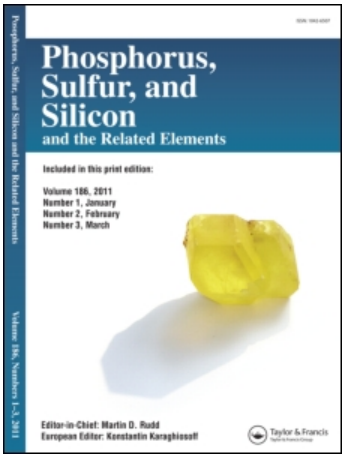

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Fluoro-λ-Monophosphazenes and Fluoro-1.3-Diaza-2δ⁵,4δ⁵-Diphosphetidines

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

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

$$R_nPF_{3-n} + N_3C_6H_4X \longrightarrow 1/z\ [R_nPF_{3-n}{=}NC_6H_4X]_z + N_2 \qquad (1)$$

(n= 0, 1, 2; R= R_2N, $(CH_2)_5N$, $O(CH_2)_4N$, RO, $(CH_2O)_2$, 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 σ_I^P. PF_3 does not react. Apart from a few exceptions (R= Et_2N, $(CH_2)_5N$; X= NO_2) the difluorides RPF_2 form diazadiphosphetidines, whereas the monofluorides R_2PF - except the cyclic $(CH_2O)_2PF$ - 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.