1,3,5-Triethylcyclotriphosph(III)azanes and Related Compounds †

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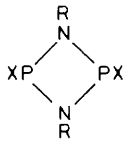
The cyclophosph(III)azanes, $(ClPNEt)_3$, $Cl_2P_4(NEt)_5$, and the previously reported diphosphinoamine, $Cl_2P{-}NEt{-}PCl_2$, are formed by suitable variation of the stoicheiometry of a mixture of phosphorus trichloride and ethylamine hydrochloride in refluxing *sym*-tetrachloroethane solution. Oxo-derivatives of the cyclic products are also formed in low yields, and in the case of $(ClPNEt)_3$, the same oxo-derivatives can be identified as a product of the reaction with oxygen or dimethyl sulphoxide. Both $(ClPNEt)_3$ and bicyclo-$Cl_2P_4(NEt)_5$ can be converted to the analogous fluorides by reaction with antimony trifluoride. The former also gives $(Cl_3PNEt)_2$ on reaction with chlorine. Cyclotriphosph(III)azanes, $(ClPNR)_3$ (R = Me or Et), were obtained in low yield by heating the diphosphinoamines, $Cl_2P{-}NR{-}PCl_2$. Isomeric forms of the cyclophosph(III)azanes have been distinguished by n.m.r. spectroscopy and their structures are discussed.

The chemistry of the cyclophosph(III)azanes (1) and (2) has undergone a period of rapid development over the past ten years,[1-5] and the cyclodiphosph(III)azanes (1) (R = alkyl or aryl; X = alkyl, amino, or halogen) in particular have been widely investigated. Convenient routes to the compounds (1) are provided by the reactions of phosphorus trichloride with



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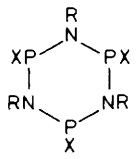
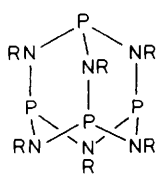


(2)

amines or amine hydrochlorides having bulky *N*-alkyl groups,[6,7] or *N*-aryl groups.[8] It appears that amines with bulky *N*-substituents are likely to form small ring compounds, primarily to relieve steric interactions, and, by this reasoning, less bulky alkylamines might be expected to favour the formation of larger ring systems. An indication that this might be the case arose some time ago in that phosphorus trichloride reacts with excess of methylamine to give the cage compound (3) (R = Me), and with t-butylamine to give (1) (R = Bu^t, X = NHBu^t).[9] It has also been claimed [10] that the disilazanes, $NR(SiMe_3)_2$, react with phosphorus trichloride to give cyclophosph(III)azanes $(ClPNR)_n$ (R = Me, n = 2; R = Et, n = 3 or 4). However, the authenticity of the products from the latter reactions is questionable.[11] More recently, evidence for the formation of (1) (R = Et, X = Cl), (2) (R = Et, X = Cl), and a bicyclic compound (4) (R = Me, X = Cl) has been presented,[12] although none of these compounds was obtained in a pure state. However, a recent study of the reaction of



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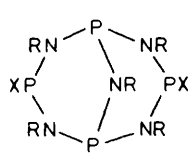


(4)

† *Non-S.I. unit employed*: mmHg ≈ 13.6 × 9.8 Pa.

heptamethyldisilazane, $NMe(SiMe_3)_2$, with phosphorus trichloride showed that (2) (R = Me, X = Cl) can be obtained as a crystalline solid in moderate yield,[13] and that the latter compound can be converted to (4) (R = Me, X = Cl) by reaction with heptamethyldisilazane.[14] An analogous bromide (3) (R = Me, X = Br) was also obtained from a similar reaction with phosphorus tribromide.[13] We have now developed a convenient route to pure (2) (R = Et, X = Cl) and (4) (R = Et, X = Cl), and investigated their properties.

Results and Discussion

(*a*) *Synthesis.*—During an attempt to prepare the bis(dichlorophosphino)amine, $Cl_2P{-}NEt{-}Cl_2$, by the reaction of ethylamine hydrochloride with phosphorus trichloride in refluxing *sym*-tetrachloroethane solution (*cf.* ref. 15), substantial amounts of a dark brown oil were obtained. The oil was distilled under reduced pressure and the distillate crystallised from light petroleum to give a pure sample of (2) (R = Et, X = Cl), identified by elemental analyses, mass and n.m.r. spectroscopy. Subsequent work showed that this ring compound can be obtained in good yield by variation of the ethylamine hydrochloride to phosphorus trichloride mol ratio. The bicyclic compound (4) (R = Et, X = Cl) was also obtained from a similar reaction, although this was more easily purified by crystallisation alone. The formation of the diphosphinoamine, $Cl_2P{-}NEt{-}PCl_2$,[15] (2) (R = Et, X = Cl), and (4) (R = Et, X = Cl) may be expressed by equations (i)—(iii). The cage compound, (3) (R = Et) could not be

$$2PCl_3 + [NH_3Et]Cl \longrightarrow Cl_2P{-}NEt{-}PCl_2 + 3HCl \quad (i)$$

$$3PCl_3 + 3[NH_3Et]Cl \longrightarrow (2)\ (R = Et, X = Cl) + 9HCl \quad (ii)$$

$$4PCl_3 + 5[NH_3Et]Cl \longrightarrow (4)\ (R = Et, X = Cl) + 15HCl \quad (iii)$$

obtained by this method, although it can be obtained by reaction of (4) (R = Et, X = Cl) with ethylamine.[16] Two minor components (<10%) of the reaction mixtures obtained in the synthesis of (2) (R = Et, X = Cl) gave rise to ^{31}P n.m.r. signals at δ_P 228.0 and δ_P 2.8, 140.6, and 148.6. The former signal appears to arise from the cyclodiphosph(III)azane, $(ClPNEt)_2$ (lit.,[12] δ_P = 227.3) although a pure sample could not be separated. The second group of signals (grouped on

Table 1. Phosphorus-31 n.m.r. data [a]

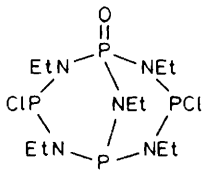
Compound	Isomer [b]	δ_P [c]/p.p.m.	J(PNP)/Hz	Temp./°C	Isomer ratio
(2) (R = Et, X = Cl)	*cis*	104.1		Ambient	1
	trans	129.0 (1)			4.5
		135.4 (2)			
	cis	102.2		−60	1
	trans	127.2 (1)	6.7		2.3
		134.6 (2)			
(2) (R = Pr^n, X = Cl)	*cis*	105.3		Ambient	1
	trans	130.6 (1)			5
		136.5 (2)			
(2) (R = Me, X = Cl) [d]	*cis*	101.4		Ambient	1
	trans	127.8 (1)			1.6
		132.4 (2)			
	cis	99.4		−65	1.7
	trans	125.8 (1)	6		1
		131.4 (2)			
(2) (R = Et, X = F)	*cis*	100.4		Ambient	1
	trans	111.2 (1)			8
		117.8 (2)			
	cis	99.2		−67	1
	trans	108.2 (1)	6.2 [e]		7.5
		116.1 (2)			
(4) (R = Et, X = Cl)	A	54.4		Ambient	3.5
		129.7			
	B	119.4 (1)			1
		36.9 (2)			
		130.8 (1)			
	A	51.8	8.0	−60	9
		130.8			
	B [f]	120.9 (1)	13.1		1
		33.7 (2)	7.4		
		132.1 (1)			
(4) (R = Et, X = F)	A	46.6	7.9	−65	2
		116.0			
	B	106.8 (1) [g]	0		1
		35.4 (2)	6.9		
		119.3 (1) [h]			
Monoxide of		140.6	28.5		
(2) (R = Et, X = Cl)		2.8	23.9 2.0 (at −60 °C)	Ambient	*i*
		148.6			
Monoxide of	A	−4.5 (1)	8.9	−65	8
(4) (R = Et, X = Cl)		121.1 (1)	10.6 26.0		
[Compound (5)]		147.2 (2) [j]			
	B	165.3 [j]	29.9		1
		−12.8	10.9 4.0		
		119.6	5.0 28.6		
		144.7 [j]			
Dioxide of		11.4	34.7	−65	*i*
(4) (R = Et, X = Cl) [k]		137.3			

[a] $CDCl_3$ solutions. Only absolute values of coupling constants are given. The ^1H n.m.r. spectra of the *N*-ethyl compounds all gave complex CH_2– multiplets in the range δ 3.4—3.7 which were not analysed in detail. [b] See text. Compounds (4): isomer A gives two signals of equal intensity; isomer B gives three signals. [c] Relative to 85% H_3PO_4 (downfield shifts are positive). Relative intensities are given in parentheses. [d] Ambient temperature data first reported in ref. 13. [e] See Table 2 for value of $^2J(P^2P^2)$. [f] ^4J(PNPNP) 1.5 Hz. [g] ^1J(PF) 1 105.7 Hz. [h] ^1J(PF) 1 061.8 Hz, ^5J(PF) 2 Hz. [i] Signals for only one isomer were observed. [j] *P*–Cl. [k] Present as an impurity in the solution of the monoxide of (4) (R = Et, X = Cl).

the basis of their mutual spin-coupling interactions, see Table 1), is assigned to a monoxide of (2) (R = Et, X = Cl). This is consistent with the fact that the same compound could be identified as a major product of the dimethyl sulphoxide-induced oxidation of (2) (R = Et, X = Cl). The bicyclic compound (4) (R = Et, X = Cl) can be converted to (2) (R = Et, X = Cl), and finally, Cl_2P–NEt–PCl_2, in refluxing phosphorus trichloride solution. Compounds (2) and (4) (R = Et) have not, however, been detected in reaction mixtures containing ethylamine hydrochloride and excess of phosphorus trichloride; if (2) and (4) (R = Et) are formed, they are more reactive towards the latter reagent than ethylamine hydrochloride. The crude reaction products in the synthesis of the bicyclic compound (4) (R = Et, X = Cl) often contained small quantities of its monoxide (5). In one case this was formed in sufficient quantity to allow its isolation by fractional crystallisation.

Attempts to carry out analogous reactions with methylamine hydrochloride were unsuccessful, the only products being the diphosphinoamine Cl_2P–NMe–PCl_2[15] and traces of (2) (R = Me, X = Cl). The reason for this difference is not clear, but it is worth noting that in refluxing *sym*-tetrachloroethane solution, methylamine hydrochloride largely remains as a solid suspension, but under similar conditions ethylamine

hydrochloride forms an oily liquid on the surface of the solvent. If (2) and (4) (R = Me, X = Cl) are formed in this reaction, they undergo relatively rapid conversion to the



(5)

diphosphinoamine. It was also found that cyclotriphosph(III)-azanes could be obtained in low yields by prolonged heating of the diphosphinoamines $Cl_2P{-}NR{-}PCl_2$ (R = Me or Et) [equation (iv)]. This reaction does not constitute a very useful

$$n Cl_2P{-}NR{-}PCl_2 \xrightarrow{ca.\ 150\ ^\circ C} (ClPNR)_n\ (n = 3) + n PCl_3 \quad \text{(iv)}$$

method for the synthesis of cyclophosph(III)azanes, however, because of the low yields and frequent formation of solid red unidentified decomposition products.

(*b*) *Reactions of Chlorocyclotriphosph(III)azanes.*—The cyclotriphosph(III)azane (2) (R = Et, X = Cl) was converted to the corresponding fluoride, (2) (R = Et, X = F), by reaction with antimony trifluoride in refluxing light petroleum [equation (v)]. A similar reaction with (4) (R = Et, X = Cl)

$$(ClPNEt)_3 + SbF_3 \longrightarrow (FPNEt)_3 + SbCl_3 \quad \text{(v)}$$

gave (4) (R = Et, X = F) as the major product, although the latter compound could not be separated from other impurities. Both (2) (R = Et, X = Cl) and (4) (R = Et, X = Cl) are readily hydrolysed by water, reaction with the former compound being particularly violent.

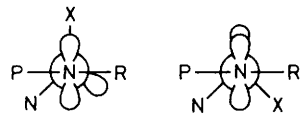
Although the oxidation of cyclodiphosph(III)azanes (1) by dimethyl sulphoxide or with elemental sulphur occurred cleanly,[7] this was not the case with (2) (R = Et, X = Cl) or (4) (R = Et, X = Cl). A monoxide of (2) (R = Et, X = Cl) was found amongst the products of a reaction of (2) (R = Et, X = Cl) with oxygen, or with dimethyl sulphoxide, although this was not obtained in a pure state. In one case the synthesis of (4) (R = Et, X = Cl) gave its monoxide and traces of a dioxide (see above).

The oxidation of (2) (R = Et, X = Cl) by chlorine resulted in cleavage of the P_3N_3 ring and the formation of the known [17] cyclodiphosph(III)azanes (6) [equation (vi)]. The incorporation

$$\underset{\text{(2) (R = Et, X = Cl)}}{2(ClPNEt)_3} \xrightarrow{6Cl_2} \underset{\text{(6)}}{3(Cl_3PNEt)_2} \quad \text{(vi)}$$

of five-co-ordinate phosphorus [presumably with a trigonal bipyramidal (t.b.p.) distribution of bonds] into a six-membered ring could easily result in destabilising chlorine–chlorine interactions. These interactions will be reduced in smaller PN rings such as the cyclodiphosph(v)azanes, where chlorine and nitrogen atoms occupy both axial and equatorial t.b.p. sites. The recently identified phosph(v)azene, $Cl_3P{=}NEt$,[16] which readily dimerises to $(Cl_3PNEt)_2$, would be a plausible intermediate in this ring-contraction process, although it was not detected by ^{31}P n.m.r. spectroscopy.

(*c*) *Structures of Cyclotriphosph(III)azanes.*—The structures of the compounds prepared in this study are of interest, particularly since they may be expected to reflect the conformational constraints of the $P^{III}{-}N$ bonds. In considering the structures of compounds (2) and (4) in solution we assume that nitrogen has a planar distribution of bonds, or a very low barrier to inversion (*cf.* ref. 18). Unfortunately, no crystal structures of cyclotriphosph(III)azanes have yet been reported, but the nitrogen atoms in the crystal structure of $(MePNMe)_4$ do have a planar distribution of bonds.[19] The cage-type structures, $P_4(NMe)_6X$ (X = MeI [20] or S [21]), derived from (3) (R = Me), contain P_3N_3 ring fragments, and here the bonds to nitrogen deviate only slightly from planarity (average sum of angles at N = 353 and 352° respectively). Thus (2) (R = Et, X = Cl or F) can exist as 2-*cis*-4-*trans*-6 (*trans* isomer) and 2-*cis*-4-*cis*-6 (*cis* isomer) with chair, twist boat, or, less likely, boat conformations. It is well known that electronegative substituents on phosphorus in dioxaphosphorinanes generally adopt axial positions.[22] A rationale for this observation is provided by the '*gauche* effect', and similar reasoning may well apply to the cyclotriphosph(III)azanes. The *gauche* effect indicates [23] that the conformer with the maximum number of *gauche* interactions between lone pairs on adjacent atoms will be favoured. Of the Newman-type projections along N–P bonds, (7) and (8), that may be used to represent the pseudo-axial and equatorial positioning respectively of the X substituent in (2), (7) is favoured by the *gauche* effect.



(7) (8)

The ^{31}P n.m.r. spectra of both (2) (R = Me and Et, X = Cl) show that two isomers can be distinguished at ambient temperatures (*e.g.* see Figure 1). In each case (R = Me or Et) the spectra comprised a singlet and a 2 : 1 doublet with the latter predominating; the signals arise from *cis* and *trans* isomers respectively. At present we cannot distinguish between possible ring conformers. At ambient temperatures the spectra of both (2) (R = Me and Et, X = Cl) in deuteriochloroform solution are broad ($W_{\frac{1}{2}}$ *ca.* 30 Hz), and the addition of 0.5 mol equivalent of anhydrous aluminium chloride to the *N*-ethyl compound collapsed the three signals from *cis* and *trans* isomers into a broad singlet at δ_P 126. Presumably, chloride-ion exchange is promoted under these conditions and the formation of transient species containing the $\gtrless N{-}\overset{+}{P}{-}N\lessgtr$ grouping would provide a pathway for the interconversion of *cis* and *trans* isomers. Cationic species of this type generally have low-field ($\delta_P > 200$) ^{31}P signals,[24] but no signals were detected in this region from mixtures of (2) (R = Et, X = Cl) and aluminium chloride at temperatures down to −100 °C (CD_2Cl_2 solutions).

At sub-ambient temperatures the ^{31}P n.m.r. signals from (2) (R = Me and Et, X = Cl) sharpened, and spin-coupling effects were resolved in the *trans* isomers, confirming that the signals do indeed arise from phosphorus atoms in the same molecule. The proportion of the *cis* isomers also increased from *ca.* 18% at ambient temperatures to >90% at −100 °C (R = Et, CD_2Cl_2 solution). In view of the effects of aluminium chloride the most likely isomerisation mechanism involves chloride-ion exchange, and this might contribute to the ambient temperature linewidth. The activation energy for phosphorus inversion (typically [25] >100 kJ mol^{-1}) is too high

Table 2. Fluorine-19 n.m.r. data [a]

Compound	Isomer	δ_F [b]/p.p.m.	^1J(PF)/Hz	Other couplings/Hz
(2) (R = Et, X = F) [c]	*cis*	−65.6	−1 069.7 [d]	
	trans [e]	−70.5 (1)	−1 095.1	$\lvert^3J(F^1P^2)\rvert = 10.7$
				$\lvert^4J(F^1F^2)\rvert = 20.0$
		−74.8 (2)	−1 137.1	$^3J(F^2P^2) = -0.6$
				$\lvert^3J(F^2P^1)\rvert = 8.0$
				$\lvert^4J(F^2F^2)\rvert$ } = {20.3 [f]
				$\lvert^2J(P^2P^2)\rvert$ } = {11.9 [f]
(4) (R = Et, X = F) [g]	A [h]	−67.1	−1 077.2	$\lvert^3J(FP)\rvert = 11.0$
				$\lvert^5J(FP)\rvert = 1.9$ [i]
	B [j]	−65.0	−1 070.7	$\lvert^3J(FP)\rvert = 10.7$
		−77.2	−1 106.2	$\lvert^3J(FP)\rvert = 10.1$
				$\lvert^5J(FP)\rvert = 2$

[a] Obtained in $CDCl_3$ solutions with proton noise decoupling. Relative intensities are given in parentheses. [b] With respect to external CCl_3F (positive to high frequency). [c] At −65 °C. [d] $^1J(PF) + 2[^3J(PF)]$. [e] AA'KK'RX analysis (A, A', R = F; K, K', X = P). [f] The analysis does not give the assignment of $^4J(F^2F^2)$ and $^2J(P^2P^2)$. [g] At ambient temperature. Isomer ratio A : B = *ca.* 1 : 1. [h] AA'KK'X_2 analysis (A, A' = F; K, K', X = P). [i] The symmetrical nature of this splitting shows that $^4J(PP)$ and $^6J(FF)$ are essentially zero. [j] First-order spectrum.

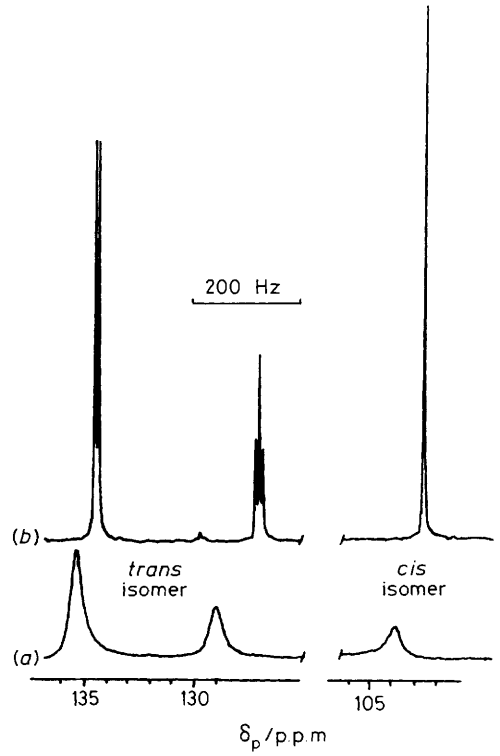


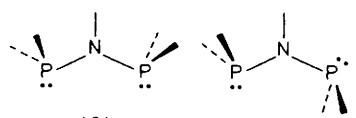
Figure 1. ^{31}P-{^1H} n.m.r. spectra of isomers of (2) (R = Et, X = Cl) at (*a*) ambient temperature, and (*b*) −60 °C in $CDCl_3$ solution

to cause isomerisation or dynamic n.m.r. effects around ambient temperatures. The broadness at ambient temperature presumably also has a contribution from quadrupolar relaxation effects (from ^{14}N and/or $^{35,37}Cl$). Since P–Cl bonds are generally considered more labile than analogous P–F bonds, it is not surprising that the *cis–trans* isomer ratio in (2) (R = Et, X = F) is, within experimental error, independent of temperature. The one-bond spin couplings between phosphorus and fluorine generally assume the order $|J(PF)\text{axial}| < |J(PF)\text{equatorial}|$ in dioxaphosphorinanes.[26] If such a correlation existed for the cyclotriphosph(III)azanes, then *trans*-(2) (R = Et, X = F), the major isomer, would have two 'equatorial' [J(PF) = 1 137.1 Hz] and one 'axial' [J(PF) = 1 095.1 Hz] P–F bonds. This assignment is clearly not in line with the reasoning from the *gauche* effect. The value of $^1J(PF)$ for the *cis* fluoride cannot be determined because of the uncertainty in the value of $^3J(PF)$, see Table 2.

The ^{31}P n.m.r. spectra of the bicyclic compound (4) (R = Et, X = Cl) shows that there are two isomers present in solution. The major and minor components give rise to A_2X_2 and AMX_2 spin systems respectively. These can be interconverted, for on changing the temperature from *ca.* 25 to −60 °C the proportion of the isomer giving rise to the A_2X_2 spin system increases from 80 to 90%. However, the shifts and spin couplings of the two isomers appear to change very little over this temperature range suggesting that each isomer is dominated by a single conformer. Compounds of the general type (4) can exist as a series of conformers (Figure 2) which are analogous to the bicyclo[3.3.1]nonanes. In the latter system the boat form becomes more favourable than in the cyclohexane system because of the axial–axial interactions in conformers analogous to (*a*), (*d*), and (*g*) of compound (4). Molecular models suggest that conformers such as (*d*) and (*g*) are sterically improbable but at this stage it is very difficult to establish which conformers from the groups (4) (*a*),(*b*),(*c*) [or (*d*),(*e*),(*f*)] and (4) (*g*),(*l*),(*i*),(*j*) make major contributions to the A_2X_2 and AMX_2 spectra respectively. It may be noted that only one isomer of (4) (R = Me, X = Cl) has been detected,[12,14] this having only two chemically shifted ^{31}P n.m.r. signals (analogous to the predominant isomer of the ethyl compound).

The chemical shifts and spin couplings in the two isomers of the monoxide of (4) (R = Et, X = Cl), compound (5), are consistent with the structure shown in which oxygen is bonded to one of the non-halogenated phosphorus atoms.

The *PNP* spin couplings in the cyclotriphosph(III)azanes are all relatively small (<10 Hz), and the same is true of (4) (R = Me or Et, X = Cl). Where this coupling can be measured (no relative sign determinations have been made) it shows [27] that the arrangement of phosphorus lone pairs is more closely related to (10) than (9). The *PNP* spin couplings in cyclodiphosph(III)azanes also fall in a similar range ($|J| <$ 50 Hz).[1,2] These spin couplings are in marked contrast to the



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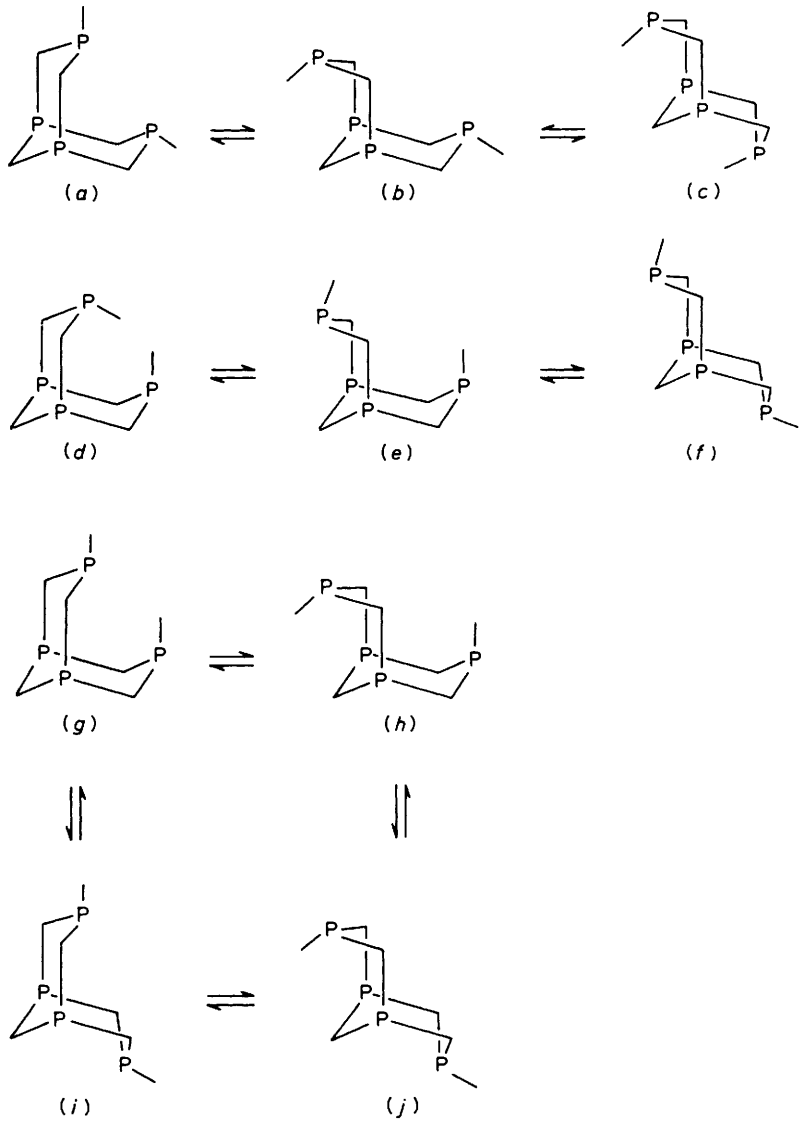

Figure 2. Possible structures of compound (4), showing the effects of P_3N_3 ring inversion

PNP spin couplings, typically of several hundred Hz, observed [27] in certain diphosphinoamines which adopt the preferred conformation (9).

The ^{19}F n.m.r. spectra of both (2) and (4) (X = F) were analysed using explicit equations (Table 2), except that the spectrum of the *cis* isomer of (2) (X = F) could not be analysed in this way. The latter constitutes the XX'X'' part of an AA'A''XX'X'' spin system of which the only obvious feature is a doublet of separation $^1J(PF) + 2[^3J(PF)]$. Half of the spectrum is shown in Figure 3. The spectrum is broader at ambient temperatures than at −65 °C, and it has not been analysed. It has been observed [28] that $^4J(FF')$ is large (94.8 Hz) in *cis*-$(FPNBu^t)_2$, and that there may be a through-space contribution to this coupling. Although these couplings might eventually provide a basis for the identification of preferred conformations, there are insufficient data to attempt this at present.

Experimental

Hydrogen-1, ^{19}F, and ^{31}P n.m.r. spectra were obtained as previously described.[18] Mass spectra were obtained on an A.E.I. MS12 spectrometer. Where possible, all operations were carried out under an atmosphere of dry nitrogen.

2,4,6-*Trichloro*-1,3,5-*triethylcyclotriphosph*(III)*azane* (2) (R = Et, X = Cl).—Phosphorus trichloride (152.1 g, 1.11 mol), ethylamine hydrochloride (90.0 g, 1.10 mol), and *sym*-tetrachloroethane (1 l) were mixed in a 2 l round-bottomed flask fitted with a 50 cm air condenser topped by a water condenser. The water condenser was connected to a paraffin oil bubbler. The mixture was boiled under reflux (6 d), cooled to ambient temperature, filtered, and the solvent removed. The oily brown residue was distilled under reduced pressure, b.p. 115 °C (0.003 mmHg), and the distillate, which slowly solidified, recrystallised from light petroleum (b.p. 40—60 °C) to give the compound (yield 78 g, 65%), m.p. 25—30 °C (Found: C, 21.8; H, 5.1; N, 12.9%; *m/e* 327. $C_6H_{15}Cl_3N_3P_3$ requires C, 21.9; H, 4.6; N, 12.8%; *m/e* 327 *). Omission of the recrystallisation step invariably resulted in contamination of the compound by its *monoxide* (see below).

* ^{35}Cl species; three-chlorine isotope pattern.

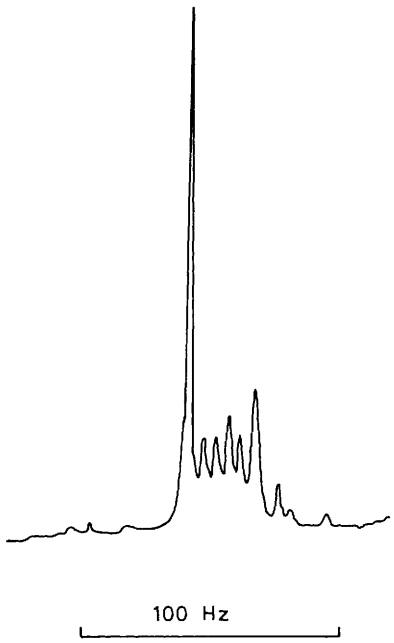

Figure 3. High-field half of the ^{19}F n.m.r. spectra of the *cis* isomer of (2) (X = F) at −65 °C (the low-field signals form a mirror image of this spectrum)

2,4,6-*Trichloro*-1,3,5-*tri-n-propylcyclotriphosph*(III)*azane* (2) (R = Pr^n, X = Cl).—This compound, b.p. 130 °C (0.02 mmHg), was obtained in 30% yield from a similar reaction to that above using n-propylamine hydrochloride (Found: C, 28.9; H, 6.1%; *m/e* 369. $C_9H_{21}Cl_3N_3P_3$ requires C, 29.1; H, 5.7%; *m/e* 379*). This compound failed to crystallise from n-pentane solution. Distillation of the reaction products also gave small quantities (*ca.* 5%) of *bis(dichlorophosphino)-n-propylamine*, b.p. 65 °C (0.01 mmHg), δ_P 153.9 [Found: *m/e* 259 (base peak of four-chlorine isotope pattern). $C_3H_7Cl_4NP_2$ requires *m/e* 259].

Attempts were made to repeat these reactions with methylamine hydrochloride substituted for ethylamine hydrochloride. After 14 d only a small proportion of the methylamine hydrochloride had dissolved and the solution assumed a dark brown colour. Removal of the solvent gave a small quantity of an oil containing (2) (R = Me, X = Cl) (identified by ^{31}P n.m.r., see below) in *ca.* 3% yield. The oil did not crystallise and a pure sample of (2) (R = Me, X = Cl) was not obtained.

1,3,5-*Triethyl*-2,4,6-*trifluorocyclotriphosph*(III)*azane* (2) (R = Et, X = F).—Antimony trifluoride (2.8 g, 16 mmol) was added to a solution of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane (2) (R = Et, X = Cl) (5.2 g, 16 mmol) in light petroleum (b.p. 40—60 °C) (20 cm^3) and the mixture boiled under reflux (1 h). On cooling, the supernatant liquid was decanted off and the solvent removed leaving a colourless liquid. The liquid was distilled under reduced pressure to give the compound (yield 1.5 g, 34%), b.p. 70 °C (1 mmHg) (Found: *m/e* 279.0428. $C_6H_{15}F_3N_3P_3$ requires *m/e* 279.0 423).

Reaction of 2,4,6-*Trichloro*-1,3,5-*triethylcyclotriphosph*(III)*azane* (2) (R = Et, X = Cl) *with Chlorine*.—Elemental chlorine, dried by passage through a phosphorus pentoxide column, was passed into a solution of (2) (R = Et, X = Cl) (0.20 g, 0.61 mmol) in methylene chloride (5 cm^3) at 0 °C over a period of 30 s. An immediate white solid appeared and excess of chlorine was removed by flushing with nitrogen. The white solid was identified as 2,2,2,4,4,4-hexachloro-1,3-diethylcyclodiphosph(v)azane (0.21 g, 82%), m.p. 121 °C, δ_P 80.2 (lit.,[17] m.p. 122—124 °C, δ_P 78.8).

Reaction of 2,4,6-*Trichloro*-1,3,5-*triethylcyclotriphosph*(III)*azane* (2) (R = Et, X = Cl) *with Dimethyl Sulphoxide and with Oxygen*.—Dimethyl sulphoxide (0.33 g, 4.2 mmol) in methylene chloride solution (5 cm^3) was added dropwise to a stirred solution of (2) (R = Et, X = Cl) (1.38 g, 4.2 mmol) in the same solvent (20 cm^3) at 0 °C. After removal of the methylene chloride a colourless oil was obtained which was distilled under reduced pressure (b.p. 115 °C, 0.04 mmHg). N.m.r. examination of the distillate showed that it contained a mixture of products including a *monoxide* of (2) (R = Et, X = Cl) (Found: *m/e* 343. $C_6H_{15}Cl_3N_3OP_3$ requires *m/e* 343 for ^{35}Cl species). No further purification was achieved by distillation or attempted crystallisation. A mixture containing the same monoxide (*ca.* 50%) was also formed when dry oxygen was passed through a solution of (2) (R = Et, X = Cl) in methylene chloride solution for 1 h.

Reactions of (2) (R = Et, X = Cl) with aluminium chloride were carried out on an n.m.r. tube scale using CD_2Cl_2 solutions [*ca.* 0.2 mol dm^{-3} in (2) (R = Et, X = Cl)] as described in the text. No attempt was made to isolate any of the products of these reactions.

2,6-*Dichloro*-1,3,5,7-*tetraethyl*-4,8-*ethyliminocyclotetraphosph*(III)*azane* (4) (R = Et, X = Cl).—A mixture of phosphorus trichloride (136.0 g, 0.99 mol) and ethylamine hydrochloride (100.0 g, 1.22 mol) was boiled under reflux (5 d) in *sym*-tetrachloroethane (1.5 l) as in the preparation of (2) (R = Et, X = Cl) (above). Removal of the solvent and crystallisation of the residual oil from light petroleum (b.p. 40—60 °C) gave (4) (R = Et, X = Cl) (46 g, 45%), m.p. 62—65 °C (Found: C, 29.3; H, 6.6; N, 17.1%; *m/e* 409. $C_{10}H_{25}Cl_2N_5P_4$ requires C, 29.3; H, 6.1; N, 17.3%, *m/e* 409†). In one experiment, careful concentration of the light petroleum solution obtained after crystallisation of (4) (R = Et, X = Cl) gave a monoxide, 2,4-*dichloro*-1,3,5,7-*tetraethyl*-4,8-*ethylimino*-4-*oxocyclotetraphosph*(III)*azane*, (5) *ca.* 5%, m.p. 79—81 °C (Found: C, 27.9; H, 5.4; N, 16.1%; *m/e* 425. $C_{10}H_{25}Cl_2N_5OP_4$ requires C, 28.2; H, 5.9; N, 16.4%; *m/e* 425 †). Phosphorus-31 n.m.r. spectroscopy showed that the solution of (5) in deuteriochloroform also contained traces of what was tentatively identified as a dioxide of (4) (R = Et, X = Cl) (Found: *m/e* 441. $C_{10}H_{25}Cl_2N_5O_2P_4$ requires *m/e* 441 †) (see Table 1).

Attempted Synthesis of Hexaethylphosphorimide, $P_4(NEt)_6$, (3) (R = Et).—Phosphorus trichloride and ethylamine hydrochloride (2 : 3 mol ratio) were boiled under reflux in *sym*-tetrachloroethane solution as in the synthesis of (2) (R = Et, X = Cl) above. Phosphorus-31 n.m.r. examination of the products showed that the major compound was (4) (R = Et, X = Cl). There was no evidence for the formation of $P_4(NEt)_6$, δ_P 79.0.[16]

An attempt to fluorinate (4) (R = Et, X = Cl) by reaction with antimony trifluoride in light petroleum [*cf.* reaction with (2) (R = Et, X = Cl) above] resulted in a complex mixture of products, but two isomers of (4) (R = Et, X = F) were identified by ^{31}P and ^{19}F n.m.r. (Tables 1 and 2).

Effect of Heat on Bis(dichlorophosphino)methylamine.—Bis(dichlorophosphino)methylamine, $Cl_2P{-}NMe{-}PCl_2$, was

* ^{35}Cl species; three-chlorine isotope pattern.

† ^{35}Cl species; base peak of two-chlorine isotope pattern.

heated to 160 °C at atmospheric pressure over a period of *ca.* 8 h. During this time phosphorus trichloride distilled out of the reaction vessel. Eventually a reddish yellow unidentified solid was formed in the reaction flask, but by stopping the reaction before phosphorus trichloride evolution was 50% complete [as required by the equation $n Cl_2P{-}NMe{-}PCl_2 \longrightarrow (ClPNMe)_n + nPCl_3$], low yields (<10%) of (2) (R = Me, X = Cl) could be obtained by distillation of the residue under reduced pressure. Compound (2) (R = Me, X = Cl) was identified by ^{31}P n.m.r. spectroscopy (*cf.* lit.[13]). Analogous results were obtained on heating $Cl_2P{-}NEt{-}PCl_2$.

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