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Insights into the reactivity and structure of silylene phosphonium ions†

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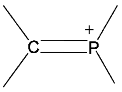
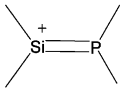
Experimental evidence for the intermediate occurrence of a so far unknown silylene phosphonium ion is presented and its reactivity and bond situation is discussed on the basis of *ab initio* calculations.

Methylene phosphonium ions are cationic tricoordinate tetravalent phosphoranes with a formal PC double bond (structure **I**). Initially they had been postulated as intermediates,[1] but soon after could even be isolated.[2] Some years later the existence of discrete methylene phosphonium has been proven unambiguously by X-ray crystallography.[3] Moreover, the reactivity of methylene phosphonium ions[4] and their unusual bonding situation has been analyzed in detail.[5] In contrast nothing is known about the corresponding silicon analogues so far.

Formally one might describe an analogous silylene phosphonium ion (**II**) as an adduct between a silylene unit and a phosphenium ion. Both of these fragments should possess singlet ground states[6] and therefore have the tendency to form a twisted non-classical double bond. According to the CGMT model,[7,8] this tendency should be even more pronounced in silylene phosphonium ions than in the case of methylene phosphonium ions.



I



II

In this contribution we report on the formation of an intermediate silylene phosphonium ion which due to its pronounced electrophilic behavior is not stable under the reaction conditions. However, the nature of the subsequent products supports the occurrence of this species and explains its decomposition. Furthermore, energetic aspects and the bond situation in a model silylene phosphonium ion are explored by quantum chemical calculations.

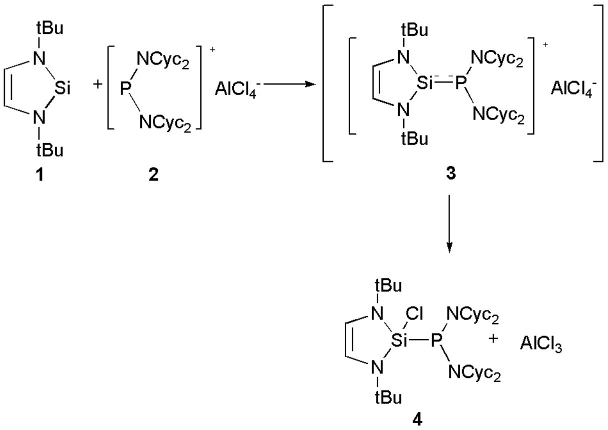
Hypothetical cleavage of a silylene phosphonium ion should furnish a silylene unit along with a phosphenium ion. Both of these fragments show nucleophilic and electrophilic behavior at the same positions and therefore they can be considered as singlet heterocarbenes.[6] Due to the synthetic accessibility of both of these components,[9] it seems worthwhile to investigate whether a silylene phosphonium ion can actually be generated from these components. To explore this possibility we have chosen the "classical" stable silylene **1** by West[10] which is well known for its nucleophilic character at the silicon atom[11] and a diaminophospheniumtetrachloroaluminate **2** which is characterized by a high electrophilicity as our starting materials.

Due to the electrophilic behavior of **2** the reaction was performed at a low temperature (−80 °C) in solution, where the onset of the reaction can be observed by a color change to dark red. After the reaction is finished the products can be identified spectroscopically directly from the reaction mixture using ^{31}P and ^{29}Si NMR. As it turns out, silylene phosphonium ion **3** is not the final product but instead phosphanochlorosilane **4** can be identified (Scheme 1). In the ^{29}Si NMR spectra **4** shows a doublet ($^{1}J_{\mathrm{SiP}}$: 43 Hz) at −26.5 ppm. The ^{31}P NMR signal appears at 103.9 ppm ($^{4}J_{\mathrm{PH}}$ = 12.2 Hz).

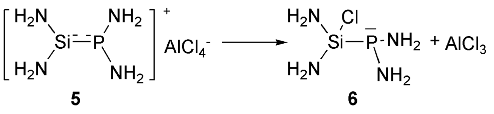
The formation of **4** can be explained when the abstraction of a chloride ion from the tetrachloroaluminate anion of **2** is assumed. Therefore it seems likely that in an initial step silylene phosphonium ion **3** is actually formed. However, unlike its carbon analogue **3** appears not to be stable under the reaction conditions. Its electrophilicity is obviously higher than that of $AlCl_3$ which leads to the transfer of a chloride ion from $AlCl_4^-$ to the silicon center.

To support this hypothesis we performed quantum chemical calculations using the program package Gaussian 98.[12] In order to assess the relative electrophilicity of the species involved, we explored the energy separation between the reactants and products of the hypothetical reaction depicted in Scheme 2. On Hartree Fock level using a triple zeta basis (6-311+G(d,p)) the mixture of chlorosilylphosphane **6** and $AlCl_3$ is about 67.42 Kcal mol^{-1} more stable than the silylene phosphonium tetrachloroaluminate **5**. Similar results are obtained if electron correlation is taken into account using DFT methods. Thus with the hybrid functional B3LYP employing a triple zeta basis set (6-311+G(d,p)) the phosphinochlorosilane–$AlCl_3$ is favored by 67.87 Kcal mol^{-1} (Table 1). The energy separation for this reaction is even more pronounced if electron correlation is included using the MP2(fc) approach (70.87 Kcal mol^{-1}).

As a result of our calculations we obtained the geometry of the silylene phosphonium ion **5**, which shows some interesting features. While the silicon atom shows a planar coordination environment, the phosphorus atom in contrast adopts a pyramidal geometry. The P–Si bond length is 2.255 Å, in the typical range for a single bond,[13] and only marginally shorter than in **6** (2.267 Å). On the basis of a Mulliken population analysis[14] both, the phosphorus



Scheme 1 Adduct formation between silylene **1** and phosphenium ion **2**.



Scheme 2 Model reaction to assess the electrophilicity of **5** relative to $AlCl_3$.

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† Dedicated to Professor Edgar Niecke on the occasion of his 65th birthday.

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Table 1 Computed energies for reactants and products of the model reaction in Scheme 2 and computed PSi distances [Å] and atomic charges in **5**[a]

	[> P=Si <]$^+$ + $AlCl_4^-$ [hartree]	> P–SiCl < + $AlCl_3$ [hartree]	Δ*E*/Kcal mol^{-1}	*d*(P–Si)	*q*(P)	*q*(Si)	Symmetry
HF//6-311+G(d,p)	−2932.393388	−2932.500824	−67.42	2.256	+0.66	+1.31	C_1
MP2//6-311+G(d,p)	−2933.869408	−2933.982339	−70.87	2.234	+0.66	+1.32	C_1
B3LYP//6-311+G(d,p)	−2938.372453	−2938.480609	−67.87	2.255	+0.55	+1.10	C_1

[a] Computational details are available as supporting information.

and the silicon atoms are positively charged due to the adjacent nitrogen atoms that are more electronegative. However the phosphorus atom in **5** shows only approximately half of the positive charge of the silicon atom (Table 1). This is in good agreement with our experimental findings where a chloride ion adds to the silicon atom in **3** rather than to the phosphorus atom. The electrophilic site in such ions obviously seems to be at the silicon atom. The reactivity of **3** and the geometry obtained for **5** differ substantially from the findings for methylene phosphonium ions, which show a short but twisted central P–C bond and a positively charged but planar phosphorus atom concomitant with a negatively charged planar carbon atom.[3,5]

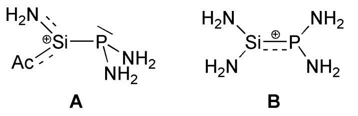
Our findings support the formulation of **5** as an adduct in which the lone pair at the silicon atom of a silylene donates into the vacant orbital located at the phosphorus atom in a phosphenium ion. Therefore it is structurally more related to classical base adducts of phosphenium ions[15–17] than to methylene phosphonium ions and could be described as phosphanyl silyl cation. The bond situation in **5** is represented better by description A rather than B in Scheme 3.

By exploring the chemistry of the chloride adduct of silylene phosphonium ion, we found that under ambient conditions the PSi bond in **4** is cleaved hydrolytically and the phosphane fragment is replaced by a hydrogen atom (Scheme 4). As final products hydridochlorosilane **7** and bisdicyclohexylaminophosphane oxide **8** can be isolated. Compounds **7** and **8** have been previously described in the literature[18,19] and were identified NMR spectroscopically (^{29}Si, ^{31}P, ^{1}H) and by high resolution mass spectroscopy.[20]

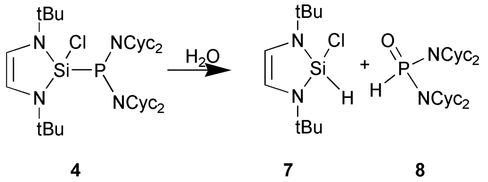
An interesting aspect in the formation of **7** is the fact that the cleavage of the P–Si bond in **6** follows the opposite direction than would be expected from the electronegativity values of these atoms (P: 2.1; Si: 1.7).[21] For comparison, the hydrolytic bond cleavage in trisorganosilylphosphanes is in accord with the bond polarity on the basis of the standard electronegativity values and produces hydridophosphanes along with silanols and/or their condensation products.

Considering the complete reaction sequence, **1** is transformed into **7**, which is formally an oxidative addition of one equivalent of HCl to the silicon atom of the unsaturated silylene. Since the reactivity of the aromatic silylene **1** is mostly based on the nucleophilicity of its lone pair, the interaction with the phosphenium ion causes a reversed reactivity at the silicon atom by altering its character from nucleophilic to strongly electrophilic. Or in other words, by forming this adduct the electrophilic character of the phosphenium ion is transferred to the otherwise nucleophilic silicon atom.

In summary, we could show that silylene phosphonium ions are likely intermediates in the reaction of singlet silylenes with phosphenium ions. Their reactivity and structure differs quite substantially from that of their carbon analogues and is characterized by a strong electrophilicity at the silicon atom. In fact there should be a reasonable chance to isolate such adducts by employing modern non coordinating counter ions.



Scheme 3 Phosphanyl silyl cation *vs.* silylene phosphonium ion.



Scheme 4 Hydrolytic cleavage of the Si–P bond in **4**.

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20 Chlorosilylphosphane **4**: a solution of 0.56 g (1 mmol) of **2** in 10 mL of dry methylene chloride, obtained in a similar fashion as described in ref. 9, is slowly added to 0.20 g (1 mmol) of silylene **1** dissolved in 10 mL of diethyl ether at −80 °C. The reaction mixture is concentrated under vacuum and transferred into an NMR tube with a capillary containing C_6D_6 as lock substance. ^{29}Si (49.7 MHz): −26.5 ppm (dt, $^1J_{SiP}$ = 43 Hz); ^{31}P (101.2 MHz): 103.9 ppm, $^4J_{PH}$ = 12.2 Hz. All attempts to isolate the product from the reaction mixture resulted in hydrolytic cleavage of the P–Si bond under formation of **7** and **8**. ^{1}H (250.1 MHz): 6.39 (t, $^4J_{HH}$ = 7.0 Hz, 1H, > SiClH), 5.84 (d, $^4J_{HH}$ = 7.0 Hz, 2H, C–H), 1.32 (s, 18 H, *t*-Bu). ^{29}Si (49.7 MHz): −42.0 ppm (dt, $^1J_{SiH}$ = 319 Hz, $^3J_{SiH}$ = 319 Hz, MS (EI): 231.1082 (calc.: .1084), $M^+ - H$.
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