Studies of Phosphazenes. Part 21.[1] Associative and Dissociative Pathways in the Aminolysis Reactions of Halogenocyclotriphosphazenes

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The rates of stepwise replacement of chlorine from hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) by $-NMe_2$, the last chlorine atom from $N_3P_3(OPh)_5Cl$ by alkylamines, and the first fluorine atom from $N_3P_3F_6$ by $-NMe_2$, in methyl cyanide, have been determined at three temperatures. Detailed analysis of the kinetic data suggests a concerted $S_N2(P)$ mechanism for the first and second Cl substitutions. A sharp changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism occurs at the fourth substitution; the replacement of chlorine from $N_3P_3(OPh)_5Cl$ also occurs by an $S_N1(P)$ pathway. The first F substitution from $N_3P_3F_6$ by $-NMe_2$ proceeds *ca.* 20 times slower than the analogous reaction for $N_3P_3Cl_6$; the kinetic data for these two reactions are in accord with a two-step $S_N2(P)$ pathway. Many diverse findings reported for the aminolysis reactions of halogenocyclophosphazenes are explained in terms of the continuous spectrum of mechanisms established in the present study.

Continuing our quest for a better understanding of the mechanisms of the nucleophilic substitution reactions of halogenocyclophosphazenes,[2-5] we have carried out a detailed kinetic study of the stepwise replacement of chlorine atoms from hexachlorocyclotriphosphazene† by dimethylamino-nucleophile in methyl cyanide medium. The kinetics of the reaction of $N_3P_3(OPh)_5Cl$ with alkylamines and $N_3P_3F_6$ with dimethylamine in methyl cyanide have also been carried out. The mechanistic implications of the results are discussed in this paper. On the basis of the present study, a unified framework is formulated for explaining the 'regioselectivity' observed in the nucleophilic substitution reactions of chlorocyclophosphazenes.

Experimental

Materials.—Previously described methods were employed to prepare and purify $N_3P_3Cl_6$,[4] $N_3P_3F_6$,[6] $N_3P_3(NMe_2)_nCl_{6-n}$ (n = 1—4),[7,8] and $N_3P_3(OPh)_5Cl$.[9] The purity of the derivatives $N_3P_3(NMe_2)_nCl_{6-n}$ (n = 1—4) and $N_3P_3(NMe_2)F_5$ were checked by gas–liquid chromatography (g.l.c.) using a Pye Unicam 204 instrument. Details of the g.l.c. conditions and the retention times of the (dimethylamino)cyclophosphazene derivatives are given in Table 1.

Methods used for the purification of various solvents and alkylamines have been described previously.[4]

Procedure for the Kinetic Studies.—The kinetics of the various reactions studied in the present investigation are listed below. The rates of the reactions (iii)—(vi) were determined using the potentiometric titration method.[4] Reactions (i) and (ii) were very rapid and hence low concentrations ($\sim 10^{-4}$ mol dm^{-3}) of the reactants are required in order to follow the progress of these reactions potentiometrically. Since the potentiometric titration technique is subject to large errors at these low concentrations, the conductivity method was used instead.[4] Potentiometric techniques could not be used to follow the progress of reaction (vii) due to lack of an ion-selective electrode; hence the alternative conductivity method was used conveniently for this reaction also.

$$N_3P_3Cl_6 + 2NHMe_2 \longrightarrow N_3P_3(NMe_2)Cl_5 + NH_2Me_2^+Cl^- \quad (i)$$

$$N_3P_3(NMe_2)Cl_5 + 2NHMe_2 \longrightarrow N_3P_3(NMe_2)_2Cl_4 + NH_2Me_2^+Cl^- \quad (ii)$$
2-*trans*-4

$$N_3P_3(NMe_2)_2Cl_4 + 2NHMe_2 \longrightarrow N_3P_3(NMe_2)_3Cl_3 + NH_2Me_2^+Cl^- \quad (iii)$$
2-*trans*-4 → 2-*trans*-4,6

$$N_3P_3(NMe_2)_3Cl_3 + 2NHMe_2 \longrightarrow N_3P_3(NMe_2)_4Cl_2 + NH_2Me_2^+Cl^- \quad (iv)$$
2-*trans*-4,6 → 2-*cis*-4,6,6

$$N_3P_3(OPh)_5Cl + 2NHMe_2 \longrightarrow N_3P_3(OPh)_5(NMe_2) + NH_2Me_2^+Cl^- \quad (v)$$

$$N_3P_3(OPh)_5Cl + 2NH_2Me \longrightarrow N_3P_3(OPh)_5(NHMe) + NH_3Me^+Cl^- \quad (vi)$$

$$N_3P_3F_6 + 2NHMe_2 \longrightarrow N_3P_3(NMe_2)F_5 + NH_2Me_2^+F^- \quad (vii)$$

Table 1. G.l.c. retention times[a] of $N_3P_3(NMe_2)_nCl_{6-n}$ (n = 1—6) and $N_3P_3(NMe_2)F_5$

Phosphazene derivative	Retention time (min)
$N_3P_3(NMe_2)Cl_5$	4.5
trans-$N_3P_3(NMe_2)_2Cl_4$	6.0
cis-$N_3P_3(NMe_2)_2Cl_4$	6.8
trans-$N_3P_3(NMe_2)_3Cl_3$	7.5
cis-$N_3P_3(NMe_2)_3Cl_3$	12.0
trans-$N_3P_3(NMe_2)_4Cl_2$	8.5
cis-$N_3P_3(NMe_2)_4Cl_2$	10.0
$N_3P_3(NMe_2)_6$	9.2
$N_3P_3(NMe_2)F_5$	2.5[b]

[a] A glass column packed with 5% OV 17 on diatomite CQ (Pye Unicam) with nitrogen as carrier gas (flow rate, 30 cm^3 min^{-1}); flame-ionisation detector; column temperature 200 °C. [b] Column temperature 120 °C.

The products of the reactions (i)—(iv) and (vii) were identified by t.l.c. and g.l.c. (Table 1) and those of reactions (v) and (vi) by ^1H n.m.r. and C, H and N analysis.

† A more systematic name for this compound is 2,2,4,4,6,6-hexachlorocyclotri(λ^5-phosphazene), the prefix λ^5 indicating that each phosphorus atom possesses a bonding of five.

Table 2. Summary of the kinetic results obtained for reactions (i)—(vii) in methyl cyanide

Reaction	Rate constant[a] (θ/°C) k_2/dm^3 mol^{-1} s^{-1}	$10^4 k_1$/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
(i)[b]	51.9 (0)			
	84.4 (10)		20.7 ± 1.2	−128.0 ± 2.3
	105.7 (20)			
(ii)[c]	21.9 (0)			
	27.1 (10)		10.6 ± 1.4	−189.7 ± 3.2
	32.4 (20)			
(iii)[d]	1.08 (0)			
	1.58 (15)		14.0 ± 1.0	−196.4 ± 3.6
	2.21 (20)			
(iv)[e]		1.06 (0)		
		3.32 (30)	21.0 ± 1.1	−217.2 ± 4.1
		4.27 (38)		
(v)[f]		1.11 (30)		
		1.23 (34)	18.8 ± 1.3	−224.0 ± 4.6
		1.38 (38)		
(vi)[g]		1.13 (30)		
		1.35 (35)	24.7 ± 1.2	−214.1 ± 2.3
		1.63 (40)		
(vii)[h]	1.56 (0)			
	3.98 (10)		53.1 ± 1.7	−128.7 ± 3.2
	8.27 (20)			

[a] Error in the individual rate constants ~2%. [b] $[N_3P_3Cl_6]_0$ = (0.20—1.0) × 10^{-4} mol dm^{-3}; $[NHMe_2]_0$ = (0.40—2.0) × 10^{-4} mol dm^{-3}. [c] $[N_3P_3(NMe_2)Cl_5]_0$ = (0.20—1.0) × 10^{-4} mol dm^{-3}; $[NHMe_2]_0$ = (0.40—2.0) × 10^{-4} mol dm^{-3}. [d] [*trans*-$N_3P_3(NMe_2)_2Cl_4]_0$ = (1.5—4.0) × 10^{-3} mol dm^{-3}; $[NHMe_2]_0$ = (3.0—8.0) × 10^{-3} mol dm^{-3}. [e] [*trans*-$N_3P_3(NMe_2)_3Cl_3]_0$ = (0.50—2.0) × 10^{-2} mol dm^{-3}; $[NHMe_2]_0$ = (1.0—4.0) × 10^{-2} mol dm^{-3}. [f] $[N_3P_3(OPh)_5Cl]_0$ = (1.0—2.0) × 10^{-3} mol dm^{-3}; $[NHMe_2]_0$ = (2.0—4.0) × 10^{-3} mol dm^{-3}. [g] $[N_3P_3(OPh)_5Cl]_0$ = (1.0—2.3) × 10^{-3} mol dm^{-3}; $[NH_2Me]_0$ = (2.0—4.6) × 10^{-3} mol dm^{-3}. [h] $[N_3P_3F_6]_0$ = (1.0—2.5) × 10^{-4} mol dm^{-3}; $[NHMe_2]_0$ = (2.0—5.0) × 10^{-4} mol dm^{-3}.

Product of reaction (v), $N_3P_3(OPh)_5(NMe_2)$ (liquid) (Found: C, 59.4; H, 4.4; N, 6.4. Calc. for $C_{32}H_{31}N_4O_5P_3$: C, 59.6; H, 4.6; N, 6.5%); product of reaction (vi); $N_3P_3(OPh)_5(NHMe)$ (liquid) (Found: C, 58.9; H, 4.5; N, 6.6. Calc. for $C_{31}H_{29}N_4O_5P_3$: C, 59.0; H, 4.6; N, 6.6%). ^{1}H N.m.r. (60 MHz, solvent $CDCl_3$, standard $SiMe_4$): $N_3P_3(OPh)_5(NMe_2)$, δ(NMe_2) = 2.4 (d), ^3J(P–H) = 12.0 Hz; $N_3P_3(OPh)_5(NHMe)$, δ(NHMe) = 2.3 (d), ^3J(P–H) = 12.0 Hz.

The rate constants and activation parameters were evaluated on a DCM microsystem 1121 using a least-squares curve-fitting program with appropriate rate expressions.[10-12] The data are summarised in Table 2.

Results and Discussion

The kinetic data for the stepwise first, second, and third substitutions of Cl [reactions (i)—(iii)] from $N_3P_3Cl_6$ by NMe_2 obey a second-order rate law. Reactions (iv)—(vi) follow a first-order rate law; the rates depend only on the concentration of the phosphazene and are independent of the amine concentration. The replacement of the first fluorine atom from $N_3P_3F_6$ by NMe_2 [reaction (vii)] also follows a second-order rate law.

The second-order kinetic data for reactions (i)—(iii) and (vii) are in accord with a bimolecular $S_N2(P)$ type mechanism which usually involves a five-co-ordinate phosphorus intermediate in a rapid pre-equilibrium step, the rate-determining step being the decomposition of this intermediate with the formation of products [Figure (*i*)].

The bimolecular kinetic behaviour observed for reactions (i)—(iii) suggests at first sight that all these reactions occur *via* the formation of a five-co-ordinate phosphorus intermediate. However, a closer examination of the activation parameters (Table 2) for these reactions reveals certain important mechanistic differences. The enthalpy of activation for first Cl substitution [reaction (i)] is higher than those of the second and third substitutions [reactions (ii) and (iii)], but the reactivity of the substrates in these reactions varies in the order $N_3P_3Cl_6$ > $N_3P_3(NMe_2)Cl_5$ > $N_3P_3(NMe_2)_2Cl_4$ (for k_2 values see Table 2). The higher reactivity of $N_3P_3Cl_6$ compared to the other two is a direct consequence of the ease of formation of the five-co-ordinate phosphorus intermediate.[13-18] If reactions (ii) and (iii) were to occur *via* such an intermediate, a higher value of

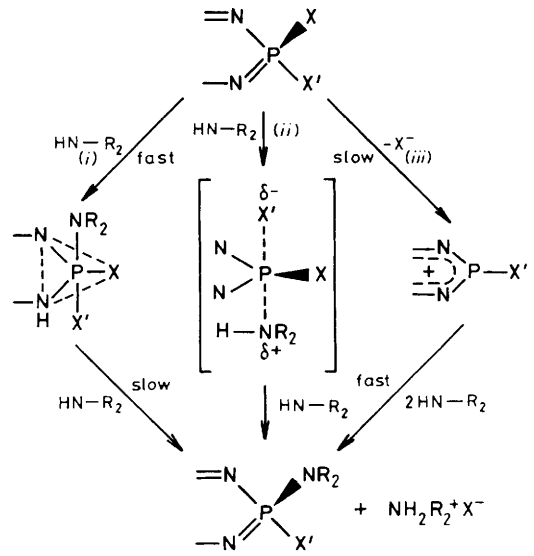


Figure. (*i*) $S_N2(P)$ mechanism *via* a five-co-ordinated phosphorus intermediate, X = X′ = Cl; (*ii*) $S_N2(P)$ concerted mechanism, X = X′ = Cl; and (*iii*) $S_N1(P)$ mechanism, X = Cl, X′ = OPh or NMe_2

$\Delta H^{\ddagger}$ for these reactions would be expected compared to (i). This is because the substrates, $N_3P_3(NMe_2)Cl_5$ and $N_3P_3(NMe_2)_2Cl_4$ [for reactions (ii) and (iii) respectively], would experience considerable steric hindrance [due to the presence of $-NMe_2$ group(s)] in the formation of a five-co-ordinate phosphorus intermediate.[17,18] On the contrary, the observed lower values of $\Delta H^{\ddagger}$ for reactions (ii) and (iii) compared to (i) can be best explained by invoking a one-step concerted $S_N2(P)$ type mechanism for (ii) and (iii). A concerted $S_N2(P)$ pathway is a direct displacement mechanism at phosphorus without the intervention of an intermediate [Figure (*ii*)] and is similar to S_N2 reactions in carbon chemistry.[13,14] A comparison of the activation parameters for reactions (i) and (ii) with those reported by Goldschmidt and Licht[17,19] for the same reactions in tetrahydrofuran (thf) provides further evidence in favour of an $S_N2(P)$ concerted mechanism for (ii) and (iii) in MeCN. In thf the activation enthalpy (21.3 kJ mol^{-1}) for the second Cl substitution [reaction (ii)] is greater than that (7.1 kJ mol^{-1}) of the first [reaction (i)];[17,19] this trend would be expected because the substrate in the former reaction would experience greater steric hindrance for the formation of the five-co-ordinate phosphorus intermediate compared to the substrate in the latter reaction. The enthalpies of activation for reactions (i) and (ii) in methyl cyanide (Table 2) follow a reverse trend compared to those observed for the same reactions in thf. A concerted $S_N2(P)$ mechanism which involves a polar transition state[20,21] would be much more favoured in a polar solvent like methyl cyanide than in a solvent of low polarity like thf. On account of the increased steric hindrance for the formation of the five-co-ordinate phosphorus intermediate, a lower energy pathway [*i.e.* a concerted $S_N2(P)$ mechanism] is preferred in methyl cyanide.

The values of entropy of activation ($\Delta S^{\ddagger}$) for reactions (i)—(iii) are also in agreement with the proposed mechanisms. A relatively small negative value of $\Delta S^{\ddagger}$ for reaction (i) would mean a lesser degree of solvation of the intermediate; a large negative value of $\Delta S^{\ddagger}$ for reactions (ii) and (iii) is indicative of an efficient solvation process occurring in these two reactions.[4,17-19,21-24] The five-co-ordinate phosphorus intermediate is essentially a neutral species (without much charge separation) and hence demands a lesser degree of solvation [as reflected in the low negative value of $\Delta S^{\ddagger}$ for reaction (i)]. On the other hand, a concerted $S_N2(P)$ pathway would involve a polar transition state[20,21] requiring greater solvation and hence large negative values of $\Delta S^{\ddagger}$ [as observed for reactions (ii) and (iii)].

A sharp changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism occurs when the fourth Cl is replaced as shown by the first-order kinetic behaviour for reaction (iv). Such a sharp changeover in mechanism can be explained in terms of the interplay of both steric and electronic effects. With the increased degree of substitution the attainment of the five-co-ordinate phosphorus intermediate by the substrate, $N_3P_3(NMe_2)_3Cl_3$, becomes more difficult; at the same time the mesomeric electron release by the three NMe_2 groups into the phosphazene ring would promote the dissociation of the P–Cl bond [Figure (*iii*)]. The removal of the last chlorine atom from $N_3P_3(OPh)_5Cl$ by NMe_2 or NHMe proceeds by an $S_N1(P)$ mechanism, as revealed by the first-order kinetic behaviour of reactions (v) and (vi). Again, the five phenoxy groups in $N_3P_3(OPh)_5Cl$ not only offer enough steric hindrance to an associative $S_N2(P)$ pathway but also assist in the dissociation of the P–Cl bond by mesomeric electron release into the phosphazene ring. The large negative values of $\Delta S^{\ddagger}$ observed for reactions (iv)—(vi) can be readily attributed to the efficient solvation of the phosphazenium ion, presumably as a result of extensive delocalisation of its positive charge.[14]

A dissociative $S_N1(P)$ mechanism is rarely encountered in general phosphorus chemistry.[16,25] In a few instances where an $S_N1(P)$ mechanism is observed, it is the steric effect which dictates the course of the reaction and the electronic effect plays an insignificant role.[14,16] However, in the present study the occurrence of an $S_N1(P)$ mechanism is brought about by both electronic and steric effects as explained above. A measure of electron release by various substituents towards the phosphazene ring is provided by the substituent constant, α, derived from basicity measurements. The values of α for $-NMe_2$ and $-OPh$ groups are 5.6 and 3.1 respectively.[26-28] If the substituent effects are assumed to be additive,[26] it may be readily seen that the extent of the electron release by the three $-NMe_2$ groups in $N_3P_3(NMe_2)_3Cl_3$ is almost the same as the five phenoxy groups in $N_3P_3(OPh)_5Cl$. From previous work it seems clear that in the reaction of $N_3P_3Cl_6$ with alkoxides, a bimolecular mechanism operates at least until the fourth chlorine replacement.[29] Therefore, the substituent constants can provide guidelines for predicting the stage of chlorine replacement at which a changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism may occur, although such an argument is empirical in nature and does not take into consideration the nature of the attacking nucleophile.

In order to understand the differing reactivities of $N_3P_3Cl_6$ and $N_3P_3F_6$ in their nucleophilic substitution reactions, a kinetic study of the replacement of the first fluorine atom from $N_3P_3F_6$ by NMe_2 [reaction (vii)] in MeCN has been carried out. The second-order kinetic behaviour for this reaction can be interpreted in terms of an $S_N2(P)$ mechanism involving a five-co-ordinate phosphorus intermediate. A comparison of the rate constants for reaction (vii) with those of the analogous reaction of $N_3P_3Cl_6$ [reaction (i)] reveals that $N_3P_3F_6$ reacts *ca.* 20 times slower than $N_3P_3Cl_6$. A similar decrease in the reactivity of $N_3P_3F_6$ is also reflected in the difficulty of obtaining products beyond the second F substitution in its reactions with amino-nucleophiles,[30,31] and in the formation of *gem*-$N_3P_3(NMe_2)_2F_4$ from the reaction of *gem*-$N_3P_3F_4Cl_2$ with dimethylamine.[32] This decreasing reactivity (F < Cl) parallels the expected decreasing availability of phosphorus *d* orbitals during amine attack as the strong electronegativity of fluorine should favour the strongest involvement of the phosphorus *d* orbital density in skeletal $d\pi$–$p\pi$ bonding. Furthermore, the strengthening of the skeletal $d\pi$–$p\pi$ bonding may lead to an enhanced rigidity of the fluorocyclotriphosphazene ring.[33] Therefore, the approach to the five-co-ordinate transition state becomes more difficult for $N_3P_3F_6$ than $N_3P_3Cl_6$. This view is consistent with the observed activation parameters for reactions (i) and (vii); $\Delta H^{\ddagger}$ for reaction (vii) is greater than that for (i), whereas the entropies of activation remain the same. The higher value of $\Delta H^{\ddagger}$ is indicative of the difficulty of attaining a five-co-ordinate phosphorus intermediate for $N_3P_3F_6$[4,34,35] compared to $N_3P_3Cl_6$.

The results of the present kinetic investigation fit into a continuous spectrum of mechanisms for displacement reactions at a four-co-ordinate P^V centre: ranging from reactions proceeding through a five-co-ordinate intermediate [$S_N2(P)$ mechanism] to an extreme case of a unimolecular dissociation of the leaving group [$S_N1(P)$ mechanism], with a concerted $S_N2(P)$ mechanism lying in between these two extremities (Figure). On the basis of this unified framework, it is possible to rationalise the diverse findings reported for the aminolysis reactions of halogenocyclophosphazenes by points (*a*)—(*e*).

(*a*) The g.l.c. analysis of the products of reactions (ii)—(iv) shows that all three reactions are highly stereoselective in affording more than 95% yields of *trans*-$N_3P_3(NMe_2)_2Cl_4$, *trans*-$N_3P_3(NMe_2)_3Cl_3$, and *cis*-$N_3P_3(NMe_2)_4Cl_2$ respectively. Although the '*cis* effect' invoked by Keat and Shaw[36] can explain the observed *trans* preference in reactions (ii) and (iii), the 'substituent solvating effect'[19] or the 'modified substituent solvating effect' proposed by Goldschmidt and Goldstein[37] gives a better explanation for the observed stereoselectivity in

reactions (ii) and (iii). As discussed earlier, the transition state in a concerted $S_N2(P)$ pathway [invoked for reactions (ii) and (iii)] would be highly polar, thus demanding an efficient *solvation*. Consequently the substituent solvating effects would be pronounced in a concerted $S_N2(P)$ mechanism and hence reactions (ii) and (iii) are highly stereoselective in affording > 95% yields of *trans* isomers.

The stereoselectivity of reaction (iv) which gives > 95% yields of *cis*-$N_3P_3(NMe_2)_4Cl_2$ can be readily explained in terms of the preferential cleavage of the P–Cl bond that is *cis* to the maximum number of $-NMe_2$ substituents in the phosphazene ring. The *X*-ray crystal structure of *trans*-$N_3P_3(NMe_2)_3Cl_3$ reveals that this P–Cl bond is slightly longer than the other two P–Cl bonds,[38] and can therefore be easily heterolysed resulting in the formation of the *cis* isomer of $N_3P_3(NMe_2)_4Cl_2$.

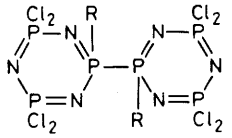
It seems obvious that the predominant formation of *trans* isomers in reactions (ii) and (iii) is kinetically controlled and that the appreciable yields of the *cis* isomer which were observed in boiling methyl cyanide during synthetic studies of the aminolysis reactions of $N_3P_3Cl_6$[2,7,8,35] must be attributed to a secondary isomerisation step.[39,40]

(*b*) The difficulty in isolating $N_3P_3(NMe_2)_5Cl$, and also its hydrolytic instability have been attributed to the possible removal of the last chlorine atom in a rapid $S_N1(P)$ process.[2,33] This postulate is now vindicated in view of the observed changeover to an $S_N1(P)$ mechanism even when the fourth chlorine is replaced.

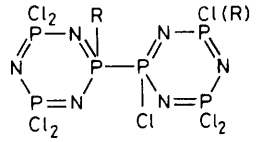
The aminolysis reactions of $N_3P_3Cl_5[N{-}PPh_3]$ have recently been investigated.[41] In diethyl ether, the geminal derivative $N_3P_3Cl_4R[N{=}PPh_3]$ [R = $-NMe_2$, $-NEt_2$, or 1-piperidyl, is formed exclusively, whereas in methyl cyanide both geminal and non-geminal isomers are formed. Furthermore, there is no evidence for the formation of derivatives of the type $N_3P_3Cl_3(R)_2[N{=}PPh_3]$ [R = $-NMe_2$, $-NEt_2$, or 1-piperidyl], containing a $\equiv PCl[N{=}PPh_3]$ group.[41] These results can be rationalised on the basis of the mechanistic changeover observed in the present investigation. Presumably the $S_N1(P)$ mechanism assumes importance even when the first chlorine is replaced from $N_3P_3Cl_5[N{=}PPh_3]$, because the electron releasing power of $-N{=}PPh_3$ is much greater than that of $-NMe_2$ or $-OPh$ [substituent constant (α) of $-N{=}PPh_3$ = 10.0].[28] It is also likely that the steric effect due to the bulky $-N{=}PPh_3$ substituent impedes the operation of an associative $S_N2(P)$ mechanism. The formation of geminal products in the dimethylaminolysis of $N_3P_3Cl_4(N{=}PPh_3)_2$[42] can be explained on similar grounds.

(*c*) The preponderance of non-geminal products formed at the second Cl substitution and the exclusive formation of geminal tetrakis(amino) derivatives in the reactions of $N_3P_3Cl_6$ with ethylamine and isopropylamine[43] could also be a consequence of a mechanistic changeover occurring after the second substitution. In these primary amino-systems, a factor which further assists in the mechanistic changeover is the operation of a base-catalysed proton abstraction step; such a mechanism (termed E_1cB) will essentially have unimolecular characteristics.[44] The proton abstraction mechanism has been invoked to explain the formation of geminal products at the second and subsequent Cl substitutions in the reactions of $N_3P_3Cl_6$ with t-butylamine.[45] With the smaller nucleophiles like ethylamine or isopropylamine, the $S_N2(P)$ mechanism is still operative at the second Cl substitution and only subsequently does the E_1cB mechanism take over leading to the exclusive formation of geminal tetrakis(amino) derivatives. The non-isolation of geminal tris(amino) derivatives in these reactions can also be explained on the above basis.

(*d*) Goldschmidt and co-workers[39] have studied the *cis–trans* isomerisation of three pairs of non-geminal isomers of $N_3P_3(NMe_2)_nCl_{6-n}$ (n = 2—4) and have found that the rates of



(A)



(B)

isomerisation are in the order $N_3P_3(NMe_2)_4Cl_2$ > $N_3P_3(NMe_2)_2Cl_4$ > $N_3P_3(NMe_2)_3$. This trend is explained by these authors by assuming an $S_N1(P)$ mechanism for the isomerisation of $N_3P_3(NMe_2)_4Cl_2$ without any supporting kinetic evidence. The mechanistic changeover observed in the present investigation lends experimental support for this assumption.

(*e*) Recently Allcock *et al.*[46] have reported that in the reaction of $N_3P_3Cl_6$ with methyl- and phenyl-magnesium bromides, a derivative is obtained in which two phosphazene rings are linked *via* the phosphorus atoms bearing the alkyl (aryl) substituent [structure (**A**)]. No evidence is found for the formation of a derivative involving the linking of one $\equiv PCl_2$ and one $\equiv P(R)Cl$ phosphorus centres [structure (**B**)]. This result can be readily explained if an $S_N1(P)$ attack of the phosphazene anion $N_3P_3Cl_4R^-$ (formed as a result of metal–halogen exchange)[46] on $N_3P_3Cl_5R$ is invoked. Heterolysis of the P–Cl bond in $\equiv P(R)Cl$ will be much more favoured compared to that in $\equiv PCl_2$ and hence would lead to the exclusive formation of the derivative with structure (**A**).

Conclusions

$S_N1(P)$ and concerted $S_N2(P)$ mechanisms have been demonstrated for the first time for the aminolysis reactions of cyclophosphazenes. The 'regioselectivity' observed in the nucleophilic displacement reactions of halogenocyclophosphazenes can be readily explained by assuming a changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism; the stage of chlorine replacement at which this changeover occurs may be predicted by considering the combined effects (steric and electronic) of the substituents present on the phosphazene ring and the incoming nucleophile. The substituent constants derived from basicity measurements may provide guidelines for assessing the electronic effects of substituents present on the phosphazene ring.

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