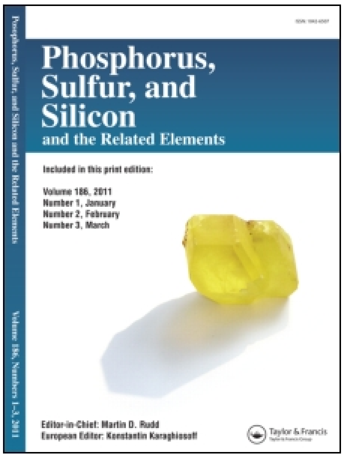

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Recent Developments in Phosphasilene Chemistry

Yvar Van Den Winkel[a]; Harold M. M. Bastiaans[a]; Friedrich Bickelhaupt[a]
[a] Scheikundig Laboratorium, Vrije Universiteit De Boelelaan 1083, Amsterdam, The Netherlands

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RECENT DEVELOPMENTS IN PHOSPHASILENE CHEMISTRY

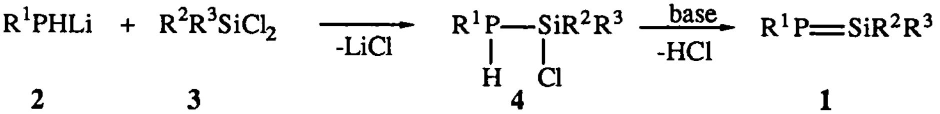
YVAR VAN DEN WINKEL, HAROLD M. M. BASTIAANS, AND
FRIEDRICH BICKELHAUPT

Scheikundig Laboratorium, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

ABSTRACT An alternative route to phosphasilenes is discussed and several new phosphasilenes, with variation of the substituents on phosphorus, have been synthesized. The influence of the substituents on the phosphorous and silicon chemical shifts, as well as on the stability of the phosphasilenes is analyzed. The chemical reactivity of one of the phosphasilenes was explored.

A survey of the recent literature shows an increasing interest in compounds of groups 14 and 15 in a low coordination state, thus violating the classical Double Bond Rule[1]. Phosphasilenes (**1**), i.e. compounds with a phosphorus-silicon double bond (P=Si), combine the aspects of both a pπ-bonded phosphorus and a pπ-bonded silicon atom and are therefore interesting representatives of the phosphahetero-alkenes. In 1984, we reported on the first, moderately stable phosphasilene[2]; several others have been synthesized since and their stability and spectroscopic properties were studied[3].

The original procedure for the preparation of phosphasilenes followed the sequence outlined in 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**.



$$\underset{\mathbf{2}}{R^1PHLi} + \underset{\mathbf{3}}{R^2R^3SiCl_2} \xrightarrow[-LiCl]{} \underset{\mathbf{4}}{R^1\underset{H}{P}\!-\!\underset{Cl}{Si}R^2R^3} \xrightarrow[-HCl]{base} \underset{\mathbf{1}}{R^1P{=}SiR^2R^3}$$

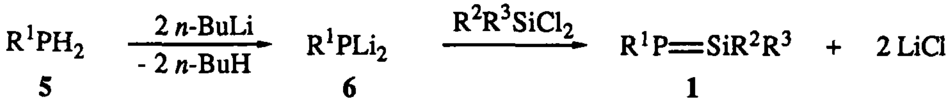
Scheme 1 (for R^1, R^2, and R^3 see TABLE I)

However, several difficulties were encountered in this procedure. The major problem was that **2** is a highly efficient base for promoting the elimination of HCl from **4**. Therefore, the yield of **1** could be increased by employing the stoichiometry **2** : **3** = 2 : 1 (Scheme 2). This method, however, suffers from yielding equimolar amounts of **5** which could so far not be separated from the sensitive **1**[3].

$$\underset{\mathbf{2}}{2\,R^1PHLi} + \underset{\mathbf{3}}{R^2R^3SiCl_2} \longrightarrow \underset{\mathbf{1}}{R^1P{=}SiR^2R^3} + \underset{\mathbf{5}}{R^1PH_2}$$

Scheme 2

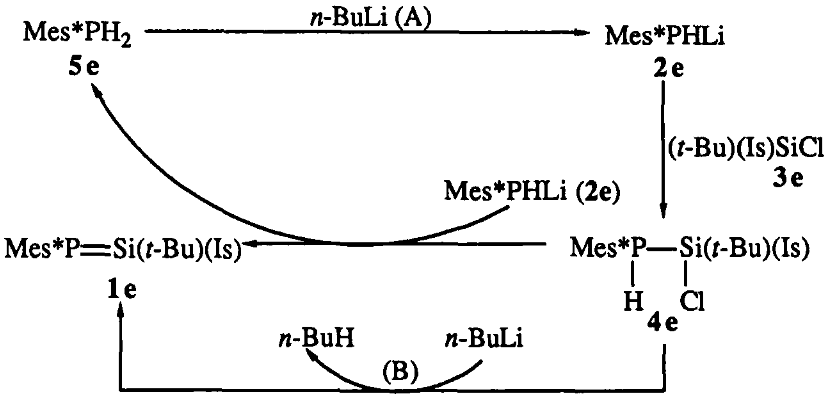
We therefore investigated the alternative approach outlined in Scheme 3. Two equivalents of *n*-BuLi were reacted with **5** in order to obtain **6**; **6** was expected to combine with a dichlorosilane **3** to give **1** with LiCl as the only and easy separable byproduct.



$$\underset{\mathbf{5}}{R^1PH_2} \xrightarrow[-\,2\,n\text{-BuH}]{2\,n\text{-BuLi}} \underset{\mathbf{6}}{R^1PLi_2} \xrightarrow{R^2R^3SiCl_2} \underset{\mathbf{1}}{R^1P{=}SiR^2R^3} + 2\,LiCl$$

Scheme 3

Indeed, this approach turned out to be successful as a one-pot reaction, combining both steps, for the synthesis of one specific phosphasilene, **1e** (R^1 = Mes*, R^2 = Is, R^3 = *t*-Bu). However, isolation, detection by NMR, or trapping with D_2O of the interesting dilithiophosphide **6e** was impossible; only the monolithiophosphide **2e** was obtained. On the other hand, it was possible to synthesize and detect two other dilithiophosphides, **6g** and **6k**, bearing the isityl and phesityl group (TABLE I), respectively, on phosphorus. Unexpectedly, the attempted reaction of these latter phosphides with $Cl_2Si(t\text{-}Bu)(Is)$(**3e**) did not occur at all. Furthermore, it was observed in a separate experiment that *n*-BuLi does not react with **1e**. So the conclusion was drawn that in this particular, very crowded system, a reaction pattern as shown in Scheme 4 applies, in which *n*-BuLi has the double function of metalating **5e** (pathway A) and of eliminating HCl (pathway B).



Scheme 4

Since the last report[3], several new phosphasilenes have been synthesized and characterized. In TABLE I known (**1a**-**1e**)[3] as well as new compounds (**1f**-**1k**) together with their ^{31}P and ^{29}Si NMR data are summarized. Apart from their chemical reactions (*vide infra*), the identity of **1** follows unambiguously from their NMR spectra. The ^{31}P chemical shifts are somewhat scattered and suprisingly shielded[3]; together with the ^{29}Si chemical shifts they show a certain compensatory tendency such that the sum of $\delta(^{31}P)$ +

$\delta(^{29}Si)$ is approximately constant, especially within a set having identical substituents at silicon (i.e. =Si(*t*-Bu)(Is)). More diagnostic are the ^{29}Si chemical shifts which are amongst the most deshielded ones ever reported for silicon with **1j** ($\delta(^{29}Si)$ = 199 ppm) being, to our knowledge, so far the world record. Similarly diagnostic are the large coupling constants $^{1}J(PSi)$ in the range of 149-155 Hz, testifying to the high s-character in the P=Si bond. In one case (**1f**), a 1 : 1 mixture of the expected *E*/*Z* isomers has been observed, whereas for all others, only one stereoisomer seems to be formed, apparently due to the difference in bulk between the large isityl group and the smaller second substituent at silicon. *E*/*Z* Isomerization of **1f**, however, was not found so far, even at 80°C. The qualitative evaluation of the thermal stability of **1** lead to the conclusion that protection at silicon is more important than at phosphorus.

TABLE I Selected ^{31}P- [a] and ^{29}Si [b]-NMR data for $R^1P{=}SiR^2R^3$ [c] (**1**).

Compound	R^1	R^2	R^3	$\delta(^{31}P)$[ppm]	$\delta(^{29}Si)$[ppm]	$^{1}J(PSi)$[Hz]
1a	Mes*	Mes	Mes	136.0	151.2	149
1b	Mes*	Es	Es	133.7	150.1	152
1c	Mes*	Ph	Is	93.5	153.0	151
1d	Mes*	Mes	Is	122.7	148.7	152
1e	Mes*	*t*Bu	Is	105.4	175.9	155
1f	Mes*	Es	Es'	134.2	149.2[d]	153
	Mes*	Es'	Es	135.8	149.0[d]	153
1g	Is	*t*Bu	Is	66.2	190.3	153
1h	Es	*t*Bu	Is	65.8	194.1	153
1i	Mes	*t*Bu	Is	69.0	196.8	153
1j	R"	*t*Bu	Is	69.7	199.0	154
1k	Phes	*t*Bu	Is	86.7	180.0	151

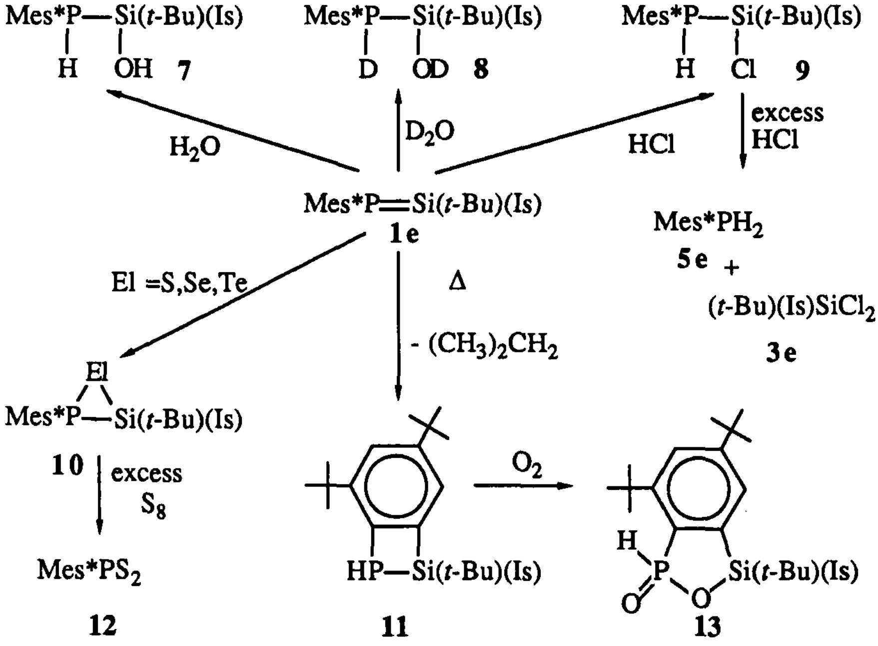
[a] Standard: ext. 85% H_3PO_4. [b] Standard: ext. Me_4Si. [c] Nomenclature: Mes* = 2,4,6-*t*-$Bu_3C_6H_2$; Is = 2,4,6-*i*-$Pr_3C_6H_2$; Es = 2,4,6-$Et_3C_6H_2$; Es' = 2,6-$Et_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$; Phes = 2,4,6-$Ph_3C_6H_2$; R" = 2,6-Me_2-4-(OC_8H_{17})C_6H_2. [d] The assignment for the $\delta(^{29}Si)$ signal to one of the $\delta(^{31}P)$ signals is arbitrary and may have to be reversed.

So far, the chemical investigation of **1** was handicaped because they had not been isolated in pure form[3]. By the improved approach of Scheme 4 it was possible to obtain **1e** as an almost pure compound, and several reactions (Scheme 5) on **1e** were performed.

The reactivity pattern of **1e** shows the polarization expected on the basis of electronegativities: phosphorus is the negative end of the P=Si dipole and adds electrophiles, while nucleophiles attack at silicon; adducts **7**, **8**, and **9** were obtained as diastereomeric pairs. Compound **9** could be cleaved by an excess of HCl to give **3e** and **5e**.

In analogy to the behaviour of phosphaalkenes[4] and related compounds[5], **1e** adds chalcogens to form rather unstable, three-membered ring compounds **10**; with excess of sulfur, further cleavage occurs.

On heating in benzene or toluene to 60°C, **1e** has been found to eliminate isobutene under formation of **11**. Although the reaction was performed in perdeuterated solvents, no deuterium incorporation was observed; the implications for the mechanism of this reaction are still unclear, but abstraction of hydrogen from the solvent, as suggested for a related germaphosphene[6], can be excluded. A stepwise reaction (either ionic or radical) is more likely than a concerted one, because two isomers (*cis/trans*) were formed, which were shown not to be in equilibrium. Compound **11** reacts with oxygen to give two isomers of compound **13**.



Scheme 5

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