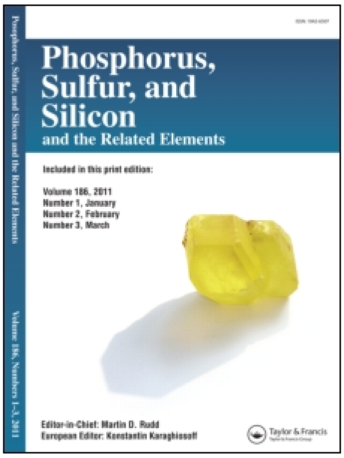

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P=Si- and As=Si-Bonds as Building Blocks for Unusual Phosphorus and Arsenic- Silicon- Heterocycles

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P=Si- AND As=Si-BONDS AS BUILDING BLOCKS FOR UNUSUAL PHOSPHORUS- AND ARSENIC- SILICON- HETEROCYCLES

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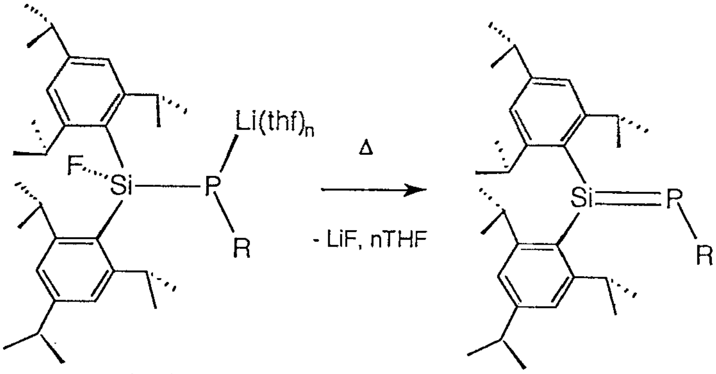
Abstract The high-yield access to new stable, activated phosphanylidensilanes and the first arsanylidensilane enabled us to investigate the reactivity of these very reactive compounds. Cycloaddition and oxidation reactions leads to new classes of heterocycles. For example, the first azaphosphasiliridine as well as arsaazasiliridine derivative has been characterized by X-ray crystal structure determination.

We have reported the preparation of new stable, activated phosphanylidensilanes ("phosphasilenes" $RP{=}SiR_2$)[1] **1a-d** and the first arsanylidensilane ("arsasilene" $RAs{=}SiR_2$)[2] **2** by elimination of LiF from the corresponding lithio-pnictogenofluorosilanes.

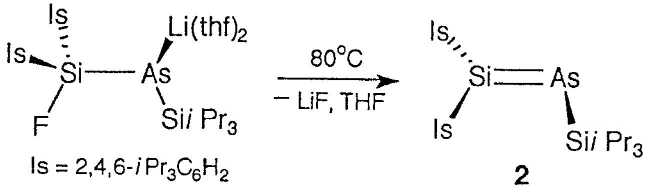


colourless crystals

orange-red oils

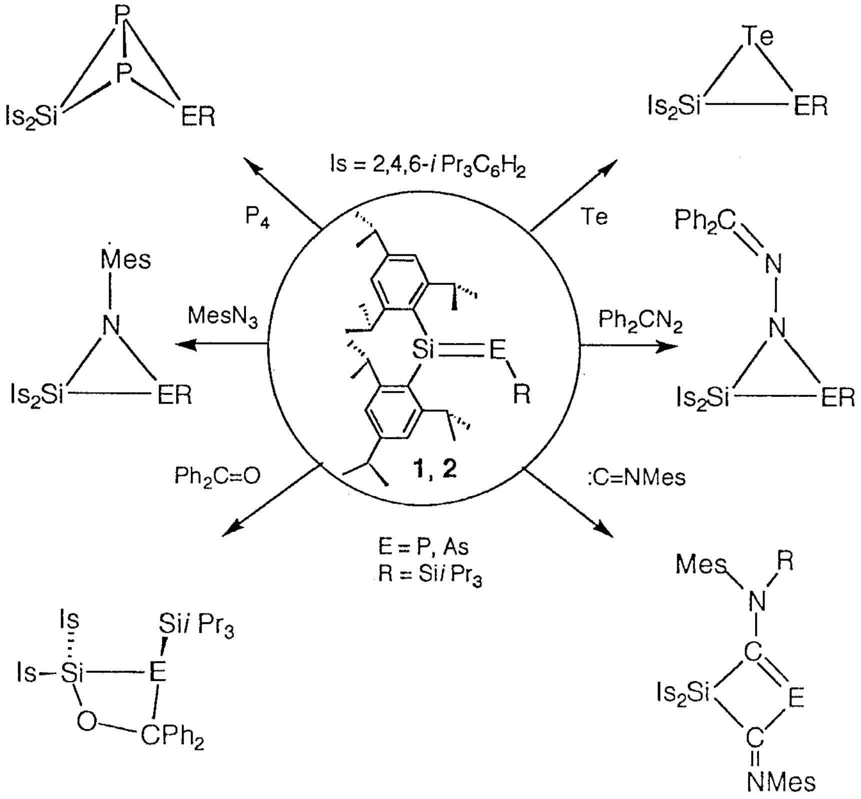
R = Si*i*Pr$_3$
R = SiMe$_3$
R = Si*t*BuMe$_2$
R = P*t*Bu$_2$

1a: δ(^{31}P) =	11.1,	δ(^{29}Si) = 167.8, J = 160Hz
1b:	28.1	172.4, J = 152Hz
1c:	17.7	178.4, J = 148Hz
1d:	72.2	184.6, J = 158Hz
	26.6 (P*t*Bu$_2$)	J = 43Hz



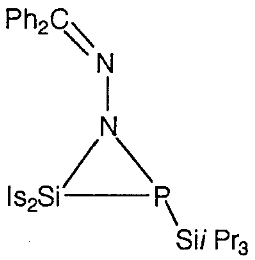
All derivatives are thermally quite stable (up to 110°C) due to the bulky aryl groups on silicon and the strong σ-donor influence of the triorganosilyl- and di-*tert* - butylphosphanyl substituents on phosphorus (arsenic). The compounds **1** and **2** were obtained as deep orange-red oils. The ^{31}P- and ^{29}Si-NMR data [$\delta(^{29}Si) = 167\text{-}185$, $^{1}J(SiP) = 149\text{-}160Hz$; $\delta(^{31}P) = 72.2\text{-}11.1$] reflects the low-coordination on phosphorus (arsenic) and silicon as well as the unusual bonding mode of the $(p\text{-}p)_\pi$- systems. In comparison to the known phosphasilenes made by *Bickelhaupt et al.* the ^{31}P-NMR signal of **1a** is tremendous shifted to higher field by $\Delta\delta = 124.9$!

The thermal stability enabled us to investigate the reactivity of **1** and **2** as shown in scheme 1.

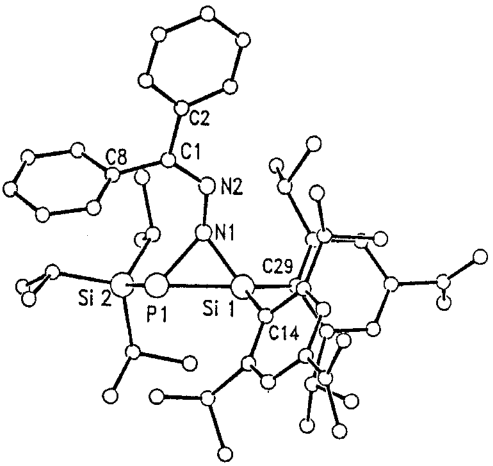


Scheme 1: Some reactions of 1 and 2

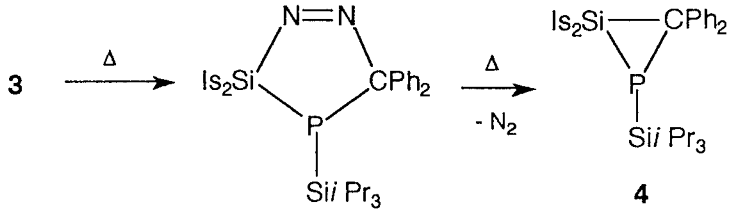
Somewhat unexpected is the reaction of **1** and **2** with white phosphorus to form 1,2,3-triphospha-4-silabicyclo[1.1.0]butanes[1] and two constitutional isomers of butterfly-like compounds with an AsP_2Si- skeleton. Another interesting feature is the formation of the azaphosphasiliridine **3**[3] by reactin of **1a** with diphenyldiazomethane. **3** can be regarded as end-on adduct (π-complex) of the nitrene-form of the diazomethane and the π-bond of the phosphasilene as shown in the result of the X-ray crystal structure determination.

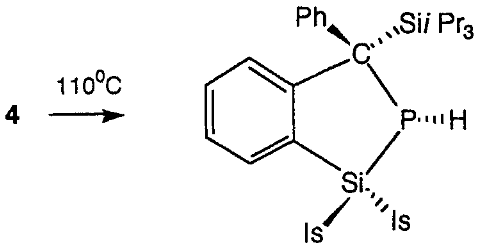


3

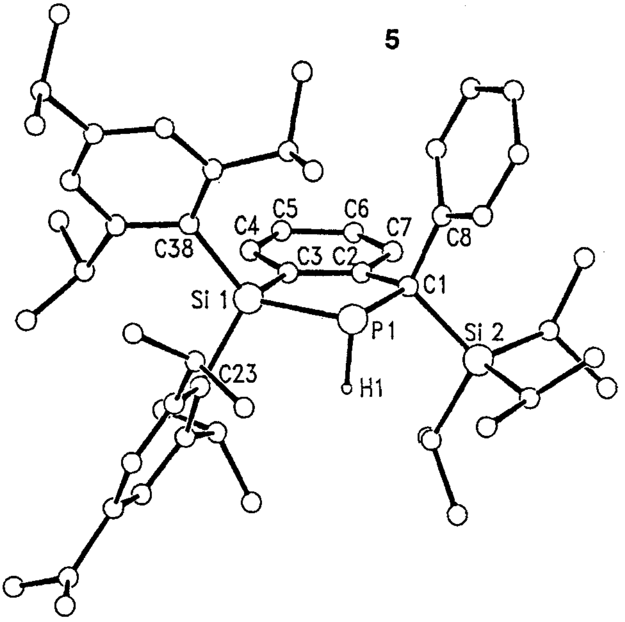


Thermolysis of **3** leads under rearrangement and loss of N_2 to the corresponding phosphasilirane **4**, which further rearranges at 110°C to give the unusual benzophosphasilolane **5**, quantitatively.[3]





5



The formation of **5** is remarkable regarding two aspects. Firstly, a hetero-phenyl-cyclopentene-rearrangement occurs with shift of the Si(*i* Pr)$_3$ group from the phosphorus to the *saturated* C1 atom. Secondly, it should be noted that these process probably occuring in a radical fashion, obviously proceeds so effectively that only **5** is generated.

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