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Fluoro- λ -Monophosphazenes and Fluoro-1.3-Diaza- $2\delta^5$, $4\delta^5$ -Diphosphetidines

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Fluoro- λ^5 -Monophosphazenes and Fluoro-1.3-Diaza- $2\lambda^5$, $4\lambda^5$ -Diphosphetidines

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34 new fluoro- λ^5 -monophosphazenes and 37 new fluoro-1.3-diaza- $2\lambda^5$, $4\lambda^5$ -diphosphetidines have been prepared by applying the STAUDINGER reaction on λ^3 -phosphorus compounds (eq. (1)).

$$R_n PF_{3-n} + N_3 C_6 H_4 X \longrightarrow 1/z \left[R_n PF_{3-n} = NC_6 H_4 X \right]_z + N_2$$
 (1)
 $(n = 0, 1, 2; R = R_2 N, (CH_2)_5 N, O(CH_2)_4 N, RO, (CH_2 O)_2, alkyl, aryl; X = H, CH_3, Cl, Br, NO_2)$

The logarithm of the rate constant k_1 ' is lineary correlated with the sum of the substituent constants $\mathcal{S}_{\mathbf{I}}^{\mathsf{P}}$. PF $_3$ does not react. Apart from a few exceptions (R= $\mathrm{Et}_2\mathsf{N}$, (CH $_2$) $_5\mathsf{N}$; X= NO_2) the diffuorides RPF $_2$ form diazadiphosphetidines, whereas the monofluorides R $_2$ PF - except the cyclic (CH $_2$ O) $_2$ PF - are more likely to yield monophosphazenes.

In solution the majority of the diphosphetidines dissociates into monophosphazenes. The influence of the substituents R and X on the structure of the compounds and their n.m.r. data is discussed.