

Synthesis of Trimethylphosphazeny- and Triphenylphosphazeny-fluorocyclotriphosphazatrienes by a Silylation Method

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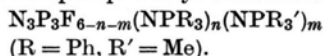
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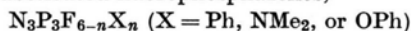
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Trimethylphosphazenyfluorocyclotriphosphazatrienes,
Triphenylphosphazenyfluorocyclotriphosphazatrienes,
Isomers, Silylation Method, Steric Effects

The synthesis of trimethylphosphazeny- and triphenylphosphazeny-fluorocyclotriphosphazatrienes, $N_3P_3F_{6-n}(NPR_3)_n$, by a silylation method using Me_3SiNPR_3 ($R = Me$ or Ph) is reported. More phosphazeny groups can be introduced if $R = Me$ than if $R = Ph$. Isomers have been isolated, as have been mixed phosphazeny derivatives,



Substituted fluorophosphazenes,



also undergo similar reactions.

Silylation methods have been used extensively to link certain substituents to non-metals, especially to phosphorus *e.g.* $=P-A + R_3SiB \rightarrow =P-B + R_3SiA$ ^{1,2} ($A =$ usually Cl or F ; $B = NMe_2, OMe, SR, \text{ etc.}$). Few syntheses of phosphazeny derivatives have however been reported by this method³⁻⁵, and these were confined to mononuclear phosphorus compounds. Phosphazeny-cyclophosphazenes have recently aroused a good deal of interest, because of the large electron-releasing capacity of the phosphazeny group in protonation studies⁶, and in particular because of a novel type of conformational isomerism displayed by such substituents^{7,8}; this has been discussed in detail elsewhere^{9,10}.

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We now report an extensive series of phosphazeny derivatives prepared from hexafluoro-, $N_3P_3F_6$, and substituted hexafluoro-cyclotriphosphazatriene, $N_3P_3F_{6-n}X_n$ ($X = Ph, NMe_2, \text{ or } OPh$; $n = 1$ or 2) substrates and silylating agents Me_3SiNPR_3 ($R = Me$ or Ph) (see Table).

All reactions were carried with the stoichiometric quantities of reagents in the absence of solvent at 80–100 °C. Isomeric pairs were isolated *e.g.* **2** and **3**, **6** and **7**, **8** and **9**, **11** and **12**, **16** and **17**, and are probably present in other cases, *e.g.* **14** where the presence of other isomers was indicated, but these have, as yet, not been isolated.

The products are soluble in the usual organic solvents. Compound **7** is remarkably soluble in water but decomposes on boiling the solution.

It is worth noting that under our reaction conditions only two $NPPH_3$ substituents can be introduced *e.g.* $N_3P_3F_4(NPPH_3)_2$; we noted earlier that in the reaction between triphenylphosphazene, Ph_3PNH , and hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, a similar limit pertained¹¹. The cause is probably the same in both systems, largely steric in origin. However, the smaller (and probably also more nucleophilic) trimethylphosphazeny reagent, Me_3SiNPM_3 , enables up to three such groups to be introduced, *e.g.* compounds **6** and **7** (*cf.* also compounds **8** and **9**).

The phosphazenylation appears to take place nongeminally, and where applicable, reaction occurs at $\equiv PF_2$ groups in preference to $\equiv PFX$ groups (*cf.* compounds **10–18**). A detailed discussion of the compounds reported here will be published elsewhere.

Table. Phosphazenyfluorocyclotriphosphazatrienes.

Compound	m.p. [°C]
$N_3P_3F_5(NPPH_3)$	(1) 81.5
$N_3P_3F_4(NPPH_3)_2$	(2) 195
$N_3P_3F_4(NPPH_3)_2$	(3) 235
$N_3P_3F_5(NPMe_3)$	(4) 45
$N_3P_3F_4(NPMe_3)_2$	(5) 117
$N_3P_3F_3(NPMe_3)_3$	(6) 245
$N_3P_3F_3(NPMe_3)_3$	(7) 202
$N_3P_3F_3(NPPH_3)(NPMe_3)_2^*$	(8) 70
$N_3P_3F_3(NPPH_3)(NPMe_3)_2^*$	(9) 197
$N_3P_3F_4Ph(NPMe_3)$ viscous oil	(10)
$N_3P_3F_3Ph(NPMe_3)_2$ „ „	(11)
$N_3P_3F_3Ph(NPMe_3)_2$ „ „	(12)
$N_3P_3F_3Ph_2(NPMe_3)^+$ „ „	(13)
$N_3P_3F_2Ph_2(NPMe_3)_2^+$	(14)
$N_3P_3F_3Ph_2(NPMe_3)^\neq$	(15) 93
$N_3P_3F_4(NMe_2)(NPPH_3)^*$	(16) 95
$N_3P_3F_4(NMe_2)(NPPH_3)^*$	(17) 119
$N_3P_3F_4(OPh)(NPMe_3)^*$ viscous oil	(18)

Starting materials ⁺gem.- $N_3P_3F_4Ph_2$, [≠]*cis*- $N_3P_3F_4Ph_2$, ^{*} $N_3P_3F_5X$ ($X = NMe_2, OPh, \text{ or } NPPH_3$).

Experimental

All manipulations were carried out under an atmosphere of argon. Trimethylphosphine was obtained from its hydrochloride by a specially developed method¹². $N_3P_3F_6$ ¹³, $N_3P_3PhF_5$ ¹⁴, gem.- $N_3P_3Ph_2F_4$ ¹⁵, cis.- $N_3P_3Ph_2F_4$ ¹⁴, and $N_3P_3F_5(NMe_2)$ ¹⁶ were prepared by literature methods. The synthesis of $N_3P_3F_5(OPh)$ is new¹². Me_3SiNPR_3 (R = Me or Ph) was prepared by BIRKHOFFER'S method¹⁷. Three typical syntheses are described.

a) $N_3P_3F_3(NPMe_3)_3$ (6 and 7)

The reaction of $N_3P_3F_6$ (10 g) with Me_3SiNPM_3 (20 g) at a 100 °C for 24 h yielded 18 g crude product. Column chromatography of 6 g of this on silica gel, eluent methanol-acetone (5:8) gave first 4.1 g (66%) of 7, m.p. 202 °C (from acetone) and then 0.5 g (8%) of isomer 6, m.p. 245 °C (identified by mass-spectrometry only).

$C_9H_{27}F_3N_6P_6$ (462)

Calcd C23.4 H5.9 F12.4 N18.2 P40.3,
Found isomer 7 C23.6 H5.8 F12.3 N18.2 P39.8.

b) $N_3P_3Ph_2F_3(NPMe_3)$ (13)

The reaction of gem.- $N_3P_3Ph_2F_4$ (8 g) with Me_3SiNPM_3 (3.6 g) at 90–100 °C for 3 h, followed by pumping in high vacuum, and chromatography on silica gel, eluent methanol-acetone (1:1) gave compound 13 as a viscous oil, 8 g (84%).

$C_{15}H_{19}F_3N_4P_4$ (436)

Calcd C41.3 H4.4 F13.1 N12.8 P28.4,
Found C41.9 H4.5 F13.3 N12.8 P28.1.

c) $N_3P_3F_4(NMe_2)(NPPPh_3)$ (16 and 17)

The reaction of $N_3P_3F_5(NMe_2)$ (8 g) with Me_3SiNPh_3 (10.2 g) at 90–100 °C for 24 h, followed by pumping in high vacuum gave 15.2 g solid crude product. 8 g of this was chromatographed on silica gel, eluent benzene-acetone (10:0.5). Yield (in order of elution) of isomer 17 1.4 g (17%), isomer 16 0.9 g (11%); an analytically pure mixture of isomers 17 and 16 (5.3 g) was also obtained.

$C_{20}H_{21}F_4N_5P_4$ (531)

Calcd C45.2 H4.0 F14.3 N13.2 P23.3,
Found isomer 17 C45.2 H3.9 F14.5 N13.3 P22.7,
Found isomer 16 C45.2 H4.0 F14.5 N13.4 P23.3.

All compounds reported in this paper had the correct mass-spectrometric molecular weight.

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