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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 Cl₃PNSO₂Cl with acetonitrile and BCl₃ we have obtained six-membered polyheteroatomic cycles $\lceil P(Cl_2)NSO_2(Cl)N(H) \rceil$ $\lceil P(Cl_2)NS(O)(Cl)OB(Cl_2)N(Me) \rceil$. 1,2 In the sys-C(Me)Nand Ph_2PCl_3 , H_2NSO_2Cl and $HN(SiMe_3)_2$ we have identified and isolated several P-N-S cycles, e.g. the reaction of Ph_2PCl_3 with H_2NSO_2Cl gives $Ph_2ClPNSO_2Cl^3$ which with $HN(SiMe_3)_2$ reacts to $\lceil S(O_2)N(H)P(Ph)_2N(H)SO_2N(H)P(Ph)_2N(H) \rceil$, $\lceil S(O_2)N(H)S(O_2)N(H)P(Ph)_2N(H)P(Ph)_2N(H) \rceil$ and $[S(O_2)N(H)]$ $P(Ph)_2NP(Ph)_2N(H)]^+$ Cl^- ; Ph_2PCl_3 with $HN(SiMe_3)_2$ gives $N[P(Ph)_2N(H)SiMe_3]_2^+$ Cl^- , and H_2NSO_2Cl with $HN(SiMe_3)_2$ leads to $SO_2(NHSiMe_3)_2$. The reaction of Ph_2PCl_3 with $HN(SiMe_3)_2$ gives $N(P(Ph)_2NHSiMe_3)_2Cl$ in a very good yield which was further used to syntheses of metal-containing heterocycles. By the reaction of $N[P(Ph)_2N(H)SiMe_3]_2^+Cl^-$ 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 $N[P(Ph)_2NHSiMe_3]_2^+Cl^-$ 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_3PNSO_2Cl (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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$$\begin{array}{c} \text{Cl} \\ \text{P=N-SO}_2\text{-Cl} & + \text{CH}_3\text{CN} \\ \text{HN} \\ \text{SiMe}_3 & \text{CH}_3 \\ \text{Cl}_3\text{P=N-SO}_2\text{-Cl} \\ + \text{MeN}(\text{SiMe}_3)_2 & \text{Cl}_2\text{P} \\ \text{NN} \\ \text{CH}_3 & \text{CH}_3 \\ \text{Cl}_3\text{P=N-SO}_2\text{-Cl} \\ + \text{MeN}(\text{SiMe}_3)_2 & \text{Cl}_2\text{P} \\ \text{NS} \\ \text{OMeN} \\ \text{SiMe}_3 & \text{Cl}_2\text{Cl} \\ \text{MeN} \\ \text{SiMe}_3 & \text{Cl}_2\text{Cl} \\ \end{array}$$

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 sixmember cation isolated as a chloride salt (Scheme 2).

SCHEME 2 Products from the reaction system ClPPh₂NSO₂Cl with HMDS.

SCHEME 3 Reaction mechanism of the formation of P—N—S six-member cation in the system ClPPh₂NSO₂Cl with HMDS.

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

$$Ph_2PCl_3 + NH_2SO_2Cl \longrightarrow ClP(Ph_2)NSO_2Cl + 2HCl$$
 (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 equilibrium 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(trimethylsilylsulfamide $SO_2[N(H)SiMe_3]_2$ 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 BCl₃ 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).

$$N[PPh_{2}N(H)SiMe_{3}]_{2}^{+}Cf \xrightarrow{+x BCl_{3}} Ph \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph \\ HN \xrightarrow{B} NH \\ Cl \qquad [BCl_{4}]^{-}$$

$$+ \underbrace{x AsCl_{3}}_{As} Ph \xrightarrow{Ph} Ph \\ HN \xrightarrow{As} NH \cdot AsCl_{3}$$

SCHEME 4 Reaction of 7 with BCl₃ and AsCl₃.

SCHEME 5 Dimeric P—N—B cation.

 $Cl_3P = N - POCl_2$

$$\begin{array}{c} \text{MeN(SiMe}_3)_2 \\ \text{Cl} \\ \text{Cl-P=N-POCl}_2 \\ \text{MeN} \\ \text{SiMe}_3 \end{array} \begin{array}{c} \text{Cl}_2 \\ \text{PCl}_2 \\ \text{MeN} \\ \text{O} \\ \text{Cl} \\ \text{Cl} \end{array}$$

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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