Silicon Double Bonds

DOI: 10.1002/anie.201007688

Reversible Formation of a Blue Arsasilene and Isolation of Air-Stable Emissive Disilenes[**]

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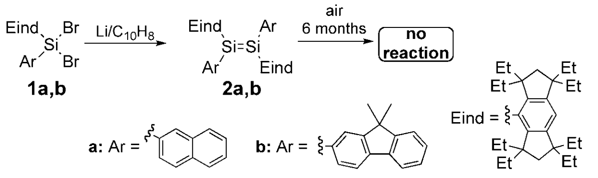
carbene homologues · fluorescence · isomerization · multiple bonds · silicon

Alkene homologues with formal double bonds involving the heavier Group 14 elements constitute a very active area of research in contemporary main group chemistry.[1] The major reasons for this ever-increasing interest are the high conformational flexibility and the inherently small HOMO–LUMO gap associated with the double bonds of heavier elements. Application of the principles of the electronic and steric stabilization of reactive main group metal centers has enabled a large number of heavier alkenes to be isolated that are thermally stable under inert conditions, but they usually retain a high reactivity. The clear downside to the resulting rich chemistry is the sensitivity towards oxygen and water, which is a major obstacle to the application of the above-mentioned unique properties and are thus sought to be overcome. The most air-stable disilene reported until recently was $Tip_2Si{=}SiTip_2$ ($Tip = 2,4,6\text{-}i\text{Pr}_3C_6H_2$) with a half-life of $t_{1/2} = 17$ min.[2] Nonetheless, double bonds involving heavier Group 14 and 15 elements are promising building blocks for incorporation into π-conjugated organic systems. Conjugated polymers based on P=C[3] and P=P[4] repeat units have been prepared, as well as the first molecular model compounds with Si=Si[5] and Si=P motifs.[6] The recent reports on air-stable disilenes with emissive properties[7] have, therefore, raised considerable hopes in regard to the incorporation of compounds containing double bonds between heavier elements for incorporation into materials for optoelectronic devices.

By reducing the hydrindacenyldibromosilanes **1a** and **1b**, the research group of Matsuo and Tamao obtained the disilenes **2a** and **2b** as red crystals in yields of 57% and 37%, respectively.[7] The longest wavelength UV/Vis absorptions ($\lambda_{max} = 504$ nm (**2a**), 510 nm (**2b**)) are remarkably red-shifted compared to that of the corresponding diphenyl-substituted disilene reported earlier ($\lambda_{max} = 461$ nm);[5b] this is most likely a consequence of the extension of the conjugated systems through the use of larger conjugated substituents (Scheme 1).



Scheme 1. Synthesis of air-stable disilenes **2a,b**.[7]

In solution, disilenes **2a,b** survive exposure to air for several minutes (half-life, $t_{1/2} = 2$ to 4 h); solid (presumably crystalline) samples even remain unchanged for several months. The extremely bulky Eind substituent not only accounts for this unusual air stability of disilenes **2a,b**, but, importantly, also forces the organic π system and the perfectly planar Si=Si bonds into a coplanar conformation. Similarly to previously reported Si=Si-containing compounds with Eind substituents, the rigidity of **2a,b** results in fluorescence with appreciable quantum yields in the solid state at room temperature ($\Phi_F = 0.23$ (**2a**); 0.21 (**2b**)). In addition, the rigidity of the hydrindacenyl framework probably diminishes the vibrational relaxation of excited states, which could explain the comparatively small Stokes shift of the emissions in solution compared to those observed in the case of the low-temperature fluorescence of alkyl and aryl disilenes with less sterically demanding substituents.[8] The availability of air-stable Si=Si units in principle offers the possibility of incorporating disilene building blocks into extended conjugated π systems by taking advantage of the synthetic repertoire available to organic chemists.

Another difficulty to address to develop the chemistry of double bonds between heavier elements effectively is the limited number of preparative tools available for their synthesis. With the notable exception of the boryl- and amino-substituted disilenes generated by the addition of boranes and amines to the Si≡Si bond of a disilyne,[9] the preparation generally involves either photolytic conditions or either strongly reducing reagents or reactants such as lithiated species.[1] One of the main objectives of current research is, therefore, the development of new synthetic methods that avoid such conditions. A recent report by Driess and coworkers on the reversible formation of a donor-stabilized Si=As bond can, thus, be regarded as a starting point.[10]

As the research groups of Driess and Roesky have shown previously, the zwitterionic N-heterocyclic Driess silylene **3**[11] reacts smoothly with simple second row element hydrides

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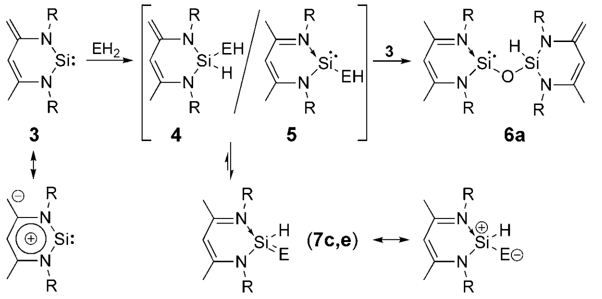
[**] Financial support by the Aventis foundation (Karl-Winnacker Fellowship) is gratefully acknowledged.

EH_2 (E = O,[12] NH[13]). The presence of the electron-rich conjugated backbone confers considerable variability in terms of the accessible reaction pathways. Reactions can occur either through direct 1,1-addition across the silicon center or by initial 1,4-addition involving the exocyclic methylene group. The possibly involved intermediates **4a** or **5a** could not be isolated from the reaction with water (E = O); an additional equivalent of silylene **3** served as the trapping reagent to afford the mixed-valent siloxane **6a** (Scheme 2).[12] Treatment of **3** with ammonia (E = NH) affords the 1,1-addition product **4b** exclusively.[13] In contrast, the reaction of **3** with H_2S yields **7c**, a compound with a formal Si=E bond (E = S).[14] However, the large difference in the electronegativity between silicon and sulfur suggests a substantial ylidic contribution to the electronic ground state of **7c**. In addition, the inherent difficulties of Group 16 elements to support more than two valencies limit the use of Si=S motifs for the design and synthesis of more extended systems.



Scheme 2. Addition of element hydrides to the zwitterionic Driess silylene **3** (R = 2,6-*i*$Pr_2C_6H_3$; **a**: E = O; **b**: E = NH; **c**: E = S; **d**: E = PH; **e**: E = AsH).

The new reactions of **1** with PH_3 and AsH_3 constitute a major breakthrough.[10] While the quantitative reaction with PH_3 stops at the 1,1-addition stage **4d**, the initial product **4e** of AsH_3 addition (characterized by NMR spectroscopy) undergoes migration of a hydrogen atom from the arsenic to the methylene moiety of the ligand backbone. This affords the donor-stabilized arsasilene **7e**, which was isolated in 48% yield. Notably, in contrast to the sulfur derivative **7c**, arsasilene **7e** is in equilibrium with the initial product **4e**, and thus the transformation is fully reversible. Despite the stabilization of the Si–As bond by the donor group, the distance between the atoms in **7e** in the solid state is closer to the only structurally characterized example of a Si–As double bond[15] than to a standard Si–As single bond. The Wiberg bond index of 1.465 also supports the notion of substantial double bond character and a less pronounced ylidic contribution to the ground state of **7e** (compared to **7c**). Most remarkable is the very small HOMO–LUMO gap of the intensely blue **7e**. The longest wavelength absorption is observed at $\lambda_{max} = 590$ nm in toluene and was assigned to a π–π^* transition on the basis of DFT calculations. Even though the LUMO is unsurprisingly ligand centered (a common feature of many donor-stabilized systems), the small band gap suggests interesting possibilities upon its incorporation into more extended conjugated π systems.

The two studies highlighted herein[7,10] are important milestones on the way towards the more widespread application of double bonds between heavier elements. We can look forward to further developments in regard to air-stable and/or readily accessible double bond motifs based on heavier elements.

Received: December 7, 2010

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