VIP **Bond Activation**

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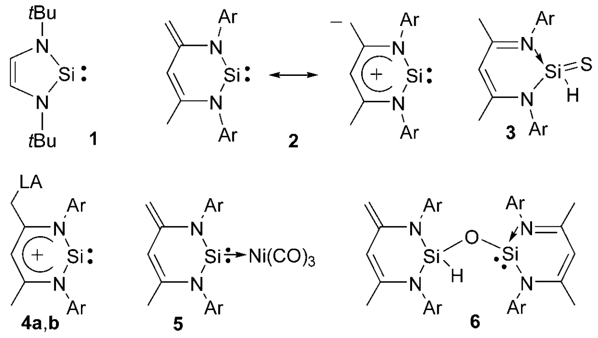
Metal-Free Activation of EH_3 (E = P, As) by an Ylide-like Silylene and Formation of a Donor-Stabilized Arsasilene with a HSi=AsH Subunit**

*Carsten Präsang, Miriam Stoelzel, Shigeyoshi Inoue, Antje Meltzer, and Matthias Driess**

In memory of Hans Georg von Schnering

Compounds containing homoleptic and heteroleptic multiple bonds between heavier main-group elements are a highly interesting current topic of research owing to their intriguing structure reactivity features. In the case of silicon, the isolation and characterization of the first stable disilene[1] and the first crystalline silylene **1** (Scheme 1)[2] are milestones that have inspired and encouraged many research groups to gain access to novel types of silicon-containing functional groups.[3] This work has recently enabled the discovery of new reactivity patterns, such as the metal-free activation of N–H bonds of ammonia or amines with multiply bonded silicon.[4]



Scheme 1. Isolable N-heterocyclic silylenes **1** and **2** and adducts **3**–**6** derived from silylene **2**. LA = H, $(C_6F_5)_3B^-$; Ar = 2,6-$i$$Pr_2C_6H_3$.

Apart from one example published by Kira et al.,[5] all known isolable silylenes are stabilized by adjacent nitrogen donor(s) and can be classified as N-heterocyclic silylenes[6] (NHSi molecules) or donor-stabilized silicon(II) compounds.[7] The reactivity of NHSis is comparable to that of well-known N-heterocyclic carbenes (NHCs), with the silicon center and the Si–N bonds being the predominant reactive sites.[8] Because of the yilde-like (zwitterionic) electronic structure of silylene **2**[9] (Scheme 1), its chemistry is distinctively different from that of other known NHSi molecules. Compound **2** exhibits an electron-rich butadiene moiety in the backbone that can be utilized for the metal-free activation of E–H bonds or the addition of Lewis acids. NHSi **2** thus features three reactive sites instead of two: The basic silicon lone pair, a formally empty (acidic) 3p orbital at silicon, and a basic butadiene moiety. The straightforward formation of silathioformamide **3** from **2** and H_2S[10] is the only example to date where all three of these sites have been involved in a single reaction. However, it is possible to selectively trigger one or two of the donor–acceptor functional groups if the right choice of reagent is made. For example, strong Lewis and Brønsted acids add to the exocyclic electron-rich methylene group[11] (compounds **4a,b**, Scheme 1), whereas the silicon(II) lone pair can be utilized as a strong σ donor for the preparation of silylene–metal complexes, as shown for complex **5** in which the zwitterionic character of the ligand is retained.[12] The 1,1-addition to the silicon center, which is also well-documented for other NHSis,[13] and the 1,4-addition across the C_3N_2Si heterocycle are the most common reactivity features of **2**. Both pathways have even been observed simultaneously during the reaction of water with two equivalents of NHSi **2** to yield donor-stabilized siloxysilylene **6** (Scheme 1).[14]

It has been shown that **2** and even the $\{Ni(CO)_3\}$ complex **5** are capable of activating the N–H bonds of ammonia and hydrazines,[15] C–H bonds of alkynes[16] and arenes, and C–F bonds of fluoroarenes[17] to eventually yield the corresponding thermodynamic 1,1-addition products. As part of our ongoing investigations on ylide-like silylene **2**, we were curious about its reactivity towards the more Brønsted acidic heavier Group 15 hydrides EH_3 (E = P, As). This reactivity could possibly lead to unprecedented donor-stabilized Si=E multiple bonds akin to the formation of silathioformamide **3** formed from **2** and H_2S. Herein we present the strikingly different reactivity of **2** towards PH_3 and AsH_3. Remarkably, whilst PH_3 leads merely to the 1,1-addition product, the activation of AsH_3 furnishes a donor-stabilized arsasilene (silylidenearsane, Si=As) with a HSi = AsH subunit in a two-step process, which could be isolated in the form of deep blue crystals.

The reaction of **2** with a twentyfold excess of PH_3 furnishes merely the 1,1-addition product, that is, silylphosphane **7a**, even at low temperatures (Scheme 2). The progress of the PH_3 addition can easily be monitored by the slow disappearance of the characteristic yellow color of **2** in

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[*] Dr. C. Präsang, M. Stoelzel, Dr. S. Inoue, Dr. A. Meltzer,
Prof. Dr. M. Driess
Technische Universität Berlin
Institute of Chemistry: Metalorganics and Inorganic Materials
Sekretariat C2, Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-314-29732
E-mail: matthias.driess@tu-berlin.de
Homepage: http://www.driess.tu-berlin.de

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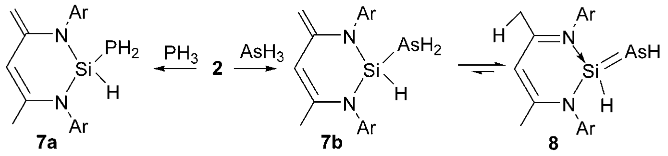

Scheme 2. Reaction of silylene **2** with PH_3 and AsH_3.

toluene solutions. The silylphosphane **7a** is the only product, as shown by ^{1}H NMR spectroscopy. The ^{31}P NMR spectrum reveals a triplet of doublets at $\delta = -257.4$ ppm ($^1J_{P,H} = 187.1$ Hz, $^2J_{P,H} = 23.5$ Hz), which clearly shows the formation of the 1,1-insertion product. Accordingly, the exocyclic methylene group is still present in **7a**, as shown by the ^{1}H and ^{13}C NMR spectra, and the ^{29}Si chemical shift ($\delta = -18.5$ ppm, $^1J_{Si,P} = 8.9$ Hz, $^1J_{Si,H} = 240.2$ Hz) is in the range typical of tetracoordinate silicon centers, with Si–H and Si–P single bonds but significantly more deshielded than the analogous 1,1-insertion product of silylene **2** and ammonia ($\delta = -45.0$ ppm).[15a] The diastereotopic PH_2 protons are observed as an AB spin system in the ^{1}H NMR spectrum at $\delta = 0.76$ and 0.81 ppm, each with a multiplet pattern and a geminal ^{1}H,^{1}H coupling constant of 12.1 Hz.

The structure of **7a** was confirmed by single-crystal X-ray analysis[18] (Figure 1). Suitable crystals were obtained from a concentrated *n*-hexane solution at -30 °C. The atoms of the C_3N_2 backbone of **7a** are nearly co-planar. The silicon center and the PH_2 group are located on opposite sides of the C_3N_2 mean plane. The PH_2 moiety occupies an equatorial position, whilst the hydrogen atom at silicon is located in an axial position. The Si–P distance (av. 224 pm) is in the characteristic range of Si–P single bonds.[19]

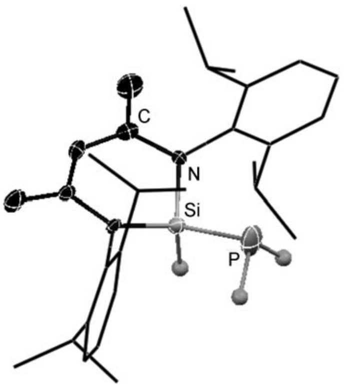

Figure 1. Molecular structure of **7a**. Hydrogen atoms are omitted except for those at P, Si. Thermal ellipsoids are set at 50% probability. Selected distances [pm] and angles [°] are mean values and ranges of four crystallographically independent molecules in the unit cell: Si–P 223.8(2)–224.2(2), Si–N 171.7(3)–173.2(3), C_{ring}–N 171.7; P-Si-N 119.1, N-Si-N 96.4, Si-C_3N_2 (mean plane) 50.0–57.8, P-C_3N_2 (mean plane) 26.0–49.9.

In contrast to the addition of PH_3, reaction of **2** with AsH_3 proceeds much faster, and no excess of the latter is necessary to complete the conversion. On preparative scales, gaseous AsH_3 was added to solutions of **2** in toluene at -78 °C. Upon warming to room temperature, the color of the reaction mixtures changed from yellow to deep blue; the arsasilene **8** could be isolated from this solution in a 48% yield (Figure 2).

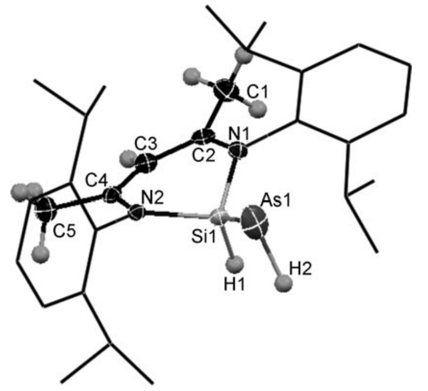

Figure 2. Molecular structure of **8**. Hydrogen atoms are omitted except for those at As1, Si1, C1, C3, and C5). Thermal ellipsoids are set at 50% probability. Selected distances [pm] and angles [°]: Si1–As1 221.78(1), Si1–N1 182.17(1), Si1–N2 180.26(1); As1-Si1-N1 119.1, As1-Si1-N2 116.2, N1-Si1-N2 96.4, Si-C_3N_2 (mean plane) 66.9, As-C_3N_2 (mean plane) 17.3.

The ^{1}H NMR spectrum of **8** is consistent with its higher symmetry as compared to the precursor **2** or the possible 1,1-addition product **7b**. Only six distinct resonances are observed for the protons of the isopropyl groups, and the exocyclic methyl groups appear as one singlet at $\delta = 1.42$ ppm. The SiH and AsH moieties each give a doublet ($\delta = 6.77$ and -2.22 ppm, $^3J_{H,H} = 6.7$ Hz); the remarkably high shielding of the As–H proton is unprecedented for As–H compounds[20] and is presumably due to relativistic effects (spin–orbit coupling). Owing to the dative N→Si coordination, the ^{29}Si resonance of **8** ($\delta = 17.6$ ppm) appears much further upfield than those of arsasilenes containing three-coordinate silicon atoms ($\delta = 179$–187 ppm).[21] DFT calculations of a model system (see below) confirm that the intense blue color of solutions of arsasilene **8** is attributed to a $\pi \rightarrow \pi^*$ transition (λ_{max}(toluene) = 590 nm, $\varepsilon = 246$, very broad, TD-DFT: $\lambda_{calcd} = 634$ nm) of the Si=As bond (HOMO) and mainly the ligand C_3N_2 backbone (LUMO; see Figure 4).

Suitable crystals for single-crystal X-ray analysis[18] were obtained from a concentrated toluene solution at -30 °C. As in the case of silylphosphane **7a**, the ligand backbone of arsasilene **8** exhibits an almost planar arrangement and the AsH moiety occupies an equatorial position. The Si–As distance of 221.78(1) pm is rather short and between the values observed for single (236 pm) and double bonds (216 pm).[21] This elongation results from dative N→Si=AsH interaction similar to the situation observed for related N-donor-stabilized silanones and silanthiones such as **3**.[3e,f,22] Accordingly, a significant lengthening of the N–Si bonds in arsasilene **8** (180.26(1), 182.17(1) pm) as compared to **7a** (171.7–173.2 pm) is observed owing to the Si=As multiple-bond character that weakens the Si–N π interactions.[22]

Remarkably, dissolution of pure **8** in benzene leads to an equilibrium with its tautomer (1,1-addition product), silylarsane **7b**, as shown by ^{1}H NMR spectroscopy. The concentration of **7b** reaches its maximum after about four hours. The equilibrium was also utilized to determine the ^{29}Si chemical shift of compound **7b** by dissolving **8** in C_7D_8, keeping this sample at room temperature for four hours, and then cooling to −50 °C. This sample contained compounds **7b** and **8** in the molar ratio of 2:8 according to ^{1}H NMR analysis. The same sample shows a new resonance in the ^{29}Si NMR spectrum at $\delta = -18.8$ ppm, which is almost identical to that of silylphosphane **7a** ($\delta = -18.5$ ppm) and thus could be assigned to **7b**. Furthermore, we learned that **7b** is the initial product from the reaction of **2** with AsH_3. Accordingly, if the reactants are combined at low temperature in C_7D_8 solutions, the formation of **7b** takes place starting at −50 °C, and the formation of arsasilene **8** can be observed above −30 °C. A maximum molar fraction of 0.70 of compound **7b** was observed by ^{1}H NMR spectroscopy when the above sample was warmed to ambient temperature and measured immediately. After this sample was kept at room temperature for five minutes, the ratio of **7b** to **8** was 3:7.

DFT calculations on model systems in which the bulky aryl groups were replaced by phenyl substituents at nitrogen were performed to rationalize the differences in the course of the reaction between silylene **2** and the different Group 15 hydrides NH_3, PH_3, and AsH_3. We calculated a series of possible products, namely the analogous model compounds **7a′–c′** (1,1-addition products, EH_2 group axial), **8a′–c′** (Si=E subunit equatorial)**,** **9a′–c′** (Si=E subunit axial), and **10a′–c′** (1,4-addition products) containing different Group 15 elements E (E = N, P, As; Figure 3).

The energies of **8a′–c′**, **9a′–c′**, and **10a′–c′** are referenced to **7a′**, **7b′**, and **7c′** ($E = 0$ kcal mol^{-1}), respectively. It is worth mentioning that no minimum could be located on the hypersurface for **7a′–c′** with the EH_2 group in equatorial position, unlike the structure observed experimentally for **7a**. This can be explained by the steric hindrance of the isopropyl groups in the 2,6-position of the aromatic rings, which force the EH_2 moieties into an equatorial position. The geometric parameters for the calculated model compounds **7a′** and **8b′** are in good agreement with the experimental values of silylphosphane **7a** and arsasilene **8**, respectively. The calculations predict that the hypothetical aminosilylene **10c′** and its tautomeric iminosilanes **8c′** and **9c′** are significantly higher in energy than the corresponding aminosilane **7c′**. In other words, the experimental observation of such species seems very unlikely, and this is in accordance with recent results.[15a]

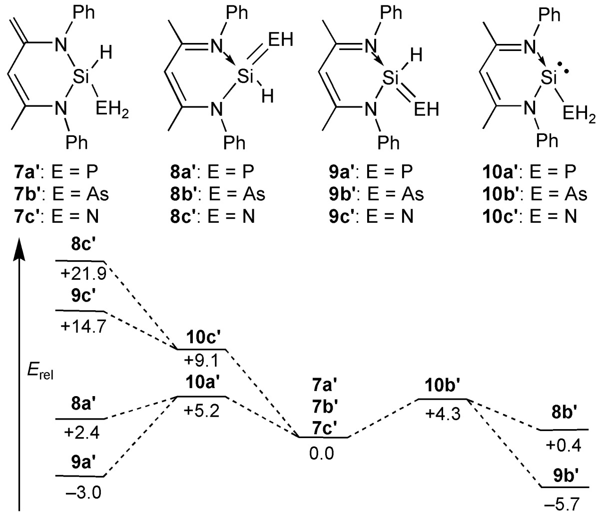

Figure 3. Calculated relative energies (kcal mol^{-1}) of model compound **7a′–c′**, **8a′–c′**, **9a′–c′**, and **10a′–c′**. Dashed lines connect isomers that exhibit the same element E and do not suggest possible reaction pathways.

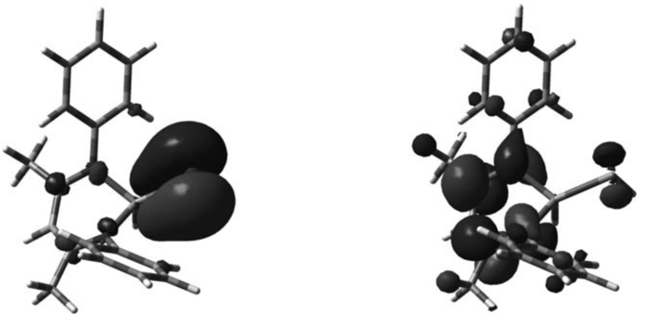

Figure 4. HOMO (left) and LUMO (right) of model compound **8b′**.

In contrast to the nitrogen systems, the calculated relative energies of the phosphasilenes **8a′**, **9a′** and arsasilenes **8b′**, **9b′** are about equal or even lower than those of the corresponding tautomeric 1,1-addition products **7a′** and **7b′**, respectively. Nevertheless, no experimental evidence could be found for the formation of the corresponding phosphasilene if **2** was allowed to react with PH_3, even at low temperatures.

As expected, the Si=As bond character of **8** as represented by the HOMO (Figure 4) is weaker with respect to Si=As systems with three-coordinate silicon atom owing to the dative N→Si interaction. Accordingly, MO analysis of the corresponding model system **8b′** revealed a reduced Wiberg bond index (WBI = 1.465) in comparison with diaminoarsasilene $(H_2N)_2Si{=}AsH$ as a reference system (WBI = 1.643). Our calculations further show that the deep blue color of **8** is due to the HOMO (Si=As π)→LUMO (ligand π*) transition (Figure 4).

In conclusion, double metal-free As–H bond activation occurs readily by reaction of the ylide-like silylene **2** with AsH_3, yielding the unique donor-stabilized, deep-blue arsasilene **8** with a HSi=AsH subunit. This subunit undergoes reversible tautomerization to give the corresponding silylarsane **7b**. In contrast, addition of PH_3 to **2** proceeds much more slowly and leads merely to silylphosphane **7a**. This drastic difference can be explained by the higher Brønsted acidity of AsH_3 versus PH_3, which facilitates As–H activation by the zwitterionic silylene **2**.

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[18] CCDC 793882 (**7a**) and 793881 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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