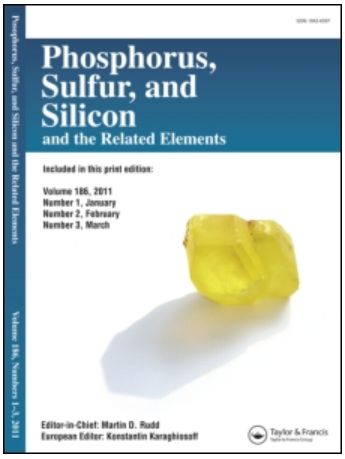

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Silicon-Containing Phosphorus(V) Hydrazine Hetero-Cycles

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SILICON-CONTAINING PHOSPHORUS(V) HYDRAZINE HETEROCYCLES

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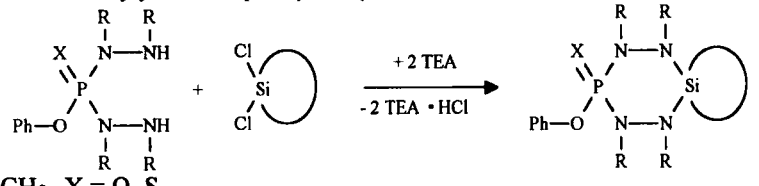
Abstract 3-Phenoxy-1,2,4,5-tetraaza-3λ^5-phospha-6-silacyclohexane-6-spiro-1′-silacyclohexane-3-sulfide **1** and 6,6-dichloro-1,2,4,5-tetramethyl-3-phenoxy-1,2,4,5-tetraaza-3λ^5-phospha-6-silacyclohexane-3-sulfide **3** are prepared from thiophosphoryldihydrazido derivatives of phosphoric and thiophosphoric acid and cyclic organodichlorosilanes or tetrachlorosilane respectively. The constitutions of the new cyclic systems are confirmed by MS, ^{1}H- and ^{13}C NMR.

Reactions of cyclic organodichlorosilanes with dihydrazidophosphoric and -thiophosphoric acid-O-phenyl esters in a 1:1 molar ratio in THF in the presence of triethylamine mainly yield the spirocyclic systems shown in eq. 1.



R = H, CH_3; X = O, S

eq. 1

The constitutions of the new compounds combining inorganic and organic heterocycles in spirocyclic ring systems are confirmed by MS, NMR, and elemental analysis. In one case a dimeric compound (Fig. 1) is also isolated. A single crystal X-ray analysis reveals this compound to consist of a dispiro system with a central centrosymmetric eigthmembered inorganic heterocycle connected with two silacyclohexanes via Si-spirocenters[1].

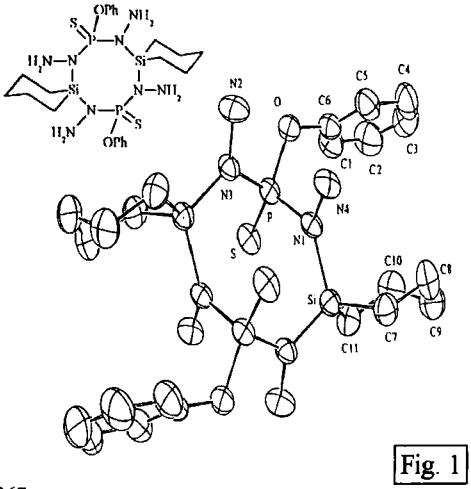


Fig. 1

It is also interesting to react N-substituted and unsubstituted dihydrazidoderivatives of phosphoric- and thiophosphoric acid[2-4] with silicontetrachloride. The purpose is to discover, if the complete substitution of chlorine atoms is possible to yield a spirocyclic system. However, the expected spirocycle **II** does not form. The N,N′-dimethyl substituted dihydrazido derivative react with silicontetrachloride directly only under partial substitution of the chlorine atoms to give the silicon containing heterocycle **III** (eq. 2).

The N,N′-unsubstituted dihydrazido derivatives do not react in a clear, well defined way. Mainly decomposition is observed.

Obviously the bulkier methyl groups at the nitrogen atoms stabilize the cyclic spezies, but may also inhibit the complete substitution of the chlorine atoms bond to the silicon[5].

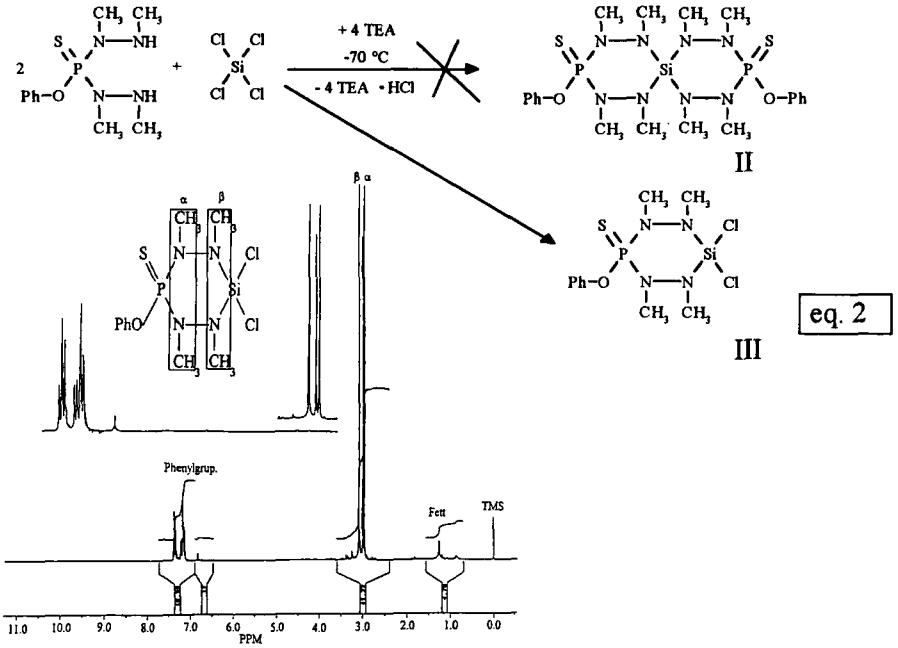


Fig. 2: Proton NMR spectrum of **III** (250 MHz, $CDCl_3$)

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