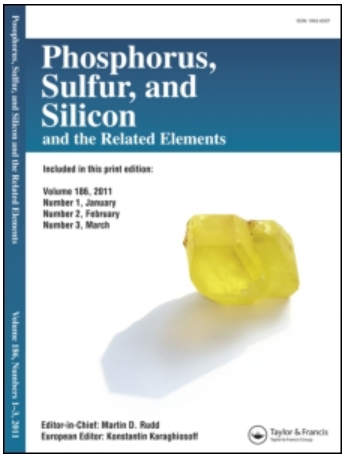

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STUDIES OF PHOSPHAZENES, PART XI. SYNTHESES AND STRUCTURES OF BIS(PRIMARY AMINO)HEXACHLOROCYCLOTETRAPHOSPHAZENES AND THEIR DIMETHYLAMINO DERIVATIVES

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STUDIES OF PHOSPHAZENES, PART XI† SYNTHESES AND STRUCTURES OF BIS(PRIMARY AMINO)HEXACHLOROCYCLOTETRAPHOSPHAZENES AND THEIR DIMETHYLAMINO DERIVATIVES

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The bis(amino)hexachlorocyclotetraphosphazenes, 2-*trans*-6-$N_4P_4(NHR)_2Cl_6$, R = Me, Pr^n, Pr^i, Bu^n, CH_2Ph, Ph, are obtained from the reaction of $N_4P_4Cl_8$ with four mol. equivalents of the appropriate amine. Isomers with 2,4-structures have been isolated for R = Bu^n, CH_2Ph. The ^1H and ^{31}P NMR spectra of these bis(amino) compounds and of their dimethylamino derivatives, 2-*trans*-6-N_4P_4 $(NMe_2)_6$ $(NHR)_2$ are discussed.

Detailed studies of the reactions of the tetrameric chloride, $N_4P_4Cl_8$, with ethylamine[1] and *t*-butylamine[2] have been reported recently.

$$N_4P_4Cl_8 + 2n\text{-}RNH_2 \longrightarrow N_4P_4(NHR)_nCl_{8-n} + n\text{-}RNH_2.HCl$$

(R = NHEt, n = 1, 2, 3, 4, 8; R = $NHBu^t$, n = 1, 2, 3, 8)

All these (amino)chloro derivatives have non-geminal structures. This observation may be contrasted with the exclusive formation of geminal compounds in the reactions of *t*-butylamine with the trimeric chloride, $N_3P_3Cl_6$, and the isolation of gem.-$N_3P_3(NHEt)_4Cl_2$.[3] The difference in behaviour between the trimeric and tetrameric systems is due to the much greater reactivity of $N_4P_4Cl_8$.[4]

An interesting feature of the reactions of the tetrameric chloride, $N_4P_4Cl_8$, with amines concerns the replacement of the second chlorine atom. Reactive amines such as ethylamine[1] and dimethylamine[5] give 2,6-substituted products almost exclusively. Both 2,6- and 2,4-substituted derivatives are obtained from reactions with less reactive amines *t*-butylamine,[2] *N*-methylaniline[6] and dibenzylamine.[7] The relative yield of these bis isomers can vary markedly with the reaction solvent.[2,6]

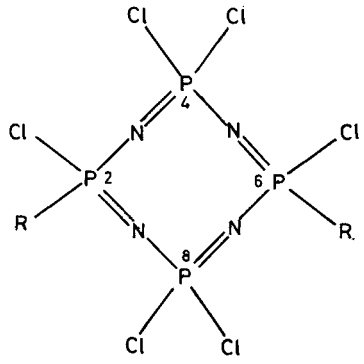
In this paper, we describe the reactions of the tetrameric chloride with four mol. equivalents of various primary amines whose reactivities differ. The structures of the bis(amino)-derivatives, $N_4P_4(NHR)_2Cl_6$, isolated in these reactions have been deduced from their ^1H and ^{31}P NMR spectra and also from NMR data for their dimethylamino derivatives, $N_4P_4(NHR)_2(NMe_2)_6$.

EXPERIMENTAL

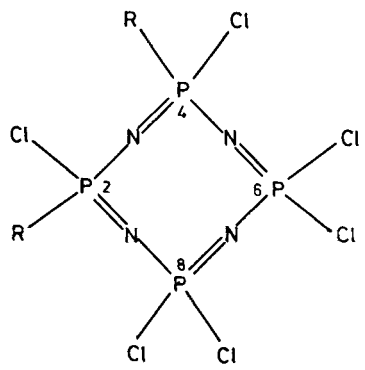
Octachlorocyclotetraphosphazene was purified by recrystallisation from light petroleum to constant m.p. 124°C. Aniline, benzylamine and triethylamine were distilled under reduced pressure; aliphatic primary amines were used as supplied. Dimethylamine was generated from an aqueous solution and dried over potassium hydroxide before condensation at −70°C. Organic solvents were purified by conventional methods; light petroleum refers to the fraction b.p. 40–60°C unless stated otherwise.

Proton NMR spectra were recorded with Joel MH 100 and Varian HR 100/220 spectrometers. Most phosphorus NMR spectra were recorded with a Bruker WH 90 spectrometer operating at 36.43 MHz, but some were obtained with a Jeol C60 HL spectrometer. Infrared spectra were recorded in

† PART X: S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc., Dalton*, 840 (1980).



2,6 - Product
R = NHEt, $NHBu^t$; NMe_2, NMePh



2,4 - Product
R = $NHBu^t$; NMePh

potassium bromide discs using a Carl Zeiss UR 10 spectrophotometer. Mass spectrometric data were obtained with an AEI MS 902 spectrometer (PCMU Service, Harwell, U.K.).

Preparation of $N_4P_4(NHR)_2Cl_6$ Derivatives

General procedure The major product from the reaction of $N_4P_4Cl_8$ (**1**) with four mol. equivalents of a primary amine is 2,6-$N_4P_4(NHR)_2Cl_6$, a product that can easily be crystallised from the reaction mixture. TLC examination of the residues obtained after removing the bulk of the major product invariably shows the presence of two other components with R_f values greater and less than that of the 2,6-bis(amino) derivative. These products can be identified as the mono(amino)-derivative, $N_4P_4(NHR)Cl_7$, and one of the other bis(amino) isomers. In some cases, column chromatographic separation of the mixtures was attempted and 2,4-bis(amino) isomers were obtained. A typical experiment is described below and other details are summarised in Table I.

*Reaction of $N_4P_4Cl_8$(**1**) with four mol. equivalents of Benzylamine*

Benzylamine (8.56 g, 80 mmol), diluted with diethyl ether (25 ml), was added (30 min) to a well-stirred solution of the octachloride (**1**) (9.28 g. 20 mmol) in diethyl ether (200 ml) at 0°C. Stirring was continued for a further 3 hr at 0°C. Benzylamine hydrochloride was filtered off and evaporation of the filtrate

TABLE I

Preparation of Bis(amino)hexachlorocyclotetraphosphazenes, $N_4P_4(NHR)_2Cl_6$

$N_4P_4Cl_8$(**1**)		Amine			Reaction solvent[a]		Time of addition of amine	Total reaction time	Products and yields			
g	mmol		g	mmol	ml		h	h	No.	g	m.p. °C	%
9.28	20	$MeNH_2$	2.42[b]	80	Et_2O	225	0.5	2.5	(**2**)	5.10	144[c]	56
9.28	20	Pr^nNH_2	4.72	80	Et_2O	225	0.75	1.5	(**4**)	3.87	115[d]	38
9.28	20	Pr^iNH_2	4.72	80	Et_2O	225	1.0	2.0	(**5**)	4.10	122[e]	40
9.28	20	Bu^nNH_2	5.84	80	Et_2O	225	0.5	2.0	(**6**)	4.78	114[f]	44
									(**7**)	0.65	liq.	6
9.28	20	$PhNH_2$	7.52	80	CH_3CN[g]	170	0.5	2.5	(**11**)	2.42	166[h]	24

[a] Reaction carried out at 0°C.
[b] Reaction carried out using aqueous amine in the presence of anhydrous sodium sulfate (*cf.* Ref. 1); in other cases, anhydrous amine was used.
[c] Lit.[8] m.p. 143°.
[d] Lit.[9] m.p. 110°.
[e] Lit.[9] m.p. 121°.
[f] Analysis–Found: C, 18.2; H, 3.9; N, 15.8. Calc. for $C_8H_{20}Cl_6N_6P_4$: C, 17.9; H, 3.8; N, 15.7%. Isomer (**7**) was characterized by mass spectrometry [m/e = 537 corresponding to $(C_8H_{20}{}^{35}Cl_6N_6P_4)^+$].
[g] Reaction carried out in boiling solvent.
[h] Lit.[8] m.p. 166°.

yielded an oil. The oil was extracted with boiling light petroleum (b.p. 60–80°) and the solution was filtered. The filtrate was concentrated to *ca.* 10 ml and cooled to 0°. Three crops of crystals were obtained. These crops were combined and recrystallized from light petroleum-benzene (3:1) to give 2,6-*bis(benzylamino) hexachlorocyclophosphazatetraene*, $N_4P_4(NHCH_2Ph)_2Cl_6$(**9**), m.p. 150° (3.64 g, 34%) [Found: C, 27.7; H, 2.9; N, 13.4. Calculated for $C_{14}H_{16}Cl_6N_6P_4$; C, 27.8; H, 3.0; N, 13.3%]. The mother liquor contained four components (TLC) and these were chromatographed over silica gel (120 g). Elution with light petroleum-benzene (3:1) gave unreacted $N_4P_4Cl_8$(**1**) (0.20 g, 2.2%) and *mono(benzylamino) heptachlorocyclophosphazatetraene*, $N_4P_4(NHCH_2Ph(Cl_7$, m.p. 68° (0.20 g, 1.9%) [Found: C, 16.3; H, 1.7; N, 13.6. Calculated for $C_7H_8Cl_7N_5P_4$: C, 15.7; H, 1.5; N, 13.9%] which was recrystallised from light petroleum. Elution with light petroleum-benzene (1:1) gave a further quantity of compound (**9**) (0.55 g) and its 2,4-isomer (**10**), liq (1.0 g, 9.3%) [m/e = 505 corresponding to parent ion $(C_{14}H_{14}{}^{35}Cl_4N_6P_4)^+$].

Reactions of $N_4P_4Cl_8$(**1**) with four mol. equivalents of benzylamine were also carried out in methyl cyanide and chloroform. The relative yields of isomers (**9**) and (**10**) were 3:2 and 2:3 respectively. [Visual estimates from TLC, eluant: light petroleum-benzene (2:1)].

Preparation of $N_4P_4(NMe_2)_6(NHR)_2$ *and* $N_4P_4(NMe_2)_6(NHR)_2$, HCl *Derivatives*

General An excess of dimethylamine was added to a solution of the appropriate bis(amino)hexachloro- compound, $N_4P_4(NHR)_2Cl_6$ in an organic solvent at 0°C. The mixture was then heated under reflux for 3–4 h (condenser cooled at 0°). Complete substitution was only achieved in diethyl ether when *R* = Me; in methyl cyanide, good yields of the hydrochloride adducts, $N_4P_4(NMe_2)_6(NHR)_2HCl$, R = Pr^n (**14A**), Pr^i (**15A**), Bu^n (**16A**) were obtained and there was no evidence for the presence of the respective free bases (**14–16**). (The latter are easily prepared by treating the hydrochloride adducts with triethylamine). Reactions carried out in boiling chloroform are complex as bicyclic phosphazenes[10] are also formed when R = Me, Pr^n, Bu^n and CH_2Ph. The details are summarised in Table II and a typical experiment is described below.

Reaction of 2,6-$N_4P_4(NHPr^n)_2Cl_6$(**4**) *with an Excess of Dimethylamine in Methyl Cyanide*

Dimethylamine (9.2 g, 200 mmol) was added to a solution of compound (**4**) 1.50 g, 3 mmol) in methyl cyanide (75 ml) at 0°C.

TABLE II

Reactions of Bis(amino)hexachlorocyclotetraphosphazenes with an excess of dimethylamine

Compound No.	g	mmol	Me_2NH g	mmol	Reaction solvent ml	Products and yields No.	g	%
(**2**)	2.26	5	11.5	250	Et_2O 200	(**12**)[a]	1.60	70
(**2**)	4.50	10	22.5	500	$CHCl_3$ 200	(**12**)[b]	2.30	46
(**4**)	3.00	6	11.5	250	$CHCl_3$ 150	(**14**)	[c]	36
(**5**)	2.10	4	9.2	200	MeCN 100	(**15A**)[d]	1.5	66
(**5**)	2.10	4	9.2	200	$CHCl_3$ 100	(**15A**)	1.2	52
(**6**)	1.20	2.2	7.0	150	MeCN 60	(**16A**)[e]	0.89	64
(**6**)	2.00	3.7	9.2	200	$CHCl_3$ 150	(**16**)	[f]	65
(**9**)	2.00	3.3	9.2	200	$CHCl_3$ 100	(**17**)	0.05	[g]
(**9**)	2.00	3.3	9.2	200	MeCN 150	(**17**)	[h]	70
(**11**)	0.50	0.87	7.0	200	$CHCl_3$ 50	(**18**)[i]	0.35	66

[a] m.p. 41–43°C. Anal. Found: C, 33.5; H, 8.8; N, 33.2. Calc. for $C_{14}H_{44}N_{12}P_4$: C, 32.6; H, 8.7; N, 32.6.

[b] $N_4P_4(NMe_2)_5(NHMe)(NMe)$[10] (30%) also isolated.

[c] Yield estimated by ^{31}P NMR after reaction mixture heated with Et_3N; $N_4P_4(NMe_2)_5(NHPr^n)(NPr^n)$[10] (54%) also formed.

[d] $N_4P_4(NMe_2)_6(NHPr^i)_2$, HCl(**15A**), m.p. 137°C. [Found: C, 35.2; H, 8.7; N, 27.3. Calc. for $C_{18}H_{53}ClN_{12}P_4$: C, 36.2; H, 8.9; N, 28.2%].

[e] $N_4P_4(NMe_2)_6(NHBu^n)_2$, HCl(**16A**), m.p. 151–152°C. [Found: C, 38.3; H, 9.1; N, 26.9; Cl, 6.1. Calc. for $C_{20}H_{57}ClN_{12}P_4$: C, 38.3; H, 9.1; N, 26.9; Cl, 5.7%]; $N_4P_4(NMe_2)_5(NHBu^n)(NBu^n)$[10] (8%) also formed.

[f] $N_4P_4(NMe_2)_6(NHBu^n)_2$ (**16**), liq. [Found: C, 41.4; H, 9.9; N, 27.9; Calc. for $C_{20}H_{56}N_{12}P_4$: C, 40.6; H, 9.6; N, 28.6%]. Yield estimated as in (c); $N_4P_4(NMe_2)_5(NHBu^n)(NBu^n)$[10] (22%) also formed.

[g] $N_4P_4(NMe_2)_6(NHCH_2Ph)_2$ (**17**), m.p. 108–110°, isolated after column chromatography (silica gel; eluant ethyl acetate.) [m/e = 655 corresponding to $(M-1)^+$; M = $C_{26}H_{51}N_{12}P_4$]. Further characterised by ^1H and ^{31}P NMR. The latter technique indicates the overall yield of compound (**17**) is 40%; $N_4P_4(NMe_2)_5(NHCN_2Ph)(NCH_2Ph)$[10] (40%) is also formed.

[h] Not isolated; visual estimate from TLC; small quantity (~10%) of $N_4P_4(NMe_2)_5(NHCH_2Ph)(NCH_2Ph)$[10] also present.

[i] $N_4P_4(NMe_2)_6(NHPh)_2$ (**18**), m.p. 162–163°. [Found: C, 44.8; H, 7.7. Calc. for $C_{24}H_{48}N_{12}P_4$: C, 45.8; H, 7.6%].

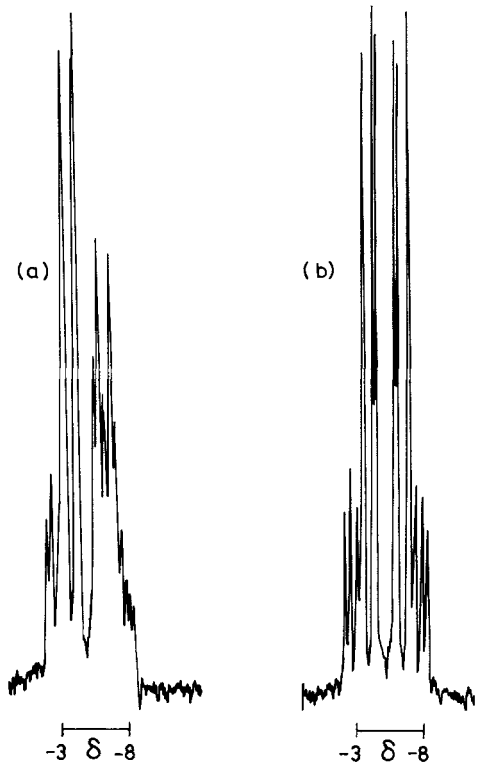
The mixture was heated under reflux for 3 hr and the precipitated dimethylamine hydrochloride removed by filtration. The filtrate was evaporated to give a viscous mass which was digested with light petroleum. This extract was filtered to remove a further quantity of Me_2NH, HCl. The remaining solution was slightly turbid but it became clear after addition of a few drops of methylene chloride. After 48 h at 0°, crystals were deposited which on recrystallisation from light petroleum-methylene chloride (2:1) gave *hexakis (dimethylamino)-2,6-bis(n-propylamino)cyclotetraphosphazatetraene hydrochloride*, $N_4P_4(NMe_2)_6(NHPr^n)_2$, HCl (**14A**), m.p. 148–149° (1.20 g, 68.3%) [Found: C, 35.6; H, 9.6; N, 27.3. Calculated for $C_{18}H_{53}ClN_{12}P_4$: C, 36.2; H, 9.0; N, 28.1%]. Compound (**14A**) was heated with an excess of triethylamine in boiling benzene for 1 h to give the parent base, *hexakis (dimethylamino)-2-trans-6-bis(n-propylamino)cyclotetraphosphazatetraene*, $N_4P_4(NMe_2)_6(NHPr)_2$(**14**), liq. [Found: C, 38.1; H, 9.2; N, 29.6. Calculated for $C_{18}H_{52}N_{12}P_4$: C, 38.6; H, 9.3; N, 30.0%].

RESULTS AND DISCUSSION

The tetrameric chloride (**1**) reacts with four mol. equivalents of primary amine, RNH_2(R = Me, Et[1], Pr^n, Pr^i, Bu^n and CH_2Ph, in diethyl ether to give bis(amino)hexachloro-derivatives, $N_4P_4(NHR)_2Cl_6$ (**2–6**) in 35–55% yield.[11] The bis(anilino)-derivative, $N_4P_4(NHPh)_2Cl_6$ (**11**), was prepared in methyl cyanide but the yield (24%) showed no improvement on that reported by Moeller and coworkers[8] for an analogous reaction in benzene. A second component with a TLC R_f value slightly lower than that of the major product was detected in every reaction. In three cases (R = Bu^n, CH_2Ph, Ph), this compound was present in sufficient quantity for separation by column chromatography. The isomeric *n*-butylamino (**7**) and benzylamino (**10**) compounds were isolated in this way.

Phosphorus and proton NMR data for these bis(amino)-derivatives (**2–11**) are given in Table III. The ^{31}P NMR spectra of the major products of the reactions are of the A_2B_2 type and indicate 2,6-structures. In every spectrum, signals arising from the $\equiv PCl_2$ groups are downfield from those arising from $\equiv PCl(NHR)$ groups. This conclusion is borne out by a comparison of the ^{31}P NMR spectra recorded with and without broad band proton decoupling (see Figure).

A 2,6-nongeminal structure was also assigned to the bis(anilino)-derivative prepared by Moeller and co-workers[8] as its ^{31}P NMR spectrum (16.2 $-NMe_2$ region of the spectra (Table III). The latter trum of this compound recorded at 36.4 MHz shows two sharp triplets with some minor second-order splittings. The considerable upfield shift of



The ^{31}P FT NMR spectrum ($CDCl_3$, 36.43 MHz) of 2-*trans*-6-$N_4P_4(NHPr^i)_2Cl_6$ (**5**); (a) normal spectrum; (b) with broad-band proton decoupling.

$\delta_{PCl(NHPh)}$ for the bis(anilino)-compound (**11**) compared to the analogous chemical shift for the straight-chain alkylamino compounds is presumably due to the shielding of the aromatic group. The nongeminal structure of these bis(amino)-derivatives may also be inferred from the chemical shift of the N-*H* protons[3] (Table III).

The $^{31}P\{^1H\}$ NMR spectrum of the second bis isomer isolated from the reaction of $N_4P_4Cl_8$ (**1**) with *n*-butylamine (or benzylamine) is of the AA'BB' type; a 2,4-structure is indicated for compounds (**7**) and (**10**). Thus, the formation of a 2,4-isomer in significant quantities is observed with sluggishly reacting amines as noted earlier for *t*-butylamine.[2,13]

The phosphorus NMR spectra of the hexadimethylamino derivatives, $N_4P_4(NMe_2)_6(NHR)_2$ (**12–18**) are of the A_2B_2 type, an observation that is consistent with the 2,6-disposition of the primary amino substituents. Their proton NMR spectra contain two doublets[14] in the ratio 2:1 in the $-NMe_2$ region of the spectra (Table III). The latter observation is only consistent with a 2-*trans*-6

TABLE III

Hydrogen-1 and phosphorus-31 NMR data[a] for the cyclophosphazene derivatives, $N_4P_4(NHR)_2Cl_6$(**2** – **11**) and $N_4P_4(NMe_2)_6(NHR)_2$(**12** – **18**)

Compound number	R	^1H δ_{NH}	^1H δ_{NCH_γ}	^1H $\delta_{N(CH_3)_2}$	^{31}P
2	Me	3.1	2.75[b] ($NHCH_3$)		−2.2 (broad singlet)
3	Et[c]	[d]	3.12		δ_{PCl_2} − 3.4, $\delta_{PCl(NHEt)}$ − 4.9, $^2J(P - P)$ 46.0 Hz
4	*n*-Pr	[d]	3.06		−3.4 (broad singlet)
5	*i*-Pr	2.9			δ_{PCl_2} − 4.0, $\delta_{PCl(NHPr^i)}$ − 7.4, $^2J(P - P)$ 38.3 Hz
6	*n*-Bu	[d]	2.98		δ_{PCl_2} − 3.4, $\delta_{PCl(NHBu^n)}$ − 4.6, $^2J(P - P)$ 40.0 Hz
7	*n*-Bu	[d]	3.03		AA′BB′, centre δ − 3.3
8	*t*-Bu[e]	3.1			δ_{PCl_2} − 6.1, $\delta_{PCl(NHBu^t)}$ − 10.6, $^2J(P - P)$ 38.3 Hz
9	CH_2Ph[f]	3.5[g]	4.22		δ_{PCl_2} − 2.9, $\delta_{PCl(NHCH_2Ph)}$ − 5.5, $^2J(P - P)$ 39.2 Hz
10	CH_2Ph	3.4[g]	4.05		AA′BB′ spectrum[e]
11	Ph	5.4			δ_{PCl_2} − 3.0, $\delta_{PCl(NHPh)}$ − 12.0, $^2J(P - P)$ 40.3 Hz

					$\delta_{P(NMe_2)_2}$	$\delta_{P(NMe_2)(NHR)}$	$^2J(P - P)$ Hz
12	Me[h]	2.1	2.48 ($NHCH_3$)	2.60[2][i] 2.64[1]	9.4	10.2	42.5
13	Et[c]	2.1	2.87	2.60[2] 2.63[1]	9.2	6.8	41.2
14	*n*-Pr	2.2	2.83	2.64[2] 2.67[1]	9.4	7.2	41.5
15	*i*-Pr	2.1		2.60[j]	7.7	4.6	41.9
16	*n*-Bu	2.0	2.8_0	2.61[2] 2.63[1]	9.4	7.4	41.2
17	CH_2Ph	*k*	4.09	2.63[2] 2.67[1]	9.6	7.1	40.3
18	Ph	4.91[l]		2.37[1] 2.67[2]	11.6	0.8	40.8

[a] ^1H NMR: $CDCl_3$ solution, TMS as internal standard; $^{31}P\{^1H\}$ NMR: CD_2Cl_2 solution, 85% H_3PO_4 as external reference (δ = 0), upfield shifts are negative.
[b] $^3J^*$ (P—H) = 18.5 Hz; signal with second order effects.
[c] Data from Ref. 1.
[d] Obscured by N-CH_2 signal.
[e] See Ref. 12.
[f] Note reversal of assignment of δ_{PCl_2} and $\delta_{PCl(NHCH_2Ph)}$ from that given in Ref. 12.
[g] $^2J(H - H)$ = 6.5 Hz.
[h] Proton NMR spectrum measured at 220 MHz.
[i] Numbers in parentheses refer to relative intensities.
[j] Broad lines.
[k] Obscured by NMe_2 signals.
[l] $^2J(P - H)$ = 7.0 Hz.

structure for these products. This arrangement of substituent groups is also implied for the chloro-precursors (**2**–**4**, **6**, **9**, **11**) provided there is no net inversion of configuration during the dimethylaminolysis reaction.[3] Corroborative evidence for the 2-*trans*-6 assignment to the derivatives, $N_4P_4(NHR)_2Cl_6$, R = Me, Et, Pr^n, Bu^n, CH_2Ph, is implicit in the observation that these compounds can undergo trans-annular nucleophilic reactions to give bicyclic phosphazenes.[10]

The ^1H and $^{31}P\{^1H\}$ NMR spectra of the hydrochlorides (**14A**–**16A**) show broader signals than those observed for the respective free bases (**14**–**16**); the N*H*R and NMe_2 resonances for the hydrochloride adducts are deshielded by *ca.* 0.5 and *ca.* 0.05 ppm respectively. The data suggest that protonation occurs at a ring nitrogen atom of these hydrochlorides.[3,15] The broadening of the signals is probably due to rapid exchange of the proton among the ring nitrogen atoms at ambient temperature.[2] Further evidence for ring protonation is provided by the upward shift of the ring stretching frequency, ν(P=N)[16], in the infrared spectra of the hydrochloride adducts (**14A**–**16A**) (1290–1300

cm^{-1}) compared to the free bases (**14–16**) (1260–1265 cm^{-1}). The appearance of bands at 920–950 cm^{-1} and 2620–2670 cm^{-1} [P=N$^+$(H)—P] in the infrared spectra of these hydrochlorides is also indicative of ring protonation.[15]

The NMR spectroscopic data for the dimethylamino derivatives, $N_4P_4(NMe_2)_6(NHR)_2$, are not only useful for deducing the structures of their chloro precursors but they also provide an informative comparison with data for the corresponding bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR)(NR)$, particularly when it is difficult to separate the latter from the reaction mixture.[10]

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13. It is interesting to note that in the reactions of $N_4P_4Cl_8$ with benzylamine or *t*-butylamine,[2] methyl cyanide as reaction medium favours the formation of the 2,6-isomer whereas chloroform promotes the formation of the 2,4-isomer.
14. The coupling constants $^3J^*(P - H)$ are 10.0–11.0 Hz and are unexceptional; all dimethylamino signals show some second order effects.
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16. The ring stretching frequency ν(P = N) for the bis(alkylamino)hexachlorocyclotetraphosphazenes appears as a broad band centered at 1310–1290 cm^{-1}.