of stabilizing Cr(IV) without decomposition to Cr(III) or Cr(V) may well be one of placing the metal ion in a coordination geometry and environment that are uncommon or constrained with tri- and pentavalent states. Recently, a Cr(IV) porphyrin derivative has been prepared and characterized.[37] Further work in the area of stabilization of uncommon oxidation states by way of manipulation of reorganizational barriers is in progress.[38]

Registry No. $Cr(O_2)_2(en)(H_2O)$, 17192-14-2; $Cr(O_2)_2(dien)$, 59419-71-5; $Cr(en)(H_2O)_4^{3+}$, 16702-61-7; $Cr(dienH)(H_2O)_4^{4+}$, 24249-47-6; $Cr(H_2O)_6^{3+}$, 14873-01-9; $H_2Cr_2O_7$, 13530-68-2.

(37) Groves, J. T.; Kruper, W. J.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.

(38) Nair, B. U.; Ramasami, T.; Ramaswamy, D. *Inorg. Chem.* **1986**, *25*, 51, and references therein; also unpublished work.

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Reactions of Pentachloro- and Pentafluoro(triphenylphosphazenyl)cyclotriphosphazenes with Sodium Methoxide. Mechanistic Aspects and Their Implications for Nucleophilic Displacement at a Tetrahedral Phosphorus(V) Center[1]

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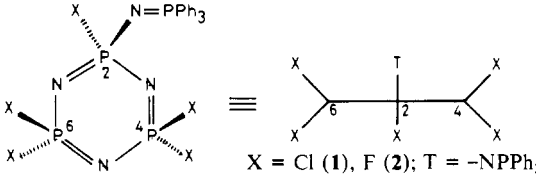
Reactions of $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**), F (**2**)] with sodium methoxide afford the derivatives $N_3P_3(NPPh_3)(OCH_3)_nX_{5-n}$ (n = 1-5; X = Cl, F) (**3**-**20**), whose structures have been elucidated by NMR (^1H, ^{31}P, and ^{19}F) spectroscopy. The successive replacement of chlorine from **1** yields geometrical isomers in unequal proportions whereas the substitution of fluorine from **2** gives geometrical isomers in roughly equal proportions. The chlorine at the $\equiv P(NPPh_3)Cl$ center is easily replaced whereas the fluorine at the $\equiv P(NPPh_3)F$ site is not replaced until the last stage. These differences are rationalized in terms of a changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism for the methoxylation of **1** at later stages of substitution and an $S_N2(P)$ mechanism persisting throughout for the fluoro system. Attack of the methoxide in the plane of the phosphazene ring is postulated to explain the stereochemical course found for the reaction of **2**.

Numerous investigations on the nucleophilic displacement reactions of halogenocyclophosphazenes have been primarily concerned with an understanding of the behavior of the attacking nucleophile.[2-4] Despite these extensive studies, a comprehensive model to explain all the findings has not yet emerged. The effects of (a) the substituent already present on the ring, (b) the leaving group, and (c) the solvent have not been assessed in any detail to rationalize the "regio- and stereoselectivity" observed in these reactions. Any progress in this area should have wider ramifications for understanding the stereochemistry of displacement at a tetracoordinate P(V) center. We have chosen the pentachloro- and pentafluoro(triphenylphosphazenyl)cyclotriphosphazenes, $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**), F (**2**)], as substrates to study the



X = Cl (**1**), F (**2**); T = $-NPPh_3$

differences in the mechanisms of displacement reactions at P-Cl and P-F centers.[5] Both **1** and **2** are high-melting solids and can be handled more conveniently than $N_3P_3Cl_6$ and $N_3P_3F_6$, the latter of which is very volatile. Furthermore, the $-NPPh_3$ group exerts a geminal-directing influence in the reactions of **1** with secondary amines[6] and hence it would be of interest to study the effect with other nucleophiles. The choice of the substrates is also dictated by the fact that the shielding effect of the $-NPPh_3$ group on the protons of the cis substituent[6] and the magnitude of phosphorus-phosphorus coupling in the ^{31}P NMR spectra facilitate structural assignments to geometrical and positional isomers.

In this paper, we report the results of a detailed investigation of the reactions of **1** and **2** with sodium methoxide.[7] This investigation constitutes the first systematic study of the reaction of a fluorocyclotriphosphazene with an alkoxide. The results are correlated with those observed in the nucleophilic displacement reactions at a tetrahedral P(V) center in other systems.

Results and Discussion

Methoxylation of **1** or **2** can lead to 19 substitution products of the type $N_3P_3(NPPh_3)(OCH_3)_nX_{5-n}$ [X = Cl, F; n = 1 and 4 (three isomers each), 2 and 3 (six isomers each), and 5]. The structural elucidation of the derivatives obtained in the present study by NMR spectroscopy is based upon the following criteria: (a) ^1H NMR (i) the number of methoxy environments and the presence or absence of "virtual coupling",[8] (ii) the magnitude of $^3J(P-H)$, and (iii) the relative chemical shifts of the cis and trans (with respect to the $-NPPh_3$ substituent) $-OCH_3$ protons; (b) ^{31}P NMR (i) the number of phosphorus environments, (ii) the chemical shift values, and (iii) the magnitude of $^2J(P-P)$; (c) ^{19}F

(1) Studies of Phosphazenes. 28. Part 27: Kumara Swamy, K. C.; Ramabrahmam, P.; Krishnamurthy, S. S. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 1023.

(2) (a) Karthikeyan, S.; Krishnamurthy, S. S. *Z. Anorg. Allg. Chem.* **1984**, *513*, 231. (b) Evans, T. L.; Allcock, H. R. *Inorg Chem.* **1979**, *18*, 2342. (c) Ramachandran, K.; Allen, C. W. *Inorg. Chem.* **1983**, *22*, 1445. (d) Van der Huizen, A. A.; Jekel, A. P.; Rusch, J.; van de Grampel, J. C. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 343.

(3) (a) Krishnamurthy, S. S.; Sundaram, P. M; Woods, M. *Inorg. Chem.* **1982**, *21*, 406. (b) Dhathathreyan, K. S.; Krishnamurthy, S. S.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2151.

(4) For a review, see: Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.

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(6) (a) Krishnamurthy, S. S.; Ramabrahmam, P.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 215. (b) Biddlestone, M.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2740. (c) Nabi, S. N.; Biddlestone, M.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2634. (d) Ramabrahmam, P.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *Z. Anorg. Allg. Chem.* **1985**, *522*, 226.

(7) A part of this work has appeared as a communication. See: Kumara Swamy, K. C.; Krishnamurthy, S. S. *Phosphorus Sulfur* **1983**, *18*, 241.

(8) Finer, E. G.; Harris, R. K.; Bond, M. R.; Keat, R.; Shaw, R. A. *J. Mol. Spectrosc.* **1970**, *33*, 72.

(9) Biddlestone, M.; Keat, R.; Rose, H.; Rycroft, D. S.; Shaw, R. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *B31*, 1001.

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Table I. $^{31}P\{^1H\}$ NMR Data for the Methoxy Derivatives $N_3P_3(NPPh_3)(OCH_3)_nCl_{5-n}$ (**1**, **3–12**)[a]

	chem shift[b]					coupling constants (^2J(P–P))							
compd no.	P(A)	P(B)	P(C)	P(D)	P(E)	AB	BC	BD	BE	CD	CE	DE	^4J(P–P)
1[c]	15.40	0.20	20.30			27.8	47.5						3.4 (AC)
3	14.76	4.53	23.75	20.38		28.8	52.4	59.4		75.8			4.5 (AD)
													3.0 (AC)
4	15.02	5.08	23.90	20.75		27.5	54.8	56.0		72.0			3.7 (AD)
													3.5 (AC)
5	13.97	8.44		24.20		29.6		63.8					4.5 (AD)
6	13.95	8.74	*d*		13.01	29.6	56.6		67.5		74.1		4.0 (AE)
7[e]	13.79	(5.2)	(23.5)	(21.4)		41.1	55.1	63.1		74.0			2.0
8[e]	13.93	(4.4)	(23.5)	(21.8)		40.5	52.7	64.1		73.0			2.0
9	11.73	7.03	24.50		13.92	39.0	56.6		67.7		74.1		1.0
11	11.00	10.00		28.56	17.24	38.1		66.9	68.4			79.3	3.0 (AE)
													3.1 (AD)
12	9.42	13.48			21.01	37.0			70.9				2.0 (AE)

[a] Chemical shifts are in δ and coupling constants (J) in Hz; field strength is 162 MHz. [b] Legend: P(A) = $P\text{Ph}_3$; P(B) = $P(\text{NPPh}_3)(\text{R})$; P(C) = $P\text{Cl}_2$; P(D) = $P(\text{OCH}_3)\text{Cl}$; P(E) = $P(\text{OCH}_3)_2$. [c] Data from ref 9. [d] Buried in signals due to isomer **5**. [e] Only a 109.4-MHz ^{31}P NMR spectrum obtained; values in parentheses are approximate (±0.5 δ).

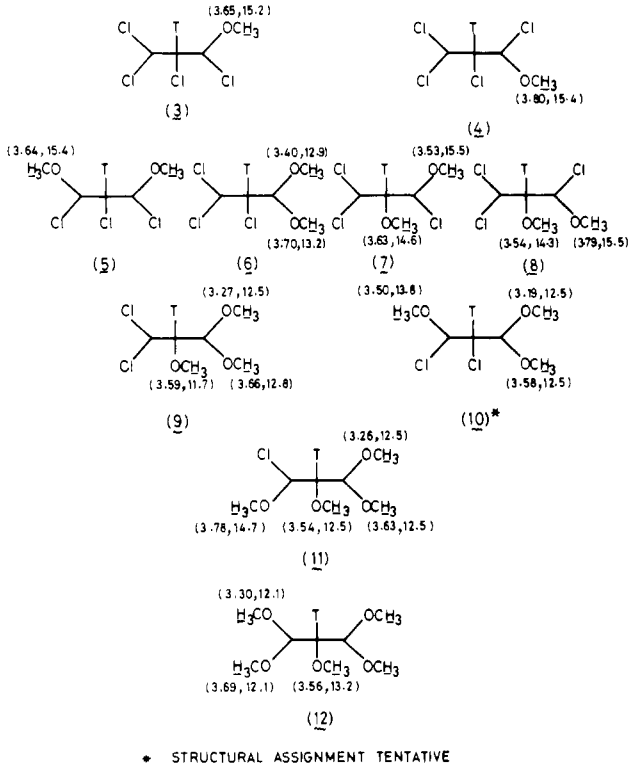


Figure 1. Structures of methoxy derivatives **3–12** along with the ^1H NMR data. Chemical shifts (δ) and coupling constants (^3J(P–H), Hz) for the methoxy protons are given in parentheses.

NMR, the relative chemical shifts of $\equiv P(\text{NPPh}_3)F$ and $\equiv P(\text{R})F$, where R = F, OCH_3.

Structures of the Methoxy–Chloro Derivatives 3–12. The structures of compounds **3–12** are shown in Figure 1 along with the ^1H NMR data for the methoxy protons. The ^{31}P NMR data are summarized in Table I. The $^{31}P\{^1H\}$ NMR spectrum of **3** (which contains a trace of the isomer **4**) is illustrated in Figure 2. Four distinct phosphorus environments for both isomers show that each of these contains only the $\equiv P(OCH_3)Cl$ and not the $\equiv P(\text{NPPh}_3)(OCH_3)$ group. The assignment of signals due to $\equiv P(\text{NPPh}_3)Cl$ and $=P\text{Ph}_3$ can be easily made on the basis of the multiplet patterns. The signals centered at δ 20.38 (and at δ 20.75 for **4**) are ascribed to the $\equiv P(OCH_3)Cl$ group because the value of ^2J(P–P) involving this group is expected to be higher than that involving the $\equiv PCl_2$ group [cf. the ^2J(P–P) values BC and BD in Table I].[10] The relative proton chemical shifts of the methoxy groups[11] and the TLC R_f values (see Experimental Section)[12] of **3** and **4** suggest the 2,cis-4[13] and the 2,trans-4 structures, respectively, for these isomers.

Four isomers (**5–8**) are formed at the bis stage of chlorine replacement in methyl cyanide. The composition of this mixture has been confirmed by its mass spectrum, which shows only a trace of a trimethoxy derivative, $N_3P_3(\text{NPPh}_3)(OCH_3)_3Cl_2$ (<2%) and no other impurity; the ^1H NMR spectrum (methoxy region) of this sample is shown in Figure 3. The doublet with intense "virtual coupling"[8] at δ 3.64 for **5** can arise from a 2,cis-4,cis-6 or a 2,trans-4,trans-6 isomer.[13] A mixture of **5** and **6** (ratio 4:1 as shown by the ^1H NMR spectrum) has been isolated by repeated fractional crystallization of the above mixture. In the ^{31}P NMR spectrum of the mixture of **5** and **6**, the signals due to individual isomers can be readily identified. Isomer **5** shows only three phosphorus environments, which is consistent with either the 2,cis-4,cis-6 or 2,trans-4,trans-6 structure. However, since the cis isomer **3** is the major product at the mono stage, the 2,cis-4,cis-6 structure is assigned for **5**.[14]

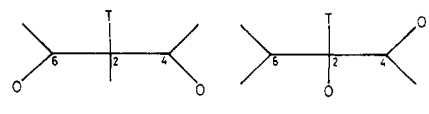
The low ^3J(P–H) values for the two methoxy doublets in the ^1H NMR spectrum of **6** strongly indicate the presence of a $\equiv P(OCH_3)_2$ group.[4,15] The $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublets at δ 13.01, a multiplet (eight lines) at δ 8.74, and a doublet at δ 13.95; more lines at 23–26 δ can be seen, but the exact δ value is uncertain because of overlap of signals due to **5**. The resonances centered at δ 8.74 and 13.95 can be easily ascribed to $\equiv P(\text{NPPh}_3)(\text{R})$ and $=PPh_3$ groups, respectively, on the basis of the splitting pattern. The signals centered at δ 13.01 can be due to a $\equiv P(OCH_3)Cl$, a $\equiv PCl_2$, or a $\equiv P(OCH_3)_2$ group. However, on the basis of the expected trends in the phosphorus chemical shifts of substituted cyclotriphosphazenes, $N_3P_3(\text{R})_nCl_{6-n}$ (R = OC_6H_5,[16] OC_6H_4-*p*-CH_3,[2a] OCH_2CF_3,[17] $OCH{=}CH_2$,[2c]

(10) Finer, E. G.; Harris, R. K. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *6*, 61.

(11) The protons on the methoxy group cis to the $-NPPh_3$ group are expected to be more shielded than the trans methoxy protons.[4,6d,7]

(12) (a) Goldschmidt, J. M. E. "Analytical Chemistry of Phosphorus Compounds"; Halmann, M., Ed.; Wiley-Interscience: New York, 1972; pp 523–591. (b) Das, R. N.; Shaw, R. A.; Smith, B. C.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1973**, 709. (c) Kauffman, G. H.; Gump, B. H.; Stedjee, B. J.; Houghton, R. A., Jr. *J. Chromatogr.* **1976**, *123*, 448.

(13) Disposition of all $-OCH_3$ groups is with respect to the $-NPPh_3$ group; the position of the $-NPPh_3$ group is fixed at P(2), e.g.



2,trans-4,trans-6 2,cis-4,2

(14) The observed δ value for $-OCH_3$ protons is close to that observed for isomer **3** and provides additional support for the structural assignment.

(15) (a) Dell, D.; Fitzsimmons, B. W.; Keat, R.; Shaw, R. A. *J. Chem. Soc. A* **1966**, 1680. (b) Keat, R.; Ray, S. K.; Shaw, R. A. *J. Chem. Soc.* **1965**, 7193.

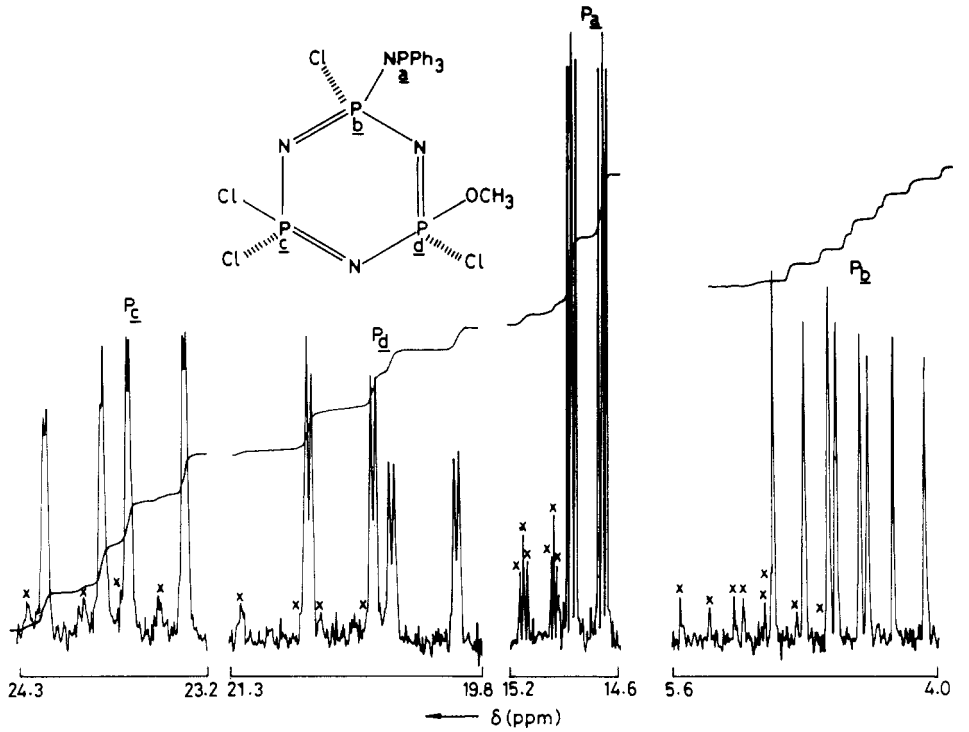


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of *cis*-$N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3**). Lines indicated by × are due to the trans isomer **4**.

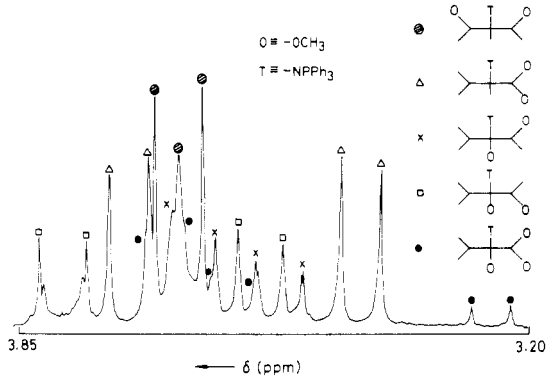


Figure 3. ^1H NMR spectrum (270 MHz) of a mixture of $N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ isomers (**5–8**) containing a trace of $N_3P_3(NPPh_3)(OCH_3)_3Cl_2$ (**9**) (methoxy region only).

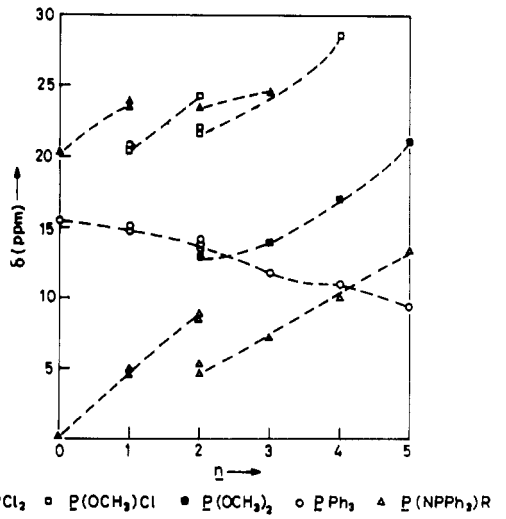


Figure 4. Trends in phosphorus-31 chemical shifts for $N_3P_3(NPPh_3)(OCH_3)_nCl_{5-n}$ (n = 1–5).

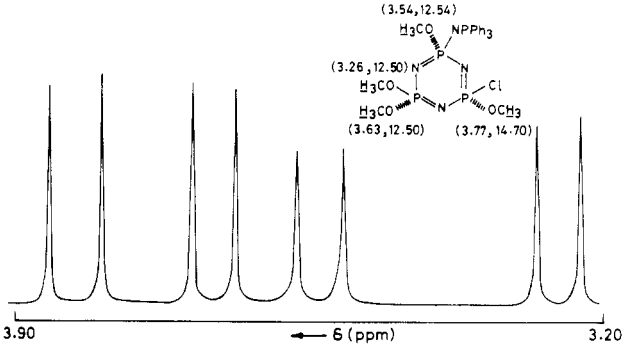


Figure 5. ^1H NMR spectrum (270 MHz) of $N_3P_3(NPPh_3)(OCH_3)_4Cl$ (**11**) in the methoxy region.

NMe_2[18]), the chemical shifts of $\equiv P(OCH_3)Cl$ and PCl_2 (δ 20–24) are expected to move downfield from **3** and **4** to **6**. Hence, this upfield resonance at δ 13.01 is definitely due to the $\equiv P(OCH_3)_2$ group. From these arguments it follows that **6** has a 2,4,4-structure.

The other two dimethoxy derivatives **7** and **8** are formed as major products (ratio 1:1, >88%) in benzene. This mixture shows mainly two ABMX spin systems in its $^{31}P\{^1H\}$ NMR spectrum. The presence of the $\equiv P(NPPh_3)(OCH_3)$ group in these two isomers is shown by the higher values of $^2J(PPh_3\text{–}P(NPPh_3)(R))$ (~41 Hz) when compared to those for **1** and **3–6** (27.5–29.6 Hz), which contain $\equiv P(NPPh_3)Cl$ groups.[10] This assignment is confirmed by the trends in $\equiv P(NPPh_3)(R)$ chemical shifts of $N_3P_3(NPPh_3)(OCH_3)_nCl_{5-n}$, which are shown in Figure 4. The δ values of $\equiv P(NPPh_3)Cl$ for compound **1** (δ 0.20) and isomeric pairs **3** + **4** (δ 4.53 and 5.08) and **5** + **6** (δ 8.44 and 8.74) fall in a line; the δ values observed for the isomeric pair **7** + **8** (δ 5.2 and 4.4) fall in line with those of $\equiv P(NPPh_3)(OCH_3)$ for compounds **9**, **11**, and **12**. From these data and the ^1H NMR chemical shifts and $^3J(P\text{–}H)$ values, it follows that the isomers **7** and **8** are

(16) Sulkowski, W.; Volodin, A. A.; Brandt, K.; Kireev, V. V.; Korshak, V. V. *Zh. Obshch. Khim.* **1981**, *51*, 1221.
(17) Schmutz, J. L.; Allcock, H. R. *Inorg. Chem.* **1975**, *14*, 2433.
(18) Keat, R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1582.
(19) (a) Dahmann, D.; Rose, H.; Walz, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *B35*, 964. (b) Dahmann, D. Ph.D. Dissertation, Ruhr University, Bochum, West Germany, 1978.

Table II. ^{19}F NMR Data for the Fluoro Derivatives $N_3P_3(NPPh_3)(OCH_3)_nF_{5-n}$ (n = 0–4)

compd no.	chem shift, δ^a			coupling constant ^1J(P–F), Hz		
	F(1)	F(2)	F(3)	P(B)F(1)	P(C)F(2)	P(D)F(3)
2[b]	−44.79	−70.39		870	884	
	(−44.70)	(−70.39)		850	890	
13	−43.78	−70.35	−67.69	865	903	874
14	−43.78	−70.35	−67.88	863	900	878
15	−42.70		−67.89	863		878
16	−43.26		−68.08[c]	850		851
			−69.78[d]			856
17	−43.44		−69.39	851		844
18	−41.00		−69.20	840		880
19	−41.00		−71.2	840		885
20	−40.86			860		

[a] Legend: F(1) = P(NPPh$_3$)*F*; F(2) = P*F*$_2$; F(3) = P(OCH$_3$)*F*; P(B) = *P*(NPPh$_3$)F; P(C) = *P*F$_2$; P(D) = *P*(OCH$_3$)F. [b] Literature values in parentheses.[19] [c] Fluorine trans to the –NPPh$_3$ substituent. [d] Fluorine cis to the –NPPh$_3$ substituent.

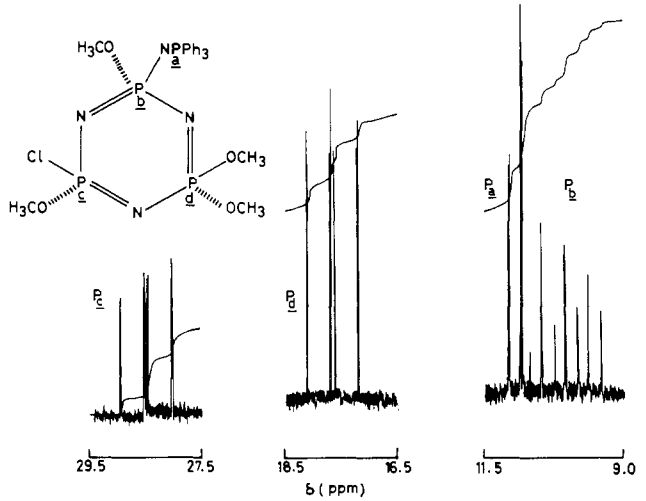


Figure 6. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of $N_3P_3(NPPh_3)(OCH_3)_4Cl$ (**11**).

2,*cis*-4,2- and 2,*trans*-4,2-$N_3P_3(NPPh_3)(OCH_3)_2Cl_3$, respectively. The closeness of the ≡*P*Cl$_2$ and ≡*P*(OCH$_3$)Cl chemical shifts results in the split doublets at δ 3.53 and 3.79 in the ^1H spectrum of these isomers (Figure 3).

The 2,2,4,4-structure for the major trimethoxy derivative **9** follows from the low ^3J(P–H) values, the ≡*P*(OCH$_3$)$_2$ chemical shift, and the magnitude of ^2J(P(NPPh$_3$)(R)–PPh$_3$)). Another isomer **10** is obtained only as a mixture (not containing **9**) in very low quantities from the reaction in methyl cyanide; only the ^1H NMR spectrum could be recorded for this mixture. The 2,cis-4,6,6 structure has been tentatively assigned to the major component (**10**) on the basis of the proton chemical shifts and ^3J(P–H) values.

Both ^1H (Figure 5) and $^{31}P\{^1H\}$ (Figure 6) NMR spectra show that the tetramethoxy derivative **11** has a ≡P(OCH$_3$)Cl group. The most downfield doublet in the ^1H NMR spectrum having the largest ^3J(P–H) (14.7 Hz) value is attributed to these protons. The chemical shift value (δ 3.78) leaves no doubt about the trans disposition of this –OCH$_3$ group with respect to the –NPPh$_3$ substituent.

Structures of the Methoxy–Fluoro Derivatives 13–20. The structures of the methoxy–fluoro derivatives **13–20** along with their ^1H NMR data are shown in Figure 7; no other derivative has been observed in the present study. The ^{19}F and the $^{31}P\{^1H\}$ NMR data are summarized in Tables II and III, respectively. The ≡P(NPPh$_3$)*F* chemical shifts (δ −40 to −45) lie very much downfield when compared to those of ≡P(OCH$_3$)*F* or ≡P*F*$_2$ (δ −67 to −71). The ^{19}F NMR data clearly show that attack by methoxide at the ≡P(NPPh$_3$)F site does not take place *until the very last stage*. Thus only two mono- (**13** and **14**), three di- (**15**, **16**, and **17**), and two trimethoxy (**18** and **19**) derivatives are formed; the geometrical isomers at each stage of substitution are formed in comparable amounts. The structural assignments are based on the trends in proton chemical shifts discussed earlier;

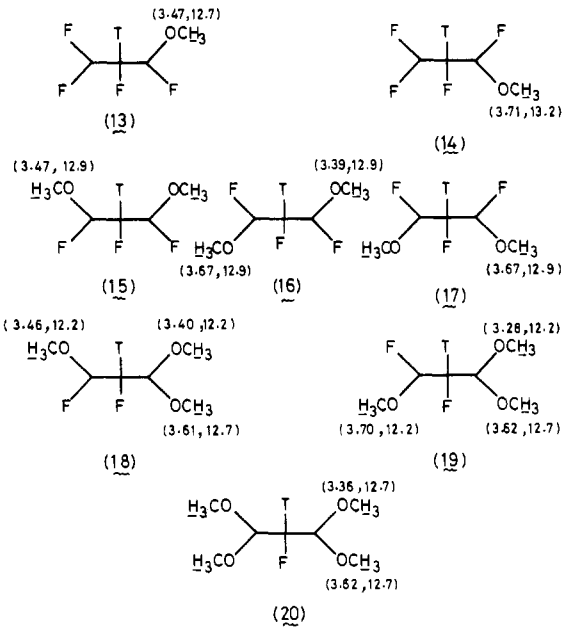


Figure 7. Structures of the methoxy–fluoro derivatives **13–20** along with their ^1H NMR data (methoxy protons only). Note the revision of assignments made previously.[7]

Table III. $^{31}P\{^1H\}$ NMR Data for the Fluoro Derivative $N_3P_3(NPPh_3)(OCH_3)_nF_{5-n}$ (n = 0, 1, 4)

compd no	chem shift, δ^a				coupling constant, Hz	
	P(A)	P(B)	P(C)	P(D)	^3J(P(A)–F)	^2J(P(A)–P(B))
2	16.14[b]	7.4	10.2		15.5	47.3
13	17.24	*c*	*c*	*c*	17.6	47.2
14	17.74	*c*	*c*	*c*	16.2	47.3
20[d]	11.70	13.34		20.64	18.1	44.5

[a] Legend: P(A) = *P*Ph$_3$; P(B) = *P*(NPPh$_3$)(F); P(C) = *P*F$_2$; P(D) = *P*(OCH$_3$)F or *P*(OCH$_3$)$_2$. [b] Literature value δ 16.8.[19] [c] Spectrum too complicated to assign these resonances. [d] Other data: ^1J(P(B)–F) = 844.8 Hz; ^2J(P(B)–P(D)) = 78.0 Hz; ^3J(P(D)–F) < 15.0 Hz.

it is interesting to note that the fluorine nuclei that are cis to the –NPPh$_3$ substituent experience shielding similar to that of the methoxy protons (cf. Figure 7 and Table II).

For the tetramethoxy–monofluoro derivative $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**) the ^1H (Figure 8), $^{31}P\{^1H\}$ (Figure 9), and ^{19}F NMR spectra independently confirm the structure. The ^1H NMR spectrum shows two doublets with intense "virtual coupling"; only the structure with the ≡P(NPPh$_3$)F group is compatible with this observation. The $^{31}P\{^1H\}$ NMR spectrum shows only three phosphorus environments, and the presence of the ≡P(NPPh$_3$)F group is clearly revealed by the large ^1J(P–F) coupling (844.8 Hz). The ^{19}F NMR spectrum exhibits a doublet of multiplets centered at δ −40.86, thus establishing the presence of a ≡P(NPPh$_3$)F group.

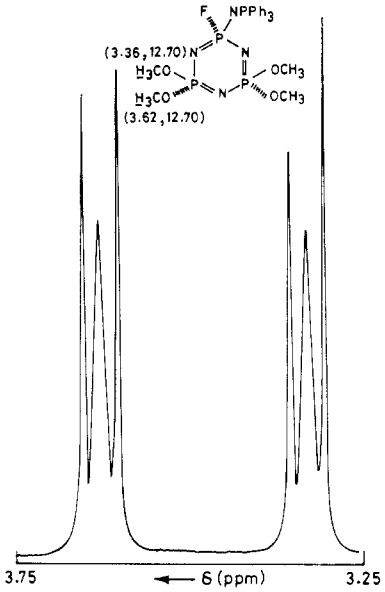


Figure 8. ^{1}H NMR spectrum (270 MHz) of $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**) in the methoxy region.

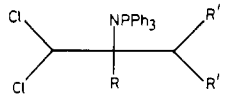
Halogen Replacement Pattern and Mechanistic Implications. (a) Methoxylation Reactions of 1. The salient features of the results obtained in this system may be summarised as follows.

(i) At the mono stage of chlorine replacement, only nongeminal isomers are obtained; the isomer 2,*cis*-4-$N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3**) predominates. The ratio of cis (**3**) to trans (**4**) isomer decreases in the order $CH_3CN > C_6H_6 > Et_2O$.

(ii) Attack by methoxide occurs at all phosphorus centers [$\equiv PCl_2$, $\equiv P(NPPh_3)Cl$, and $\equiv P(OCH_3)Cl$] at the bis stage in methyl cyanide; the isomers 2,*cis*-4,*cis*-6- (**5**), 2,4,4- (**6**), 2,*cis*-4,2- (**7**), and 2,*trans*-4,2-$N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ (**8**) are formed in significant quantities. By contrast, in benzene, only the isomers **7** and **8** predominate (>88%) and the isomer **5** is a minor product (<8%).

(iii) The isomer 2,2,4,4-$N_3P_3(NPPh_3)(OCH_3)_3Cl_2$ (**9**) is the major product at the tris stage. The tetrakis derivative 2,*trans*-4,2,6,6-$N_3P_3(NPPh_3)(OCH_3)_4Cl$ (**11**) has been isolated in low yields from reactions in both methyl cyanide and benzene; this derivative has a $\equiv P(OCH_3)Cl$ group. Exposure of this compound to the atmosphere for 1 week leads to uncharacterized hydrolyzed products (^{1}H NMR evidence).

It is worthwhile to compare the above results with the observations made in the aminolysis reactions of **1**. In the reaction of **1** with dimethylamine, a derivative of type $N_3P_3(NPPh_3)(NMe_2)_nCl_{5-n}$ ($n \geq 2$) containing a $\equiv P(NPPh_3)Cl$ group is not formed.[6d] The isomer 2,2,4,4-$N_3P_3(NPPh_3)(NMe_2)_3Cl_2$ (Ia) is

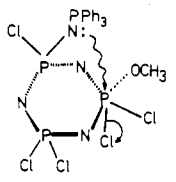


Ia, R = R′ = NMe_2
b, R = R′ = NC_2H_4
c, R = $NPPh_3$, R′ = NMe_2

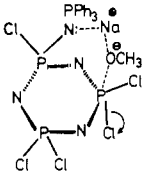
the only product observed at the tris stage of chlorine replacement; even in the aziridinolysis of **1** such an isomer (Ib) is the sole product.[20] Furthermore, the reaction of 2,2-$N_3P_3(NPPh_3)_2Cl_4$ with dimethylamine gives the geminal product 2,2,4,4-$N_3P_3(NPPh_3)_2(NMe_2)_2Cl_2$ (Ic) in high yields.[21]

The presence of a bulky substituent (such as $-NPPh_3$) on the phosphazene ring would retard $S_N2(P)$ attack; at the same time if the substituent is electron-releasing, the ionization of the P–Cl bond would be promoted and an $S_N1(P)$ mechanism would be favored. The distribution of products at a particular stage of chlorine replacement is a result of competition between these two mechanisms. From kinetic data for the dimethylaminolysis of $N_3P_3Cl_6$, it has been shown that a changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism occurs at the tetrakis stage of chlorine replacement.[22] By contrast, the reaction of *n*-butoxide with $N_3P_3Cl_6$ follows a second-order rate law until the tetrakis stage.[23] An $S_N1(P)$ mechanism has been observed for the reaction of $N_3P_3(OPh)_5Cl$ with dimethylamine[22] (Figure 10). In view of the powerful electron release by the $-NPPh_3$ substituent,[24] an $S_N1(P)$ mechanism is likely to be operative at the bis stage in the dimethylaminolysis of **1**. The changeover from an $S_N2(P)$ to an $S_N1(P)$ mechanism for the methoxylation of **1** could occur at a later stage because of the smaller size and less electron releasing power of the –OMe group when compared to the $-NMe_2$ group.[24] The changeover to the $S_N1(P)$ mechanism is essentially complete at the tris stage of methoxylation.[26] The low yield of the tetramethoxy derivative (**11**) is readily explained by a rapid $S_N1(P)$ process operating at the final stage of chlorine replacement.

Ratio of Cis (3) and Trans (4) Isomers. Two types of interactions (II and III) that involve the lone pair of electrons on the two-coordinated exocyclic nitrogen atom can be envisaged to explain the preponderance of the cis isomer **3**. The first one (II)



II



III

has been invoked recently to explain the cis–trans isomer ratios in the reaction of $N_3P_3Cl_6$ with sodium *p*-cresoxide.[2a,27] Involvement of an exocyclic substituent (e.g. III) has been suggested previously by Shaw and co-workers in the reactions of $N_3P_3Cl_6$ with amines.[25a,29] Both formulations II and III would favor cis products and entail a transition state with an apical chlorine as the leaving group. A polar solvent like methyl cyanide can promote a transition state involving a species such as III better than benzene or diethyl ether; this would explain the increased yield of compound **3** in methyl cyanide. It also explains the formation of isomer **5** in significant quantities in methyl cyanide.

(b) Methoxylation Reactions of 2. The most important observation in this system is that the fluorine at the $\equiv P(NPPh_3)F$ site is the last one to be replaced. The other significant features are (i) the isolation of the di- (**15–17**) and the tetramethoxy (**20**)

(20) Kumara Swamy, K. C.; Damodara Poojary, M.; Krishnamurthy, S. S.; Manohar, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *B39*, 615.
(21) Lensink, G.; de Ruiter, B.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1521.
(22) (a) Katti, K. V.; Krishnamurthy, S. S. *Phosphorus Sulfur* **1983**, *14*, 157. (b) Katti, K. V.; Krishnamurthy, S. S. *J. Chem. Soc., Dalton Trans.* **1985**, 285.
(23) Sorokin, M. F.; Latov, V. K. *Kinet. Catal.* **1966**, *7*, 35.
(24) A measure of the electron-releasing power of various substituents toward the phosphazene ring is provided by the substituent constants (α) derived from basicity measurements. The values of the α parameter for the relevant substituents are as follows: $-NMe_2$, 5.6; $-NPPh_3$, 10.3; $-OCH_3$, 3.3; –O-*n*-Bu, 4.0; –OPh, 3.1.[25]
(25) (a) Shaw, R. A. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1976**, *B31*, 641. (b) Dhathathreyan, K. S. Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1980.
(26) Even at the bis stage of chlorine replacement a slow $S_N1(P)$ mechanism probably competes with the $S_N2(P)$ pathway. In benzene, the reaction is inherently slow and hence isomers **7** and **8** are formed by an $S_N1(P)$ process. In the more polar methyl cyanide, the increase in the rate of the $S_N1(P)$ process is effectively matched by a fast concerted $S_N2(P)$ mechanism[22b] and thus isomers **5–8** are formed in significant quantities.
(27) This type of interaction involves a nonbonding orbital (d_{z^2}) on phosphorus. It is interesting to note that, in many reactions involving phosphonium ions, McEven and co-workers have postulated 2p(oxygen)–3d(phosphorus) through-space interactions to explain the observed stereochemical course of the reactions.[28]
(28) McEven, W. E.; Cooney, J. V. *J. Org. Chem.* **1983**, *48*, 483.
(29) Das, R. N.; Shaw, R. A.; Smith, B. C.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1973**, 709.

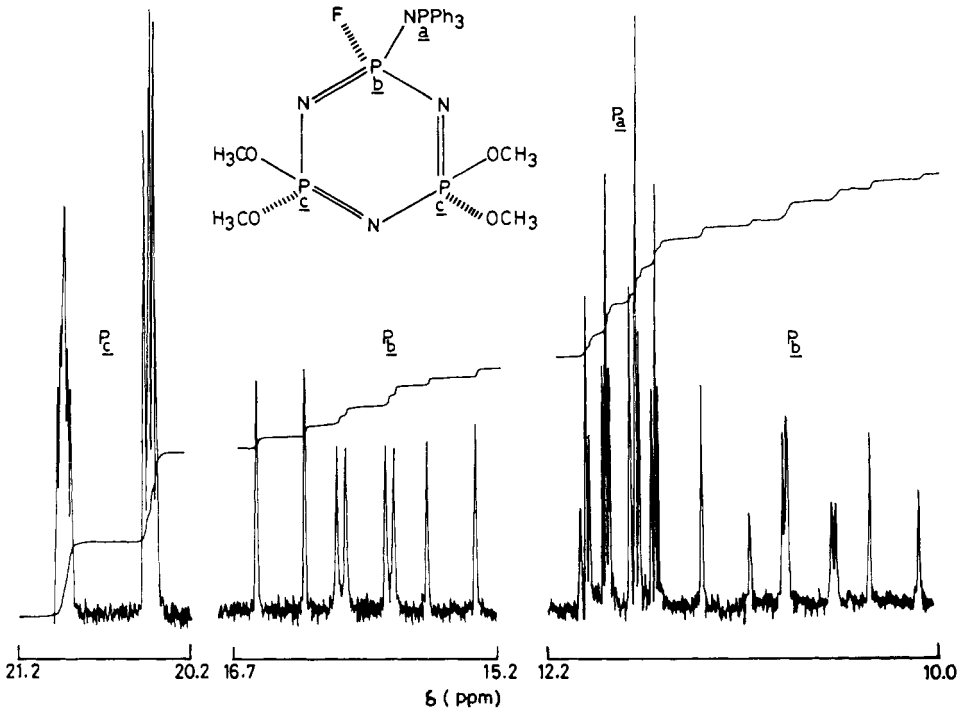


Figure 9. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**).

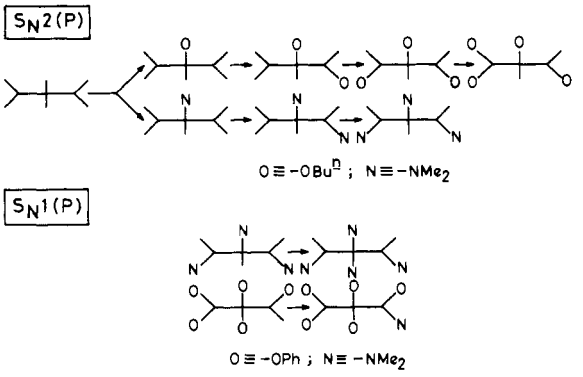


Figure 10. $S_N2(P)$ and $S_N1(P)$ mechanisms in the reaction of chlorocyclophosphazenes with *n*-butoxide and dimethylamine (chlorine atoms not shown; from ref 22, 23).

derivatives in very high yields (>65%), (ii) the formation of $N_3P_3(NPPh_3)(OCH_3)_5$ (**12**) *only in traces* in the reaction of **2** with an excess of methoxide, and (iii) the formation of all the geometrical isomers (**13**, **14**, **15–17**, **18**, **19**) in appreciable quantities. Kinetic investigations on the first stage of halogen replacement from $N_3P_3X_6$ (X = Cl, F) by dimethylamine[22b] and *n*-propylamine[30] indicate that the replacement of fluorine is much slower than that of chlorine. It is also worth noting that the final stage of hydrolysis of $P(O)Cl_3$ follows an $S_N1(P)$ mechanism whereas the analogous fluoro compound $P(O)F_3$ undergoes hydrolysis throughout by an $S_N2(P)$ mechanism.[31] The inherent difficulty of heterolysis of a P–F bond is elegantly illustrated by cyclenphosphoranes (IV);[32] whereas the fluoro derivative (X =

IV

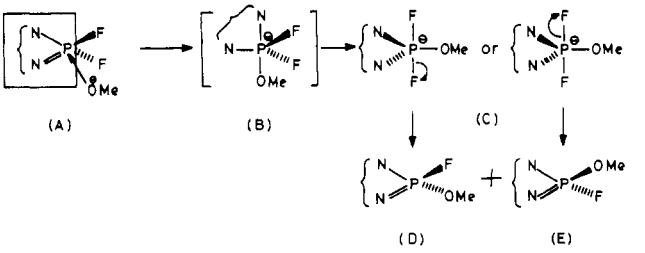


Figure 11. Suggested sequence of steps to explain the ratio of geometrical isomers in the reaction of **2** with methoxide.

F) is covalent, the chloro compound (X = Cl) is ionic. On the basis of these observations, a slow $S_N2(P)$ (high activation barrier) pathway persisting throughout can be envisaged for the reaction of methoxide with $N_3P_3(NPPh_3)F_5$ (**2**). The reaction is presumably hindered to a significant extent by bulky substituents, and hence attack by methoxide at the $\equiv P(NPPh_3)F$ site does not take place until the last stage.

However, electronic effects probably play a more decisive role than steric effects. The formation of nongeminal products in the aminolysis reactions of $N_3P_3F_6$ and paucity of (amino)fluorocyclotriphosphazenes, $N_3P_3(NRR')_nF_{6-n}$ ($n \geq 3$, R, R' = H, alkyl), have been attributed to deactivation of fluorine at a $\equiv P(NRR')F$ site.[2b,33] The greater deactivation at a PF(X) site when X is an amino group compared to that when X is an alkoxy group has been attributed to the greater π-donor ability of nitrogen. The stronger inductive electron withdrawal by fluorine (when compared to that by chlorine) would make electron release by the nitrogen more effective.[34] The greater the electron-releasing power of the substituent (X), the greater is the deactivation for nucleophilic attack at the same phosphorus atom. Thus the reactivity should decrease in the order $\equiv PF_2 > \equiv P(OCH_3)F > \equiv P(NMe_2)F > \equiv P(NPPh_3)F$. This trend would explain observations i and ii noted above and also the difficulty of replacing the fluorine at a $\equiv P(NPPh_3)F$ center. The exclusive nongeminal substitution observed here and elsewhere[2b,33,35] can thus be rationalized.

(30) Moeller, T.; Kokalis, S. C. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1397.
(31) Kirby, A. J.; Warren, S. J. "The Organic Chemistry of Phosphorus", Elsevier: Amsterdam, 1967; p 301.
(32) Richman, J. E.; Gupta, O. D.; Flay, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1291.
(33) Chivers, T.; Oakley, R. T.; Paddock, N. L. *J. Chem. Soc. A* **1970**, 2324.
(34) See ref 31, p 316; See also: Hudson, R. F.; Keay, L. *J. Chem. Soc.* **1960**, 1859.
(35) Niecke, E.; Thamm, H.; Bohler, D. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 261.

Ratios of Geometrical Isomers 13:14, 15:16:17, and 18:19. If one considers a trigonal-bipyramidal (TBP) transition state for the reactions of fluorocyclotriphosphazenes, there are two highly apicophilic fluorine substituents and the phosphazene ring contains two nitrogen atoms of less apicophilic character.[36] The six-membered cyclophosphazene ring is rigid, and the bond angle at phosphorus is generally ~120°. An apical–equatorial disposition for the ring in the transition state would mean a narrowing of this angle from 120 to 90° (which introduces strain in the ring system) and also a retaining of one of the fluorine substituents at an energetically unfavorable equatorial position.[36] Hence, a diequatorial disposition for the phosphazene ring with the two fluorine atoms at apical positions is favored in fluorocyclophosphazenes.[38] The formation of geometrical isomers in equal proportions in the reaction of **2** with methoxide can be explained by the sequence of steps shown in Figure 11. Attack by methoxide occurs in the plane of the phosphazene ring to form a TBP transition state (B) in which the methoxide and one of the ring nitrogens occupy axial positions. Pseudorotation[40] followed by departure of a fluorine from one of the apical positions leads to the final products D and E. Alternatively, attack by methoxide can still occur in the plane of the ring but along the FPF tetrahedral face, which will also lead to transition state C without pseudorotaton.[41] Although "apical entry and apical depature" is the accepted rule for displacement reactions at the tetrahedral P(V) center, other possibilities can not be entirely discounted.[43]

Trends in NMR Chemical Shifts and Coupling Constants. The difference in ^3J(P–H) values for $\equiv P(OCH_3)_2$ and $\equiv P(OCH_3)X$ protons for the methoxy–chloro derivatives **3–12**, although not so marked as for the amino derivatives,[4,15] are quite useful in structural elucidation; for the methoxy–fluoro derivatives **13–20** this difference is insignificant. It appears that the relative effectiveness of the π bonding from the counterpart substituent (R′) for a group R at the $\equiv P(R)(R')$ site determines these ^3J(P–H) values.

The deshielding of $\equiv PCl_2$, $\equiv P(OCH_3)Cl$, $\equiv P(OCH_3)_2$, and $\equiv P(NPPh_3)Cl$ [or $\equiv P(NPPh_3)(OCH_3)$] observed here (Figure 4) and similar results obtained by others[2a,c,16-18] show that the phosphorus chemical shifts in cyclotriphosphazenes are affected considerably by substituents present elsewhere on the ring, presumably via a "long-range effect".[44] A noteworthy feature in the present system is the progressive shielding of the $\equiv PPh_3$ group upon substitution. Similar results have also been obtained for the aziridino derivatives $N_3P_3(NPPh_3)(NC_2H_4)_nCl_{5-n}$ (n = 1–5).[45] It has been established previously that the exocyclic P–N–P unit in (triphenylphosphazenyl)cyclotriphosphazenes forms a "π island" with the P_{ring}–N_{exo} bond length (1.60 Å) being comparable to those of P_{ring}–N_{ring} bonds (1.55–1.61 Å).[46] Upon substitution of –Cl by $-OCH_3$ groups, the effectiveness of the π bonding of the $-NPPh_3$ group with the ring phosphorus decreases, which, at least in part, would explain the trend in the phosphorus chemical shift of $\equiv PPh_3$.

Another interesting observation is that the $\equiv P(OCH_3)_2$ groups in $N_3P_3(NPPh_3)(OCH_3)_5$ (**12**) are slightly nonequivalent (a difference of 2 Hz at 162 MHz) as found by a computer analysis of the phosphorus-31 NMR spectrum. The four-bond phosphorus–phosphorus coupling [^4J(P–P)] is observed in all the derivatives **1–12**, but its magnitude is very low for $N_3P_3(NPPh_3)(OCH_3)_3Cl_2$ (**9**) (<1.0 Hz).

The fluorine chemical shifts present a more interesting picture. The δ values for $\equiv P(F)R$ groups lie in the order R = F (δ –67.7 to –73.6)[47] < OCH_3 (δ –67.7 to –71.2) < NMe_2 (δ –59.2 to –66.4)[47] < $NPPh_3$ (δ –40.8 to –44.8). This trend is in exactly the reverse order of deactivation of the $\equiv P(F)R$ site toward attack by the methoxide, which has been discussed earlier. The signficant downfield shift for $\equiv P(NPPh_3)F$ is due to reduction in the paramagnetic contribution to shielding at the fluorine nucleus[47] as a result of strong π bonding of the $-NPPh_3$ group with the ring phosphorus atom.[46]

Conclusion

The stereochemistry of nuclephilic displacement at a tetracoordinate P(V) center and its analogy to silicon systems has received considerable attention in recent years.[42,43,48] The results reported in this paper add another interesting facet to this overall theme. The main conclusions of the present study is that a comprehensive model to rationalize the observed "regio- and stereoselectivity" in the reactions of cyclophosphazenes can emerge only by considering the combined effects of (a) the substituent present on the phosphazene ring, (b) the nucleophile, (c) the leaving group, and (d) the solvent. Apart from furnishing valuable insight into the mechanistic aspects, the (triphenylphosphazenyl)cyclotriphosphazene derivatives (**1–20**) provide excellent examples of different types of multispin systems in NMR spectroscopy.

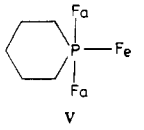
Experimental Section

All the solvents were purified by conventional procedures. The triphenylphosphazenyl derivative **1** was obtained by Keat's procedure[49] but with chloroform as the solvent,[1] and the fluoro derivative **2** was prepared by the fluorination of **1** with potassium fluoride in methyl cyanide.[1] The NMR measurements were carried out with the following spectrometers (solvents and standards are given in parentheses): ^{1}H, Bruker FT-270 spectrometer ($CDCl_3$, Me_4Si); ^{31}P, Bruker FT-400 spectrometer (162 MHz, Warwick, U.K.) or Bruker FT-270 spectrometer (109.4 MHz, University of Southern California, Los Angeles) ($CHCl_3$, 85% H_3PO_4); ^{19}F, Varian FT-80A spectrometer ($CHCl_3$, $CFCl_3$). The chemical shifts are quoted on the δ scale with upfield shifts negative.

Elemental analyses were obtained from the Ciba-Geigy Research Centre, Bombay, India, and University of London (U.K.). Mass spectra were obtained from PCMU Service, Harwell, U.K. (AEI MS902 instrument). IR spectra were recorded on a Carl-Zeiss UR-10 spectrometer.

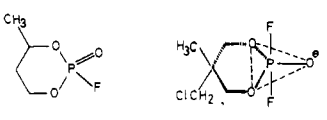
The compounds/mixtures of compounds were isolated from the reaction mixture by column chromatography (silica gel). Light petroleum ether (bp 60–80 °C), benzene, ethyl acetate, or a combination of these in different proportions was used as the eluant. The details of the re-

(36) Note that relative apicophilicities are in the order F > OPh > Cl > OCH_3 > NMe_2.[37]
(37) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: New York, 1976.
(38) It is interesting to note that, in V, the six-membered ring occupies diequatorial positions even at 100 °C.[39]



V

(39) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.
(40) (a) Frey, P. A., *Tetrahedron* **1982**, *38*, 1541. (b) Harris, P. J.; Fadely, C. L. *Inorg. Chem.* **1983**, *22*, 561.
(41) An in-plane attack of the methoxide has been envisaged by Corriu and co-workers for the reaction with the fluoro compound VI.[42a] Also a TBP intermediate (VII) with two apical fluorines has been suggested for the nucleophilic associated reactions of $Cl(O)P(-OCH_2C(CH_3)(CH_2Cl)CH_2O)$.[42b]



VI VII

(42) (a) Corriu, R. J. P.; Dutheil, J. P.; Lanneau, G. F.; Ould Kuda, S. *Tetrahedron* **1979**, *35*, 2889. (b) Corriu, R. J. P.; Dutheil, J. P.; Lanneau, G. F. *J. Am. Chem. Soc.* **1984**, *106*, 1060.
(43) Corriu, R. J. P.; Lanneau, G. F.; Declercq, D. *Phosphorus Sulfur* **1983**, *18*, 197.
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(45) Kumara Swamy, K. C.; Damodara Poojary, M.; Krishnamurthy, S. S.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1881.
(46) (a) Babu, Y. S.; Manohar, H.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1981**, 599. (b) Biddlestone, M.; Shaw, R. A.; Bullen, G. J.; Denn, P. E. *J. Chem. Soc., Chem. Commun.* **1974**, *56*.
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(49) Keat, R.; Miller, M. C.; Shaw, R. A. *J. Chem. Soc. A* **1967**, 1404.

Table IV. Experimental Details of the Reactions of $N_3P_3(NPPh_3)X_5$ [X = Cl (**1**), F (**2**)] with Sodium Methoxide[a]

phosphazene (amt, g, mmol)	amt of methoxide,[b] mmol	solvent (vol, cm^3)	column chromatogr results[c,d] products	yield, g	yield, %
1 (2.0, 3.4)	3.4	CH_3CN (160)	**1**	0.28	14.0
			3 (10) + **4** (1)	0.25	12.6[e]
1 (2.0, 3.4)	3.4	C_6H_6 (170)	**1**	0.66	32.5
			3 (5) + **4** (1)	0.20	10.1
1 (2.0, 3.4)	3.4	Et_2O (170)	**1**	0.68	34.2
			4	0.02	1.0
			3 (5) + **4** (1)	0.18	9.1
1 (2.0, 3.4)	6.8	CH_3CN (170)	**1** + **3** (10) + **4** (1)	0.22	11.0
			5 (15) + **6** (18) + **7** (9) + **8** (11) + **9** (2)	0.35	17.8[f]
1 (2.0, 3.4)	6.8	C_6H_6 (170)	**1** (2) + **3** (5) + **4** (1)	0.30	16.6
			(**3** + **4** + **5** + **7** + **8**)	0.02	1.1
			5 (1) + **7** (15) + **8** (10)	0.40	20.3
1 (2.0, 3.4)	10.2	CH_3CN (170)	(**3**–**8**)	0.25	12.7
			(**5**–**8**)	0.02	1.1
			9	0.25	12.8
			10 (50%) + others[g]	0.03	1.6
1 (2.0, 3.4)	10.2	C_6H_6 (180)	(**3**–**5** + **7** + **8**)	0.25	12.7
			(**5** + **7** + **8**)	0.03	1.6
			9	0.32	19.2
1 (2.0, 3.4)	13.6	CH_3CN (170)	(**5**–**10**)	0.30	15.2
			11	0.10	5.1
1 (2.0, 3.4)	13.6	C_6H_6 (180)	(**5** + **7**–**9**)	0.32	16.2
			11	0.10	5.1
1 (2.0, 3.4)[h]	23.8	CH_3CN (150)	**9** (1) + **11** (11)	0.20	10.1
			11	0.10	5.1
			12	0.10	5.2
2 (2.0, 3.95)	3.95	CH_3CN (150)	**2**	0.28	14.0
			14	0.30	14.6
			13 (5) + **14** (3)	0.25	12.2
			13	0.25	12.2
			(**15** + **16** + **17**)	0.05	2.4
2 (2.0, 3.95)	7.90	CH_3CN (160)	**13** (1) + **14** (1)	0.08	4.0
			15 (4) + **16** (5) + **17** (4)	1.30	61.9[i]
			(**18** + **19**)	0.02	1.0
2 (2.0, 3.95)	11.85	CH_3CN (150)	**15** (4) + **16** (5) + **17** (4)	0.30	14.3
			(**15**–**19**)	0.10	4.7
			19	0.10	4.7
			18 (1) + **19** (1)	0.60	28.0
2 (2.0, 3.95)	15.80	CH_3CN (160)	(**15**–**19**)	0.20	9.4
			18 (1) + **19** (1)	0.25	11.6
			18 (1) + **19** (1) + **20** (1)	0.10	4.6
			20	0.25	11.3
2 (0.7, 1.40)[h]	10.1	CH_3CN (100)	**20**	0.60	78.0
			(**20** + **26**)	0.10	13.0

[a] All the reactions were carried out at the reflux temperature of the solvent: time of addition of methoxide 30–40 min; total reaction time 24 h (unless otherwise stated). [b] Aliquots of the required amount taken from a 0.5 M solution of sodium methoxide in the solvent used. [c] For the structures of compounds **3**–**20** see Figures 1 and 7. [d] The ratios of isomers (established by ^1H NMR and TLC) are indicated in parentheses; the mixtures for which the exact ratio of products was not determined are shown together in parentheses. [e] Pure compound **3** was obtained by repeated fractional crystallization using dichloromethane–light petroleum ether (1:1). [f] A mixture of **5** and **6** (ratio 4:1) was separated by fractional crystallization. [g] Structures of the other compounds not assigned; see text for details. [h] See text (procedure b) for details. [i] **17** was isolated from this mixture by fractional crystallization; from the residue, **15** was isolated by preparative-scale TLC.

action conditions, the products obtained, and the yields are summarized in Table IV. Two typical reactions are described below.

(a) Reaction of $N_3P_3(NPPh_3)Cl_5$ (1) with 1 mol equiv of Sodium Methoxide in Methyl Cyanide. A solution of sodium methoxide (0.5 M) in methyl cyanide was first prepared by dissolving 1.15 g of sodium in 2.3 cm^3 of methanol with 50 cm^3 of methyl cyanide as the solvent and then making up the solution to 100 cm^3 by adding more methyl cyanide.

An aliquot of the above solution of sodium methoxide (6.8 cm^3, 3.4 mmol) diluted with methyl cyanide (50 cm^3) was added dropwise to a suspension of $N_3P_3(NPPh_3)Cl_5$ (**1**) (2.0 g, 3.4 mmol) in methyl cyanide (110 cm^3) at ~25 °C over a period of 40 min with continuous stirring. The mixture was heated under reflux for 24 h and filtered, and the solvent was evaporated in vacuo to obtain an oil, which soon solidified (~1.8 g). TLC examination of this mixutre (eluant benzene) showed three major spots at R_f values 0.85 [$N_3P_3(NPPh_3)Cl_5$ (**1**)], 0.66 [$N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3**)], and 0.36 [$N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ (**5**–**8**)] in the ratio 1:4:1; a minor component at an R_f value of 0.70 [$N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**4**)] could also be identified. Using benzene–light petroleum ether (1:1) as the eluant and developing the TLC plate thrice, it was possible to identify the spots corresponding to R_f values 0.66 and 0.70 more clearly; the approximate ratio of these two components was 10:1 (^1H NMR evidence also shows the same ratio). The reaction mixture was subjected to column chromatography, and the compounds isolated are shown in Table IV. When this reaction was carried out at 25 °C, the distribution of the products remained the same (TLC evidence).

(b) Reaction of $N_3P_3(NPPh_3)F_5$ (2) with 7 mol equiv of Sodium Methoxide. A solution of sodium methoxide (10 mmol) in methyl cyanide (50 cm^3) was added to a solution of **2** (0.7 g, 1.4 mmol) in methyl cyanide (50 cm^3) with continuous stirring, and the mixture was heated under reflux for 72 h. TLC examination of the reaction mixture showed the presence of only the compound $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**). The solvent was evaporated in vacuo from the solution. The resulting mixture was dissolved in benzene (100 cm^3) and filtered, and the solvent was evaporated from the filtrate in vacuo to obtain a solid. The ^1H NMR spectrum of this solid showed it to be mostly the compound $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**) (>90%). This compound was recrystallized from dichloromethane–light petroleum ether (1:1) to obtain pure **20** (mp 152 °C; 0.6 g, 78%).

The residual oil (0.10 g) contained compound **20** and a mixture (**26**) of hydrolyzed products (TLC and ^1H NMR evidence).

An analogous reaction with **1** gave $N_3P_3(NPPh_3)(OCH_3)_nCl_{5-n}$ [n = 3 (**9**), 4 (**11**), and 5 (**12**) in the ratio 3:4:2] along with hydrolyzed products (TLC and ^1H NMR evidence).

The following compounds/mixtures of compounds were isolated (figures in parentheses represent the relative proportions of the isomers). $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3** (9) + **4** (1)): Anal. Calcd for $C_{19}H_{18}Cl_4ON_4P_4$: C, 39.1; H, 3.1; N, 9.6. Found: C, 39.5; H, 3.9, N, 9.4. $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3**): mp 178 °C; R_f (TLC, silica gel, eluant benzene) 0.66. $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**4**): mp 174 °C, R_f 0.70. $N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ [**5** (4) + **6** (1)]: mp 149 °C; R_f 0.36. Anal. Calcd for $C_{20}H_{21}Cl_3O_2N_4P_4$: C, 41.1; H, 3.6. Found: C, 40.8; H, 3.6. $N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ [**7** (15) + **8** (10) + **5** (1)]: mp 143 °C; R_f 0.36. Anal. Calcd for $C_{20}H_{21}Cl_3O_2N_4P_4$: C, 41.4; H, 3.6. Found C, 41.3; H, 3.7. $N_3P_3(NPPh_3)(OCH_3)_3Cl_2$ (**9**): mp 138 °C; R_f 0.08, 0.65 [eluant benzene–ethyl acetate (5:1)]. Anal. Calcd for $C_{21}H_{24}Cl_2O_3N_4P_4$: C, 43.8; H, 4.2. Found: C, 44.3; H, 4.6. $N_3P_3(NPPh_3)(OCH_3)_4Cl$ (**11**): mp 128 °C; R_f 0.26. Anal. Calcd for $C_{22}H_{27}ClO_4N_4P_4$: C, 46.3; H, 4.7. Found: C, 46.8; H, 5.0. $N_3P_3(NPPh_3)(OCH_3)_5$ (**12**): mp 150 °C, R_f 0.10 (for C, H, N analyses see ref 50).

The mass spectra of the mixture **5** (15) + **6** (18) + **7** (9) + **8** (11) + **9** (2) and of the compounds **9** and **12** were recorded. They show $[M]^+$ and $[M - H]^+$ peaks (M = molecular ion).

The purity of the fluoro derivatives **13–20** has been confirmed by mass spectrometry. They showed peak corresponding to $[M]^+$, $[M - H]^+$, $[M - Ph]^+$, $[M - OCH_3 - 2H]^+$, and $[PPh_2 - 2H]^+$. The melting points and TLC R_f values of these compounds were as follows: $N_3P_3(NPPh_3)(OCH_3)F_4$ (**13**), mp 89 °C, R_f 0.62 (eluant benzene); $N_3P_3(NPPh_3)(OCH_3)F_4$ (**14**), mp 123 °C, R_f 0.66; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**15**), mp 126 °C, R_f 0.40; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**16**) (as a mixture with a small quantity of **15**), mp 105 °C, R_f 0.44; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**17**), mp 78 °C, R_f 0.44; $N_3P_3(NPPh_3)(OCH_3)_3F_2$ (**18**) (as a mixture with **19**, a ratio 1:1), mp 89 °C, R_f 0.62 [eluant benzene–ethyl acetate (5:1)]; $N_3P_3(NPPh_3)(OCH_3)_3F_2$ (**19**), mp 92 °C, R_f 0.64; $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**), mp 152 °C, R_f 0.26.

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Supplementary Material Available: IR spectroscopic data for compounds **1–20** (Table V) (2 pages). Ordering information is given on any current masthead page.

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Spectral Characterization and Kinetics of Formation of Hypoiodous Acid in Aqueous Solution

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The UV–visible absorption spectrum of the transient HOI species was obtained by utilizing the anion-exchange capacity of the mercury carbide polymer $[Hg_3CO(ClO_4)]_n$. The spectrum of HOI exhibited an absorption maximum at 278 nm in agreement with a recently reported spectrum obtained by a different method. The kinetics of hydrolysis of iodine to form HOI and I^- were studied at 20 °C and an ionic strength of 0.1 M by temperature-jump spectrophotometry. In contrast to the halogens, Cl_2 and Br_2, the rate of hydrolysis is controlled by the disproportionation of the conjugate base, I_2OH^-, with a rate constant of 994 ± 36 s^{-1}.

Introduction

The halogens, Cl_2, Br_2, and I_2, are known to undergo rapid hydrolysis, or water-assisted disproportionation, according to the equation

$$X_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOX + X^- + H^+ \quad (1)$$

The only complete set of kinetic results for this reaction was provided by Eigen and Kustin,[1] whose temperature-jump experiments established the general rate law

$$k_{obsd} = k_1 + k_{-1}\{[HOX][X^-] + [H^+][X^-] + [HOX][H^+]\} \quad (2)$$

These results are summarized in Table I together with the values of the relevant equilibrium constants. For X = Cl and Br, the values of k_1 and k_{-1} were determined directly from the respective intercepts and slopes of plots of k_{obsd} vs. $[HOX][X^-] + [H^+][X^-] + [HOX][H^+]$, whereas for X = I, k_{-1} was considered to be so much greater than k_1 that the intercept could not be determined with accuracy by this method and therefore k_1 was calculated from the relationship

$$k_1 = K_1 k_{-1} \quad (3)$$

However, it should be noted that this k_1 value is two orders of magnitude smaller than would have been obtained from the actual intercept, which is ca. 450 s^{-1}. Preliminary stopped-flow experiments, in which solutions of iodine and carbonate buffers were mixed, indicate that hydrolysis must be complete within the mixing

Table I. Summary of Rate and Equilibrium Constants at 20 °C and μ = 0.1 M

X	k_1, s^{-1}	k_{-1}, M^{-2} s^{-1}	K_1, M^2	ref
Cl	11.0	1.8×10^4	6.0×10^{-4}	1
	5.6[a]			2
			3.46×10^{-4}[b]	3
Br	110	1.6×10^{10}	6.9×10^{-9}	1
			4.46×10^{-9}	4
I	2.8[c]	4.4×10^{12}	4.3×10^{-13}[b]	1, 5
			3.13×10^{-13}[b,d]	6

[a] A calorimetric flow technique was used at 9.5 °C. [b] $\mu \simeq 0$. [c] Differs slightly from 3.0 s^{-1} quoted in the original reference[1] because a different value for K_1 was used (i.e. 6.25×10^{-13} M^2). [d] Obtained from a quadratic fit of all the current literature data.

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