Silicon Chemistry

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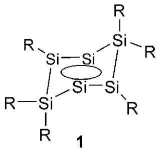
News from Silicon: An Isomer of Hexasilabenzene and A Metal–Silicon Triple Bond**

*Claudia Gerdes and Thomas Müller**

aromaticity · carbene analogues · multiple bonds · organosilicon compounds

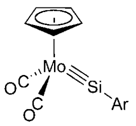
In memory of Herbert Schumann

Novel, stable, isolable, and storable key intermediates were recently introduced into organosilicon chemistry. These compounds have the potential to broaden significantly the synthetic chemistry of low-coordinated silicon.[1–3] This is demonstrated by two recent landmark achievements: The characterization of an unprecedented isomer of hexasilabenzene (**1**)[4] and by the synthesis of the molybdenum–silylidyne complex **2**.[5]



1

R = 2,4,6-triisopropylphenyl (Tipp)
Ar = C_6H_3-2,6-bis-Tipp



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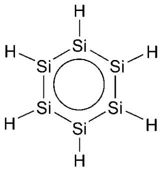
Benzene is central for chemistry, not only from a synthetic point of view. Its thermodynamic stability and in particular its physical and structural properties also invoked the development of the concept of aromaticity, with all its implications for physical and theoretical chemistry. Interestingly, theory predicts that hexasilabenzene (Si_6H_6) is not a planar molecule with sixfold symmetry such as **3**: a second-order Jahn–Teller distortion forces it into a chairlike puckered structure **4** with D_{3d} symmetry.[6,7] Moreover, calculations of the potential energy surface of Si_6H_6 indicate a clear preference for σ-bonded polyhedral cluster-type molecules over planar systems involving π bonding.[6] Thus, hexasilaprismane **5** is found to be significant more stable than the D_{3d}-symmetric hexasilabenzene **4** (by 22.7 kJ mol^{-1}, according to calculations at the CCSD(T)/6-311 + G(d,p)//MP2/6-311 + G(d,p) level).[8]



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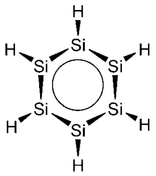

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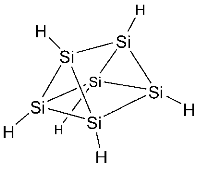

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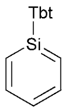
The synthesis of silabenzoids (benzene analogues, in which the carbon atoms have been replaced by silicon atoms) has been hampered for a long time by the reluctance of silicon to participate in π bonding. Major synthetic achievements during the last decade, however, have allowed the synthesis of sila- (**6**) and 1,2-disilabenzene (**7**), both substituted with bulky protection groups at the silicon atoms which provide the kinetic stabilization needed for their isolation and characterization.[9,10]



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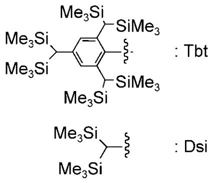

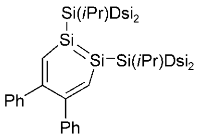

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In contrast, the synthesis of the persila compound—the hexasilabenzene, Si_6H_6—or derivatives thereof still remains one of the holy grails in organosilicon chemistry. Numerous synthetic attempts started from the conceptually clear premise that reductive dehalogenation of trihalosilanes **8** or tetrahalodisilanes **9** would provide the synthetic equivalent of monocoordinated silicon atoms (RSi), which would then eventually form triple-bonded or cyclic conjugated persila compounds. These attempts were, however, unsuccessful in as far as only polyhedral silicon compounds $(RSi)_n$ (with $n > 3$) were formed. Depending on the substituents R and the reaction conditions, persilatetrahedranes **10**, -prismanes **11**, or -cubanes **12** were isolated (Scheme 1).[11] In this respect, the recent synthesis of three disilynes **13** was an important breakthrough (Scheme 2).[12–14] In all three cases, the extreme steric bulk of the substituents R prevented the formation of polyhedral cage compounds and was a prerequisite for the success.

A new impetus to the hexasilabenzene problem came recently from work by Scheschkewitz and co-workers.[4] They used the disilenyllithium reagent **14**[1a] for the synthesis of the unsymmetrically substituted trichlorocyclotrisilane **15** with three different silicon atoms. Reduction of trisilane **15** afforded the hexasilabenzene isomer **1** as dark green crystals in 52 % yield (Scheme 3).

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[*] C. Gerdes, Prof. Dr. T. Müller
Institut für Reine und Angewandte Chemie
Carl von Ossietzky Universität Oldenburg
Carl von Ossietzky Strasse 9–11, 26211 Oldenburg (Germany)
Fax: (+ 49) 441-798-3352
E-mail: thomas.mueller@uni-oldenburg.de

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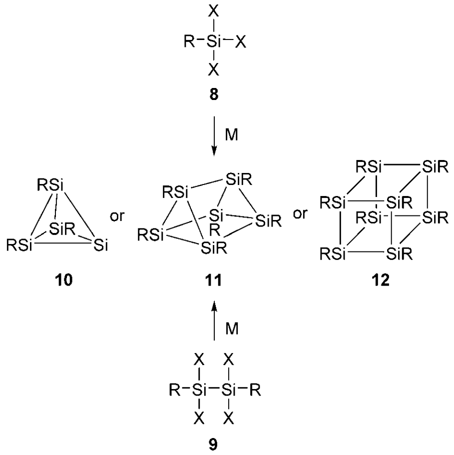
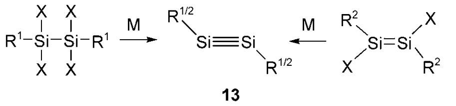
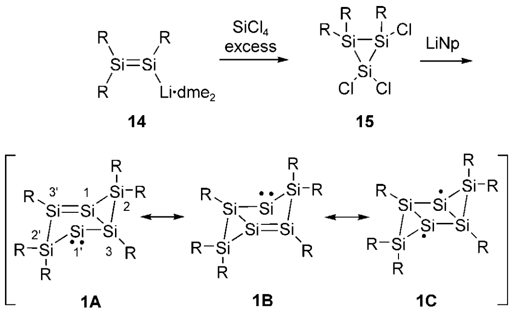


Scheme 1. Synthesis of polyhedral persila compounds **10–12** by reductive dehalogenation of halosilanes **8** and **9** (X = Cl, Br; M = Group I, II metal, lithium naphthalide (LiNp)).[11]



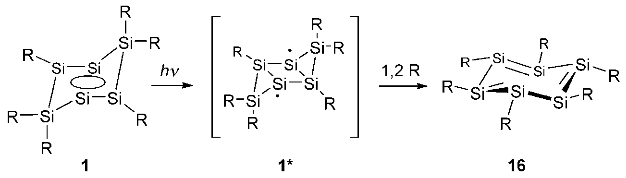
Scheme 2. Synthesis of disilynes **13** by reductive dehalogenation (X = Cl, Br; M = *t*BuLi, lithium naphthalide, C_8K; R^1 = Si(*i*pr)Dsi$_2$, R^2 = (C_6H_2-2,6-(CH(SiMe$_3$)$_2$)-4-(C(SiMe$_3$)$_3$) (Bbt) or Si(Me)Si(*t*Bu$_3$)$_2$).[12–14]



Scheme 3. Synthesis of hexasilabenzene isomer **1** by reductive elimination from trisilane **15** (R = Tipp). Significant Si-Si bond lengths in **1**: Si1-Si3 232.8 pm; Si1-Si3′ 230.3 pm; Si1-Si1′ 272.9 pm. dme = 1,2-dimethoxyethane.[4]

The NMR spectroscopic data of **1** in solution indicate three different types of silicon atoms in significantly different bonding situations in the molecule [$\delta(^{29}\mathrm{Si}) = 124.6$ (Si3), -84.8 (Si2), and -89.3 (Si1)]. This bonding situation is confirmed by results from an X-ray diffraction analysis: Six silicon atoms in three different oxidation states—+II (SiR$_2$), +I (SiR), 0 (Si)—form a tricyclic molecule **1**, which exhibits a chairlike puckered conformation with a central rhomboid Si$_4$ ring. The distances between neighboring silicon atoms in **1** are at the short end of the range of typical Si–Si bonds in cyclopolysilanes (233–239 pm; Scheme 1)[15] and the diagonal Si1–Si1′ distance is significantly larger than typical covalent Si–Si bonds (Scheme 3).

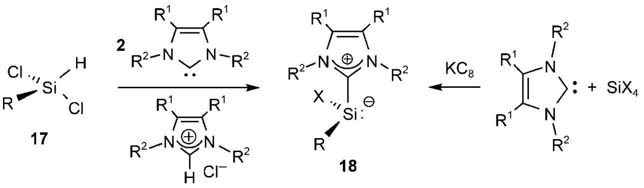
These analytical data together with results from quantum mechanical calculations suggest an intriguing bonding pattern in **1**: Six electrons (2 π and 2 σ electrons as well as a lone pair of electrons) are delocalized over the central Si$_4$ ring, which can be described by the resonance forms **1A**↔**1B** in Scheme 3). The three molecular orbitals involved provide the basis for six cyclically delocalized electrons across the Si$_4$ ring. In addition, the results of the computations indicate the minor importance of the biradicaloid representation **1C** for the ground state of **1**. Nucleus-independent chemical shift (NICS)[16] computations indicate a strong diatropic ring current across the Si$_4$ ring which is characteristic of aromatic molecules. On the basis of their structural data and their theoretical analysis, the authors propose an alternative form of aromaticity called “dismutational aromaticity” for hexasilabenzene isomer **1**, with its six silicon atoms in three different formal oxidation states. Computations on model compounds with 2,6-diisopropylphenyl (Dipp) substituents show that the tricyclic isomer **1** is less stable ($\Delta G^{298} = 48.9\ \mathrm{kJ\,mol^{-1}}$) than the corresponding hexasilabenzene ($18.0\ \mathrm{kJ\,mol^{-1}}$) or hexasilaprismane ($0\ \mathrm{kJ\,mol^{-1}}$).[4] The close structural relationship between isomers **1** and **16** opens up the intriguing possibility that the dismutational aromatic compound **1** might be an important intermediate in the final synthesis of the more stable Hückel-aromatic hexasilabenzene **16** by, for example, photochemical activation of **1** (Scheme 4).



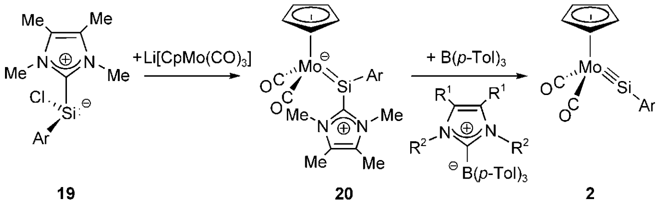
Scheme 4. Suggested photochemical isomerization of tricyclic isomer **1** to give hexasilabenzene **16**.

The second breakthrough in organosilicon chemistry that will be mentioned here would not have been possible without the significant progress made in the use of N-heterocyclic carbenes (NHC) in the synthesis low-valent organoelement compounds.[17] In particular, NHCs have been shown to stabilize silicon centers in low oxidation states.[2,3,18] Synthetically useful approaches were revealed by the research groups of Roesky[2] and Filippou.[3] The formal reductive elimination of HCl from chlorosilanes **17** leads to the formation of stable complexes **18** between chlorosilylenes and the NHC. These adducts **18** of dihalosilylenes SiX$_2$ (X = Cl, Br) with NHCs can also be prepared by reduction of the NHC complexes of the corresponding silicon(IV) halides (Scheme 5).

The first outstanding result based on the application of a precursor of type **18** has been reported: Filippou et al. synthesized and fully characterized the first molybdenum–silylidyne complex **2** with a genuine molybdenum–silicon triple bond,[5] thereby closing the remaining gap in metal–tetrelyne complexes.[19] A remarkably simple salt elimination reaction between the silicon(II) chloride **19** and Li-[CpMo(CO)$_3$] (Cp = cyclopentadienyl) in toluene at 100 °C affords the base-stabilized silylidene complex **20** (Scheme 6). The final and intriguing step of this sequence is cleavage of the Si–NHC linkage with tris-*p*-tolylborane in boiling *o*-xylene and the formation of the molybdenum–silylidyne complex **2**. The driving force for this reaction is thought to be



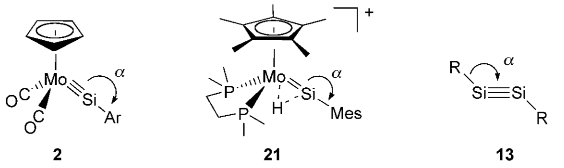
Scheme 5. Synthesis of NHC-stabilized silylenes **18** (R = Cl, Br, C_6H_3-2,4-Tipp, C_6H_3-2,4-Mes; X = Cl, Br; R^1 = H, Me; R^2 = Me, Dipp, Mes) by reductive elimination of **17** or by reduction. Mes = 2,4,6-trimethylphenyl.



Scheme 6. Synthesis of the molybdenum–silylidyne complex **2** starting from silylene–carbene complex **19** (Ar = C_6H_3-2,4-Tipp).[5]

the formation of a relatively strong carbon–boron bond at the expense of the weaker silicon–carbon bond.[5]

The experimental molecular structure of complex **2** resembles an almost C_s-symmetric three-legged piano stool with a very short Mo≡Si bond of 222.4 pm (Scheme 7). A similar short Mo–Si bond was found previously only in the complex cation salt **21**$[B(C_6F_5)_4]$ (Mo–Si: 221.9 pm) isolated by Mork and Tilley.[20] In this case, the Mo–Si bond is bridged by an additional three-center Mo–H–Si bond. Remarkably, in the molecular structures of **2** and **21**, the multiply bonded silicon atom has an almost linear coordination. This indicates a classical triple bond consisting of one σ bond and two orthogonal π bonds.[21] This coordination geometry differs significantly from the strongly bent structure reported for disilyne **13** (R = Bbt; Scheme 7), but it nicely corresponds to the molecular structures of other molybdenum– or tungsten–tetrelyne complexes.[19,21]



Scheme 7. Selected bond parameters of the molybdenum–silylidyne complex **2**,[5] the complex cation **21**,[20] and disilyne **13**[14] (**2**: Mo-Si 222.4 pm, α 173.5°; **21**: Mo-Si 221.9 pm, α 170.9; **13** (R = Bbt): Si-Si 210.8 ppm, α 133.0°).

The results reported by the research groups of Scheschkewitz[4] and Filippou[5] not only show very exciting, novel, and important chemistry but also provide unique solutions for long-standing major synthetic challenges in organosilicon chemistry. In both cases the key for the success was the correct choice of the precursor compound. In particular, the NHC complexes of silicon(II) halides[2,3] have the potential to become a central class of compounds in organosilicon chemistry.

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