Studies of Phosphazenes. Part 10.[1] Spirocyclic Derivatives of Cyclotriphosphazatrienes

By **S. S. Krishnamurthy, Kolikkara Ramachandran,** and **A. R. Vasudeva Murthy,** Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India
Robert A. Shaw and **Michael Woods,** Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, and its geminal bis-t-butylamino- and diphenyl derivatives, with ethylenediamine and ethanolamine are reported. In each case, both chlorine atoms attached to the same phosphorus atoms are replaced, giving rise to spirocyclic derivatives. A small quantity of a bis spirocyclic derivative, $N_3P_3(NHCH_2CH_2O)_2Cl_2$, is also obtained; this compound occurs in both *cis* and *trans* forms. Attempts to prepare fully substituted tris spirocyclic derivatives have been unsuccessful and only resinous materials were obtained. The ^1H and ^{31}P n.m.r. spectra of the products are discussed.

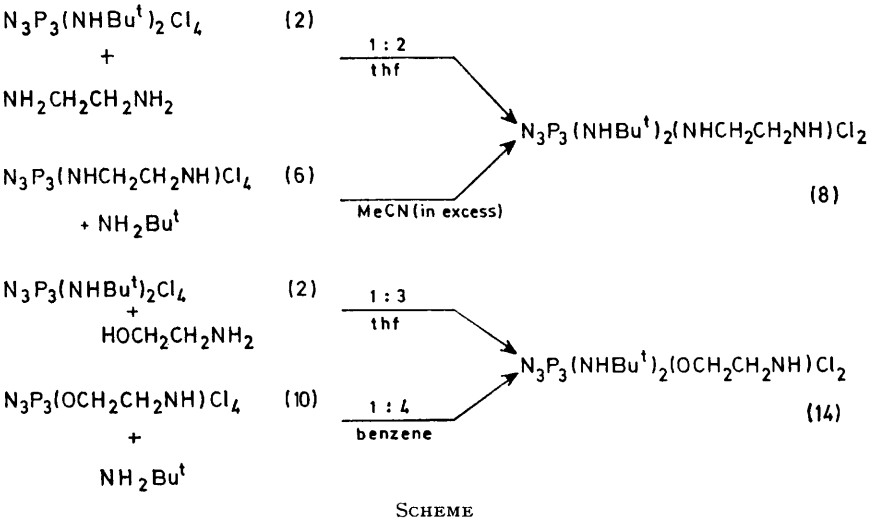
DETAILED studies of the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1), with many monofunctional amines have been reported and several hypotheses have been proposed to rationalise the substitution pattern.[2-7] The reactions of chlorocyclophosphazenes with difunctional reagents are less well documented.[2] These reactions merit detailed study in view of their relevance to the chemistry of phosphazene polymers, which has aroused much interest in recent years.[8] We have carried out a systematic investigation of the reactions of chlorocyclotriphosphazatrienes with the difunctional reagents ethylenediamine and ethanolamine, in order to determine the structure of the products.

RESULTS

The hexachloride, $N_3P_3Cl_6$, (1) reacts with two equivalents of ethylenediamine in diethyl ether at *ca.* 25 °C to give the derivative $N_3P_3(NHCH_2CH_2NH)Cl_4$ (6) in 80% yield. The use of tetrahydrofuran (thf) as the reaction solvent decreases the yield of compound (6) (35%). Compound (1) reacts with three equivalents of ethanolamine in thf to give the derivative $N_3P_3(OCH_2CH_2NH)Cl_4$ (10) (55%). The reaction is much slower in diethyl ether and column chromatography (silica gel) is essential to isolate product (10) (35%); the hexachloride (1) is also recovered (40%). The yield of derivative (10) can be increased if equimolar quantities of the hexachloride (1) and ethanolamine are allowed to react in the presence of two equivalents of triethylamine in thf (see Experimental section).

Two crystalline isomers of $N_3P_3(OCH_2CH_2NH)_2Cl_2$, (11) and (12), have been isolated in very small quantities from the reaction of the hexachloride (1) with ethanolamine in the presence of triethylamine (mol ratio 1 : 2 : 4) in thf. Compounds (11) and (12) can be separated by fractional crystallisation from methylene chloride: compound (11) crystallises first. Alternatively, separation can be accomplished by extraction with benzene: compound (11) dissolves preferentially. The major product of the above reaction is a sticky resin. Only resinous materials are obtained from the reactions of the hexachloride (1) with more than two equivalents of ethylenediamine or more than three equivalents of ethanolamine. Thin-layer chromatography (t.l.c.) indicates no moving component even with ethyl acetate as eluant. Hence, the presence of simple monocyclic spirophosphazenes is very unlikely. These resins are initially soluble in organic solvents but harden and become insoluble on exposure to atmospheric moisture or on storing for 2—3 days. The i.r. spectrum of one of these resins shows a strong broad absorption band at *ca.* 1 200 cm^{-1} suggesting that the six-membered P–N ring is retained. The value of ν(P=N) for analogous linear polyphosphazenes is *ca.* 1 250 cm^{-1}.[9]

Ethylenediamine or ethanolamine reacts readily with the

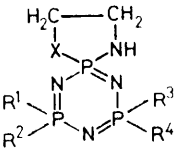


SCHEME

geminal bis-t-butylamino-compound [5] $N_3P_3(NHBu^t)_2Cl_4$ (2) to give the derivatives $N_3P_3(XCH_2CH_2NH)(NHBu^t)_2Cl_2$ (8; X = NH) and (14; X = O). These derivatives can also be prepared by the reaction of t-butylamine with compounds (6) and (10) (see Scheme). However, the geminal tetrakis-t-butylamino-derivative [5] $N_3P_3(NHBu^t)_4Cl_2$ (3) does not react with ethylenediamine or ethanolamine in boiling thf (48 h).

The reaction of compound (6) with four equivalents of t-butylamine in boiling benzene yields a substance of composition $N_3P_3Cl_3(NHBu^t)(NHCH_2CH_2NH)$, m.p. 80—85 °C (decomp.) which appears to be a 1 : 1 adduct of compounds (6) and (8) (^1H and ^{31}P n.m.r. evidence) and not a genuine tris derivative as suggested earlier.[10] Adduct formation between cyclophosphazenes containing primary amino-substituents is well known.[4]

The geminal diphenyl compound,[11] $N_3P_3Ph_2Cl_4$ (4), reacts with ethylenediamine in diethyl ether and with ethanol-



(6) X = NH; R^1, R^2, R^3, R^4 = Cl; m.p. 198 °C
(7) X = NH; R^1, R^2, R^3, R^4 = NMe_2; m.p. 138 °C
(8) X = NH; R^1, R^2 = Cl; R^3, R^4 = $NHBu^t$; m.p. 154 °C
(9) X = NH; R^1, R^2 = Cl; R^3, R^4 = Ph; m.p. 145 °C
(10) X = O; R^1, R^2, R^3, R^4 = Cl; m.p. 150 °C
(11),(12) X = O; R^1, R^2 = Cl; R^3, R^4 = $-OCH_2CH_2NH$, m.p. 200 °C (decomp.), (two isomers)
(13) X = O; R^1, R^2, R^3, R^4 = NMe_2; m.p. 87 °C
(14) X = O; R^1, R^2 = Cl; R^3, R^4 = $NHBu^t$; m.p. 157 °C
(15) X = O; R^1, R^2 = Cl; R^3, R^4 = Ph; m.p. 136 °C

FIGURE 1 Structure of ethylenediamino- and ethanolamino-cyclotriphosphazatriene derivatives

amine in thf to give the derivatives $N_3P_3(XCH_2CH_2NH)Ph_2Cl_2$ (9; X = NH and 15; X = O).

A crystalline product could not be obtained from the reaction of the dimethylamino-compound,[12] 2-*trans*-4-$N_3P_3(NMe_2)_2Cl_4$ (5), with ethylenediamine in boiling thf.

TABLE 1

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

Compd.	$\delta(PCl_2)$/ p.p.m.	$\delta[P_{(spiro)}]$/ p.p.m.	$\delta(PR_2)$/ p.p.m.	$^2J(P-N-P)$/Hz
(6)	22.0 [b]	22.0 [b]		
(7)		35.5	26.7	40.0
(8)	22.2	26.0	6.0	$J(P_{spiro}-PCl_2)$ 49.2; $J(P_{spiro}-PR_2)$ 45.0; $J(PCl_2-PR_2)$ 54.8
(9)	21.4	25.3	18.9	$J(P_{spiro}-PCl_2)$ 31.8; $J(P_{spiro}-PR_2)$ 18.5; $J(PCl_2-PR_2)$ 23.7
(10)	23.3 [b]	23.3 [b]		
(11) [c]	29.0 [d]	29.0 [d]		
(13)		36.5	27.3	46.0
(14)	23.3	27.1	6.7	$J(P_{spiro}-PCl_2)$ 58.6; $J(P_{spiro}-PR_2)$ 51.2; $J(PCl_2-PR_2)$ 55.0
(15)	22.9	25.8	20.8	$J(P_{spiro}-PCl_2)$ 39.3; $J(P_{spiro}-PR_2)$ 21.1; $J(PCl_2-PR_2)$ 21.3

[a] Upfield shifts are negative and the external reference (δ = 0) is 85% H_3PO_4. [b] Single line observed. [c] Data for isomer (12) not available. [d] Approximately AB_2 spectrum.

Substantial quantities of starting material are detected by t.l.c.

DISCUSSION

The spirocyclic structure of the compounds, $N_3P_3(XCH_2CH_2NH)Cl_4$ (6; X = NH and 10; X = O) has been deduced from the ^1H and ^{31}P n.m.r. data for their tetrakis(dimethylamino)-derivatives (7) and (13).[10] This conclusion has been confirmed by a recent crystallographic study of the ethylenediamino-derivative (7).[13] The ^1H and ^{31}P n.m.r. data for the other ethylenediamino- and ethanolamino-compounds, (8) and (9), (11) and (12), and (14) and (15), prepared in this study are in general consistent with spirocyclic structures (Figure 1, Tables 1 and 2).

The spirocyclic compound (10) is undoubtedly the precursor for the bis(ethanolamino)-derivatives (11) and (12). A changeover from a geminal to a non-geminal mode of replacement of chlorine atoms with an increasing degree of aminolysis has not been observed in any reaction of $N_3P_3Cl_6$ with a primary amine.[4-7] It is therefore reasonable to assign a spirocyclic structure (geminal replacement) to the bis(ethanolamino)-deriva-

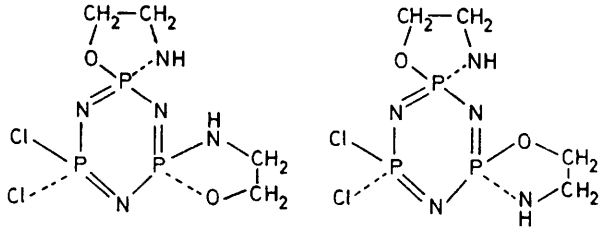
TABLE 2

Hydrogen-1 n.m.r. data for ethylenediamino- and ethanolamino-cyclotriphosphazatrienes [a]

Compound	O–CH_2 δ	O–CH_2 $^3J^*(P-H)$	N–CH_2 δ	N–CH_2 $^3J^*(P-H)$	$-C(CH_3)_3$ δ	N–H δ	N–H $^2J(P-H)$
(6) $N_3P_3(NHCH_2CH_2NH)Cl_4$			3.44 [b]	11.4		2.9_0 [c]	
(7) $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$			3.34	11.6	2.60 [b,d]	2.2_0 [c]	
(8) $N_3P_3(NHCH_2CH_2NH)(NHBu^t)_2Cl_2$			3.36	11.5	1.28	2.38	6.0
						2.4_5 [c,e]	
(9) $N_3P_3(NHCH_2CH_2NH)Ph_2Cl_2$			3.42	12.5		2.61	10.0
(10) $N_3P_3(OCH_2CH_2NH)Cl_4$	4.40 [b]	11.5	3.55 [b]	11.5		3.1_0 [c]	
(11) $N_3P_3(OCH_2CH_2NH)_2Cl_2$	4.40 [b]	11.5	3.55 [b]	11.5		3.1_5 [c]	
(12) $N_3P_3(OCH_2CH_2NH)_2Cl_2$	4.40 [b]	11.5	3.53 [b]	11.5		2.8_0 [c]	
(13) $N_3P_3(NMe_2)_4(OCH_2CH_2NH)$	4.36	11.2	3.50	11.7	2.67 [b,d]	[f]	
(14) $N_3P_3(OCH_2CH_2NH)(NHBu^t)_2Cl_2$	4.24	11.0	3.4_5	[g]	1.28	2.64	6.5
						2.80	6.5
						3.10 [e]	11.5
(15) $N_3P_3(OCH_2CH_2NH)Ph_2Cl_2$	4.36	11.4	3.44	11.8		3.10	13.0

[a] In $CDCl_3$ solution; internal reference $SiMe_4$ (100 MHz). [b] Pronounced virtual coupling. [c] Centre of broad absorption peak. [d] $\delta(NMe_2)$, $^3J^*(P-H)$ = 11.5 Hz. [e] $P-X(CH_2)_2NH$. [f] Obscured by NMe_2 signal. [g] Insufficient resolution for measurement.

tives (11) and (12). Two structures are possible depending on whether the exocyclic nitrogen atoms have a *cis* or a *trans* disposition (see below). Compound (11) is tentatively assigned the *trans* structure because of its higher t.l.c. R_f value. In general, the t.l.c. R_f value of a *trans*-aminochlorocyclotriphosphazene derivative is greater than that of its *cis* analogue.[12,14] The ^{1}H n.m.r. spectra of compounds (11) and (12) closely resemble that



(11) (12)

of the mono(ethanolamino)-derivative (10). The ^{31}P-{^{1}H} n.m.r. spectrum of compound (11) is a multiplet centred at δ 29.0. The spectrum is probably an AB_2 type tending to the A_3 limit [*cf.* the singlet observed for compound (10)].

The ^{31}P-{^{1}H} n.m.r. spectra of the derivatives $N_3P_3(NHCH_2CH_2NH)R_2Cl_2$ (8; R = NHBu^t and 9; R = Ph) and $N_3P_3(OCH_2CH_2NH)R_2Cl_2$ (14; R = NHBu^t and 15; R = Ph) are of the ABX type. A typical spectrum is shown in Figure 2. This observation establishes spirocyclic structures for the ethylenediamino-compounds. The similarity of the phosphorus chemical shifts of compounds (8) and (14) and (9) and (15) indicates that the ethanolamino-derivatives must also have spirocyclic structures (Table 1). For the t-butylamino-compounds (8) and (14), the chemical shift, δ[P(NHBu^t)$_2$], is at high field and well separated from the remaining signals [*cf.* $N_3P_3Cl_{6-n}(NHBu^t)_n$, ref. 15]; δ(PCl_2) is easily assigned from the undecoupled spectra.

Several salient features emerge from an examination of the ^{31}P shifts in Table 1: (*a*) for all the ethylenediamino- and ethanolamino-derivatives, the chemical shift of the phosphorus nucleus δ[$\overline{P\text{–X(CH}_2)_2\text{NH}}$] (spirocyclic) occurs at lowest field; (*b*) δ(spirocyclic P) undergoes a very pronounced downfield shift (*ca.* 13 p.p.m.) when the remaining PCl_2 groups of compounds (6) and (10) are converted to $P(NMe_2)_2$ groups. The values of δ[$\overline{P\text{–X(CH}_2)_2\text{NH}}$] for compounds (7) and (13) appear to be the highest positive values for any aminocyclotriphosphazatriene derivative; and (*c*) δ(PCl_2) and δ[$\overline{P\text{–X(CH}_2)_2\text{NH}}$] are not distinguished for each of the spirocyclic derivatives (6) and (10). This signal moves downfield (*ca.* 6 p.p.m.) in the spectrum of the bis-(ethanolamine) derivative (11). This observation may be contrasted with the much smaller downfield shift of δ(PCl_2) that occurs on increasing the number of amino-substituents in a series of primary aminocyclotriphosphazatriene derivatives.[7,15] Similar trends can be discerned from a close inspection of the ^{31}P n.m.r. data reported for a series of spiro(alkylenedioxy)cyclotriphosphazatrienes.[16]

Compounds (8), (9), (14), and (15) provide rare examples of cyclotriphosphazene derivatives in which three phosphorus nuclei are chemically different and consequently the three P–P coupling constants should, in principle, be different. The values obtained are shown in Table 1. These and other $^2J(P\text{–}P)$ values in Table 1 can be correlated with the electronegativity of the substituents as noted previously,[15,17,18] although other factors must also be considered.[15,19]

The ^{1}H n.m.r. spectra also reveal several interesting features (Table 2). The N–H resonances for compounds (8), (9), (14), and (15) appear as well resolved doublets and the coupling to phosphorus [$^2J(P\text{–}H)$] can be measured. For most primary aminocyclophosphazenes, the N–H resonances invariably appear as unresolved humps and the coupling to the phosphorus nuclei cannot usually be discerned.[6,7,20] Another interesting observ-

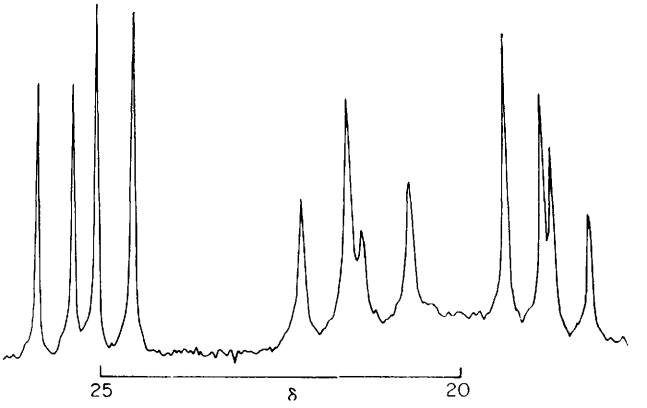


FIGURE 2 ^{31}P-{^{1}H} n.m.r. spectrum (36.4 MHz) of (9) $N_3P_3(NHCH_2CH_2NH)Ph_2Cl_2$

ation is the near constancy of $^3J^*(P\text{–}H)$ for the methylene protons of the spirocyclic group in all the compounds.† The observed values (*ca.* 11.5 Hz) are in conformity with the proposed spirocyclic structures. Intense virtual coupling is observed in the spectra of compounds (6) and (10)—(12) (OCH_2 and/or NCH_2 signals) and (7) and (13) (NMe_2 signals only) as anticipated from the closeness of the ^{31}P chemical shifts.[15,21] In contrast, the absence of virtual coupling in the spectra of compounds (7)—(9) ($N\text{–}CH_2$ signals) and (13)—(15) ($O\text{–}CH_2$ and $N\text{–}CH_2$ signals) can be related to the significant differences in ^{31}P chemical shifts (Table 1).

There are three possible paths for the reaction of hexachlorocyclotriphosphazatriene (1) with difunctional reagents such as ethylenediamine or ethanolamine: (*i*) replacement of two chlorine atoms from the same phosphorus atom to give a spirocyclic derivative, (*ii*) replacement of two chlorine atoms from two different phosphorus atoms to give an *ansa*-type compound, and (*iii*) intermolecular condensation to yield cyclo-linear and/or cyclo-matrix polymers. The results of the present investigation clearly establishes the absence of

† The asterisk to J indicates an apparent spin–spin coupling constant.

the second process and hence the previous assignment [22] of an *ansa*-type structure for the ethylenediamino-derivative (6) is untenable.

We must now consider the factors that influence the competitive reactions (*i*) and (*iii*). Ethylene glycol [23] and many other diols [2,4,24] are able to replace all six chlorine atoms of $N_3P_3Cl_6$ (1) to give tris(spiro)cyclotriphosphazatrienes [reaction (*i*)]. *NN'*-Dimethylethylenediamine reacts readily in diethyl ether to give the bis derivative, $N_3P_3(MeNCH_2CH_2NMe)_2Cl_2$.[25] In contrast, ethylenediamine replaces only the first two chlorine atoms, by reaction (*i*): further treatment of the spirocyclic derivative $N_3P_3(NHCH_2CH_2NH)Cl_4$ (6) with ethylenediamine gives only non-crystalline resins [reaction (*iii*)]. This difference in behaviour suggests that it is the presence of P*NH*R groups that is largely responsible for the formation of resins rather than the group $PXCH_2CH_2YH$ (X = Y = O, NH, or NMe). It seems probable that a proton-abstraction process of the type we have discussed elsewhere [5,20] will occur readily at a P*NH*R centre, thereby promoting reaction (*iii*).

We have previously shown that hexachlorocyclotriphosphazene (1) reacts with t-butylamine to give the chloro(t-butylamino)-derivatives, $N_3P_3Cl_{6-n}(NHBu^t)_n$, in high yield.[5] On the other hand, resin formation is a very prominent feature of the reaction of $N_3P_3Cl_6$ (1) with ethylamine, particularly after replacement of the second chlorine atom.[6] These observations suggest that bulky PNHR substituents (and/or bulky nucleophiles) suppress reaction (*iii*). This conclusion is further borne out by the preparation of $N_3P_3(NHCH_2CH_2NH)(NHBu^t)_2Cl_2$ (8) by two synthetic routes (see Scheme).

The above explanations also pertain to the analogous reactions involving ethanolamine. The observation that small quantities of two bis(spiro) isomers of $N_3P_3(NHCH_2CH_2O)_2Cl_2$ [(11) and (12)] can be isolated (in addition to copious quantities of resins) suggests that if the number of P–*NH*R groups is less, the competitive reaction (*iii*) can be partially suppressed.

TABLE 3

Experimental details

Reactants									
	Cyclophosphazene		Amine					Products and yields	
Compound	(g)	(mmol)	(g)	(mmol)	Solvent [a] (cm^3)	Time of addition of amine (h)	Total reaction time (h)	(g)	(%)
			$(CH_2NH_2)_2$						
(1)	4.40	12.5	1.50	25	thf (120)	0.3	0.5	(6) 1.50	35.4
(1)	3.48	10	2.40	40	Et_2O (170)	0.5	6.5	(6)	trace [b,c]
(6)	3.35	10	0.60	10 [d]	Et_2O (170)	0.5	6.5	(6)	trace [b,c]
(2)	1.10	2.6	0.30	5	thf (120)	0.5	8.5	(8) 0.37	35.6
								(2)	trace [b]
(2)	1.10	2.6	0.60	10	thf (100)	0.5	10.5	(8) 0.41	39.0 [e]
(4)	2.10	5.0	0.60	10	Et_2O (120)	0.5	4.5	(9) 1.35	64.6
			$OH(CH_2)_2NH_2$						
(1)	6.96	20	3.66	60	Et_2O (220)	1.0	9.0	(1) 2.44	35.0
(1)	6.96	20	3.66	60	thf (170)	1.0	13.0	(10) 3.70	55.3
(1)	3.48	10	1.83	30	benzene (120)	1.0	48.0	[c]	
(1)	3.48	10	1.83	30 [d]	thf [f] (170)	1.0	5.0	(11)	trace [b]
								(12)	trace [b,c]
(2)	1.10	2.6	0.30	5	thf [f] (70)	0.5	3.5	(14) 0.55	44.6 [e]
								(2)	trace [b]
(2)	1.10	2.6	1.22	20	thf [f] (70)	0.5	10.5	(14) 0.60	49.0 [e]
(4)	2.10	5.0	0.92	15	thf [f] (100)	0.5	10.5	(15) 1.43	68.0
			$NHMe_2$						
(6)	2.10	7.5	17.5	390	$CHCl_3$ [f] (75)	Rapid	4.0	(7) 1.70	80.0
(10)	1.35	4.0	7.0	160	MeCN [f] (100)	Rapid	4.0	(13) 1.10	74.3
			NH_2Bu^t						
(10)	2.0	6.0	2.16	24	benzene [f] (100)	0.5	4.5	(14) 0.72	44.4

[a] Reaction carried out at *ca.* 25 °C. [b] T.l.c. [c] Major product (>60%): resinous material. [d] Stoicheiometric amount of NEt_3 added. [e] Additional resinous material (*ca.* 20%). [f] Reaction carried out in boiling solvent.

EXPERIMENTAL

Hexachlorocyclotriphosphazatriene (1) was recrystallised from light petroleum (b.p. 60—80 °C) to a constant m.p. 113 °C. The geminal derivatives, $N_3P_3Cl_4(NHBu^t)_2$ (2), $N_3P_3Cl_2(NHBu^t)_4$ (3), $N_3P_3Ph_2Cl_4$ (4), and non-geminal *trans*-$N_3P_3Cl_4(NMe_2)_2$ (5), were prepared by literature methods.[5,11,12] Organic solvents were purified by conventional methods. Ethylenediamine and ethanolamine were distilled under reduced pressure. t-Butylamine was distilled over sodium. Some typical reactions are described below. Other experiments are summarised in Table 3. Analytical data are given in Table 4.

Hydrogen-1 n.m.r. spectra were recorded with Varian HA-100 and JEOL MH 100 spectrometers. The ^{31}P-{^1H} n.m.r. spectra were recorded on a Bruker HFX-90 instrument operating at 36.43 MHz. Infrared spectra were recorded with a Carl Zeiss UR 10 spectrophotometer. Mass spectrometric data were obtained from the P.C.M.U. Service, Harwell.

Reactions of Hexachlorocyclotriphosphazatriene (1).—*With two equivalents of ethylenediamine.* Ethylenediamine (2.40 g, 40 mmol), diluted with diethyl ether (20 cm^3), was added over 0.3 h to a stirred solution of the hexachloride (1) (6.96

TABLE 4

Analytical and i.r. data

Compound	Analysis (%) [a] C	H	N	ν(P=N)/cm⁻¹
(6)	7.0 (7.2)	1.9 (1.8)	21.0 (20.9)	1 215
(7)	32.4 (32.4)	8.2 (8.1)	33.8 (34.1)	1 195
(8)	29.6 (29.4)	6.5 (6.4)	24.3 (24.1)	1 200
(9)	40.1 (40.4)	3.3 (3.4)	16.4 (16.8)	1 230
(10)	7.3 (7.1)	1.5 (1.5)	17.0 (16.7)	1 230
(11) [a]				1 230
(12) [b]				1 225
(13)	31.8 (32.4)	7.9 (7.8)	29.6 (30.2)	1 200
(14)	29.5 (29.3)	6.2 (6.1)	20.2 (20.5)	1 215
(15)	40.8 (40.7)	3.7 (3.8)	13.3 (13.4)	1 205

[a] Calculated values are given in parentheses. [b] Mass spectrum shows parent ion corresponding to the formula $C_4H_{10}Cl_2N_5O_2P_3$; also characterised by ^1H [compounds (11) and (12)] and ^{31}P [compound (11)] n.m.r. spectroscopy.

g, 20 mmol) in diethyl ether (200 cm³) at *ca.* 25 °C. After 0.35 h, the precipitate of ethylenediamine dihydrochloride was filtered off. The filtrate was washed thoroughly with water and dried over fused calcium chloride. The solvent was evaporated to give a residue (6.0 g) which on recrystallisation from dry methylene chloride–light petroleum (b.p. 60—80 °C) (2 : 1) yielded 2,2-spiro(ethylenediamino)-4,4,6,6-tetrachlorocyclotriphosphazatriene (6) (5.40 g, 80.3%), m.p. 198 °C (lit.,[22] 199 °C). The product (6) is highly susceptible to hydrolysis. Furthermore, a solution of this compound in dry methylene chloride or benzene develops turbidity after some time presumably because of cross-linking reactions.

With one equivalent of ethanolamine and two equivalents of triethylamine. Triethylamine (4.04 g, 40 mmol) was added to a solution of the hexachloride (1) (6.96 g, 20 mmol) in thf (150 cm³). Ethanolamine (1.22 g, 20 mmol), diluted with thf (20 cm³), was added slowly over 1 h to the stirred solution at *ca.* 25 °C. Stirring was continued for 6 h. Triethylamine hydrochloride was filtered off and the solvent was evaporated to give an oil. Several crops of crystals were obtained after dissolving the oil in dry benzene. The combined crops were recrystallised from benzene containing a few drops of light petroleum (b.p. 60—80 °C) to give 2,2-spiro(ethanolamino)-4,4,6,6-tetrachlorocyclotriphosphazatriene (10) (4.45 g, 66.7%), m.p. 150 °C (lit.,[26] 150.5 °C).

With two equivalents of ethanolamine and four equivalents of triethylamine in tetrahydrofuran. Ethanolamine (2.44 g, 40 mmol), diluted with thf (50 cm³), was added over 1 h to a stirred solution of the hexachloride (1) (6.96 g, 20 mmol) and triethylamine (8.09 g, 80 mmol) at *ca.* 25 °C. After 4 h, triethylamine hydrochloride was filtered off and the filtrate evaporated to give an oily residue. The residue was dissolved in methylene chloride and the solution cooled to 0 °C. Two crops of crystals, m.p. *ca.* 200 °C (decomp.) were obtained which had different i.r. spectra. The mass spectra of both compounds had intense parent-ion peaks at m/e = 323 $(C_4H_{10}{}^{35}Cl_2N_5OP_3)^+$ and hence were identified as isomers of 2,2,4,4-*bis-spiro(ethanolamino)*-6,6-*dichlorocyclotriphosphazatriene* (11), m.p. 200 °C (decomp.) (0.5 g, 7.1%) and (12), m.p. 200 °C (decomp.) (0.1 g, 1.5%). T.l.c. R_f values (using ethyl acetate as eluant) are 0.40 for (11) and 0.38 for (12).

Reaction of $N_3P_3(NHCH_2CH_2NH)Cl_4$ (6) *with an Excess of t-Butylamine in Methyl Cyanide.*—t-Butylamine (7.30 g, 100 mmol), diluted with methyl cyanide (200 cm³), was added slowly over 1 h to a boiling solution of compound (6) (3.35 g, 10 mmol) in methyl cyanide (100 cm³). The mixture was heated under reflux for 4 h and cooled to 25 °C. t-Butylamine hydrochloride was filtered off and evaporation of the filtrate yielded an oil. Crystallisation of the oil from methylene chloride containing a few drops of light petroleum (b.p. 60—80 °C) at 0 °C gave 2,2-*spiro(ethylenediamino)*-4,4-*bis(t-butylamino)*-6,6-*dichlorocyclotriphosphazatriene* (8), m.p. 154 °C (1.85 g, 45.3%).

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