Formation of Cyclophosph(III)azanes and their Oxo- and Thioxo-derivatives

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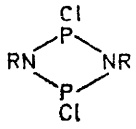
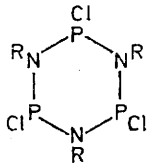
The reactions of phosphorus trichloride with three molar equivalents of methylamine and ethylamine give bis(dichlorophosphino)amines $(Cl_2P)_2NR$ (R = Me and Et), and with isopropylamine and t-butylamine, cyclodiphosph(III)azanes, $(ClPNR)_2$ (R = Pr^i and Bu^t) are obtained as major products. There is mass spectroscopic evidence for the cyclophosph(III)azanes, $(ClPNEt)_n$ (n = 2 or 3) in the products from the reaction with ethylamine, but these compounds have not been obtained pure. Several other potential routes to *N*-methylcyclophosph(III)azanes were examined, including the reaction of phosphorus trichloride or of bis(dichlorophosphino)methylamine, $(Cl_2P)_2NMe$, with heptamethyldisilazane, $(Me_3Si)_2NMe$, which gave the dichlorophosphinamines, $Cl_2P{\cdot}NMe{\cdot}SiMe_3$, $(Cl_2P)_2NMe$, and the cage compound $P_4(NMe)_6$, but no compounds of the type $(ClPNMe)_n$ were obtained. Similarly, dichloroarylphosphines and heptamethyldisilazane gave the phosphinamines, $ClArP{\cdot}NMe{\cdot}SiMe_3$ and $(ClArP)_2NMe$ (Ar = Ph or C_6H_4-*p*-Me). *m*-Chloroaniline hydrochloride reacts with phosphorus trichloride affording $(Cl_2P)_2NC_6H_4$-*m*-Cl, which with SbF_3 produces $(F_2P)_2NC_6H_4$-*m*-Cl. $(Cl_2P)_2NPh$ and the analogous fluoride were obtained similarly. The cyclodiphosph(III)azanes, $(ClPNR)_2$ (R = Pr^i or Bu^t), gave monoxides and monsulphides containing P^{III} and P^V atoms within the ring system, on reaction with dimethyl sulphoxide and elemental sulphur respectively. Oxothioxocyclodiphosphazanes were obtained by a related route. The ^1H and ^{31}P n.m.r. spectra of these compounds are reported and discussed.

FEW examples of tervalent phosphorus–nitrogen ring compounds [cyclophosph(III)azanes], based on structures (1), (2), and (3) have been reported,[1] and



(1)



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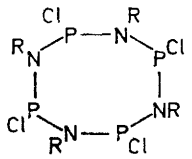


(3)

only one of these, (1; R = Bu^t), has been fully authenticated.[2] In contrast, many examples of the analogous phosphorus(V)–nitrogen compounds are known,[1] most of which contain a four-membered ring system. A very early report by Michaelis [3] of the formation of a cyclodiphosph(III)azane (1; R = Ph) from the reaction between aniline hydrochloride and PCl_3 was not substantiated in later work by Goldschmidt and Krauss [4] who identified the product as *NN*-bis(dichlorophosphino)aniline, $(Cl_2P)_2NPh$. We confirm the latter findings and have also obtained *NN*-bis(dichlorophosphino)-*m*-chloroaniline using this method. Fluorination of these chloro-compounds with antimony trifluoride affords the corresponding fluoro-compounds, $(F_2P)_2NR$ (R = Ph or *m*-ClC_6H_4), whose identity has been unequivocally established by ^{31}P and ^{19}F n.m.r. studies.[5]

The formation of four-membered ring systems related to (1) has been reported when phosphorus trichloride reacts with an excess of various primary amines.[3,6,7]

Abel *et al.*[8] reported that (1; R = Me) as well as (2 and 3; R = Et); could be isolated from the reactions of phosphorus trichloride with disilazanes:

$$n PCl_3 + n RN(SiMe_3)_2 \longrightarrow (ClPNR)_n + 2n\ Me_3SiCl$$
$$[n = 2,\ R = Me;\ n = 3 \text{ or } 4,\ R = Et]$$

It has also been shown from recent work [2] that (1; R = Bu^t) may be obtained by the two routes:

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

or

$$Bu^tNH{\cdot}PCl_2 \xrightarrow[-HCl]{Et_3N} \tfrac{1}{2}(ClPNBu^t)_2$$

The elucidation [9] of the crystal structure of (1; R = Bu^t) and the synthesis [10] of its difluoride leave no doubt as to its identity.

We have attempted to repeat the preparation of (1; R = Me) by the reaction of heptamethyldisilazane with phosphorus trichloride. If the reaction is carried out at *ca.* 0 °C and warmed to room temperature only one of the silicon–nitrogen bonds is cleaved:

$$PCl_3 + (Me_3Si)_2NMe \longrightarrow Cl_2P{\cdot}NMe{\cdot}SiMe_3 + Me_3SiCl$$

Good analytical data were not obtained for this derivative because of its thermal instability, but it was characterised as the difluoride $F_2P{\cdot}NMe{\cdot}SiMe_3$:

$$3Cl_2P{\cdot}NMe{\cdot}SiMe_3 + 2SbF_3 \longrightarrow 3F_2P{\cdot}NMe{\cdot}SiMe_3 + 2SbCl_3$$

which is more conveniently obtained [11] by reaction of heptamethyldisilazane with chlorodifluorophosphine:

$$(Me_3Si)_2NMe + F_2PCl \longrightarrow F_2P{\cdot}NMe{\cdot}SiMe_3 + Me_3SiCl$$

[1] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Part 2, Wiley, London, 1970.
[2] O. J. Scherer and P. Klusmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 752.
[3] A. Michaelis and G. Schroeter, *Chem. Ber.*, 1894, **27**, 490.
[4] S. Goldschmidt and H. L. Krauss, *Annalen*, 1955, **595**, 193.
[5] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.
[6] R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, 1963, **2**, 380.
[7] H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539.
[8] E. W. Abel, D. A. Armitage, and G. R. Willey, *J. Chem. Soc.*, 1965, 57.
[9] K. W. Muir and J. F. Nixon, *Chem. Comm.*, 1971, 1405.
[10] J. F. Nixon and B. Wilkins, *Z. Naturforsch.*, 1970, **25B**, 649.
[11] J. S. Harman, M. E. McCartney, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1971, 1547.

The formation of the dichloride parallels previous observations [12] that hexamethyldisilazane gives an unstable white solid with phosphorus trichloride formulated $Cl_2P{\cdot}NH{\cdot}SiMe_3$. Further reaction with phosphorus trichloride is relatively slow, consistent with the reaction being initiated by nucleophilic attack of the weakly basic nitrogen atom on phosphorus, and provides a new synthetic route to a known [13] series of acyclic bis(dichlorophosphino)amines:

$$Cl_2P{\cdot}NMe{\cdot}SiMe_3 + PCl_3 \longrightarrow (Cl_2P)_2NMe + Me_3SiCl$$

In no case was any evidence obtained [14] for the formation of substantial quantities of (1; R = Me), although a number of unidentified minor products were indicated from the ^{31}P n.m.r. spectra of reaction mixtures. Analogous reactions could be carried out with aryldichlorophosphines, where the intermediates were more thermally stable and could be purified by distillation.

^1H and ^{31}P N.m.r. spectroscopy showed that the di(phosphino)amines were obtained as a mixture of *meso*- and ±-isomers, although they were not identified.

Several possible alternative routes (*a*)—(*f*) to *N*-methylcyclophosphazanes based on structures (1) and (2), were examined, but no evidence for their formation was obtained.

(*a*) The major product from the reaction of phosphorus trichloride with methylamine was bis(dichlorophosphino)methylamine, $(Cl_2P)_2NMe$,[13] obtained in about 15% yield.

(*b*) The pyrolysis of dichlorophosphino(trimethylsilyl)-methylamine, $Cl_2P{\cdot}NMe{\cdot}SiMe_3$, gave a mixture of several products, all of which were in quantities too small for isolation, except bis(dichlorophosphino)methylamine, which was identified by ^1H and ^{31}P n.m.r. Trimethylsilyl chloride was eliminated, but there was no evidence that cyclophosph(III)azanes were produced.

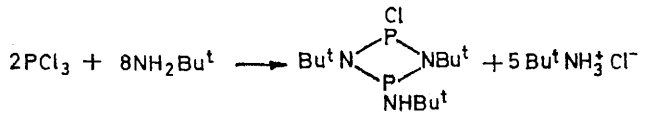
(*c*) The reaction between bis(dichlorophosphino)-methylamine and heptamethyldisilazane occurred readily at ambient temperatures to afford high yields of trimethylchlorosilane and the 'cage' aminophosphine tetraphosphorus heximide, $P_4(NMe)_6$,[15] rather than (1; R = Me).

(*d*) Attempts to effect dehydrofluorination of $MeNHPF_2$ [16] using CsF or Me_3N gave small amounts of PF_3 and $(F_2P)_2NMe$ as the only identifiable products.

(*e*) A mixture of PCl_3 and $P_4(NMe)_6$ equilibrated for two days at room temperature showed evidence (^1H n.m.r.) of the formation of small amounts of $(Cl_2P)_2NMe$. Similarly, heating $P_4(NMe)_6$ with a large excess of PF_3 produced trace amounts of $(PF_2)_2NMe$.

(*f*) Although dimethylaminotrimethylstannane and trifluorophosphine readily react to produce high yields of difluorodimethylaminophosphine, the corresponding reaction using $(Me_3Sn)_2NR$ (R = Me or Et) afforded Me_3SnF even at −130° but no ring compounds could be isolated. It is interesting to note that Schmutzler [17] observed no reaction between PF_3 and $(Me_3Si)_2NMe$.

The reaction of phosphorus trichloride with three molar equivalents of ethylamine follows a course generally similar to that with methylamine, in that bis(dichlorophosphino)ethylamine, $(Cl_2P)_2NEt$, was the major product. However, a second fraction with a higher boiling point was obtained on distillation of the reaction products, whose mass spectrum showed ions corresponding to (1; R = Et) and (2; R = Et), with the latter predominating. Unfortunately, attempts to purify this mixture further (purity examined by ^{31}P n.m.r.) were unsuccessful. The ^1H n.m.r. spectrum of this fraction was too complex to be informative, even after spin-decoupling of the methyl-protons. Analogous reactions with isopropylamine and with t-butylamine differed from those with methylamine and ethylamine in that compounds of structure (1) were obtained, which could readily be purified by distillation under reduced pressure. This route is more convenient than that previously reported [2] for the t-butyl-derivative. Examination of the products from the reaction with t-butylamine by ^{31}P n.m.r. showed that a third compound was present in addition to the t-butylamino-derivative, $Cl_2P{\cdot}NHBu^t$, and (1; R = Bu^t). This compound was exclusively formed when phosphorus trichloride was treated with four molar equivalents of t-butylamine. Elemental analysis and the presence of two doublets of equal separation and intensity in its ^{31}P spectrum confirmed the presence of a t-butylamino-derivative of (1; R = Bu^t), whose formation may be expressed:

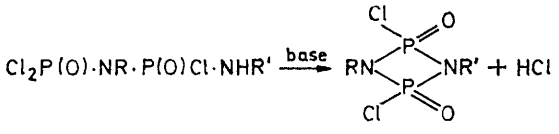


The final aminolysis product is therefore the di-t-butylamino-derivative, $(Bu^tNHPNBu^t)_2$, as shown by Holmes and Forstner.[6]

The fact that the reaction of phosphorus trichloride with methylamine and ethylamine largely produces bis(dichlorophosphino)amines, $(Cl_2P)_2NR$, whereas with isopropylamine and t-butylamine cyclodiphosph(III)azanes (1) are the major products, suggests important differences in the mechanisms of condensation. Since dichloro(t-butylamino)phosphine is known [2] to condense in the presence of triethylamine (and, presumably, t-butylamine), we surmise that the condensation proceeds *via* an acyclic derivative of the type, $Cl_2P{\cdot}NBu^t{\cdot}PCl{\cdot}NHBu^t$, and that this intermediate undergoes extremely ready cyclisation. Evidence for this comes from the observation that yields of (1; R = Bu^t) are generally comparable with those of dichloro(t-butylamino)phosphine, even in reactions with two molar equivalents of

[12] M. Becke-Goehring and H. Krill, *Chem. Ber.*, 1961, **94**, 1059.
[13] J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.
[14] R. Jefferson, J. F. Nixon, and T. M. Painter, *Chem. Comm.*, 1969, 622.
[15] R. R. Holmes and J. A. Forstner, *J. Amer. Chem. Soc.*, 1961, **83**, 1334.
[16] C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2692.
[17] R. Schmutzler, *Chem. Comm.*, 1965, 19.

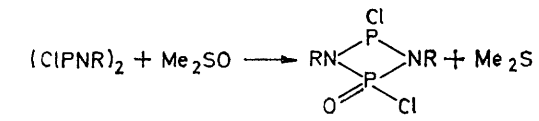
t-butylamine (leaving other unidentified materials precipitated with t-butylamine hydrochloride). It may also be noted that acyclic diphosph(III)azanes of the type $Cl_2P{\cdot}NR{\cdot}PCl{\cdot}NHR$, might be expected to undergo ready base induced cyclisation if their behaviour resembles that of the analogous diphosph(v)azanes, $Cl_2P(O){\cdot}NR{\cdot}P(O)Cl{\cdot}NHR'$:



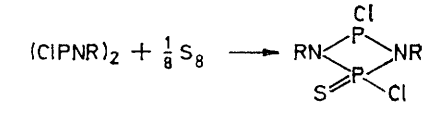
[R = R' = Me or Ph (ref. 18); R = Me, R' = Bu^t (ref. 19)]

The isolation of bis(dichlorophosphino)amines, $(Cl_2P)_2NR$ (R = Me or Et) suggests that self-condensation of the amino-derivatives, $Cl_2P{\cdot}NHMe$ and $Cl_2P{\cdot}NHEt$ is not an important step. Diphosph(III)azanes, $Cl_2P{\cdot}NR{\cdot}PCl{\cdot}NHR$, may be formed in subsequent aminolysis steps to give as yet unidentified products when R = Me, or $(ClPNEt)_n$, and indeed, they may be more reactive than bis(dichlorophosphino)amines to aminolysis. A directive factor in the cyclisation of an intermediate of the type $Cl_2P{\cdot}NR{\cdot}PCl{\cdot}NHR$, may well be the presence of relatively bulky R-substituents because of their ability to reduce the angles of the bonds at the nitrogen atoms and so lower the energy of activation for the formation of a four membered ring system [*cf.* $P\widehat{-N}-P$ = 97·3(4)° in (1; R = Bu^t)[9]]. Such an effect would also be of account when the absence of the cage molecules, $P_4(NR)_6$ (R = Pr^i or Bu^t), is considered.

The isopropyl- and t-butyl-cyclodiphosph(III)azanes of structure (1) underwent partial oxidation by dimethyl sulphoxide [20] and by elemental sulphur to give a new class of cyclodiphosphazane (4) and (5), containing tervalent and quinquivalent phosphorus atoms:

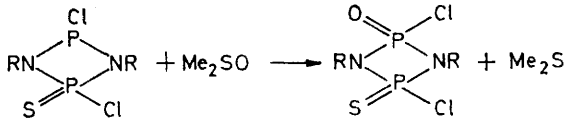


(4)



(5)

Both (4) and (5) were sufficiently thermally stable that purification could be achieved by vacuum distillation, although the higher temperatures required to effect sulphuration may also effect isomerisation (Table). Compounds of type (5) underwent ready reaction with dimethyl sulphoxide to give the oxide-sulphides (6), of which both isopropyl and t-butyl-derivatives were obtained as a mixture of geometrical isomers.



(5) (6)

Compounds (1)—(6) were most conveniently identified by their ^1H and ^{31}P n.m.r. spectra (Table). The tervalent phosphorus compounds displayed characteristic low-field ^{31}P shifts relative to phosphoric acid; those of the cyclodiphosph(III)azanes (1) were to low field of all other phosphorus(III)–nitrogen compounds.[21] The phosphorus(v) shifts were in the ranges expected. The fact that the $P^V{-}N{-}P^V$ coupling constants exceed those involving the $P^V{-}N{-}P^{III}$ grouping (R = Bu^t) may be contrasted with the situation in acyclic analogues where the converse is true.[22] Significantly different coupling constants were obtained for the geometrical isomers of (6; R = Bu^t).

A feature of the coupling constants involving phosphorus and protons is that both three and four bond couplings, $^3J(PNCH)$ and $^4J(PNCCH)$ respectively, are larger when a phosphorus nucleus in a phosphoryl-moiety is involved than one in a thiophosphoryl-moiety. Again the reverse order obtains in most acyclic phosphorus compounds [23] and, indeed, in cyclodiphosph(v)-azanes with smaller alkyl-groups, $[ClP(O)NR]_2$ and $(ClP(S)NR)_2$ (R = Me or Et).[24,25]

It was recently shown [26] that ^1H n.m.r. spectroscopy could be used to assign structures to cyclodiphosph(v)-azanes with *N*-ethyl-substituents. In the same way it may be predicted that the ^1H methyl signals within the isopropyl groups will be nonequivalent in the case of a *trans*-structure for (1; R = Pr^i), which contains a centre of symmetry, but equivalent in the *cis*-isomer which would have a plane of symmetry (assuming a planar ring in both cases). The fact that only one methyl signal is detected in the ^1H n.m.r. spectrum of (1; R = Pr^i) is consistent with, although not conclusive evidence for, its having a *cis*-structure like that of (1; R = Bu^t).[9] Neither geometrical isomer in compounds (4)—(6) contains a plane or a centre of symmetry and this is reflected in the nonequivalence of the methyl signals in (4) and (5). In (6) the presence of two isomers is indicated in the ^1H n.m.r. spectrum, and their presence makes

[18] V. P. Kukhar', *J. Gen. Chem. U.S.S.R.*, 1970, **40**, 761.
[19] R. Keat, unpublished results.
[20] E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 4296.
[21] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, ' Topics in Phosphorus Chemistry,' 1967, **5**, 272—279.
[22] R. Keat, *J. Chem. Soc.* (*A*), 1970, 2732.
[23] J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, 1966, **22**, 565; R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1968, 703.
[24] R. Keat, *J.C.S. Dalton*, 1972, 2189.
[25] M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc.* (*A*), 1966, 1766.
[26] C. D. Flint, E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, and C. D. Thakur, *J. Chem. Soc.* (*A*), 1971, 3513.

the measurement of $^2J(PNP)$ in the ^{31}P n.m.r. spectrum ambiguous. We have yet to distinguish between the geometrical isomers possible for structures (4)—(6).

EXPERIMENTAL

Solvents were dried by conventional means. Phosphorus trichloride and aryldichlorophosphines were redistilled before use. Anhydrous amines, obtained commercially, were used without further purification. Heptamethyldisilazane was prepared as described in the literature.[27] All experiments were carried out under a flush of dry nitrogen. ^1H N.m.r. spectra were obtained at 60 MHz on Varian A 60, T 60, or Perkin-Elmer R 10 spectrometers, and at 100 MHz on a Varian HA 100. ^{19}F and ^{31}P N.m.r. spectra were obtained on the R 10 at 56·4 and 24·3 MHz respectively. Mass spectra were obtained on an A.E.I. MS 12 spectrometer.

Attempted Preparations of Methylcyclophosph(III)azanes.—(a) *From phosphorus trichloride and heptamethyldisilazane.* Phosphorus trichloride (4·6 g, 0·030 mol) was added dropwise to heptamethyldisilazane (5·3 g, 0·030 mol), which was stirred at *ca.* 0 °C. The reaction flask was connected to a vacuum manifold *via* traps at 0 and −78°. After 1 h most of the contents of the reaction flask were transferred to the traps with that at −78° containing trimethylsilyl chloride and that at 0° containing a colourless liquid identified as *dichlorophosphino(trimethylsilyl)methylamine* (5·1 g, 86%), m.p. −15 to −17° [Found: *M*(mass spectrum), 204. $C_4H_{12}Cl_2NPSi$ requires *M*, 204]. Satisfactory elemental analyses were not obtained for this compound because of its tendency to evolve trimethylsilyl chloride at ambient temperatures, but further characterisation was achieved by reaction with antimony trifluoride as previously described for bis(dichlorophosphino)methylamine[13] to give *difluorophosphino(trimethylsilyl)methylamine* (38%), vapour pressure 6 mmHg at 20 °C [Found: C, 28·4; H, 7·1; *M* (mass spectrum), 171. $C_4H_{12}F_2NPS$ irequires C, 28·0; H, 7·0%; *M*, 171]. In a similar reaction, phosphorus trichloride and heptamethyldisilazane were mixed in a 3 : 1 molar ratio and the mixture boiled under reflux (48 h). Removal of trimethylsilyl chloride and phosphorus trichloride left a colourless liquid which was distilled under reduced pressure giving bis(dichlorophosphino)methylamine (84%), b.p. 38—40°, 0·1 mmHg with ^1H n.m.r. and i.r. data identical to that previously recorded.[13] No direct evidence for the formation of cyclophosph(III)azanes was obtained, but the ^{31}P n.m.r. spectra of the products indicated the presence of minor unidentified tervalent phosphorus compounds at −138 and −158 p.p.m.

^1H and ^{31}P N.m.r. data

Compound	^{31}P Shift [a,b]	$^2J(P–N–P)$/ Hz	α-CH [c]	β-CH [b,c]	$^3J(P–N–C–H)$/ Hz	$^4J(P–N–C–C–H)$/ Hz	$^3J(H–C–C–H)$/ Hz
$Cl_2P·NMe·SiMe_3$	−172·8		2·84	0·22 ($SiMe_3$)	6·7	2·9 ($P–N–Si–C–H$)	
$F_2PNMeSiMe_3$	+69 [d]		2·58	0·23 ($SiMe_3$)	6·0	2·0 ($P–N–Si–C–H$) *	
$(Cl_2P)_2NMe$	−160·8		3·38		3·0		
$P_4(NMe)_6$			2·88		16·5		
$ClPhP·NMe·SiMe_3$	−135·9		2·40	0·29 ($SiMe_3$)	6·8	1·8	
$(ClPhP)_2NMe$	−135·8, −137·8		2·36, 2·40		3·3, 3·9		
$Cl(Me\text{-}p\text{-}C_6H_4)P·NMe·SiMe_3$	−134·4		2·22	0·22 ($SiMe_3$)	3·1	2·0	
$[Cl(Me\text{-}p\text{-}C_6H_4)]_2NMe$	−137·7, −139·7						
$(Cl_2P)_2NEt$	−162·5		3·93	1·53	5·8		7·0
$(ClPNEt)_3$	−136 or −129		*ca.* 3·5	1·40			
(1; R = Pr^i)	−222·5		3·58	1·30	6·5	0·9	6·2
(4; R = Pr^i)	−133·6, −11·3	<3	3·72	1·36[1], 1·42[1]	<3 (P^{III}) 15 (PO)	<0·5	6·2
(5; R = Pr^i)	−133·4, −53·4	3·7	3·80	1·40[1], 1·46[1]	<3 (P^{III}) 12·5 (PS)	<0·5, 1·0	
(6; R = Pr^i)	−39·1, +2·7		*ca.* 3·8	1·51[1], 1·53[2]	15 (PO) 10·5 (PS)	1·0, <0·4	6·6
Cl_2PNHBu^t	−164·0			1·35		2·7 (2·2) [e]	
(1; R = Bu^t)	−210·9			1·34		1·0 (1·0) [e]	
$Bu^tN·PCl·NBu^t·P·NHBu^t$	−199·0 (P–Cl), −138·2 (P-NHBu^t)	45		1·36 (NHBu^t) 1·37 (NBu^t)		1·4 (NHBu^t) 0·7, 1·3 (NBu^t)	
(4; R = Bu^t)	−132·4, −6·2	23		1·48[5], 1·50[1]		1·2, 1·0	
(5; R = Bu^t)	−146·9, −61·1	17		1·54		0·7, 0·3	
(6; R = Bu^t)	−36·0, +4·3[5]	46		1·63		0·9	
	−36·5, +3·6[1]	37		1·70		0·6	

[a] In p.p.m. relative to external 85% H_3PO_4 as neat samples or in CH_2Cl_2 solution (solids) at 33 °C. [b] Superscripts indicate relative intensities. [c] ^1H Shifts in p.p.m. downfield relative to internal Me_4Si in CCl_4 solution at 33° (there was no reaction between CCl_4 and P^{III} compounds at this temperature). [d] ^{19}F Shift in p.p.m. from internal CCl_3F, J(PF) 1208 Hz. [e] Value in parentheses from ref. 2. * ^4J (F–P–N–C–H) 1·8 Hz.

[27] L. Birkofer and G. Schmidtberg, *Chem. Ber.*, 1971, **104**, 3831.

(b) *From the pyrolysis of dichlorophosphino(trimethylsilyl)-methylamine.* Dichlorophosphino(trimethylsilyl)methylamine was heated at 130° for 24 h in a sealed tube. The volatile products were removed *in vacuo* and the residue examined by ^{31}P n.m.r. Signals were observed at −161, −158, 156·5, −131, and −101 p.p.m. in *ca.* 20 : 1 : 1 : 3 : 2 : 6 intensity ratio respectively, but only that at −161 p.p.m. has been identified as bis(dichlorophosphino)-methylamine.

(c) *From phosphorus trichloride and methylamine.* Methylamine (9·3 g, 0·30 mol) in ether (50 ml) was added dropwise to a stirred solution of phosphorus trichloride (13·8 g, 0·10 mol) in ether (250 ml) at −78°. When the addition was complete, the mixture was allowed to come to room temperature and the precipitate removed. Ether was removed from the filtrate (rotary evaporator) leaving a colourless oil which rapidly deposited methylamine hydrochloride. This slush-like residue was extracted with ether (50 ml) and the contents of the extract examined by ^{31}P n.m.r. The major product was bis(dichlorophosphino)-methylamine (*ca.* 15%, but >80% of the reaction products examined) with identical ^{1}H and ^{31}P n.m.r. parameters to an authentic sample. The presence of minor unidentified products was indicated in the ^{31}P spectrum at −178·5, −173, −161, −159, and −136 p.p.m.

(d) *From heptamethyldisilazane and bis(dichlorophosphino)methylamine.* Heptamethyldisilazane (16·0 g, 0·115 mol), and bis(dichlorophosphino)methylamine (9·3 g, 0·040 mol) in light petroleum (b.p. 100—120°) were mixed in the cold. Distillation of the volatile products afforded solvent, trimethylchlorosilane (14·5 g, 0·134 mol) 83%, unreacted disilazane (2·0 g), and $P_4(NMe)_6$ (6·5 g, purified by sublimation).

Reaction between Dimethylaminotrimethylstannane and Trifluorophosphine.—Dimethylaminotrimethylstannane (1·57 g, 0·00754 mol) and trifluorophosphine (2·07 g, 0·0235 mol) were sealed off in a Pyrex glass ampoule (*ca.* 90 ml volume) and slowly warmed from −78° to room temperature overnight to afford a white solid. The mixture was then heated at 60° for 1 h and the products separated in the high vacuum line to afford PF_3 (1·47 g, 0·0167 mol) and difluorodimethylaminophosphine (0·83 g, 0·0074 mol) 97·7%, identified by its molecular weight and i.r. spectrum. The solid Me_3SnF residue weighed 1·27 g (92%).

Reaction between Phosphorus Trichloride and m-*Chloroaniline Hydrochloride.*—A mixture of phosphorus trichloride (75 g, 0·55 mol) and *m*-chloroaniline hydrochloride (24 g, 0·15 mol) was refluxed for 40 h, cooled, and filtered to yield after concentration at −78° sticky crystals of slightly impure NN-(*bis(dichlorophosphine)*-m-*chloroaniline*, m.p. 57—60° (decomp.) (28 g, 0·09 mol), 56% [Found: C, 24·7; H, 1·2; N, 4·25. $C_6H_4Cl_5NP_2$ requires C, 21·9; H, 2·05; N, 4·65%].

Fluorination of Bis(dichlorophosphino)-m-*chloroaniline with Antimony Trifluoride.*—Bis(dichlorophosphino)-*m*-chloroaniline (7·0 g) was refluxed with antimony trifluoride (10·0 g) in dry pentane solution for ½ h. The pentane layer was decanted, the solvent removed, and the residue distilled under reduced pressure to give NN-*bis(difluorophosphino)*-m-*chloroaniline* as a colourless liquid (with an obnoxious smell) (3·0 g), 54%, b.p. 50°, 10 mmHg [Found: C, 27·4; H, 1·7; N, 4·7. $C_6H_4ClF_4NP_2$ requires C, 27·3; H, 1·5; N, 5·3%].

In a similar fashion the colourless liquid NN-*bis(difluorophosphino)aniline*, b.p. 41°, 10 mmHg, was obtained from bis(dichlorophosphino)aniline [Found: C, 31·8; H, 2·4. $C_6H_5F_4NP_2$ requires C, 31·5; H, 2·2%].

Reactions of Heptamethyldisilazane with Aryldichlorophosphines.—Dichlorophenylphosphine (4·6 g, 0·026 mol) was added to heptamethyldisilazane (4·5 g, 0·026 mol) at ambient temperatures and the mixture was heated at *ca.* 80° for 1 h. Trimethylsilyl chloride was evolved and the residue distilled under reduced pressure to give N-[*chloro(phenyl)-phosphino*]-N-(*trimethylsilyl*)*methylamine* (4·2 g, 67%), b.p. 78—80°, 0·02 mmHg [Found: C, 48·8; H, 7·0. $C_{10}H_{17}ClNPSi$ requires C, 49·1; H, 7·0%]. Reaction of heptamethyldisilazane with two molar equivalents of dichlorophenylphosphine at 140° for 2 h gave an oily residue which was distilled under reduced pressure to give *NN*-bis-[chloro(phenyl)phosphino]methylamine (63%), b.p. 158°, 0·1 mmHg, as a 1 : 1 mixture of *meso* and ±-diastereoisomers. Satisfactory analytical data was not obtained for these derivatives, although the ^{1}H and ^{31}P n.m.r. data are consistent with this formulation. Similar reactions of heptamethyldisilazane with dichloro-(*p*-tolyl)phosphine gave N-[*chloro*(p-*tolyl*)*phosphino*]-N-(*trimethylsilyl*)*methylamine* (73%), b.p. 88°, 0·001 mmHg [Found: C, 50·9; H, 7·4; Cl, 13·7; N, 5·2. $C_{11}H_{19}ClNPSi$ requires C, 50·9; H, 7·3; Cl, 13·7; N, 5·4%] and NN-*bis*[*chloro*(p-*tolyl*)*phosphino*]-*methylamine* (62%), b.p. 160—165°, 0·1 mmHg [Found: C, 52·2; H, 5·3; N, 3·9. $C_{15}H_{17}Cl_2NP$ requires C, 52·3; H, 4·9; N, 4·1%] as a mixture of diastereoisomers. No evidence for the formation of *P*-phenylcyclophosph(III)-azanes in these reactions was obtained.

Reactions of Phosphorus Trichloride with Three Molar Equivalents of Other Primary Amines.—(a) *With ethylamine.* Ethylamine (38·8 g, 0·860 mol) was added dropwise to a stirred solution of phosphorus trichloride (39·5 g, 0·257 mol) in ether (600 ml) at −78°. The mixture was brought to room temperature, filtered, and the filtrate reduced in volume to *ca.* 100 ml. This concentrate deposited more ethylamine hydrochloride on standing (1 h) which was filtered off and the ether evaporated from the filtrate leaving a colourless oil. The oil was distilled under reduced pressure giving *NN*-[bis(dichlorophosphino)]ethylamine (8·4 g, 28%), b.p. 48—50°, 0·1 mmHg, identified by comparison of its ^{1}H n.m.r. and i.r. spectra with that of an authentic sample.[13] A second fraction (4·1 g), b.p. 120—130°, 0·1 mmHg, was also obtained, but its ^{31}P spectrum showed three signals at −136, −129, and −103 p.p.m. in an approximately 5 : 2 : 1 intensity ratio respectively. The mass spectrum of this mixture showed ions at *m/e* 218 and 327, with characteristic two and three chlorine isotope patterns respectively. These are indicative of the presence of 1,3-*diethyl*-2,4-*dichlorocyclodiphosph*(III)*azane* ($C_4H_{10}{}^{35}Cl_2N_2P_2$ requires *M*, 218) and 1,3,5-*triethyl*-2,4,6-*trichlorocyclotriphosph*(III)*azane* ($C_6H_{15}{}^{35}Cl_3N_3P_3$ requires *M*, 327).

(b) *With isopropylamine and t-butylamine.* Reactions with these amines were carried out in a manner similar to that employed for ethylamine. Distillation of the products from the reaction with isopropylamine gave traces of a liquid, b.p. *ca.* 25°, 0·1 mmHg, possibly dichloro(isopropyl)-aminophosphine, and a major fraction identified as 1,3-*diisopropyl*-2,4-*dichlorocyclodiphosph*(III)*azane* (32%), b.p. 60—62°, 0·1 mmHg [Found: C, 29·2; H, 5·6; *M* (Rast), 253; *M* (mass spectrum), 247. $C_6H_{14}Cl_2N_2P_2$ requires C, 29·1; H, 5·7; *M*, 247]. The ^{31}P n.m.r. spectrum of the reaction products showed that other minor products were present at −170, −158·5, and −156 p.p.m. in *ca.* 1 : 2 : 2 intensity ratio respectively. A similar reaction with t-butylamine

gave traces of dichloro(t-butyl)aminodichlorophosphine b.p. *ca.* 30°, 0·1 mmHg (lit.,[2] b.p. 53—58°, 6 mmHg), and 1,3-di-t-butyl-2-*cis*-4-dichlorocyclodiphosph(III)azane 38%), b.p. 95°, 0·1 mmHg, m.p. 40—42° (lit.,[2] m.p. 42—44°) [Found: *M* (mass spectrum), 274. $C_8H_{18}{}^{35}Cl_2N_2P_2$ requires *M*, 274]. The ^{31}P spectrum of the reaction products indicated that a third compound with signals centred at −199 and −138 p.p.m. was present. This compound was formed exclusively from the reaction of phosphorus trichloride with four molar equivalents of t-butylamine under the conditions described above. Recrystallisation of the solid product from light petroleum (b.p. 40—60°) gave crystals of 1,3-*di-t-butyl*-2-*chloro*-4-*t*-*butylaminocyclodiphosph*(III)*azane* (68%), m.p. 68—70° [Found: C, 45·8; H, 9·2. $C_{12}H_{28}ClN_3P_2$ requires C, 46·3; H, 9·0%].

Oxidation of Cyclodiphosph(III)*azanes.*—(a) *By dimethyl sulphoxide.* Dimethyl sulphoxide (0·95 g, 0·012 mol) in methylene chloride (5 ml) was added dropwise to a stirred solution of 1,3-di-isopropyl-2,4-dichlorocyclodiphosph(III)-azane (3·0 g, 0·012 mol) in methylene chloride (10 ml) at −78°. When the addition was complete, the mixture was allowed to come to ambient temperature and the solvent and dimethyl sulphide were evaporated under reduced pressure. The oily residue was distilled under reduced pressure to give 1,3-*di-isopropyl*-2,4-*dichloro*-2-*oxocyclodiphosphazane* (2·4 g, 75%), b.p. 70—72°, 0·1 mmHg [Found: C, 27·2; H, 5·3; *M* (mass spectrum), 263. $C_6H_{14}Cl_2N_2OP_2$ requires C, 27·4; H, 5·3%; *M*, 263]. A similar reaction of dimethyl sulphoxide with 1,3-di-t-butyl-2,4-dichlorocyclodiphosph(III)azane gave 1,3-*di-t-butyl*-2,4-*dichloro*-2-*oxocyclodiphosphazane* (86%), b.p. 90—95°, 0·1 mmHg [Found: C, 33·2; H, 6·0; Cl, 24·3. $C_8H_{18}Cl_2N_2OP_2$ requires C, 32·9; H, 6·2; Cl, 24·4%].

(b) *By elemental sulphur.* A stirred mixture of flowers of sulphur (0·35 g, 0·011 mol) and 1,3-di-isopropyl-2,4-dichlorocyclodiphosph(III)azane (2·70 g, 0·011 mol) was heated to about 150° when an exothermic reaction took place. The resultant oil was distilled under reduced pressure to give 1,3-*di-isopropyl*-2,4-*dichloro*-2-*thioxocyclodiphosphazane* (2·5 g, 82%), b.p. 65—70°, 0·1 mmHg [Found: C, 26·3; H, 5·2. $C_6H_{14}Cl_2N_2P_2S$ requires C, 25·8; H, 5·0%]. Similarly a 1 : 1 molar ratio of sulphur and 1,3-di-t-butyl-2-*cis*-4-dichlorocyclodiphosph(III)azane was heated to 170—180° and the product distilled under reduced pressure to give 1,3-*di-t-butyl*-2,4-*dichloro*-2-*thioxocyclodiphosphazane* (76%), b.p. 86—90°, 0·05 mmHg [Found: C, 31·6; H, 6·0; Cl, 22·6. $C_8H_{18}Cl_2N_2P_2S$ requires C, 31·3; H, 5·9; Cl, 23·1%].

The thiocyclodiphosphazanes described above underwent ready reactions with dimethyl sulphoxide in methylene chloride solution at −78°. Thus 1,3-di-isopropyl-2,4-dichloro-2-thioxocyclodiphosphazane gave an oil which was purified by distillation under reduced pressure to give a mixture of geometrical isomers of 1,3-*di-isopropyl*-2,4-*dichloro*-2-*oxo*-4-*thioxocyclodiphosphazane* (73%), b.p. 90°, 0·1 mmHg [Found: C, 25·0; H, 5·1. $C_6H_{14}Cl_2N_2OP_2S$ requires C, 24·4; H, 4·7%]. Similarly, 1,3-di-t-butyl-2,4-dichloro-2-thioxocyclodiphosphazane gave a solid which was recrystallised from light petroleum (b.p. 40—60°) to give a mixture of geometrical isomers of 1,3-*di-t-butyl*-2,4-*dichloro*-2-*oxo*-4-*thioxocyclodiphosphazane* (89%), m.p. 85—101° [Found: C, 29·8; H, 5·7; N, 8·2. $C_8H_{18}Cl_2N_2OP_2S$ requires C, 29·7; H, 5·6; N, 8·7%].

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