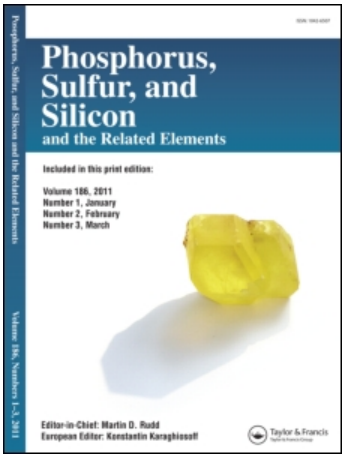

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NEW POLYHETEROATOMIC CYCLIC MOLECULES CONTAINING ELEMENTS of the 13.-16. GROUP

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NEW POLYHETEROATOMIC CYCLIC MOLECULES CONTAINING ELEMENTS OF THE 13.–16. GROUP

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During studies of the reactions of —N(H)SiMe$_3$ and —N(Me)SiMe$_3$ derivatives of Cl$_3$PNSO$_2$Cl with acetonitrile and BCl$_3$ we have obtained six-membered polyheteroatomic cycles ⌈P(Cl$_2$)NSO$_2$(Cl)N(H)C(Me)N⌉ and ⌈P(Cl$_2$)NS(O)(Cl)OB(Cl$_2$)N(Me)⌉.[1,2] In the system Ph$_2$PCl$_3$, H$_2$NSO$_2$Cl and HN(SiMe$_3$)$_2$ we have identified and isolated several P—N—S cycles, e.g. the reaction of Ph$_2$PCl$_3$ with H$_2$NSO$_2$Cl gives Ph$_2$ClPNSO$_2$Cl[3] which with HN(SiMe$_3$)$_2$ reacts to ⌈S(O$_2$)N(H)P(Ph)$_2$N(H)SO$_2$N(H)P(Ph)$_2$N(H)⌉, ⌈S(O$_2$)N(H)S(O$_2$)N(H)P(Ph)$_2$N(H)P(Ph)$_2$N(H)⌉ and ⌈[S(O$_2$)N(H)P(Ph)$_2$NP(Ph)$_2$N(H)]$^+$⌉ Cl$^-$; Ph$_2$PCl$_3$ with HN(SiMe$_3$)$_2$ gives N[P(Ph)$_2$N(H)SiMe$_3$]$_2^+$ Cl$^-$, and H$_2$NSO$_2$Cl with HN(SiMe$_3$)$_2$ leads to SO$_2$(NHSiMe$_3$)$_2$. The reaction of Ph$_2$PCl$_3$ with HN(SiMe$_3$)$_2$ gives N(P(Ph)$_2$NHSiMe$_3$)$_2$Cl in a very good yield which was further used to syntheses of metal-containing heterocycles. By the reaction of N[P(Ph)$_2$N(H)SiMe$_3$]$_2^+$Cl$^-$ with some covalent halogenides we have obtained six-membered heterocycles containing B, As, In, and Sn. The same cyclic compounds can also obtained by the reaction of N[P(Ph$_2$)NH$_2$]$_2^+$Cl$^-$ or HN(P(R$_2$)N(H)SiMe$_3$)$_2$ with covalent halogenides.[4–6] However, the synthetic route via *N[P(Ph)$_2$NHSiMe$_3$]$_2^+$Cl$^-$ is more convenient and gives the compounds in almost quantitative yields. The identity of all compounds was unambiguously establised by their X-ray structure determination.*

Keyword: Heterocyclophosphazenes

During our previous studies of the reactions of —N(H)SiMe$_3$ and —N(Me)SiMe$_3$ derivatives of Cl$_3$PNSO$_2$Cl (**1**) with acetonitrile and BCl$_3$, we have obtained and structurally fully characterized two new six-member polyheteroatomic cycles according to the Scheme 1.[1,2]

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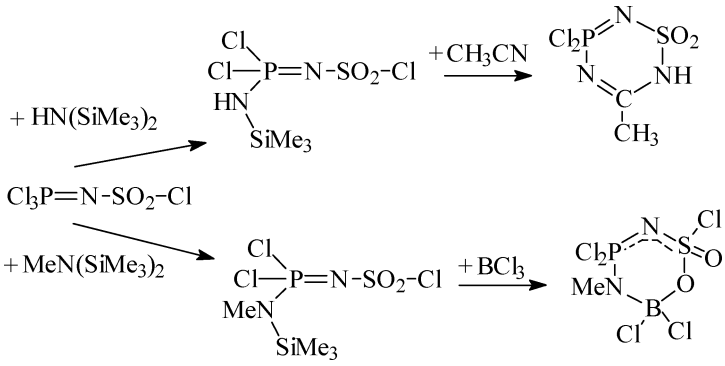
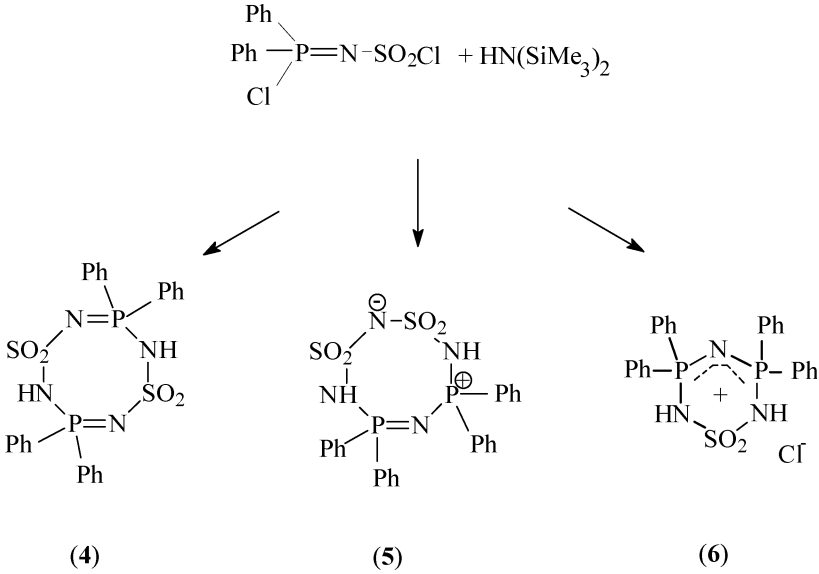


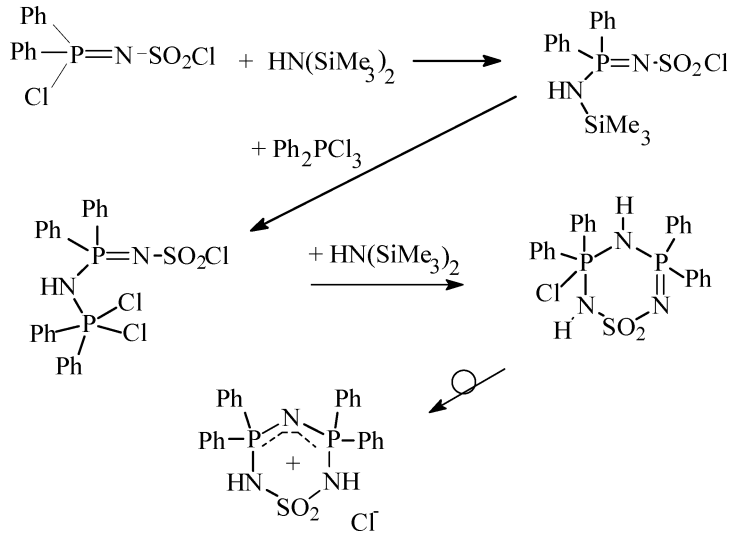
SCHEME 1 Formation of P—N—C and P—N—S—O—B six-member cycles.

In the present research we have concentrated on the reaction of diphenyl derivative of **1**, $Ph_2ClPNSO_2Cl$ (**2**) and a phosphorus analogue of **1**, $Cl_3PNPOCl_2$ (**3**) with $HN(SiMe_3)_2$ (HMDS) and $MeN(SiMe_3)_2$ (HpMDS), respectively, and their subsequent reactions with some covalent halogenides.

From the reaction mixture of **2** with HMDS we have isolated three P—N—S cycles, two eight-member neutral molecules and one six-member cation isolated as a chloride salt (Scheme 2).



SCHEME 2 Products from the reaction system $ClPPh_2NSO_2Cl$ with HMDS.



SCHEME 3 Reaction mechanism of the formation of P—N—S six-member cation in the system $ClPPh_2NSO_2Cl$ with HMDS.

The compound **2** is prepared according to Haubold and Fluck.[3]

$$Ph_2PCl_3 + NH_2SO_2Cl \longrightarrow ClP(Ph_2)NSO_2Cl + 2HCl \qquad (1)$$

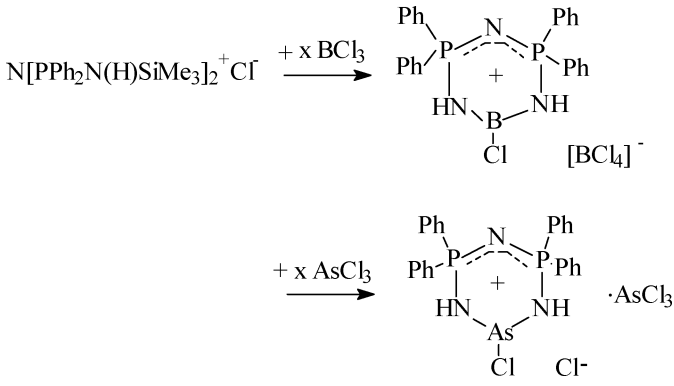
While the formation of eight-member cycles **4** and **5** can be explained easily by a subsequent condensation of, e.g., one molecule of **2** substituted by —N(H)$SiMe_3$ group both on P and S atoms with an unsilylated one (head-to-tail or head-to-head), the formation of **6** is more complex and requires, e.g., a presence of unreacted phosphorane in the reaction mixture (Scheme 3).

However, the reaction 1 is in fact an equillibrium reaction with approx. 80% conversion and thus the reaction mixture contains not only product **2** but the reactants, too. We have therefore separately examined reactions of the reactants, Ph_2PCl_3 and H_2NSO_2Cl, with HMDS.

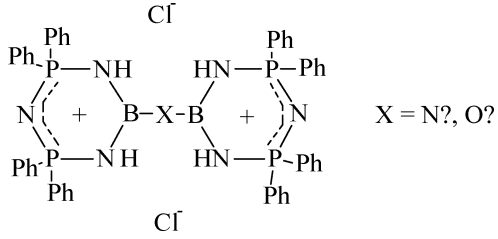
H_2NSO_2Cl reacts with HMDS to give N,N′-bis(trimethylsilyl)-sulfamide $SO_2[N(H)SiMe_3]_2$ with almost quantitative yield, while the reaction of Ph_2PCl_3 yields acyclic phosphazenium salt $[Me_3SiN(H)PPh_2NPPh_2N(H)SiMe_3]^+Cl^-$ (**7**).

This salt **7** was subsequently used to the synthesis of boron and arsenic containing six-member heterocyclic cations (Scheme 4).

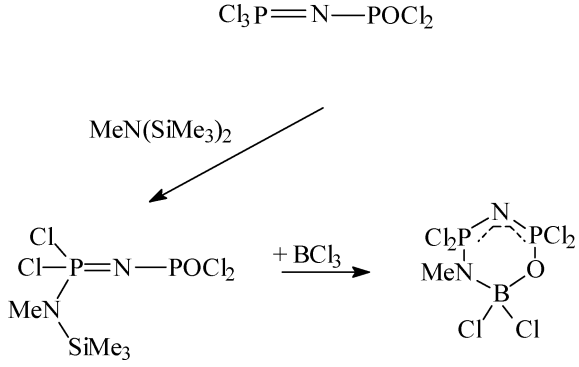
If the reaction of **7** with BCl_3 was performed in 1:1 molar ratio, we have obtained by a still not quit clear reaction mechanism a dimeric planar cyclic cation (Scheme 5).



SCHEME 4 Reaction of **7** with BCl_3 and $AsCl_3$.



SCHEME 5 Dimeric P—N—B cation.



SCHEME 6 Formation of P—N—O—B six-member cycle.

$Cl_3PNPOCl_2$ (**3**) reacts with HpMDS forming $Me_3SiN(Me)PCl_2NPOCl_2$ which gives with BCl_3 a cyclic P—N—O—B compound (Scheme 6).

The identity of all compounds, which have been described was unambiguously established by their x-ray structures.

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