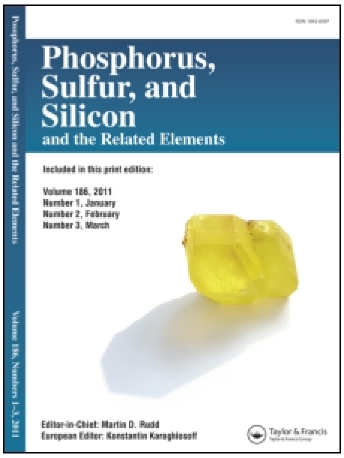

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SYNTHESIS AND REACTIVITY OF N-PHOSPHANYL PHOSPHAZENES

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Abstract The reaction of phosphorus(III) halides, $R'_{3-n}PX_n$ (X = F, Cl), with silyl azides, R_3SiN_3, are described. N-silylated halophosphazenes, $R'_{3-n}PX_n{=}N{-}SiR_3$, are only obtained with fluorophosphanes having bulky substituents. Usually azidophosphanes, $R'_{3-n}P(N_3)_n$, are formed as intermediates. These may react both as azide and as phosphane components in the Staudinger reaction forming N-phosphanyl phosphazenes, $R'_2P{-}N{=}PR_3$, or azidophosphazenes, $R'_{3-n}P(N_3)_n{=}NY$ (n = 1, 2), which can be converted into di- and triphosphazenes, $R'_{3-n}P(N{=}PR_3)_n{=}NY$. A one pot procedure for preparing N-phosphanyl phosphazenes had been developed. Replacement as well as oxidation reactions of $Cl_2P{-}N{=}PPh_3$ and its derivatives are presented.

REACTIONS OF FLUOROPHOSPHANES WITH SILYL AZIDES

Continuing our investigations on the oxidation of fluorophosphanes with aryl azides,[1] we investigated the reaction of the fluorophosphanes Ph_2PF (1), $PhOPF_2$ (2), $C_5H_{10}NPF_2$ (3), Et_2NPF_2 (4), $(Et_2N)_2PF$ (5), and $(i\text{-}Pr_2N)_2PF$ (6) with silyl azides. The products and the conditions of the reaction with Me_3SiN_3 are listed in Table I.

TABLE I Reactions of fluorophosphanes, RR'PF, with Me_3SiN_3.

Nr.	R	R'	ϑ/°C	products
1	Ph	Ph	20	N_2, Me_3SiF, c-$(RR'PN)_n$
2	PhO	F	70	N_2, Me_3SiF, and oligomeric or polymeric phosphazenes, $(>PN)_n$, (in all cases fluorine-free!).
3	$C_5H_{10}N$	F	> 90	
4	Et_2N	F	> 90	
5	Et_2N	Et_2N	80	N_2, Me_3SiF, $(RR'PN)_n$, $RR'PN_3$
6	i-Pr_2N	i-Pr_2N	100	N_2, $RR'PF{=}N{-}SiMe_3$; $(RR'PF{=}N{-}PRR'$, $RR'PF{=}N{-}PRR'{=}N{-}SiMe_3)$

The fluorides 1 - 5 were found to lead to oligomeric phosphazenes based on the intermediate formation of azidophosphanes and their autooxidative decomposition (eqs. (1) and (2)).

$$RR'PF + Me_3SiN_3 \longrightarrow RR'PN_3 + Me_3SiF \qquad (1)$$

$$RR'PN_3 \longrightarrow 1/n\ (RR'P{=}N)_n + N_2 \qquad (2)$$

The primary formation of N-silylated fluorophosphazenes and their following condensation as alternative reaction pathway (eq. (3)) can be excluded surely.

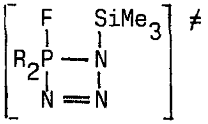
$$RR'PF + Me_3SiN_3 \not\xrightarrow[-N_2]{} RR'PF{=}N{-}SiMe_3 \xrightarrow[-Me_3SiF]{} 1/n\ (RR'P{=}N)_n \qquad (3)$$

In the case of 5 the azidophosphane $(Et_2N)_2PN_3$ could be detected by NMR spectroscopy. With the difluorides 2, 3, and 4 F-free oligophosphazenes are obtained in all cases. Obviously, the replacement of the second fluoride by azide is much faster than the autooxidation of $RFPN_3$.

$(i\text{-}Pr_2N)_2PF$ (6) behaves entirely different. It forms with trimethylsilylazide the N-silylated fluorophosphazene (eq. (4)) beside small amounts of $R_2PF{=}N{-}PR_2$ and $R_2PF{=}N{-}PR_2{=}N{-}SiMe_3$. The latter is assumed to be formed with R_2PN_3 as intermediate, because the N-silylated fluorophosphazene does not react with an excess of $(i\text{-}Pr_2N)_2PF$.

$$(i\text{-}Pr_2N)_2PF + Me_3SiN_3 \longrightarrow (i\text{-}Pr_2N)_2PF{=}N{-}SiMe_3 + N_2 \qquad (4)$$

In all probability both reactions, i. e. the exchange of fluoride by azide as well as the oxidative imination (Staudinger reaction) pass through the same transition state:



Bulky substituents at phosphorus complicate the Me_3SiF elimination. The same effect is observed with bulky substituents at silicon. Accordingly, $(Et_2N)_2PF$ (5) forms with $t\text{-}BuPh_2SiN_3$ the N-silylated phosphazene, $(Et_2N)_2PF{=}N{-}SiPh_2(t\text{-}Bu)$, whereas with Me_3SiN_3 the replacement reaction takes place only.

SYNTHESIS OF AZIDOPHOSPHANES AND THEIR APPLICATION IN THE STAUDINGER REACTION[2]

Starting from P(III) chlorides azidophosphanes are much easier formed than from fluorophosphanes. The substitution of chloride by azide using Me_3SiN_3 or metal azides already takes place at low temperatures. Recently azidophosphanes have been of primary interest concerning their special application as precursor for the intermediate formation of phosphonitriles, $R_2P{\equiv}N$.[3-6] On the other hand, azidophosphanes are also versatile reactants in the Staudinger reaction. They contain in the same molecule a nucleophilic P atom and the electrophilic azide group. Therefore, they may react both as azide (eq. (5)) and as phosphane component (eq.7).

We studied the formation of azidophosphanes from PCl_3, Et_2NPCl_2, $(Et_2N)_2PCl$, and other P(III) chlorides and found that the azide formation is not complete at room temperature. The extent of the exchange of chloride by azide varies in the range of about 15% for Et_2NPCl_2 up to 60% for PCl_3. Solutions of azidophosphanes with concentrations < 1M are sufficiently stable at room temperature. The rate of autooxidation (eq. (2)) of Cl_2PN_3 is slower than that of $(Et_2N)ClPN_3$, whereas the rate of their reaction with PPh_3 (eq. (5)) behaves oppositely (see Table II).

$$RR'PN_3 + PPh_3 \longrightarrow RR'P{-}N{=}PPh_3 + N_2 \qquad (5)$$

TABLE II Rate constants of the reactions (2) and (5) in toluene

Compound	k_2/s^{-1} (60°C)	$\tau_{1/2(2)}$/min	$k_5/lmol^{-1}s^{-1}$ (25°C)
Cl_2PN_3	$3{,}1\cdot 10^{-5}$	372 ± 20	$23{,}6\cdot 10^{-4}$
$(Et_2N)ClPN_3$	$7{,}6\cdot 10^{-5}$	152 ± 8	$2{,}2\cdot 10^{-4}$

This fact allows to carry out the reaction of phosphorus chlorides with Me_3SiN_3 or NaN_3 in the presence of organylphosphanes as a one pot reaction (eq. (6)).

$$RR'PCl + MN_3 + PR''_3 \longrightarrow RR'P{-}N{=}PR''_3 + MCl + N_2 \qquad (6)$$

(M = Me_3Si, Na; R, R' = Cl, Et_2N; R" = Ph, Bu, c-Hex, Et_2N)

The reactivity of the azidophosphanes decreases with an increasing number of amido groups in the molecule. $(Et_2N)_2PN_3$ does not react with PPh_3, but with the more nucleophilic $(Et_2N)_3P$ forming $(Et_2N)_2P{-}N{=}P(NEt_2)_3$.

Azidophosphanes are sufficiently nucleophilic to be oxidized by azides. Concerning this, $(Et_2N)P(N_3)_2$, which is intermediately formed in the reaction of Et_2NPCl_2 with Me_3SiN_3 in the molar ratio 1 : 2, can be oxidized by PhN_3 yielding the diazidophosphazene $(Et_2N)(N_3)_2P{=}NPh$. This reacts very easily with PPh_3 forming di- and triphosphazenes (eq. (7)).

$$RP(N_3)_2 + PhN_3 \xrightarrow[-N_2]{} RP(N_3)_2P{=}NPh \xrightarrow[-N_2]{+PPh_3} R(N_3)_x(Ph_3P{=}N)_{2-x}P{=}NPh \quad (7)$$

$(R = Et_2N)$

REACTIONS OF N-DICHLOROPHOSPHANYL TRIPHENYLPHOSPHAZENE, $Cl_2P{-}N{=}PPh_3$ [7]

$Cl_2P{-}N{=}PPh_3$ was firstly prepared by Fluck and Hösle[8], however, in a more difficult way. Now, it can be obtained in high yields using the procedure described above (eq. (6)). It reacts with MeOH, EtOH, PhOH, EtSH, H_2O, $P(NEt_2)_3$, and SbF_3 forming N-phosphanyl ($Ph_3P{=}N{-}PX_2$ (X = OEt, OPh, SEt, NEt_2, F)) or N-phosphinoyl phosphazenes ($Ph_3P{=}N{-}PH(O)X$ (X = Cl, OH, OMe, OEt, F)), resp.(eq. (8)).

$$Ph_3P{=}N{-}PCl_2 + 2\,X^- \xrightarrow[-\,2Cl^-]{} Ph_3P{=}N{-}PX_2 \longrightarrow Ph_3P{=}N{-}PH(O)X \quad (8)$$

The N-phosphanyl compounds are oxidized by NO_2 or sulfur yielding the corresponding N-phosphoryl derivatives ($Ph_3P{=}N{-}P(O)X_2$ (X = Cl, OPh, OEt, SEt, F)) or the N-thiophosphoryl compounds, $Ph_3P{=}N{-}P(S)X_2$ (X = Cl, F, OPh), resp. (eqs. (9) and (10)).

$$Ph_3P{=}N{-}PX_2 + NO_2 \longrightarrow Ph_3P{=}N{-}P(O)X_2 + NO \quad (9)$$

$$Ph_3P{=}N{-}PX_2 + S \longrightarrow Ph_3P{=}N{-}P(S)X_2 \quad (10)$$

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