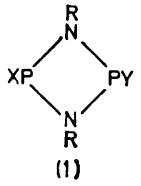
New Aminocyclodiphosph(III)azanes and the Influence of Geometrical Isomerism on their Properties

By **Rodney Keat,* David S. Rycroft,** and **David G. Thompson,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

A series of aminocyclodiphosph(III)azanes $(R^1R^2N)PNBu^tP(NR^1R^2)NBu^t$ (R^1 = H, alkyl, or $SiMe_3$; R^2 = alkyl) have been prepared by the reactions of $ClPNBu^tP(Cl)NBu^t$ with primary or secondary amines, or with $NMe(SiMe_3)_2$. In some cases geometrical isomers have been separated by fractional crystallisation and thermal methods. Other cyclodiphosph(III)azanes, $(Me_2N)PNRP(NMe_2)NR$ (R = Me or Et), have been synthesised by heating diphosphinoamines $(Me_2N)_2P–NR–P(NMe_2)_2$ (R = Me or Et) *in vacuo*. Selected physical (^1H, ^{13}C, ^{31}P n.m.r., i.r., dipole-moment, and mass-spectral) properties of these derivatives are reported and discussed.

AN intriguing feature of the rapidly developing chemistry of the cyclodiphosph(III)azanes (1) is the marked influence of geometrical isomerism on the physical and chemical properties of these compounds.[1-4] Although the occurrence of geometrical isomerism has been widely recognised in other inorganic, particularly phosphorus(V)–nitrogen, ring systems, it does not



(1)

generally result in profound differences in properties.[5] The reasons for these differences in compounds (1) are clearly intimately related to the presence of lone pairs of electrons on phosphorus, but not in a manner yet established by quantum calculations. In order to explore these differences further, we have extended a previously reported series of aminocyclodiphosph(III)-azanes,[6] and devised a new route to these compounds.

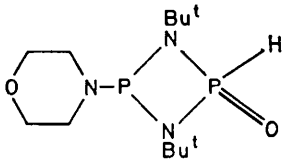
RESULTS

The reactions of (1; R = Bu^t, X = Y = Cl) with methylamine, ethylamine, pyrrolidine, morpholine, and piperidine give diamino-derivatives in good yield [equation (i)]. Reactions with methylamine and, as previously

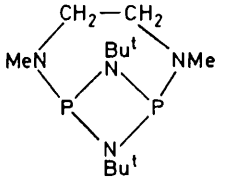
$$(1;\ R = Bu^t,\ X = Y = Cl) + 4NR^1R^2H \longrightarrow (1;\ R = Bu^t,\ X = Y = NR^1R^2) + 2[NR^1R^2H_2]Cl \quad (i)$$

reported,[6] dimethylamine gave solid products on removal of solvent, which on recrystallisation from pentane gave isomers with a ' low-field ' ^{31}P chemical shift (170—200 p.p.m.). The mixed amino-derivative (1; R = Bu^t, X = NMeH, Y = NMe_2) was formed in the same way, but gave a mixture of products on standing. These isomers were stable in the solid state, but in solution they underwent an isomerisation to a ' high-field ' isomer (^{31}P shift 90—110 p.p.m.). ' High-field ' isomers were obtained by heating the ' low-field ' isomers in benzene solution and finally purified by distillation under reduced pressure.

Pyrrolidine and piperidine gave very low yields of the ' low-field ' isomer and with ethylamine and morpholine no ' low-field ' isomers could be detected by n.m.r. The reaction with morpholine gave a morpholino-derivative, (1; R = Bu^t, X = Y = NC_4H_8O), and a small quantity of another compound. The yield of the latter compound increased on heating a benzene solution of (1; R = Bu^t, X = Y = NC_4H_8O) and it is tentatively assigned structure (2). It is evidently obtained by water-induced cleavage of an exocyclic P–N bond. Reaction of (1; R = Bu^t, X = Y = Cl) with *NN'*-dimethylethylenediamine gave the bicyclic compound (3),[7] which was separated from other,



(2)



(3)

presumably polymeric, material by distillation under reduced pressure. Yields of (3) were improved when the diamine rather than triethylamine was used to remove the elements of hydrogen chloride. Heptamethyldisilazane was also used to effect the aminolysis of (1; R = Bu^t, X = Y = Cl) [equation (ii)]. Only a ' high-field ' isomer was obtained in this reaction.

$$(1;\ R = Bu^t,\ X = Y = Cl) + 2NMe(SiMe_3)_2 \longrightarrow [(Me_3Si)MeN]P(NBu^t)_2P[NMe(SiMe_3)] + 2SiMe_3Cl \quad (ii)$$

It has also been found that mixtures of isomeric aminocyclodiphosph(III)azanes (1; X = Y = NMe_2) can be obtained by heating the acyclic diphosphinoamines $(Me_2N)_2P–NR–P(NMe_2)_2$ (R = Me or Et) in sealed tubes, or

on standing at ambient temperatures over a period of several months [equation (iii)]. An additional higher-

$$2(Me_2N)_2P{-}NR{-}P(NMe_2)_2 \longrightarrow (1;\ R = Me \text{ or } Et,\ X = Y = NMe_2) + 2P(NMe_2)_3 \quad (iii)$$

boiling product was obtained when R = Me. Its mass spectrum showed the presence of molecular ions corresponding to $[(Me_2N)PNMe]_3$ + 3 H, but satisfactory elemental analyses were not obtained. Surprisingly, an almost identical mass spectrum was obtained from its precursor, $(Me_2N)_2P{-}NMe{-}P(NMe_2)_2$, but when the inlet temperature of the mass spectrometer was reduced from the usual 150 °C to 80 °C a molecular ion corresponding to $(Me_2N)_2P{-}NMe{-}P(NMe_2)_2$ was observed. Similarly, the *N*-ethyl analogue $(Me_2N)_2P{-}NEt{-}P(NMe_2)_2$ gave a (parent + 3 H) ion at 50 °C, but at 80 °C (1; R = Et, X = Y = NMe_2) and $[(Me_2N)PNEt]_3$ were evident amongst a range of ions of higher molecular weight (up to *m/e* 440). Both (1; R = Me and Et, X = Y = NMe_2) were obtained as a 1 : 1 mixture of *cis* and *trans* isomers. Crystallisation of the methyl compound on standing at ambient temperatures appeared to have altered the proportion of these isomers for it was almost entirely converted into the ' low-field ' form after some weeks. A separate sample which did not crystallise, but was kept at the same temperatures, retained the original proportions of *cis* and *trans* isomers.

DISCUSSION

The n.m.r. and mass spectroscopic data (Tables 1 and 4) indicate that all the amino-derivatives obtained by reaction of (1; R = Bu^t, X = Y = Cl) with amines contain a four-membered ring system (1). No evidence was obtained for the formation of phosph(III)azenes $(R^1_2N)P{=}NR^2$, which are best characterised by their low-field ^{31}P chemical shifts [δ(P) *ca.* 300 p.p.m.].[3,8] The phosph(III)azene $[(Me_3Si)MeN]P{=}NBu^t$, was formed [3] by heating the products of the reaction of $Cl_2P{-}NMe{-}$ iMe$_3$ with Li[NBu^t(SiMe$_3$)]. This phosph(III)azene dimerised over a period of 1—2 weeks leaving [1; R = , X = Y = NMe(SiMe$_3$)], with properties almost identical to those reported here. Both *cis* and *trans* isomers of (1) are produced as a result of the mutual arrangements of the phosphorus substituents; it is assumed that the ring nitrogen atoms have a planar or near-planar distribution of bonds. In compounds (1; R = Bu^t) isomerisation occurs and it is invariably the

TABLE 1

Proton, ^{13}C, and ^{31}P n.m.r. data [a]

Compound	δ(P) [b]	δ(PNC*H*)	|^3J(*P*NC*H*)| [c]	δ(PNCC*H*)	|^4J(*P*NCC*H*)|	δ(PNC)	|^2J(*P*NC)|	δ(PNCC)	|^3J(*P*NCC)|	δ(PNC) (*exo*)	|^2J(*P*NC)| [d] (*exo*)
(1; R = Bu^t, X = Y = NMeH)	(*cis*) 98.1	2.61	10.3	1.19	0.4	51.1	13.8	31.1	6.6	25.18	10.5 [e]
	(*trans*) 172.4	*ca.* 2.60	br	1.17	0.9	50.7	6.1	30.5	5.8	22.24	1.6 [e]
(1; R = Bu^t, X = Y = NEtH)	(*cis*) 94.7	2.98	6.4	1.2 (Bu^t),[6] 1.10 (Et)	*ca.* 0.5 0	51.2	13.5[5]	31.0 (Bu^t), 18.5 (Et)	6.7[5] 3.3	34.0	11.8
(1; R = Bu^t, X = NMeH, Y = NMe_2)	(*cis*) 99.2 [f]	2.57	8.0	1.19	*ca.* 0.3						
	(*trans*) 170.7,[g] 184.3										
(1; R = Bu^t, X = Y = NMe_2)	(*cis*) 95.0		*h*			50.6	14.0	30.6	6.5	32.3 [i] 38.6 [i]	∓10.1 [i] ● 50.0 [i]
	(*trans*) 184.7		*h*			49.8	6.1	30.2	5.8	33.6 37.2	∓6.2 ±49.3
(1; R = Bu^t, X = NMe_2, Y = Cl)	(*cis*) 131.5 186.6 (*P*Cl)		*h*			52.3	9.0	30.6	6.3	35.1 38.3	∓10.1 ±49.4
(1; R = Bu^t, X = Y = NEt_2)	(*cis*) 91.3		*h*			51.5	15.0	30.8 (Bu^t), 15.0 (Et).	6.9 0	33.5 [j] 41.0 [j]	∓8.1 [j] ±53.8 [j]
(1; R = Bu^t, X = Y = NC_4H_8)	(*cis*) 76.7	3.26		1.21	*ca.* 0.3	50.6	14.2	30.6 (Bu^t), 26.3	6.5, 3.2	44.9	15.2
	(*trans*) 165.1			1.14	0.9						
(1; R = Bu^t, X = Y = NC_4H_8O)	(*cis*) 94.8	3.17 [k]		1.24	≲0.3						
(1; R = Bu^t, X = Y = NC_5H_{10})	(*cis*) 91.9	3.13 [l]	5.0 ± 1 [m]	1.20	*ca.* 0.3	50.8	14.4	31.0, 27.0	6.5	44.8 22.5 [δ(PNCC)]	18.4
	(*trans*) 182.3			1.15	0.9						
(3) (*cis*)	155.0	2.69 (Me), 3.12 (CH_2)	13.8, 5.6	1.19	0.5	49.9	11.9[5]	30.3	6.1	38.0 (Me), 52.3 (CH_2)	39.2, 8.1
[1; R = Bu^t, X = Y = NMe(SiMe$_3$)]	(*cis*) 89.9 [n]	2.67	4.8	1.24 [o]	*ca.* 0.3	51.7	14.8	30.7 (Bu^t), 0.3	6.6, 11.7	25.5	3.6
$(Me_2N)_2P{-}NMe{-}P(NMe_2)_2$	118.1	2.47,[p] 2.55	9.5 [p] *ca.* 3			26.7	2.6			38.1 [p]	19.7 [p]
$(Me_2N)_2P{-}NEt{-}P(NMe_2)_2$	121.7	2.50, 3.18	9.6 [p]	1.14	<0.5	36.4	5.7	17.1	1.9	38.3 [p]	21.5 [p]
(1; R = Me, X = Y = NMe_2)	114.8	2.73,[p] 2.60	7.4,[p] 10.6			29.8	23.8			35.8	19.8
	200.9	2.78,[p] 2.22	7.7,[p] 10.2			28.0	10.2			35.8	19.8
(1; R = Et, X = Y = NMe_2)	107.9	2.72,[p] 2.96	8.3 [p]	1.07	≲0.3	38.6	21.7	17.1	5.7	35.8	19.5
	191.8	2.73,[p] 2.57	8.0 [p]	0.94	≲0.3	36.5	9.1	16.9	4.5	35.8	19.5
(2)	75.5	[q]									

[a] For $CDCl_3$ solutions, unless otherwise stated. δ in p.p.m., *J* in Hz. [b] Positive shifts are downfield from external 85% H_3PO_4. [c] \|*J*(PNC*H*) + *J*(PNPNC*H*)\| when X = Y. [d] \|*J*(*P*NC) + *J*(*P*NPNC)\| when X = Y. [e] In C_6D_6 solution. [f] All data on C_6H_6 solutions. [g] \|*J*(*PNP*)\| = 10 ± 2 Hz. [h] See ref. 13. [i] At −90 °C in CD_2Cl_2 solution. [j] At −60 °C. [k] δ(PNCC*H*) 3.61 p.p.m. [l] $\Delta G^{\ddagger}_{213} = 10.2 \pm 1$ kcal mol^{-1} ($\Delta\nu = 70$ Hz at 60 MHz). [m] Measured by decoupling the other methylene protons. [n] \|^2J(*P*NSi)\| < 50 Hz. [o] δ(PNSiC*H*) 0.19 p.p.m., \|^4J(*P*NSiC*H*) + ^6J(*P*NPSiC*H*)\| = 2.1 Hz. [p] NMe_2 signals. [q] Not measured.

' high-field ' isomer which is thermodynamically favoured. The mixed amino-derivative (1; R = Bu^t, X = NMeH, Y = NMe_2) was initially spectroscopically identified as the ' low-field ' isomer, but this underwent an exchange process (iv) in addition to the expected isomerisation.

(1; R = Bu^t, X = NMeH, Y = NMe_2) ⟶
(1; R = Bu^t, X = Y = NMe_2) +
(1; R = Bu^t, X = Y = NMeH) (iv)

The components of the resulting mixture were identified by ^{31}P n.m.r. (^{1}H n.m.r. data were too complex to establish this). Surprisingly, the ' high-field ' isomer of (1; R = Bu^t, X = NMeH, Y = NMe_2) gave only one ^{31}P n.m.r. signal. It is not clear whether the exchange process occurs by simple interchange of amino-groups with the ring remaining intact, or by the intervention of monomeric phosph(III)azenes, $(Me_2N)P{=}NBu^t$ or $(HMeN)P{=}NBu^t$.

Generally, the proportion of the ' low-field ' isomer obtained initially decreases as the size of the amino-group substituent increases, although there is no apparent reason why such small proportions of these isomers should be obtained with the heterocyclic amines. If anything, the amino-groups derived from these amines should be less sterically demanding at phosphorus than a dimethylamino-group. An *X*-ray crystallographic study [1] of the ' high-field ' isomer of (1; R = Bu^t, X = Y = NC_5H_{10}) has shown that the piperidino-groups have a mutual *cis* arrangement with respect to the cyclodiphosph(III)azane ring. Moreover, the *cis* structure is thermodynamically favoured in spite of a steric interaction between the piperidino-rings. Assuming that the thermodynamically favoured ' high-field ' isomers all have *cis* structures, it is difficult to appreciate why they should be the exclusive products of aminolysis by relatively bulky amines, for example diethylamine and di-isopropylamine. Analogous results have been reported [4] for (1; R = $SiMe_3$, X = Y = NPr^i_2), where the *cis* isomer is the exclusive product. However, when X = Y = NMe_2 the *cis* : *trans* isomer ratio is initially 10 : 0, but 3 : 7 after heating in 1,2-dichlorobenzene solution.

Dipole-moment measurements on the ' high- ' and ' low-field ' isomers of (1; R = Bu^t, X = Y = NMe_2) (2.2 and 0.5 D respectively) * and on the ' high-field ' isomer of (1; R = Bu^t, X = Y = NC_5H_{10}) (2.8 D) provide good evidence that the *cis* isomers are thermodynamically favoured in solution as well as in the solid state. The chloride (1; R = Bu^t, X = Y = Cl), which has a *cis* structure,[9] has a larger dipole (3.3 D) than the *cis*-amino-derivatives. Comparisons of i.r. data do not provide any easy distinctions between *cis* and *trans* isomers. Perhaps the most diagnostic feature of these spectra is the asymmetric stretch ν_{asym}(P–N–P) associated with the cyclodiphosphazane ring in the range 800—900 cm^{-1} (Table 2). In the two cases where both isomeric forms are available the *cis* isomer has the lower-energy absorption. The reverse was true of (1; R = Bu^t, X = Y = OMe),[2] but generally the *cis* isomer has the more complex absorption in this region.

Initially, it was hoped that the n.m.r. properties of the bicyclic compound (3) [7] would provide information on the structures of isomeric compounds (1; R = Bu^t). The ^{31}P shift of compound (3), δ(P) 155.0 p.p.m., and the coupling, *J*(*PNC*), for the quaternary carbon (see below) are, however, intermediate between the isomeric forms of, for example, (1; R = Bu^t, X = Y = NMe_2). The i.r. spectra are uninformative on this point also.

The synthesis of cyclodiphosph(III)azanes by heating acyclic diphosphinoamines $(Me_2N)_2P{-}NR{-}P(NMe_2)_2$ (R = Me or Et) has not been previously reported although (1; R = Ph, X = Y = NMe_2) has been obtained from the reaction of $NPh(PCl_2)_2$ with $NMe_2(SiMe_3)$.[10] The precursors of these amino-derivatives, $Cl_2P{-}NR{-}PCl_2$ (R = Me or Et), are thermally stable up to 140 °C for *ca.* 1 h, but the loss of $NMe_2(PCl_2)$ from $(Me_2N)ClP{-}NR{-}PCl(NMe_2)$ was noted [11] at ambient temperatures. The compound $(Me_2N)_2P{-}NMe{-}P(NMe_2)_2$ gave mainly (1; R = Me, X = Y = NMe_2) on heating, but also small amounts of another derivative(s) with a higher boiling point than the four-membered ring compound. ^{1}H-{^{31}P} double resonance showed that the higher-boiling fraction was connected with ^{31}P signals at δ(P) 89 and 112 p.p.m. and its mass spectrum contained a molecular ion corresponding to $[(Me_2N)PNMe]_3$. Although the relative ease of rearrangements in the mass spectrometer precludes any definite assignments, the molecular weight determined by osmometry was close to that of a trimer. The only well authenticated cyclotriphosph(III)azanes are of the type $(XPNMe)_3$ (X = Cl or Br), obtained [12] from the reaction of heptamethyldisilazane, $NMe(SiMe_3)_2$, or of $[(Me_2Si)NMe]_3$, with PX_3.

Increasing the steric demand of the R group from Me through Et to Bu^t clearly increases the stability of the four- relative to six- or eight-membered rings. Both (1; R = Me, X = Y = NMe_2) and (1; R = Et, X = Y = NMe_2) were formed as 1 : 1 mixtures of *cis* and *trans* isomers. This illustrates the tendency for ' low-field ' isomers to be obtained when ring substituents of small steric demand are present; a similar effect was

TABLE 2

Infrared data (cm^{-1}) for cyclodiphosph(III)azanes

$XP(NR)PYNR$

	X(=Y)	Structure	ν_{asym}(P–N–P) *
(1; R = Bu^t)	NMe_2	*cis*	870, 872, 862
	NMe_2	*trans*	880
	NMeH	*cis*	882
	NMeH	*trans*	909
	NEtH	*cis*	890—900
	NEt_2	*cis*	860
	NC_4H_8	*cis*	873
	NC_4H_8O	*cis*	867
	NC_5H_{10}	*cis*	865, 852
	$NMe(SiMe_3)$	*cis*	837
(1; R = Me)	NMe_2	*trans*	894
(3)		*cis*	846

* Data obtained on Nujol mulls.

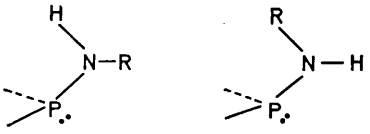
* Throughout this paper: 1 D ≈ 3.34 × 10^{-30} C m; 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

evident in the synthesis of (1; R = aryl, X = Y = NMe_2).[6]

The foregoing structural assignments provide further insight into the origins of the rotational barriers associated with the exocyclic P–N bonds in aminocyclodiphosph(III)azanes.[13] The *cis* isomers have lower barriers than the *trans* isomers, presumably because of the destabilisation of the preferred conformation in the *cis* isomer by a cross-ring steric interaction, such as that in (1; R = Bu^t, X = Y = NC_5H_{10}).[1] The free energy of activation for rotation about the exocyclic P–N bonds in the latter compound is 10.2 ± 1 kcal mol^{-1} at 213 K. If anything, this is slightly lower than the barrier observed [13] (11.4 kcal mol^{-1}) for the analogous *cis*-bis(dimethylamino)-derivative; this behaviour is to be expected when steric effects have an important role in determining the magnitude of the barrier. The importance of steric effects is also emphasised for rotational barriers in (1; R = Me or Et, X = Y = NMe_2). Coalescence phenomena are not observed until well below ambient temperatures, and when R = Et it is the isomer with the 'low-field' ^{31}P shift that first shows broadening effects (*ca.* −40 °C) on cooling. No detailed measurements were made, but it seems probable that it is this isomer which has the higher rotational barrier, and that the barriers are lower than for *trans*-(1; R = Bu^t, X = Y = NMe_2). An unambiguous distinction between the relative broadening effects in (1; R = Me, X = Y = NMe_2) was not possible. It appears that the relative magnitudes of the rotational barriers for a given pair of isomers can provide a good indication of which isomer is which, the *trans* isomer having the higher barrier.[1,13] The same distinction can be made between geometrical isomers of the oxidation products of (1; R = Bu^t, X = Y = NMe_2).[14]

The sign of the coupling constant $^2J(PNP)$ has been related [15] to *cis* and *trans* isomers of cyclodiphosph(III)-azanes. However, this coupling was generally too small ($\lesssim$10 Hz) to obtain unambiguous results by ^1H-{^{31}P} INDOR spectroscopy, but for the acyclic compound $(Me_2N)_2P$–NMe–$P(NMe_2)_2$, $^2J(PNP)$ was large and positive as expected.[14,16,17]

The ^{13}C n.m.r. data, obtained with ^1H noise decoupling (Table 1), includes previously unreported results for *cis*- and *trans*-(1; R = Bu^t, X = Y = NMe_2). The ^{13}C signals from the t-butyl groups consisted of triplets because of coupling to two equivalent ^{31}P nuclei. The coupling constant $^2J(PNC)$ for the quaternary carbon is small, as expected from the conformational relationship between the phosphorus lone pairs and the t-butyl group.[18] Its modulus is larger in the *trans*, relative to the *cis* isomers, as is $J(PNCCH)$, and the same trend was noted for alkoxy-derivatives, (1; R = Bu^t, X and/or Y = alkoxide).[2] The exocyclic PN*C* signals were deceptively simple where X = Y, taking the form of a broadened doublet. The separation of the components of this 'doublet' is a close approximation to $J(PNC)$ if $J(PNPNC)$ is small (<1 Hz), and the spectrum of (1; R = Bu^t, X = Cl, Y = NMe_2) indicates that this is the case. $^2J(PNC)$ should be relatively large (*ca.* 50 Hz) and positive if the carbon atom has a *cis* relationship to the phosphorus lone pair, and small (*ca.* 10 Hz) and negative if *trans*.[18] This is consistent with the low-temperature ^{13}C n.m.r. data for (1; R = Bu^t, X = Y = NMe_2), where the preferred conformation of the *cis* isomer is expected to be close to that of *cis*-(1; R = Bu^t, X = Y = NC_5H_{10}). The crystal structure of the latter compound shows that the best plane containing the *exo*-PNC_2 skeleton is perpendicular to the P_2N_2 ring. $|^2J(PNC)|$ in *cis*-(1; R = Bu^t, X = Y = NMeH) is larger than in the analogous *trans* isomer (10.5 and 1.6 Hz, respectively). If these couplings are positive, then conformation (4) is preferred over (5) for the *cis*, relative



(4) (5)

to the *trans*, isomer presumably because of a cross-ring steric interaction. The small *exo-PNC* coupling observed for [1; R = Bu^t, X = Y = NMe($SiMe_3$)] indicates that conformation (4) (with H and R replaced by Me and $SiMe_3$ respectively) is more important than (5).

EXPERIMENTAL

General experimental methods [2,13] and spectroscopic techniques [13,18] were as previously described.

2-cis-4 (*and* 2-trans-4)-*Bis*(*methylamino*)-1,3-*di-t-butylcyclodiphosph*(III)*azanes*, (1; R = Bu^t, X = Y = NMeH). —Excess of methylamine was bubbled through a stirred solution of 2-*cis*-4-dichloro-1,3-di-t-butylcyclodiphosph(III)-azane (10.5 g, 38.2 mmol) in light petroleum (300 cm^3, b.p. 40—60 °C) at ambient temperature. Methylamine hydrochloride was filtered off and the solvent removed leaving a solid white residue. The solid was divided into two equal parts, and the first heated (*ca.* 80 °C) in benzene solution (50 cm^3) (6 h). The benzene was removed leaving a yellowish oily residue which was distilled under reduced pressure to give 2-cis-4-*bis*(*methylamino*)-1,3-*di-t-butylcyclodiphosph*(III)*azane*, (1; R = Bu^t, X = Y = NMeH) (2.6 g, 26%), b.p. 95 °C (0.1 mmHg), which solidified, m.p. 39—42 °C (Found: C, 45.2; H, 9.9; N, 21.0; P, 23.7%; *m/e* 264. $C_{10}H_{26}N_4P_2$ requires C, 45.45; H, 9.85; N, 21.2; P, 23.5%; *m/e* 264). The second part was recrystallised from light petroleum to give 2-trans-4-*bis*(*methylamino*)-1,3-*di-t-butylcyclodiphosph*(III)*azane*, (1; R = Bu^t, X = Y = NMeH) (2.8 g, 28%), m.p. 90—95 °C (suspected isomerisation) (Found: C, 45.0; H, 9.5; N, 20.7%; *m/e* 264). 2-trans-4-*Bis*(*dimethylamino*)-1,3-*di-t-butylcyclodiphosph*-(III)*azane*, (1; R = Bu^t, X = Y = NMe_2) (30%), m.p. 114—116 °C (Found: C, 49.4; H, 10.3; N, 19.0; *m/e* 292. $C_{12}H_{30}N_4P_2$ requires C, 49.3; H, 10.3; N, 19.2%; *m/e* 292), was prepared similarly, except that crystallisation was from n-pentane; the synthesis of the *cis* isomer has been reported previously.[6] Details of other syntheses of this type are given in Table 3.

Di[*bis*(*dimethylamino*)*phosphino*]*methylamine*, NMe-[$P(NMe_2)_2$], b.p. 94 °C (0.1 mmHg), m.p. 33—35 °C, was obtained in 68% yield by dimethylaminolysis of the

corresponding chloride, $NMe(PCl_2)_2$, in light petroleum solution at −78 °C (Found: C, 40.4; H, 10.25; N, 26.6%; *m/e* 267. $C_9H_{27}N_5P_2$ requires C, 40.4; H, 10.1; N, 26.2%; *m/e* 267) (only the n.m.r. parameters of this compound have been reported previously).[16,19] *Di[bis(dimethylamino)phosphino]ethylamine*, $NEt[P(NMe_2)_2]$, b.p. 102 °C (0.2 mmHg), had a b.p. 90 °C (0.02 mmHg) [Found: *M* (osmometry in benzene) 315; *m/e* 315. $C_9H_{27}N_6P_3$ requires *M* 312; *m/e* 312]. The ^{31}P n.m.r. spectrum of this sample indicated that a mixture of products was present and included strong signals at δ(P) 112 and 89 p.p.m. In view of this, and the absence of satisfactory elemental analyses, we do not consider that any definite conclusions regarding the presence or absence of a cyclotriphosph(III)azane can be drawn.

TABLE 3

Experimental details

Substrate [amount/mmol]	Reactant [amount/mmol]	Reaction conditions: θ_c/°C, solvent (V/cm³)	Subsequent treatment at θ_c °C, stirring (t/h), recrystallisation solvent	Final products (yield/%) [isomer ratio]	M.p. (θ_c/°C)
(1; R = Bu^t, X = Cl, Y = NMe_2) [15.7]	$NMeH_2$ [31.4]	20, OEt_2 (100)	20 (0.5)	(1; R = Bu^t, X = NMeH, Y = NMe_2) (1; R = Bu^t, X = Y = NMeH) (1; R = Bu^t, X = Y = NMe_2) (see text)	
(1; R = Bu^t, X = Y = Cl) [14.5]	$NEtH_2$ [58.0]	−78, OEt_2 (100)	−78 (0.5), light petroleum (b.p. 40—60°)	(1; R = Bu^t, X = Y = NEtH) (50)	91
[10.7]	C_4H_8NH [42.8]	0, OEt_2 (200)	20 (0.5), light petroleum (b.p. 40—60°)	(1; R = Bu^t, X = Y = NC_4H_8) (60) [initially 10 : 1]	107—108
[18.5]	OC_4H_8NH [37.0] NEt_3 [37.0]	0, light petroleum (b.p. 40—60°) (150)	20 (0.5), pentane	(1; R = Bu^t, X = Y = NC_4H_8O) (9) [initially (2) : (1; R = Bu^t, X = Y = NC_4H_8O) *ca.* 1 : 1]	155—157
[21.8]	$C_5H_{10}NH$ [87.1]	0, OEt_2 (400)	20 (0.5), light petroleum (b.p. 40—60°)	(1; R = Bu^t, X = Y = NC_5H_{10}) (50) [initially 20 : 1]	97—98
[17.0]	$NMe(SiMe_3)_2$ [34.0]	20, C_6H_6 (20)	80 (170), pentane	[1; R = Bu^t, X = Y = $NMe(SiMe_3)$] (30)	123—124
(1; R = Bu^t, X = Y = NC_4H_8O) [0.3]		20, C_6H_6 (0.5)	75 (120)	(2) (identified by mass spectroscopy only)	

was similarly obtained in 73% yield (Found: C, 42.5; H, 9.8; N, 24.6%; *m/e* 281. $C_{10}H_{29}N_5P_2$ requires C, 42.7; H, 10.3; N, 24.9%; *m/e* 281).

2,4-Bis(dimethylamino)-1,3-dimethylcyclodiphosph(III)azane, (1; R = Me, X = Y = NMe_2).—Di[bis(dimethylamino)phosphino]methylamine (4.1 g, 15 mmol) in a sealed, evacuated, glass tube was heated at 130 °C for 3 h. The products were separated by distillation under reduced pressure. Tris(dimethylamino)phosphine (2.2 g, 13 mmol), volatile at ambient temperatures, was identified by comparison of its ^1H and ^{31}P n.m.r. spectra with that of an authentic sample. This was followed by *2,4-bis(dimethylamino)-1,3-dimethylcyclodiphosph(III)azane*, (1; R = Me, X = Y = NMe_2) (1.1 g, 34%, *ca.* 1 : 1 mixture of *cis* and *trans* isomers), b.p. 35 °C (0.05 mmHg) (Found: C, 34.5; H, 8.8; N, 26.8%; *m/e* 208. $C_6H_{18}N_4P_2$ requires C, 34.6; H, 8.7; N, 26.9%; *m/e* 208). After *ca.* 7 d at ambient temperature crystals of the *trans* isomer were deposited from the distillate, m.p. 55 °C. The final fraction (0.6 g) had a b.p. 102 °C (0.1 mmHg), was similarly obtained from di[bis(dimethylamino)phosphino]ethylamine although no fractions of higher boiling point were obtained in this case (Found: C, 40.3; H, 9.0; *m/e* 236. $C_8H_{22}N_4P_2$ requires C, 40.7; H, 9.3%; *m/e* 236).

TABLE 4

Analytical data [a]

Compound	Found C	Found H	Found N	Found *m/e*	Calc. C	Calc. H	Calc. N	Calc. *m/e*
(1; R = Bu^t, X = NMeH, Y = NMe_2) [b]	47.5	10.2	20.0	279 (P + H)	47.5	10.1	20.1	278
(1; R = Bu^t, X = Y = NEtH) (*cis*)	49.3	10.3	19.0	292	49.3	10.3	19.2	292
(1; R = Bu^t, X = Y = NC_4H_8) (*cis*)	56.0	9.8_5	16.2	344	55.8	9.9	16.3	344
(1; R = Bu^t, X = Y = NC_4H_8O) (*cis*)	50.9	9.3	14.7	376	51.1	9.0	14.9	376
(1; R = Bu^t, X = Y = NC_5H_{10}) (*cis*)	58.1	10.3	15.2	372	58.1	10.2	15.0_5	372
[1; R = Bu^t, X = Y = $NMe(SiMe_3)$] (*cis*)	46.9	10.3	13.9	408	47.1	10.3	13.7	408
(2)				307				307
(3)	49.3	9.8	19.5	290	49.7	9.7	19.3	290

[a] Elemental analysis in %. [b] Mixture of (1; R = Bu^t, X = NMeH, Y = NMe_2), (1; R = Bu^t, X = Y = NMeH), and (1; R = Bu^t, X = Y = NMe_2) (all *cis* isomers) in *ca.* 6 : 1 : 1 ratio respectively (^{31}P n.m.r.).

Both diphosphinoamines, $NR[P(NMe_2)_2]$ (R = Me or Et), were converted into tris(dimethylamino)phosphine and cyclophosph(III)azanes on standing at ambient temperatures over a period of *ca.* 10 weeks. The synthesis of compound (3) is reported elsewhere.[7]

We thank the S.R.C. for a studentship (to D. G. T.) and for support with n.m.r. equipment.

[9/618 *Received*, 19*th April*, 1979]

REFERENCES

[1] R. Keat, A. N. Keith, A. MacPhee, K. W. Muir, and D. G. Thompson, *J.C.S. Chem. Comm.*, 1978, 372.
[2] R. Keat, D. S. Rycroft, and D. G. Thompson, *J.C.S. Dalton*, 1979, 1224.
[3] O. J. Scherer and W. Glässel, *Chem. Ber.*, 1977, **110**, 3874.
[4] W. Zeiss, Ch. Feldt, J. Weis, and G. Dunkel, *Chem. Ber.*, 1978, **111**, 1180.
[5] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Wiley, New York, 1970, Parts 1 and 2.
[6] G. Bulloch, R. Keat, and D. G. Thompson, *J.C.S. Dalton*, 1977, 99.
[7] R. Keat and D. G. Thompson, *Angew. Chem. Internat. Edn.*, 1977, **16**, 797.
[8] E. Niecke and O. J. Scherer, *Nachr. Chem. Techn.*, 1975, **23**, 395.
[9] K. W. Muir, *J.C.S. Dalton*, 1975, 259.
[10] A. R. Davies, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J.C.S. Perkin I*, 1973, 379.
[11] R. Keat, *J.C.S. Dalton*, 1974, 876.
[12] W. Zeiss, K. Barlos, and H. Henjes, personal communication.
[13] G. Bulloch, R. Keat, and D. G. Thompson, *J.C.S. Dalton*, 1977, 1044.
[14] R. Keat and D. G. Thompson, unpublished work.
[15] R. Keat and D. G. Thompson, *J.C.S. Dalton*, 1978, 634.
[16] I. J. Colquhoun and W. McFarlane, *J.C.S. Dalton*, 1977, 1674.
[17] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1424.
[18] G. Bulloch, R. Keat, and D. S. Rycroft, *J.C.S. Dalton*, 1978, 764.
[19] H. G. Metzinger, *Org. Magn. Reson.*, 1971, **3**, 485.