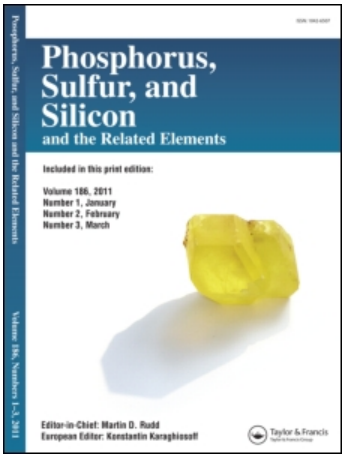

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Structures and Bonding Properties of Halotriazines

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STRUCTURES AND BONDING PROPERTIES OF HALOTRIAZINES

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Abstract Syntheses and structures of halotriazines $(XCN)_n(XSN)_{3-n}$, $(XCN)_n(X_2PN)_3$ and $(XSN)_n(XS(O)N)_{3-n}$ (X = Cl, F; n = 0-3) are systematically investigated. From the structural data simple bonding models are derived.

Triazines $(RAN)_3$ with RA = RC, RS, RS(O) and R_2P are known in the literature[1,2]. Remarkable for this class of compounds is that the RA- units can be randomly exchanged. We are especially interested in ringhalogenated heterocycles $(XAN)_n(XA'N)_{3-n}$ (with XA≠XA'= XC, XS, XS(O), X_2P and X=Cl, F) because here the special influence of the different building blocks on structure and reactivity can be directly compared. Recently we prepared (ClCN) $(ClSN)_2$ [3] the last missing member in the trichlorotriazine series

$$ClCN + 2/3\ (ClSN)_3 \longrightarrow (ClCN)(ClSN)_2 \quad \mathbf{1}$$

$$\mathbf{1} + AgF_2 \longrightarrow (ClCN)(FSN)_2 \quad \mathbf{2}$$

$$\mathbf{2} + AgF_2 \longrightarrow (FCN)(FSN)_2 \quad \mathbf{3}$$

1 is fluorinated by AgF_2 to give **2**, primary attack at the sulfur is observed. When the reaction time is extended the fully fluorinated product **3** is isolated in high yield. Strong Lewis acids abstract sulfur bonded halogen to form stable salts, e.g.:

$$(FCN)_2(FSN) + AsF_5 \longrightarrow \underset{\mathbf{4}}{(FCN)_2(SN)^+ AsF_6^-}$$

$$(FCN)(FSN)_2 + AsF_5 \longrightarrow \underset{\mathbf{5}}{(FCN)(FSN)(SN)^+ AsF_6^-}$$

$$(FCN)_2(FSN) + Me_3SiCl \longrightarrow \underset{\mathbf{6}}{(FCN)_2(ClSN) + Me_3SiF}$$

$$(FCN)(FSN)_2 + 1/2\ SiCl_4 \longrightarrow \underset{\mathbf{7}}{(FCN)(ClSN)_2 + 1/2\ SiF_4},$$

while weak chloroacids, e.g. Me_3SiCl or $SiCl_4$, selectively exchange the sulfur bonded fluorine.

The x-ray structures of $(ClCN)_n(ClSN)_{3-n}$ (n = 1-3) [1] are reported and compared with $(NSCl)_3$ [4], the complete fluoro series $(FCN)_n(FSN)_{3-n}$ (n = 0-3) [5] was investigated by electron diffraction. A bonding model for these triazines was developed to explain the experimental structures [3]. Comparison of the x-ray structures of **1**, **2**, **3**, and **7** shows, that ClF exchange has only little influence on the intramolecular bond distances.

In the chlorophosphazine system $(ClCN)_n(Cl_2PN)_{3-n}$ (n = 1,2) were prepared according to literature methods [6, 7], fluorination by SbF_3 and other fluorinating agents were only partially successfull for n = 2 .

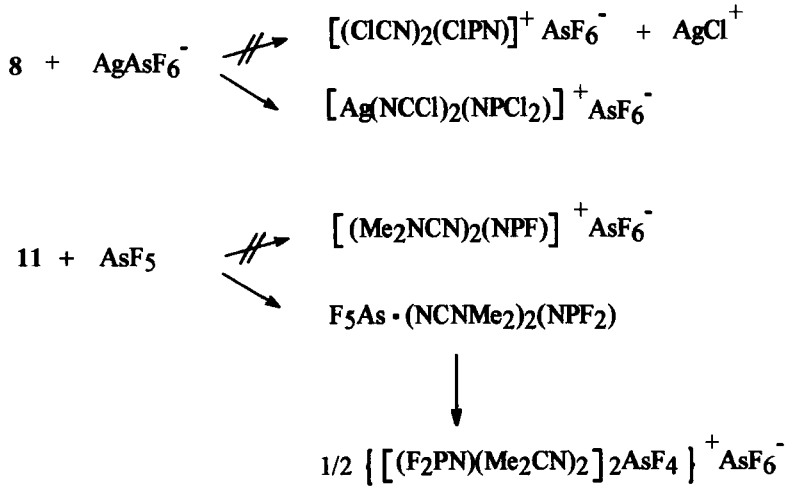
$$\underset{\mathbf{8}}{(ClCN)_2(Cl_2PN)} + 2/3\ SbF_3 \longrightarrow \underset{\mathbf{9}}{(ClCN)_2(F_2PN)} + 2/3\ SbCl_3$$

$$2\ Me_2NSiMe_3 \downarrow -2\ Me_3SiF \qquad 2\ Me_2NSiMe_3 \downarrow -2\ Me_3SiF$$

$$\underset{\mathbf{10}}{(Me_2NCN)_2(Cl_2N)}\ [8] \qquad \underset{\mathbf{11}}{(Me_2NCN)_2(F_2PN)}$$

The structures of $(ClCN)(Cl_2PN)_2$, **8-10** are reported. The dependence of the intramolecular bond distances in phosphatriazines $ClCN)_n(Cl_2PN)_{3-n}$ can be described by a similar model as developed for the chlorotriazines.

The structure determination of **4** shows a planar $[(FCN)(SN)]^+$-ring (similar to $[(PhCN)_2(SN)]^+$ [9], suggesting that the pseudo-three coordinated sulfur is part of the 6π-system. Attempts to abstract Cl^- or F^- in **8** or **11** from the tetracoordinated phosphorus were unsuccessfull:



In the oxotrichlorotritriatriazine-system $(NSCl)_n(NS(O)Cl)_{3-n}$ [10,11] we recently reported the structures with n = 1,2 [9] and that of β-$(NS(O)Cl)_3$ [12]. Now we succeedet in solving the structure of cis-$(NS(O)F)_3$ in the solid state and in the gasphase. Fluorination of $(NSCl)_2(NS(O)Cl)$ by AgF_2 is known to give $(NSF)_2(NS(O)Cl)$ [10], this rearranges slowly to $(NSCl)_2(NS(O)F)$ with an unusual long S(VI)-F bond.

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