Alkylaminocyclodiphosph(III)azanes †

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The preparation of a series of aminocyclodiphosph(III)azanes, $\overline{ClP{\cdot}NR^1{\cdot}P(NMe_2)}{\cdot}NR^2$ (R^1 = Me, R^2 = Bu^t; $R^1 = R^2 = Bu^t$; $R^1 = R^2$ = Ph) and $(R^1_2N){\cdot}\overline{P{\cdot}NR^2{\cdot}P(NR^1_2)}{\cdot}NR^3$ [R^1 = Me, R^2 = Me, R^3 = Bu^t; R^1 = Me, R^2 = Et, R^3 = Bu^t; R^1 = Me, $R^2 = R^3 = Bu^t$; R^1 = Et, $R^2 = R^3 = Bu^t$; R^1 = Me, $R^2 = R^3 = C_6H_4X$-*p* (X = H, Me, Cl, or OMe); and R^1 = Et, $R^2 = R^3$ = Ph] by aminolysis of chlorocyclodiphosph(III)azanes is described. In many cases geometrical isomers are obtained which display exceptionally large differences (65—90 p.p.m.) in ^{31}P chemical shift. Aspects of the ^1H and ^{31}P n.m.r., mass, and i.r. spectra of those compounds are recorded and discussed.

THE first report of the formation of a cyclodiphosph(III)-azane (1; X = Cl, $R^1 = R^2$ = Ph) and its amino- and alkoxy-derivatives appeared during the last century,[1] but the detailed characterisation of compounds of this type has only recently been started.[2] Difficulties have been encountered [2-4] in the identification of the derivatives (1; X = Cl, $R^1 = R^2$ = Me or Et), but a crystal-structure examination [5] of (1; X = Cl, $R^1 = R^2 = Bu^t$)

† No reprints available.

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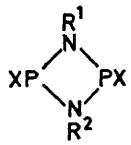
TABLE 1

Phosphorus-31 and ^{1}H n.m.r. data for aminocyclodiphosph(III)azanes (1) and (2) [a]

Compound	X	R^1	R^2	δ_P [b] p.p.m.	J_{PNP} Hz	Isomer ratio [c]		$\delta_H(NMe_2)$ p.p.m.	$J_{PNCH}(NMe_2)$ [d] Hz
(1)	NMe_2	Me	Bu^t	105.6		2	3	2.68	8.1
(1)	NMe_2	Me	Bu^t	192.3		3	2	2.70	7.6
(1)	NMe_2	Et	Bu^t	101.4		1	2	2.78 [e]	7.8
(1)	NMe_2	Et	Bu^t	186.4		2	1	2.79 [f]	7.0
(1)	NMe_2	Bu^t	Bu^t	95.0		2	10	2.66	8.4
(1)	NMe_2	Bu^t	Bu^t	184.7		3	1	2.67	*ca.* 3,12 [g]
(1)	NEt_2	Bu^t	Bu^t	91.3				3.17 [h]	8.0
(2)		Me	Bu^t	189(*P*Cl)	+31.5 ± 0.5				
				146				2.81	8.0
(2)		Bu^t	Bu^t	178(*P*Cl)	32.5 ± 0.5				
				128				2.81, 2.83	2.9, 13.2
(1)	NMe_2	Ph	Ph	101.0	*i*	1	0	2.87	8.7
(1)	NMe_2	Ph	Ph	166.5	*i*	1	1	2.78	8.4
(1)	NMe_2	C_6H_4Cl-*p*	C_6H_4Cl-*p*	100.8		1	0	2.88	8.5
(1)	NMe_2	C_6H_4Cl-*p*	C_6H_4Cl-*p*	166.1		1	1	2.82	8.5
(1)	NMe_2	C_6H_4Me-*p*	C_6H_4Me-*p*			0	0		
(1)	NMe_2	C_6H_4Me-*p*	C_6H_4Me-*p*	166.8		1	1	2.86	8.5
(1)	NMe_2	C_6H_4OMe-*p*	C_6H_4OMe-*p*	101.5		1	0	2.88	8.9
(1)	NMe_2	C_6H_4OMe-*p*	C_6H_4OMe-*p*	168.9		10	1	2.83	8.6
(1)	NEt_2	Ph	Ph	162.2				3.28 [h]	8.0
(2)		Ph	Ph	136.3 [j]				2.91	9.0
				178.6(*P*Cl)					
(1)	Bu^tNH	Bu^t	Bu^t	89.4					

[a] At ambient temperatures in $CDCl_3$ solutions (no reaction). [b] Downfield shifts are positive; relative to external 85% H_3PO_4. [c] The first column shows the ratios immediately after reaction, the second column shows the ratios after standing over a period of weeks. [d] More correctly $|J_{PNCH} + J_{PNPNCH}|$ for compounds (1). [e] $\delta(NCH_2)$ 3.01, J_{PNCH_2} 10.7 Hz; showed signs of broadening (see text). [f] $\delta(NCH_2)$ 2.58, J_{PNCH_2} 10.5 Hz. [g] Broadened by exchange effects, which arise from restricted rotation about the exocyclic P–N bonds.[18] [h] NCH_2. [i] ^1H-{^{31}P} INDOR experiments indicate that $J_{PNP} < 50$ Hz. [j] $PNMe_2$, determined by double resonance only.

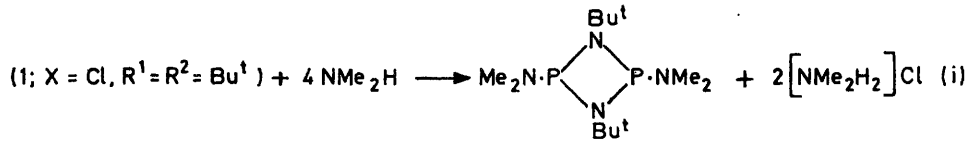
has unambiguously demonstrated the presence of a four-membered ring. Recently authenticated examples of (1; X = alkylamino) are limited to (1; X = NBu^tH, $R^1 = R^2 = Bu^t$) obtained in the t-butylaminolysis of phosphorus trichloride,[6] the dimethylamino-derivative (X = NMe_2, $R^1 = R^2 = Ph$),[7] the *N*-arylsulphonyl derivatives [X = NMeR′ (R′ = alkyl), $R^1 = R^2 = R''SO_2$ (R″ = aryl)],[8] and the dimethylhydrazino-derivative (X = $NMeBu^t$, $R^1 = R^2 = NMe_2$).[9] Cyclodiphosph(III)azanes are examples of dimeric monophosph(III)azenes, and, in view of the reports (*a*) that the latter compounds $R^1R^2N{\cdot}P{:}NR^3$ ($R^1 = R^2 = R^3 = SiMe_3$;[10,11] $R^1 = R^3 = Bu^t$, $R^2 = SiMe_3$;[12] $R^1 = R^2 = SiMe_3$, $R^3 = Bu^t$)[13] have recently been prepared, (*b*) that dimethylaminolysis of (1; X = Cl, $R^1 = R^2 = Bu^t$) led to complicated mixtures,[14] and (*c*) that no evidence has been obtained for more than one geometrical isomer of a cyclodiphosph(III)azane, we have investigated the products of aminolysis of chlorocyclodiphosph(III)azanes in some detail. Throughout this paper it will be assumed that geometrical isomerism arises from the different mutual orientations of the exocyclic phosphorus substituents and that the ring nitrogen atoms have a planar, or near planar,[5] distribution of bonds.



(1)

RESULTS AND DISCUSSION

Hydrogen-1 n.m.r. spectroscopy showed that the reaction of (1; X = Cl, $R^1 = R^2 = Bu^t$) with 4, or more, molar equivalents of dimethylamine in diethyl ether solution resulted in the formation of two products, a mixture of which analysed for $(Me_2NPNBu^t)_n$. Mass spectroscopy showed that $n = 2$, so that the reaction is straightforward, except that a mixture of geometrical



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isomers is formed [equation (i)]. The two isomers had ^{31}P chemical shifts of δ 95 and 184 p.p.m.; the difference between these shifts is exceptionally large and the shift of the low-field isomer is well outside the range expected for aminophosphines, $P(NR_2)_3$ (δ_P 78—134 p.p.m.).[15] Generally, isomeric cyclodiphosph(v)azanes have ^{31}P chemical shifts which differ by less than 5 p.p.m., and in other cyclic tervalent phosphorus compounds the shift difference between isomeric forms is less than 15 p.p.m., *e.g.* ref. 16. The isomer with the shift of δ 95 p.p.m. is well within the range expected for the incorporation of an aminophosphine in a six-membered ring;[3,4] molecular-weight measurements in benzene solution, however, confirmed that a cyclodi- rather than a cyclotri-phosphazane was present.

The dimethylaminolysis experiments were repeated on (1; X = Cl, R^1 = Bu^t, R^2 = Me or Et) and there were significant differences in isomer ratios. Isomerisation of these 2,4-bis(dimethylamino)cyclodiphosphazanes was found to occur. Qualitative observations show that the rate of isomerisation increases with increasing bulk of the nitrogen substituents, thus while isomerisation of (1; X = NMe_2, R^1 = Bu^t, R^2 = Me) was only apparent after standing for several weeks at ambient temperatures, isomerisation of (1; X = NMe_2, R^1 = Bu^t, R^2 = Et) was noticeable after a few days, and (1; X = NMe_2, R^1 = R^2 = Bu^t) isomerised almost completely to one isomer within 2 d, especially in solution. In each case isomerisation resulted in an increased proportion of the isomer with the ' high-field ' ^{31}P signal ($\delta_P \sim 100$ p.p.m.) being formed.

The preparation of (1; X = NMe_2, R^1 = Bu^t, R^2 = Me) was also achieved by reaction (ii). The substrate,

$$(Me_2N)ClP{\cdot}NMe{\cdot}PCl(NMe_2) + 3NBu^tH_2 \longrightarrow (1;\ X = NMe_2,\ R^1 = Bu^t,\ R^2 = Me) + 2[NBu^tH_3]Cl \quad (ii)$$

$(Me_2N)ClP{\cdot}NMe{\cdot}PCl(NMe_2)$, decomposes on removal of solvent,[17] so that it was necessary to carry out this reaction on a freshly prepared solution containing this compound.

Similar reactions with 2 molar equivalents of dimethylamine readily gave monodimethylamino-derivatives (2) [equation (iii)]. These products differed from the bis(dimethylamino) derivatives in that only one isomer was formed in each case. In one case (R^2 = Bu^t) there was initially some doubt about this because of the appearance of two dimethylamino-proton signals at ambient temperatures. It is now clear that these two signals arise because rotation about the P–N bond is slow on the n.m.r. time scale. Details of these effects will be described elsewhere.[18]

Reactions of (1; X = Cl, R^1 = R^2 = Bu^t) with 4 molar equivalents of diethylamine gave $(Et_2NPNBu^t)_2$ in one isomeric form only and this with a ' high-field ' ^{31}P signal. The preparation of $(HBu^tNPNBu^t)_2$ by the reaction of phosphorus trichloride with t-butylamine[6] was repeated. Only one isomer was detected, and this also had a ' high-field ' ^{31}P shift (δ_P 89.4 p.p.m.) relative to the t-butylamino-derivatives above.

The preparation of *N*-arylcyclodiphosph(III)azanes (1; X = Cl, R^1 = R^2 = C_6H_4Y-*p*) by the reaction of arylamine hydrochlorides with PCl_3 in refluxing *sym*-tetrachloroethane has recently been described.[7] In our hands, these preparations were repeatable when Y = H or Cl, but not when Y = Me or OMe. When Y = Me,

(1; X = Cl, R^1 = Bu^t, R^2 = Me or Bu^t) + 2 NMe_2H → $Me_2N{\cdot}P$(NR^1, NR^2)PCl + $[NMe_2H_2]Cl$ (iii)

(2)

the cyclodiphosph(III)azane was only obtained by heating the intermediate bis(dichlorophosphino)amine under reduced pressure [equation (iv)]. When Y =

$$2Cl_2P{\cdot}NC_6H_4Me\text{-}p{\cdot}PCl_2 \longrightarrow (ClPNC_6H_4Me\text{-}p)_2 + 2PCl_3 \quad (iv)$$

OMe, no cyclodiphosph(III)azane could be obtained.

Dimethylaminolysis of the chlorocyclodiphosph(III)azanes (1; X = Cl, R^1 = R^2 = C_6H_4Y-*p*) readily gave the bisdimethylamino-derivatives, $(Me_2NPNC_6H_4Y\text{-}p)_2$ (Y = H, Cl, or Me). The *p*-methoxyphenyl derivative was obtained by dimethylaminolysis of the bis(dichlorophosphino)amine, $Cl_2P{\cdot}N(C_6H_4OMe\text{-}p){\cdot}PCl_2$. Careful examination of the products of the reaction of $Cl_2P{\cdot}NPh{\cdot}PCl_2$ with 4 molar equivalents of dimethylamine by ^1H n.m.r. spectroscopy showed that the cyclisation step is extremely facile, for only $\overline{ClP{\cdot}NPh{\cdot}P(NMe_2){\cdot}NPh}$ (2; R^1 = R^2 = Ph) [also prepared by the reaction of (1; X = Cl, R^1 = R^2 = Ph) with 2 molar equivalents of dimethylamine], $PCl_2(NMe_2)$, and $PCl(NMe_2)_2$ could be detected. It is therefore not possible to distinguish between the various routes by which dimethylaminocyclodiphosph(III)azanes may be formed in this reaction. Although $(Me_2N)ClP{\cdot}NPh{\cdot}PCl(NMe_2)$ could not be detected, it is worth noting that $(Me_2N)ClP{\cdot}NMe{\cdot}PCl(NMe_2)$ has been identified[17] as a product of dimethylaminolysis of $Cl_2P{\cdot}NMe{\cdot}PCl_2$, and that it eliminates $PCl_2(NMe_2)$ and $PCl(NMe_2)_2$ over a period of several hours at ambient temperatures. Only the *N*-phenyl derivative, $(Me_2NPNPh)_2$, has been previously reported[7] and this apparently as one isomer. In three out of four cases (Y = H, Cl, or OMe) we have now found that a mixture of geometrical isomers is obtained, again with a large difference in ^{31}P chemical shifts for each pair of isomers. The isomer which predominates and which appears to be thermodynamically favoured is, surprisingly, that with the ' low-field ' ^{31}P shift. The

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thermodynamically favoured isomer has the ' high-field ' ^{31}P shift in the *N*-alkyl derivatives. Diethylaminolysis of $(ClPNPh)_2$ gave only one isomer of $(Et_2NPNPh)_2$, and *this had* a ' low-field ' ^{31}P signal (δ_P **161.2** p.p.m.).

The ^{31}P n.m.r. data suggest that different geometrical isomers are thermodynamically favoured when *N*-alkyl are replaced by *N*-aryl substituents. An assignment of structures to these isomers would have been simplified if the thermodynamically less-stable form could have been isolated also, but the rate of isomerisation at ambient temperatures is such that this has not been achieved, even with the more crystalline *N*-aryl derivatives. There are two possible mechanisms of isomerisation, either the conventional inversion of configuration at phosphorus, or a process of the type (v). It is well known that organophosphines are configurationally stable at ambient temperatures and, if anything, they are likely to be more stable because of the presence of electronegative substituents and the fact that phosphorus forms part of a small strained ring system.[19] It is known that monomeric phosph(III)azenes of the type shown are characterised by very low-field ^{31}P shifts (*e.g.* δ_P = **325** p.p.m. when R = R^1 = $SiMe_3$),[10] and accordingly we searched the ^{31}P spectra of these compounds in the region δ_P 200—400 p.p.m., but no signals were found. If the monomer (*e.g.* $Me_2N{\cdot}P{:}NBu^t$) is formed it must have a very short lifetime. The observation that the rate of isomerisation increases with increasing steric bulk of the nitrogen substituent could equally well be interpreted in terms of a lower barrier to inversion at phosphorus or in terms of a greater stabilisation of a monomeric species, $R_2N{\cdot}P{:}NR^1$.

There are several results which suggest that the isomers of the 1,3-dialkylcyclodiphosph(III)azanes with the low-field ^{31}P signals have a mutual *cis* orientation of dialkylamino-groups. (*a*) On steric grounds the *trans* isomer would be expected to be thermodynamically more stable than the *cis* (assuming that there are no pronounced cyclodiphosphazane ring-puckering effects). This would mean that the *trans* isomers had the highest-field ^{31}P shifts, and be consistent with the exclusive formation of an isomer of $(Et_2NPNBu^t)_2$ with a ' high-field ' ^{31}P shift. (*b*) Nucleophilic displacement of chlorine by amino-groups in phosphetans is known to proceed with inversion of configuration at phosphorus.[20] If aminolysis were also stereospecific in the cyclodiphosph(III)azanes, then the kinetically favoured product from the dimethylaminolysis of $(ClPNBu^t)_2$ (known to be *cis* [5]) would also be a *cis* isomer. The major product from this reaction appears to be the product of kinetic control, and it has a ' low-field ' ^{31}P signal. (*c*) The ethyl CH_2 signals of the two isomers of $(Me_2N)\overline{P{\cdot}NBu^t{\cdot}P(NMe_2){\cdot}}NEt$ were examined at 220 MHz. Those CH_2 signals corresponding to the isomer with the ' high-field ' ^{31}P shift were broader than those from the isomer with the ' low-field ' shift. Non-equivalence of methylene protons may be taken to imply the presence of a *trans* isomer.[21]

Although the foregoing results are all indicative of a *cis* configuration for the isomer with the low-field ^{31}P signal, the results for the 1,3-diarylcyclodiphosphazanes are different. Of the dimethylamino-derivatives, the thermodynamically favoured form has a ' low-field ' ^{31}P signal and reaction with diethylamine results in the exclusive formation of an isomer of $(Et_2NPNPh)_2$ with a ' low-field ' signal. The thermodynamically favoured 1,3-diaryl derivatives are all crystalline at ambient temperatures. A crystal structure of one of these derivatives, and variable-temperature n.m.r. studies, may shed further light on the ^{31}P shift differences, which, at present, may be rather speculatively ascribed to differences in preferred conformation adopted by the dialkylamino-groups.

A feature of the ^{31}P n.m.r. spectra of the cyclodiphosph(III)azanes is that the ^{31}P signals are moved farther upfield by increasing methyl-group substitution at the α-carbon atom in the 1,3-alkyl groups. For example, the ^{31}P signals in both isomers of the series $(Me_2N)\overline{P{\cdot}NBu^t{\cdot}P(NMe_2){\cdot}}NR$ move upfield by 2—5 p.p.m. per methyl-group substitution in the series R = Me, Et, and Bu^t. A similar effect may be noted for (**1**; X = Cl, R^1 = Bu^t, R^2 = Me, Et, or Bu^t).[4] This shift may well be related to the so-called ' gamma effect ' apparent in alkylphosphines,[22] where methyl-group substitution at the γ position [methyl-group substitution in the cyclodiphosph(III)azanes is also ' γ ' to phosphorus] results in a progressive upfield shift as a consequence of increasing steric interactions. The effect of the *para* substituent in the 1,3-diarylcyclodiphosph(III)azanes is very small, but an upfield ^{31}P shift is apparent with the more electron-releasing substituents.

(v)

The dimethylamino-proton signals in the symmetrical compounds, $(Me_2N)\overline{P{\cdot}NBu^t{\cdot}P(NMe_2){\cdot}}NR$ (R = Me, Et, or Bu^t) were all doublets of separation 8—12 Hz, with very little of the second-order effects which give rise to a group of signals between the components of the doublet. When the bridging *N*-alkyl protons are ignored these systems constitute $X_6AA'X'_6$ spin systems and

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[22] L. D. Quin and J. J. Breen, *Phosphorus*, 1973, **5**, 17.

typically give rise to second-order effects when $|J_{AX} + J_{AX'}| < J_{AA'}$. These results therefore imply that $J_{AA'}$ (or J_{PNP}) is small, probably <10 Hz. Stronger second-order effects were apparent in the dimethylamino-proton signals of 1,3-diarylcyclodiphosph(III)azanes, particularly for the isomers with the low-field ^{31}P shifts, but ^{1}H-{^{31}P} INDOR experiments [23] on the 1,3-diphenylcyclodiphosph(III)azanes indicated that J_{PNP} was again relatively small (<50 Hz). By comparison of the relative signs of J_{PNP} and J_{PNCH} in ClP·NBu^t·P(NMe$_2$)·NR (R = Me) it was possible to show that the former coupling is +31.5 Hz and we assume that the same sign holds when R = Bu^t. Relatively small *PNP* coupling constants are anticipated when the P–N–P unit forms part of a four-membered ring.[24] A general feature of the dimethylamino-proton shifts of isomeric compounds was that the isomer with the low-field ^{31}P signal always gave ^{1}H signals at higher field than the isomer with the high-field ^{31}P signals.

An important aspect of the mass spectra of the cyclodiphosph(III)azanes is the relatively high abundance of molecular ions corresponding to the monomers, XP:NR^1 (or R^2) (Table 2). In the 1,3-diarylcyclodiphosph(III)azanes the ratio [(1)] : [monomer] was less than 1 : 1. This ratio was generally greater than 1 : 1 in the 1,3-dialkylcyclodiphosph(III)azanes suggesting that aryl substituents are more effective than alkyl in stabilising monomeric phosph(III)azenes. In (1; X = NMe$_2$, R^1 = Bu^t, R^2 = Me) both possible phosph(III)azenes were formed in similar quantities; the same result was obtained when R^2 = Et. It remains to be seen how the stability of 1,3-dialkyl- relative to 1,3-diaryl-cyclodiphosph(III)azanes as molecular ions correlates with their solution properties.

TABLE 2

Selected mass-spectroscopic ratios for compounds (1)

R^1	R^2	[(1; X = NMe$_2$)] : [Me$_2$NP=NR^1]	[(1; X = Cl)] : [ClP=NR^1]
Bu^t	Me	1.75	7.60
Bu^t	Et	0.76	1.82
Bu^t	Bu^t	3.17	
Bu^t	Bu^t	5.12 (X = NEt$_2$)	
C$_6$H$_4$Cl-*p*		0.08	0.04
Ph		0.73	0.36
Ph		0.38 (X = NEt$_2$)	
C$_6$H$_4$Me-*p*		0.66	0.31 [a]
C$_6$H$_4$OMe-*p*		0.27	*b*

[a] (XPNR^1)$_3$, *m/e* 507, observed in small quantities. [b] (1; X = Cl) was not prepared.

EXPERIMENTAL

Solvents were dried by conventional means. Phosphorus trichloride and diethylamine were distilled before use, the amine from sodium hydroxide pellets. Anhydrous dimethylamine and amine hydrochlorides, obtained commercially, were used without purification. *p*-Toluidine was purified by sublimation under reduced pressure. The cyclodiphosph(III)azanes, ClP·NBu^t·PCl·NR (R = Me, Et, or Bu^t) were obtained as previously described,[4] and (Cl$_2$P)$_2$N·C$_6$H$_4$Y-*p* (Y = Cl, H, Me, or OMe) and (ClPN-C$_6$H$_4$Y-*p*)$_2$ (Y = H, Cl, or Me) were prepared by slightly modified literature methods.[3,7] N.m.r., mass, and i.r. spectroscopic data were obtained as previously,[3,4,24] and molecular weights were determined by osmometry in benzene solution.

TABLE 3

Experimental details

Substrate [amount/mmol]	Reactant (amount/mmol)	Reaction conditions [θ_c/°C, solvent (*V*/cm^3)]	Subsequent treatment [stirring(*t*/h) at θ_c/°C]	Final product(s) (yield/%), [isomer ratio]	M.p. (θ_c/°C) or [b.p.(θ_c/°C) *P*/mmHg]
(1; X = Cl, R^1 = Me, R^2 = Bu^t) [22.5]	NMe$_2$H (104)	−78, OEt$_2$ (180)	20 (3)	(Me$_2$N)P·NBu^t·P(NMe$_2$)·NMe (55) [3 : 2]	[60—66, 0.01]
(Me$_2$N)ClP·NMe·PCl(NMe$_2$) [52]	NBu^{t}H (155)	−78 CH$_2$Cl$_2$ (50)	20 (2)	(Me$_2$N)P·NBu^t·P(NMe$_2$)·NMe (64) [2 : 2]	
(1; X = Cl, R^1 = Et, R^2 = Bu^t) [19.4]	NMe$_2$H (98)	−78, OEt$_2$ (170)	20 (2)	(Me$_2$N)P·NBu^t·P(NMe$_2$)·NEt (53) [2 : 1]	[54—56, 0.005]
(1; X = Cl, R^1 = R^2 = Bu^t) [20.4]	NEt$_2$H (82)	−78, OEt$_2$ (170)	20 (15)	(Et$_2$N)P·NBu^t·P(NEt$_2$)·NBu^t (30) [1 : 0]	32—34 [78—80, 0.2]
(1; X = Cl, R^1 = Me, R^2 = Bu^t) [26.4]	NMe$_2$H (53)	−78, OEt$_2$ (50)	20 (1)	(Me$_2$N)P·NBu^t·PCl·NMe (67) [1 : 0]	[50—56, 0.02]
PCl$_3$ [230]	NBu^{t}H$_2$ (1 150)	−78, OEt$_2$ (600)	20 (48)	(HBu^{t}N)P·NBu^t·P(NBu^{t}H)·NBu^t (52) [1 : 0]	148—150
(1; X = Cl, R^1 = R^2 = Ph) [32]	NMe$_2$H (64)	−78, CH$_2$Cl$_2$ (10)–OEt$_2$ (30)	20 (1)	(Me$_2$N)P·NPh·PCl·NPh (89) [1 : 0]	84
(1; X = Cl, R^1 = R^2 = C$_6$H$_4$Cl-*p*) [13]	NMe$_2$H (52)	−78 CH$_2$Cl$_2$ (30)	20 (1)	(Me$_2$N)P·N(C$_6$H$_4$Cl-*p*)·P(NMe$_2$)·N(C$_6$H$_4$Cl-*p*) (86) [1 : 0]	117—118
(1; X = Cl, R^1 = R^2 = C$_6$H$_4$Me-*p*) [20]	NMe$_2$H (80)	−78, OEt$_2$ (30)	20 (0.5)	(Me$_2$N)P·N(C$_6$H$_4$Me-*p*)·P(NMe$_2$)·N(C$_6$H$_4$Me-*p*) (86) [1:0]	111—113
(Cl$_2$P)$_2$N·C$_6$H$_4$OMe-*p* [31]	NMe$_2$H (250)	−78, OEt$_2$ (30)	20 (1)	(Me$_2$N)P·N(C$_6$H$_4$OMe-*p*)·P(NMe$_2$)·N(C$_6$H$_4$OMe-*p*) (65) [1 : 0]	112
(1; X = Cl, R^1 = R^2 = Ph) [30]	NEt$_2$H (120)	20, CH$_2$Cl$_2$ (20)	20 (1)	(Et$_2$N)P·NPh·P(NEt$_2$)·NPh (58) [1 : 0]	104—105

Typical preparations of dimethylaminocyclodiphosph(III)azanes are described below and the remaining preparative details are given in Table 3. Analytical data are in Table 4.

2,4-Bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)-azane (1; X = NMe$_2$, R^1 = R^2 = Bu^t).—2,4-Dichloro-1,3-di-t-butylcyclodiphosph(III)azane (5.3 g, 0.019 mol) was mixed with dimethylamine (4.5 g, 0.10 mol) in diethyl ether

[23] Of the type used by W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

[24] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1424.

(180 cm³) at −78 °C. The mixture was boiled under reflux (3 h) and dimethylamine hydrochloride and solvent were removed, leaving a white low-melting-point solid. The solid was remelted and distilled under reduced pressure to give 2,4-*bis*(*dimethylamino*)-1,3-*di-t-butylcyclodiphosph*(III)*azane* (2.7 g, 48%) as a clear viscous liquid, b.p. 85—90 °C (0.01 mmHg),* which crystallised on standing (5.6 g, 0.12 mol) was added to a stirred suspension of 2,4-dichloro-1,3-diphenylcyclodiphosph(III)azane (9.9 g, 0.031 mol) in methylene chloride (20 cm³) at −78 °C. The solution was stirred (0.5 h), brought to ambient temperature, and diethyl ether (30 cm³) was added. The precipitate was removed and evaporation of the solvent left a white solid. Recrystallisation from methylene

TABLE 4

Analytical data for compounds (1) and (2)

				Found [a]				Calc.			
Compound	X	R^1	R^2	C	H	N	M [b]	C	H	N	M
(1)	NMe_2	Bu^t	Me	43.5	9.7	22.1	250 (251)	43.2	9.7	22.4	250
(1)	NMe_2	Bu^t	Et	45.4	10.0	21.4	264 (245)	45.45	9.9	21.2	264
(1)	NEt_2	Bu^t	Bu^t	55.0	11.2	15.9	348 (351)	55.15	11.0	16.1	348
(2)		Bu^t	Me	34.1	8.5	16.9	241	34.4	8.7	17.2	241 [c]
(1)	NBu^tH	Bu^t	Bu^t	55.3	11.1	16.4 [c]	348	55.2	10.9	16.1	348
(2)		Ph	Ph	52.1	5.1	13.45	323	51.9	4.9	13.0	323
(1)	NMe_2	C_6H_4Cl-*p*		48.1	4.9	14.1	400 (427)	47.9	5.0	14.0	400 (401)
(1)	NMe_2	C_6H_4Me-*p*		59.1	7.1	15.7	360	60.0	7.2	15.6	360
(1)	NMe_2	C_6H_4OMe-*p*		55.1	6.7	14.3	392	55.1	6.6	14.3	392
(1)	NEt_2	Ph	Ph	61.7	7.6	14.85	388	61.9	7.7	14.4	388

[a] Analyses in %. [b] *m/e* for ^{35}Cl-containing species; for other *m/e* data see Table 2. Values in parentheses were obtained by osmometry in benzene solution. [c] P 18.1 (calc. 17.8%).

[Found: C, 49.4; H, 10.7; N, 19.0%; *M* 291 (in benzene), *m/e* 292. $C_{12}H_{30}N_4P_2$ requires C, 49.3; H, 10.3; N, 19.2%; *M* 292, *m/e* 292], m.p. 38—42 °C; i.r. (thin film) 2 958s, 2 915s(sh), 2 860s, 2 821m, 2 783m, 1 455s(br), 1 385m, 1 359s, 1 273s, 1 240s, 1 210vs,br, 1 137w, 1 069m, 1 058m, 1 029m, 998s, 972s, 961s(sh), 923w, 897m, 866s, 810vw, 792m, 728vw, 688m, 659s, 645m, 596m, 552vw, 488w, 472w, 417w, 393vw, 238w, and 210w cm^{-1}.

2-*Chloro*-4-*dimethylamino*-1,3-*di-t-butylcyclodiphosph*(III)-*azane* (2; $R^1 = R^2 = Bu^t$).—2,4-Dichloro-1,3-di-t-butylcyclodiphosph(III)azane (5.3 g, 0.019 mol) was treated with dimethylamine (1.81 g, 0.039 mol) in diethyl ether (150 cm³) at −78 °C. The liquid residue obtained after work-up was distilled under reduced pressure to give 2-*chloro*-4-*dimethylamino*-1,3-*di-t-butylcyclodiphosph*(III)*azane* (3.7 g, 57%) a clear viscous liquid, b.p. 55—65 °C (0.03 mmHg) (Found: C, 41.7; H, 8.6; N, 15.1%; *m/e* 283. $C_{10}H_{24}{}^{35}ClN_3P_2$ requires C, 42.3; H, 8.5; N, 14.8%; *m/e* 283).

2,4-*Bis*(*dimethylamino*)-1,3-*diphenylcyclodiphosph*(III)-*azane* (1; X = NMe_2, $R^1 = R^2$ = Ph).—Dimethylamine 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%), m.p. 125—127 °C (lit.,[7] 188, 206—208 °C?) (Found: C, 58.1; H, 6.5; N, 16.6%; *m/e* 332. $C_{16}H_{22}N_4P_2$ requires C, 57.8; H, 6.6; N, 16.9%; *m/e* 332). ^1H n.m.r. spectrum indicated that the crude product contained two isomers in equimolar proportions. I.r. spectrum in CCl_4 solution: † 3 065w, 3 030w, 3 000vw, 2 970w, 2 920w, 2 890w, 2 835w, 2 800w, 2 792w, 1 592s, 1 490s, 1 476m, 1 445m, 1 405vw, 1 278vs, 1 194m, 1 175m, 1 152vw, 1 098w, 1 075w, 1 060w, 1 025w, 992w, 968m, 904s, 892s, 688s, 675m, 655m, 615vw, 525vw, 490m, and 390w cm^{-1}.

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* Throughout this paper: 1 mmHg ≃ 13.6 × 9.8 Pa.
† No reaction at ambient temperatures.