Synthesis of Trimethylphosphazenyl- and Triphenylphosphazenyl-fluorocyclotriphosphazatrienes by a Silylation Method

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

$N_3P_3F_{6-n-m}(NPR_3)_n(NPR_3')_m$
(R = Ph, R′ = Me).

Substituted fluorophosphazenes,

$N_3P_3F_{6-n}X_n$ (X = Ph, NMe_2, or OPh)

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, *etc.*). Few syntheses of phosphazenyl derivatives have however been reported by this method[3–5], and these were confined to mononuclear phosphorus compounds. Phosphazenyl-cyclophosphazenes have recently aroused a good deal of interest, because of the large electron-releasing capacity of the phosphazenyl group in protonation studies[6], 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 phosphazenyl derivatives prepared from hexafluoro-, $N_3P_3F_6$, and substituted hexafluoro-cyclotriphosphazatriene, $N_3P_3F_{6-n}X_n$ (X = Ph, NMe_2, 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 pertained[11]. The cause is probably the same in both systems, largely steric in origin. However, the smaller (and probably also more nucleophilic) trimethylphosphazenyl reagent, $Me_3SiNPMe_3$, 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. Phosphazenylfluorocyclotriphosphazatrienes.

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)	
$N_3P_3F_3Ph_2(NPMe_3)$ ≠	(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, or $NPPh_3$).

Experimental

All manipulations were carried out under an atmosphere of argon. Trimethylphosphine was obtained from its hydrochloride by a specially developed method[12]. $N_3P_3F_6$ [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 new[12]. Me_3SiNPR_3 (R = Me or Ph) was prepared by BIRKHOFER's method[17]. 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 $Me_3SiNPMe_3$ (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	C 23.4	H 5.9	F 12.4	N 18.2	P 40.3,
Found isomer **7**	C 23.6	H 5.8	F 12.3	N 18.2	P 39.8.

b) $N_3P_3Ph_2F_3(NPMe_3)$ (**13**)

The reaction of gem.-$N_3P_3Ph_2F_4$ (8 g) with $Me_3SiNPMe_3$ (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	C 41.3	H 4.4	F 13.1	N 12.8	P 28.4,
Found	C 41.9	H 4.5	F 13.3	N 12.8	P 28.1.

c) $N_3P_3F_4(NMe_2)(NPPh_3)$ (**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	C 45.2	H 4.0	F 14.3	N 13.2	P 23.3,
Found isomer **17**	C 45.2	H 3.9	F 14.5	N 13.3	P 22.7,
Found isomer **16**	C 45.2	H 4.0	F 14.5	N 13.4	P 23.3.

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

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