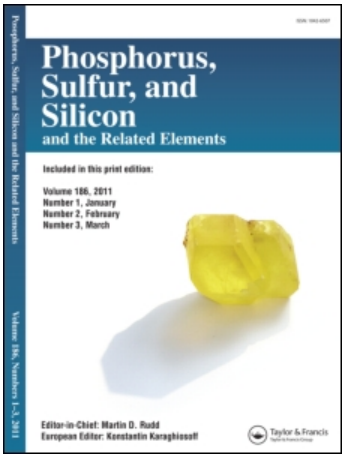

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Methanolysis of (Triphenyl Phosphazenyl) Celoro and Fluorocyclotriphosphazenes

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METHANOLYSIS OF (TRIPHENYL PHOSPHAZENYL)CHLORO AND FLUOROCYCLOTRIPHOSPHAZENES

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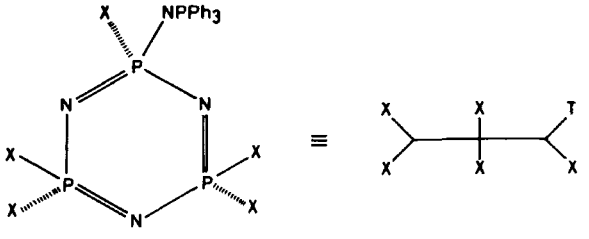
Abstract The different mechanistic features involved in the replacement of chlorine and fluorine atoms from $N_3P_3(NPPh_3)X_5$[X = Cl(I) or F(II)] by methoxide have been identified. An oxo-phosphazadiene derivative is also isolated.

Cyclophosphazenes bearing the triphenyl phosphazenyl(-$NPPh_3$) group have aroused interest in view of (a) the substituent effect exerted by the -$NPPh_3$ group in the aminolysis reactions, (b) conformation of the -$NPPh_3$ group with respect to the phosphazene ring and its relation to the four bond phosphorus-phosphorus coupling and (c) basicity studies[1-3]. We report here the results obtained on the reactions of triphenyl phosphazenyl derivatives $N_3P_3(NPPh_3)X_5$[X = Cl(I) or F(II)] with sodium methoxide in methyl cyanide.



X = Cl (I) or F (II)
T ≡ -$NPPh_3$

The methoxy derivatives $N_3P_3(NPPh_3)(X)_{5-n}(OCH_3)_n$ (X = Cl, F; n = 1-5) (II - XVI) are isolated either as pure compounds or as a mixture of isomers by column chromatography and their structures established from ^1H and ^{31}P NMR spectroscopy. The ^1H NMR data are shown in Fig.1.

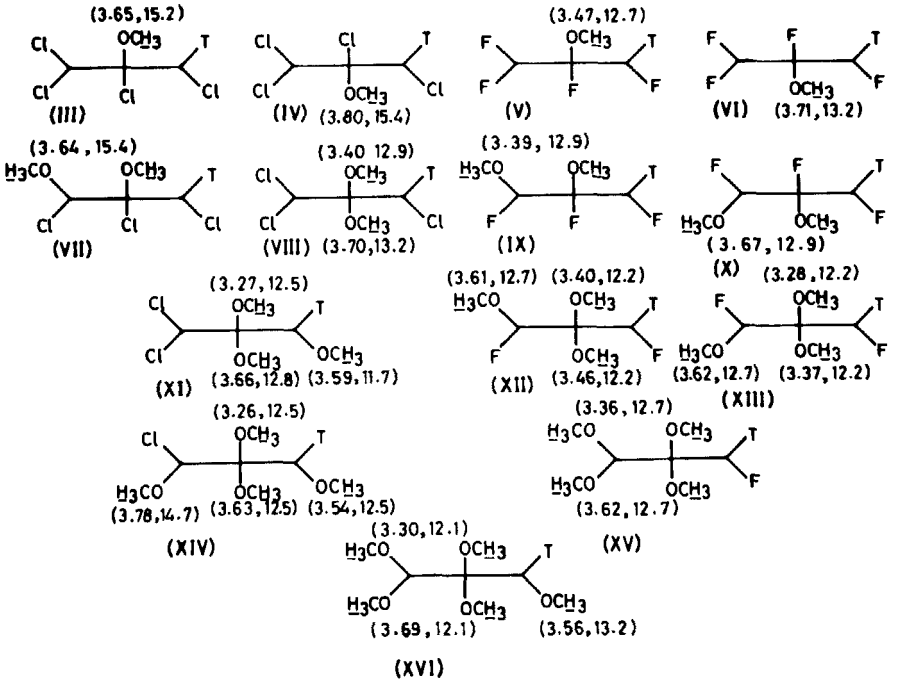


FIGURE 1 The structures of the methoxy derivatives $N_3P_3(NPPh_3)(X)_{5-n}(OCH_3)_n$; Chemical shifts ($\delta$,ppm) and coupling constants ($^3J^*(P-H)$,Hz) for $-OCH_3$ protons are given in parentheses.

The predominant isomer formed at the mono stage of chlorine replacement from compound I has a *cis*-non-geminal disposition of the methoxy and the $-NPPh_3$ substituents(Compound III). The replacement of the first fluorine atom from compound II proceeds exclusively by the nongeminal pathway and the geometrical isomers

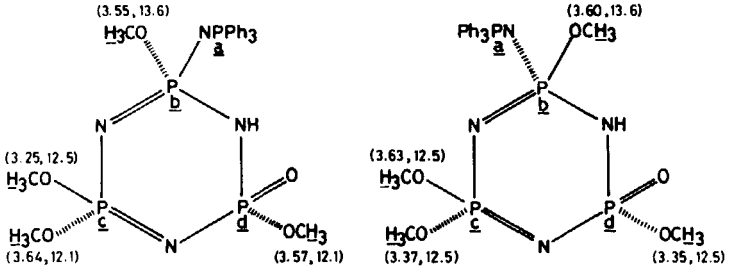
(V,VI) are formed in roughly equal proportions.

After the replacement of the first chlorine atom from compound I, attack by methoxide occurs at all phosphorus centres [$\equiv PCl_2$, $\equiv PCl(OCH_3)$ and $\equiv P(NPPh_3)Cl$] to yield a complex mixture products of which isomers VI and VII are the major components. Attack at a $\equiv PCl(R)$ [R = $-NPPh_3$, $-OCH_3$]assumes greater importance at the tris stage and the isomer, gem-$N_3P_3(NPPh_3)Cl_2(OCH_3)_3$(XI) is formed predominantly. For the fluoro compound II, substitution by methoxide at $\equiv P(NPPh_3)F$ does not occur till the *very last stage*. The fluoro (methoxy) derivative, $N_3P_3(NPPh_3)F(OCH_3)_4$(XV), contains a $\equiv P(NPPh_3)F$ group whereas the corresponding chloro derivative, $N_3P_3(NPPh_3)Cl(OCH_3)_4$(XIV), contains a $\equiv PCl(OCH_3)$ group.

The above results can be explained on the basis of a change-over from an $S_N2(P)$ to an $S_N1(P)$ mechanism for the reaction of the chloro derivative (I) and the absence of such a change-over for the fluoro analogue (II). With the sterically less-demanding methoxide, the incursion of an $S_N1(P)$ mechanism may occur at a later stage than that postualted for the dimethylaminolysis of compound I[4]. Thus compounds I and II provide a suitable pair of examples for studying the different mechanistic features which govern the nucleophilic substitution reactions of chloro and fluoro cyclophosphazenes.

Another notable feature of the present investigation is the isolation of the "hydroxy" derivative $N_3P_3(NPPh_3)(OCH_3)_4(OH)$ (XVII) from the reaction of compound I with an excess of sodium methoxide.

The ^{1}H and ^{31}P NMR data indicate that this derivative exists as an isomeric pair of *cis* and *trans* oxophosphazadienes (XVIIa and XVIIb). The ^{1}H NMR data [δ, ^{3}J*(P-H)] are shown below:



cis (XVIIa) trans (XVIIb)

(≡ P=O cis and trans to -$NPPh_3$)

The exclusive protonation at the ring nitrogen adjacent to the ≡P($NPPh_3$) (OCH_3) site can be explained by the much stronger electron releasing character of the -$NPPh_3$ substituent[1].

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