>cis</u>-$[R_2N(X)PNBu^t]_2$(X=S or Se) on increasing the size of the R-group from methyl to ethyl (Table 28). Similarly, an increase in barrier is found on going from R=Me to R=Pr^i in $R_2NP.NBu^t.PCl.NBu^t$ (Table 28). Increasing the steric congestion in these compounds obviously outweighs the deficit in barrier arising from destabilising the preferred conformation as discussed in i) and ii) above. When the barriers found in <u>cis</u>-$Me_2NP.NBu^t.PX.NBu^t$ (X=Me_2N, F, or Cl) are compared, a sharp increase of <u>ca.</u> 5 kcal mol^{-1} is observed when X=F or Cl relative to X=Me_2N. This probably does reflect the presence of a small group at one end of the ring stabilising the preferred conformation of the amino-group.

iv) The effect of size of the group on the ring-nitrogen:- Bulloch[22] found that increasing the size of one of the ring-nitrogen substituents from methyl to t-butyl resulted in an increase in barrier of ca. 2 kcal mol^{-1} (Table 27). This steric dependence is also illustrated when both phenyl-groups are replaced by t-butyl-groups in the trans isomers of $(Me_2NPNR)_2$, $[Me_2N(O)PNR]_2$, and $Me_2NP.NR.P(S)NMe_2.NR$ (R=Ph or Bu^t) (Table 28). Interestingly, the barrier in $[Me_2N(O)PNPh]_2$ is greater than that in $[Me_2N(O)PNCH_2Ph]_2$, though the structures of these compounds are unknown.

v) The effect of oxidation at phosphorus:- Only a few rotational barriers about P(V)-N bonds at four co-ordinate phosphorus have been measured[160,200,201] as generally they are not accessible by variable-temperature n.m.r. None have been reported about a P(V)-NMe_2 bond except for one claim[162] that restricted rotation occurs about the P-N bond at ambient temperatures (on the n.m.r. time-scale) in compound (67). However, variable-temperature n.m.r. experiments will be needed to confirm this and further doubt is added to the claim in that geometrical isomerism was not considered as giving rise to the observed ^1H n.m.r. effect.[162]



(67)

In many cyclodiphosphazanes containing the P(V)-NMe_2 group, barriers about the P(V)-NMe_2 bond have been measurable (Table 28), probably as a consequence of the steric congestion inherent in these small ring systems. An upper limit of 8 kcal mol^{-1} is the largest barrier yet reported[160] for a P(S)-NMe_2 bond and this compares with the range of values from <9 to 16.7 kcal mol^{-1} reported here.

In all the mixed oxidation state cyclodiphosphazanes the barriers about the P(III)-N bonds are greater than those about the P(V)-N bonds. This may be because phosphorus-nitrogen lone-pair-lone-pair repulsions

contribute to the barriers about P(111)-N bonds.[165,191] In the cis isomers it is particularly notable that oxidation at one phosphorus atom results in an increase in the other P-N rotational barrier. This is especially marked on oxidation of cis-$(Me_2NPNBu^t)_2$ by one molar equivalent of methyl iodide, where the P(111)-N barrier increases from 11.4 to 17.3 kcal mol^{-1}. Trans-$Me_2N\overline{P.NBu^t.P^+(Me)NMe_2}.NBu^t$ is interesting in that the barrier about the P(111)-N bond is 17.7 kcal mol^{-1}, only marginally greater than that in the cis isomer. The lower barrier than anticipated in the trans isomer may be explained, as before, in terms of a cross-ring interaction by the methyl-group destabilising the preferred conformation of the dimethylamino-group. On the other hand, the P(V)-NMe_2 rotational barrier is 15.9 kcal mol^{-1}, ca. 4 kcal mol^{-1} greater than in the cis isomer. This is to be expected as there are no destabilising cross-ring interactions with the P(V)-NMe_2 group in the trans isomer.

Studies of cis and trans-$[Me_2N(X)PNBu^t]_2$ (X=O, S, or Se) show that all the cis isomers have similar rotational barriers (ca. 12 kcal mol^{-1}) indicating little or no electronegativity effect depending on the X-substituent. These barriers are also similar to that found in cis-$(Me_2NPNBu^t)_2$ and this implies that P(111)-N rotational barriers are not (always) augmented by lone-pair-lone-pair repulsions. In the trans isomers the barriers (13.5-15.9) kcal mol^{-1} are greater than those found in the cis isomers, as expected, but less than that found in trans-$(Me_2NPNBu^t)_2$ (17.6 kcal mol^{-1}). This again is predictable as there is now a destabilising cross-ring steric interaction between the X-substituent and the dimethylamino-group. As oxygen is smaller than sulphur or selenium this may explain why the P-N torsional barrier in trans-$[Me_2(X)PNBu^t]_2$ is greatest when X=O.

In light of the above, the P-N rotational barriers in $Me_2N(S)\overline{P.NBu^t.PCl.NBu^t}$ enable a structural assignment to be made; the isomer with the higher barrier having a mutually cis arrangement of sulphur and chlorine atoms. Such an assignment is not readily made for $Me_2N(O)\overline{P.NBu^t.P(O)Cl.NBu^t}$, and so reasons for the largest measured rotational barrier about the P(V)-NMe_2 bond (17.5 kcal mol^{-1}) in one isomeric form of this compound are unclear.

Table 28

Variable-temperature ^{1}H n.m.r. data [a]

Compound	High T.		Low T.		$\Delta\nu$ [c]	Tc	ΔG^{*}_{Tc} [d]
	δ_{NMe_2} p.p.m.	$^{3}J(PNCH)$ [b] Hz	δ_{NMe_2} p.p.m.	$^{3}J(PNCH)$ [b] Hz	Hz	K	kcal mol^{-1}
trans-$(Me_2NPNPh)_2$ [e]	2.78	8.4	2.52	1.9	30	252	12.6
			3.02	12.9			
trans-$(Me_2NPNC_6H_4Cl\text{-}p)_2$ [e]	2.83	8.5	2.60	2.3	30	253	12.6
			3.10	13.0			
trans-$(Me_2NPNC_6H_4Me\text{-}p)_2$	2.86	8.5	2.57	2.6	29	250	12.5
			3.05	13.0			
trans-$(Me_2NPNC_6H_4OMe\text{-}p)_2$ [e]	2.83	8.6	2.66	2.0	27	254	12.7
			3.11	12.7			
cis-$Me_2NP.NPh.PCl.NPh$	2.91	9.0	2.83	3.1	14	260	13.4
			3.06	13.8			

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(PNCH)$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(PNCH)$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
trans-$(Et_2NPNPh)_2$	3.28 [f]	8.0	3.09	2.3	23	272	13.8
			3.47	13.3			
trans-$(Me_2NPNBu^t)_2$	2.73 [g]	7.0	2.69 [g]	3.0	5.5	327 [g]	17.6
			2.80 [g]	12.2			
cis-$(Me_2NPNBu^t)_2$	2.66	8.0	2.49	2.4	5.2	215	11.4
			2.57	13.1			
cis-$(C_5H_{10}NPNBu^t)_2$	3.13	5.0±1	ca. 2.45	[h]	ca.70	ca. 213	10.2±1.5
			ca. 3.65	[h]			
cis-$Me_2NP(NBu^t).PNHMe.NBu^t$	2.54	8.0	2.44	2.9	11.5	227	11.7±0.4
			2.63	13.0			
cis-$Me_2NP(NBu^t).PF.NBu^t$	2.64 [i]	8.0	2.55 [i]	2.8	9.1	308 [i]	16.2
			2.70 [i]	13.7			

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(PNCH)$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(PNCH)$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
cis-$Me_2NP(NBu^t).PCl.NBu^t$	2.68 [j]	8.3	2.58 [j]	13.6	7.4	319 [j]	16.9
			2.71 [j]	2.7			
cis-$Pr^i_2NP(NBu^t).PCl.NBu^t$	k	k	3.08 [j,l]	2.5	15.7	375 [i]	19.5±0.5
			4.30 [j,l]	ca. 15			
$Me_2NP(NBu^t).P^+.NBu^t$ $AlCl_4^-$	k	k	2.46 [m]	3.7	22.7	393 [m]	20.2±0.5
			2.84 [m]	15.1			
$[Me_2N(O)PNPh]_2$	2.87	11.1	2.66	ca. 12	25.5	197	9.8
			3.08	ca. 9			
$[Me_2N(O)PCH_2Ph]_2$	2.85	11.1	k	k	k	<177	<9
trans-$Me_2NP(NPh).P(S)NMe_2.NPh$	2.88 (P^{III})	9.1	2.69	3.4	19.7	258	13.1 (P^{III})
			3.02	14.4			
	2.87	12.0	2.51	11.1	40.5	202	9.9

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(PNCH)$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(PNCH)$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
			3.19	13.7			
cis-$Me_2NP.NBu^t.P(S)NMe_2.NBu^t$	2.64 (P^{III})	9.0	2.56	1.9	7.5	282	14.9
			2.68	13.3			
	2.90	11.6	[k]	[k]	[k]	<183	<9
trans-$Me_2NP.NBu^t.P(S)NMe_2.NBu^t$	2.69 (P^{III})[i]	8.7	2.54[i]	14.3	9	352[i]	18.6 (P^{III})
			2.69[i]	3.4			
	2.69[i]	11.6	2.23[i]	10.5	40	295[i]	14.6
			2.89[i]	12.4			
cis-$Me_2NP.NBu^t.P(Se)NMe_2.NBu^t$	2.68 (P^{III})	8.8	2.63	3.2	8.2	301	15.9 (^{III})
			2.77	13.7			
	2.99	12.0	[k]	[k]	[k]	<183	<9
trans-$Me_2NP.NBu^t.P(Se)NMe_2.NBu^t$	2.72 (P^{III})[i]	8.6	2.53[i]	13.9	13	349[i]	18.2 (P^{III})

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(PNCH)$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(PNCH)$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
			2.75 [i]	3.0			
	2.72 [i]	11.6	2.25 [i]	10.1	40	286 [i]	14.2
			2.91 [i]	13.1			
trans-$Me_2NP.NBu^t.P(Te)NMe_2.NBu^t$	2.83 (P^{111})	10.3	2.77	14.0	4.0	>255 [n]	>13 (P^{111})
			2.84	2.7			
	2.83	10.3	2.63	9.7	22.5	>255 [n]	>12.5
			3.01	15.1			
cis-$Me_2NP.NBu^t.P^+(Me)NMe_2.NBu^t$ I^-	2.48 (P^{111})[i]	8.8	2.34 [i]	1.7	6.3	323 [i]	17.3 (P^{111})
			2.45 [i]	15.4			
	3.02	11.3	2.92	9.7	1.4	216	12.0±0.5
			2.94	12.3			

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(\underline{P}NC\underline{H})$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(\underline{P}NC\underline{H})$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
trans-$Me_2NP.NBu^t.P^+(Me)NMe_2.NBu^t$ I^-	2.72 [o]	8.8	2.55 [o]	3.4	10.3	336 [o]	17.7
			2.72 [o]	14.3			
	2.79 [o]	10.5	2.71	10.0	20.8	312	15.9
			3.06	11.4			
cis-$[Me_2N(O)PNBu^t]_2$	2.72	10.5	2.72	10.5	2.6	213	11.6
			2.76	9.1			
trans-$[Me_2N(O)PNBu^t]_2$	2.78	10.8	2.76	11.5	4.3	294	15.9
			2.83	9.5			
cis-$[Me_2N(S)PNBu^t]_2$	2.93	11.8	2.89	10.0	3.7	219	11.8
			2.95	13.7			
trans-$[Me_2N(S)PNBu^t]_2$	2.92	12.0	2.88	11.3	4.1	256	13.8
			2.95	13.4			
cis-$[Me_2N(Se)PNBu^t]_2$	2.92	12.8	2.90	10.0	4.6	224	12.0

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(PNCH)$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(PNCH)$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
			2.98	15.1			
trans-$[Me_2N(Se)PNBu^t]_2$	3.01	12.8	2.99	11.0	3.3	248	13.5
			3.05	14.8			
cis-$Me_2N(S)\overline{P.NBu^t.P(Se)NMe_2}.NBu^t$	2.94 (S)	12.3	2.86	11.0	3.8	226	12.1 (S)
			2.92	13.7			
	2.97 (Se)	12.8	2.87	10.8	4.6	215	11.5 (Se)
			2.95	14.8			
cis-$[Et_2N(S)PNBu^t]_2$	3.40 [f]	14.0	3.26	[k]	11.3	256	13.3
			3.45	[k]			
cis-$[Et_2N(Se)PNBu^t]_2$	3.41 [f]	14.4	3.27	[k]	13.1	263	13.6
			3.49	[k]			
$Me_2N(S)\overline{P.NBu^t.PCl.NBu^t}.P$	2.88	12.1	2.84	11.1	6.0	225	11.9

Table 28 cont'd

Compound	High T. δ_{NMe_2} p.p.m.	High T. $^3J(\underline{P}NC\underline{H})$ [b] Hz	Low T. δ_{NMe_2} p.p.m.	Low T. $^3J(\underline{P}NC\underline{H})$ [b] Hz	$\Delta\nu$ [c] Hz	Tc K	ΔG^*_{Tc} [d] kcal mol^{-1}
$Me_2N(S)\overline{P.NBu^t.PCl.NBu^t}$	2.60 [i]	11.1	2.94	12.8			
			2.18 [i]	10.7	36.1	333 [i]	16.7
			2.78 [i]	13.4			
$Me_2N(O)\overline{P.NBu^t.P(O)Cl.NBu^t}$ [g]	2.74	11.9	2.63	13.1 ± 1	9.4	264	13.8
			2.79	10.2 ± 1			
$Me_2N(O)\overline{P.NBu^t.P(O)Cl.NBu^t}$	2.70 [i]	ca. 11	2.52 [i]	11.7 ± 1	8.9	331 [i]	17.5
			2.67 [i]	10.3 ± 1			

[a] In $CDCl_3$ or CH_2Cl_2 solution, unless otherwise stated.

[b] $|^3J(\underline{P}NC\underline{H}) + {}^5J(\underline{P}NPNC\underline{H})|$, for symmetrical dialkylaminocyclodiphosphazanes.

[c] Assuming that k at Tc = $\pi\Delta\nu/\sqrt{2}$, where $\Delta\nu$ is the difference in chemical shift in the absence of exchange.

[d] Errors are ± 0.3 kcal mol $^{-1}$, unless otherwise stated.

[e] Cis isomer, Tc < 183 K (CH_2Cl_2 solution); $\Delta G_{Tc}^{*} < 9$ kcal mol $^{-1}$.

[f] δ NC<u>H</u>$_2$.

[g] In C_6H_6 solution.

[h] Signals very broad at low temperature; signal at low-field broadest, indicating a larger coupling to phosphorus.

[i] In C_6H_5Cl solution.

[j] In C_6H_5Me solution.

[k] Not measured.

[l] δ NC<u>H</u>.

[m] In o-$C_6H_4Cl_2$ solution.

[n] Accurate measurement not possible owing to tellurium exchange.

[o] In Me_2SO solution.

[p] Isomer, δ <u>P</u>(S)NMe_2=63.3 p.p.m.

[q] Isomer, δ <u>P</u>(O)NMe_2=0.3 p.p.m.

Table 29

Variable-temperature ^{13}C n.m.r. data [a]

Compound	High temperature		Low temperature	
	δ PN(exo)C p.p.m.	^2J(PNC) [b] Hz	δ PN(exo)C p.p.m.	^2J(PNC) [b] Hz
cis-$(Me_2NPNBu^t)_2$	35.4	20.2	32.3 [c]	± 10.1
			38.6 [c]	± 50.0
trans-$(Me_2NPNBu^t)_2$	d	d	33.6	± 6.2
			37.2	± 49.3
cis-$Me_2NP(NBu^t)(PCl)NBu^t$	d	d	35.1	± 10.1
			38.3	± 49.4
cis-$(Et_2NPNBu^t)_2$	38.4	21.5	33.5	± 8.1
			41.0	± 53.8
cis-$C_5H_{10}NP(NBu^t)P(Se)NC_5H_{10}NBu^t$	d	d	42.0 (P^{III}) [e]	± 10.0
			48.1 (P^{III})	± 50.5
	46.8 (P^V)	2.5	d	d
cis-$Me_2NP(NBu^t)P(S)NMe_2NBu^t$	d	d	32.6 (P^{III})	± 10.1

Table 29 cont'd

Compound	High temperature		Low temperature	
	δ PN(exo)C p.p.m.	^2J(PNC) [b] Hz	δ PN(exo)C p.p.m.	^2J(PNC) [b] Hz
			38.6 (P^{III})	± 53.4
	38.4 (P^{V})	5.6	[d]	[d]
cis-$[Me_2N(S)PNBu^t]_2$	38.6	6.2	37.3	0
			39.3	11.6
trans-$[Me_2N(S)PNBu^t]_2$	38.2	5.2	36.9	0
			38.8	10.3

[a] In CDl_3 solution, except where otherwise stated.

[b] More correctly, $|\,^2J(PNC) + {}^4J(PNPNC)\,|$ for symmetrical alkylaminocyclodiphosphazanes.

[c] In CD_2Cl_2 solution.

[d] Not measured.

[e] ΔG^*_{343} =16.2 kcalmol.$^{-1}$

APPENDIX A

Preparative methods, solvent and reagent purification.

All operations were carried out in an atmosphere of nitrogen (dried by passing through silica gel and phosphorus pentoxide columns) and/or by use of a conventional vacuum manifold.

Anhydrous solvents were always used and dried by contact with sodium wire or molecular seive type 4A. The ethanol stabiliser was removed from chloroform before use by contact with silica gel.

All amines were distilled from sodium hydroxide pellets before use except for dimethylamine and methylamine which were passed through sodium hydroxide columns. Phosphorus trichloride, trimethylchlorosilane, methyl iodide and dimethyl sulphoxide were all purified by distillation. Anhydrous alcohols, t-butylhydroperoxide, aluminium trichloride, and elemental sulphur, selenium, and tellurium were obtained commercially and used without further purification. Amine hydrochlorides and antimony trifluoride were vacuum dried before use.

APPENDIX B.

Instrumentation and analysis.

Continuous-wave ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra were recorded on a Jeol C60HL spectrometer at ca. 60, 56.4 and 24.3 MHz respectively. Selective-noise ^{1}H and ^{31}P decoupling were carried out using a Schomandl ND100M frequency synthesiser and a Jeol SDHC amplifier unit. ^{31}P resonance frequencies were measured by a Racal frequency counter. ^{1}H n.m.r. spectra at 90, 100 and 220 MHz were recorded on Perkin Elmer R32 and Varian XL-100 and HR-220 spectrometers respectively. Pulsed-Fourier-transform ^{31}P and ^{13}C n.m.r. spectra were obtained on a Varian XL-100 spectrometer at ca. 40.5 and 25.2 MHz respectively. $^{31}P-\{^{1}H, ^{31}P\}$ triple-resonance experiments were performed on the XL-100; the decoupler transmitter coil was double-tuned to accept 100 MHz from the power amplifier of the Gyrocode decoupler and 40 MHz direct from the output of the (above) frequency synthesiser. $^{31}P-\{^{1}H, ^{77}Se\}$ triple-resonance experiments were performed similarly, except the decoupler coil of the spectrometer was tuned to accept the ^{77}Se resonance frequency of ca. 19.1 MHz. Phosphorus-31 chemical shifts measured by $^{1}H-\{^{31}P\}$ double-resonance were determined in a manner similar to that outlined in ref. 301. Selenium-77 chemical shifts were also obtained similarly, but with the modification that,

$$\Xi_{\text{lock}} \cdot \nu(^{77}Se)/\nu_{\text{lock}} = \Xi(^{77}Se),$$

as the spectra were run in the Fourier-transform mode using deuteriochloroform as lock ($\Xi\, CDCl_3$=15.350719 MHz).

Mass, infrared, and Raman spectra were recorded on A.E.I. MS 12, Perkin Elmer 257, and Spex Ramalog IV spectrometers respectively. The photoelectron spectra were obtained by Dr. S. Cradock, University of Edinburgh, on a Perkin Elmer PS 16 photoelectron spectrometer with He(1) (21.22 eV) excitation.

X-ray diffraction data were collected on a Hilger and Watts Y290 diffractometer, equipped with a graphite monochromator, using Mo radiation. Dipole moments were measured using a universal bridge TF 2700 and a variable condenser to measure capacitance.

Microanalyses were determined by the microanalysis laboratory, Department of Chemistry, University of Glasgow.

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