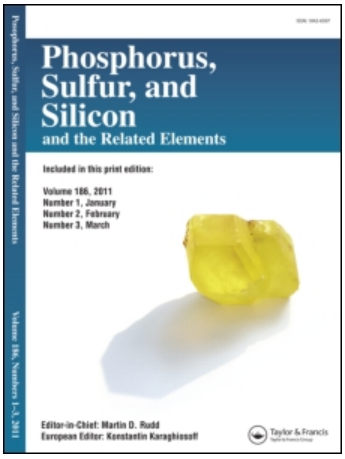

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Phosphasilaethenes

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PHOSPHASILAETHENES

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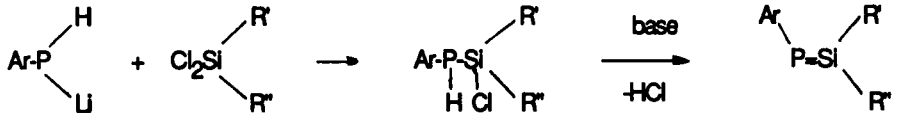
Abstract. - The synthesis, stability, and spectroscopic properties of several phosphasilaethenes ArP=SiR'R" are described. It is concluded that the P=Si bond is a typical p(π)-p(π) bond which is highly polarized ($P^{\delta-}$, $Si^{\delta+}$).

As a result of intensive recent efforts, the famous Double Bond Rule has to be modified. In its original form it states that elements of the third and higher Periods do not form stable compounds containing p(π)-p(π) double bonds[1]; it is now evident that a more correct formulation is: the tendency to form such bonds decreases in the Periodic Table from top to bottom and from right to left.

In this light, phosphasilaethenes (**1**) deserve particular interest. In the first place, they combine two elements which are notoriously reluctant to form p(π) bonds; this is particularly true for silicon. But while several stable compounds containing tri-coordinate silicon, such as the disilenes [2], have recently been prepared, the combination P=Si poses the additional challenge of containing elements of different polarity, and bond polarity is one of the major causes of kinetic instability in such compounds.

After reporting on the first detectable phosphasilaethene (**1a**, Scheme 1) [3], we have been engaged in a broader investigation of the synthesis and properties of **1**. The general approach has been as follows (Scheme 1). Combination of the lithium phosphide **2** with a suitable dichlorosilane **3** in THF results in the formation of **4** which by elimination of HCl serves as a precursor to **1**.

Scheme 1



2 **3** **4** **1**

Ar = 2,4,6-tri-t-butylphenyl

a: R' = R" = mesityl (Mes)

b: R' = R" = 2,4,6-triethylphenyl (Ar')

(**c**: R' = R" = 2,4,6-triisopropylphenyl (Ar"))

d: R' = Ph, R" = Ar"

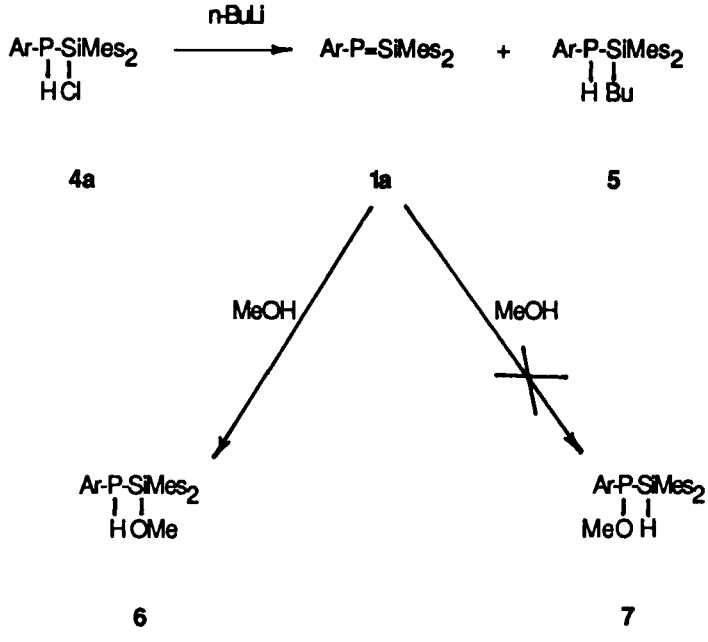
e: R' = Mes, R" = Ar"

f: R' = t-Bu, R" = Ar"

Several difficulties were encountered in this procedure. For instance, the combination of **2** with **3c** proved to be impossible; apparently due to excessive steric hindrance, the two compounds showed no reaction even after prolonged heating to 55°C. Another problem was that in several cases the isolation and purification of the intermediate **4** was not possible, because the elimination of HCl in situ could not be prevented as **2** turned out to be an extremely efficient base in bringing about elimination.

In our first example **1a** [3], these difficulties were not encountered, but the elimination of HCl from **4a** was accompanied by a side reaction, i.e. substitution at silicon leading to **5** (Scheme 2). This must be due to insufficient steric protection at silicon, which is also illustrated by the extreme instability of **1a**. **1a** Was characterized by its spectral data (vide infra) and by the addition of methanol which leads to **6** and gives no trace of the regioisomer **7**, thus demonstrating the polarization of the P=Si bond.

Scheme 2



The most promising compounds are **1b** and **1f**. The latter is the most stable one obtained so far, but its precursor **4f** elimininates HCl immediately under the influence of **2** (vide supra), so that it has so far only been obtained as a 1:1 mixture with $ArPH_2$. Compound **1b** is of intermediate stability; however in this case, **4b** can be isolated and **1b** can be prepared by reaction with n-butyllithium in THF at -60°C. Compound **1b** adds tellurium to form a PSiTe three-membered ring system.

The data from the ^{31}P- and ^{29}Si-NMR spectra are highly diagnostic for the characterization of the new compounds as phosphasilaalkenes with a phosphorus-silicon p(π)-p(π) double bond. They are collected in Table 1.

Table 1 ^{31}P- and ^{29}Si-NMR data of the phosphasilaalkenes **1**

Compound	^{31}P a		^{29}Si b	
	δ [ppm]	$^{1}J(PSi)[H_2]$	δ [ppm]	$^{1}J(PSi)$
1a c	136.0	148.5	151.0 e	148.5
1b c	133.7	152	150.1	152
1d c	93.5	151	153.0	151
1e c	122.7	152	148.7	152
1f d	105.4	154	175.9	155

a At 101.2 MHz. b At 49.7 MHz. c In THF. d In C_6D_6. e Corrected value (cf.ref.3).

The δ(^{31}P) values are, rather surprisingly, at the high field side of the usual range for di-coordinated phosphorus. We feel that this is a result of the high degree of polarization of the P=Si bond; phosphorus is more electronegative and pulls the electrons towards itself. The δ(^{29}Si) values are less variable, but fall into the low field region typical for tricoordinated silicon with **1f** presenting, to our knowledge, a world record in deshielding for silicon. A comparison with other P=X and Si=X compounds (X = element from Group IV or V) suggests that both the relative electronegativity and a paramagnetic contribution to δ (mainly due to a small HOMO-LUMO gap) are important factors in determining δ. Unparalled is also the high coupling constant $^{1}J(PSi)$ of ca. 150 Hz, which is indicative of a high s-character in the σ-bond between the two (approximately) sp^2-hybridized elements.

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