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Conjugated π Systems with Heavy Main Group Elements—A Stable Neutral Silaarene and the First Tetrasilabutadiene[**]

Thomas Müller[*]

The question of conjugation and aromaticity in organosilicon compounds has recently attracted considerable interest. For instance, the influence of cyclic conjugation on the stability of aminosilylenes has aroused controversy.[1] However, even simple stable neutral silaarenes like derivatives of silabenzene have been elusive until very recently. This is in sharp contrast to the successful synthesis of kinetically stabilized silenes and 1-silaallenes.[2] In addition calculations predict for silabenzene a resonance stabilization of about 75% of that calculated for benzene.[3] Early fundamental investigations showed that silaarenes can be produced as short-lived intermediates in the gas phase or in the matrix at low temperatures and that they can be characterized by IR, UV, or PE spectroscopy.[4] None of these compounds could be however investigated in solution or even isolated in substance. Investigations by Märkl and co-workers[5] revealed the extraordinary reactivity of silaarenes. Even the with bulky groups substituted silabenzene **1** is at −100°C only of limited stability.

On the other hand the search for anionic silaarenes has been more successful during the last years. Almost simultaneously the groups of Boudjouk, Tilley, and West[6] reported the synthesis of silolyl anions **2**, analogues of the cyclopentadienyl anion, and silole dianions **3**. Surprisingly, the silicon in **2** is pyramidalized and the anions have localized C=C bonds. Cyclic conjugation with involvement of the silicon atom seems to play only a minor role in **2**. In contrast, silole dianions **3** as well as germole dianions[7] have delocalized π electron systems with almost identical CC bond lengths. The silicon atom in **3** is markedly deshielded relative to tetracoor-

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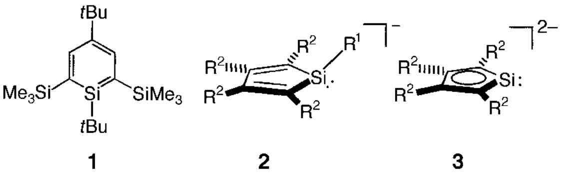


R^1 = alkyl, aryl, R_3Si; R^2 = Me, Et, Ph

dinated silicon atoms ($\delta(^{29}Si) = 64$, $R^2 = Ph$). Ab initio calculations for **3** ($R^2 = H$) and for its higher homologues suggest considerable resonance stabilization of the dianions, and the calculated magnetic properties give evidence for an aromatic ring current.[6c,d,7]

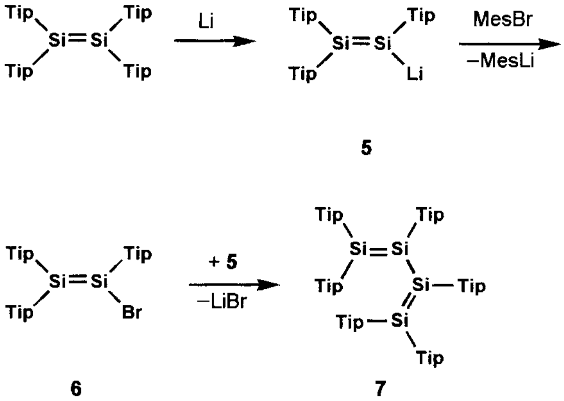
Another highlight of the experimental and theoretical studies in this area is the synthesis of a neutral silaarene stable at room temperature by the group of Tokitoh and Okazaki at Tokyo University. Like often in the chemistry of low-valent silicon, the sufficient protection from bimolecular reactions of the inherently stable target compound is also the key to success in this case. By taking advantage of the particular properties of the 2,4,6-tris[bis(trimethylsilyl)methyl)]phenyl (Tbt) protecting group the Tokyo group synthesized the 2-Tbt-2-silanaphthalene **4** by a HBr eliminiation in 80 % yield as a colorless crystalline powder.[8] An X-ray analysis of the compound established the molecular structure and proved the planar environment of the silicon atom; the severe disorder of the 2-silanaphthalene ring in the crystal, however, prevents any discussion of structural details. The reported spectroscopic data are certainly unambiguous. The ^{29}Si NMR chemical shift ($\delta(^{29}Si) = 87.4$) is characteristic for sp^2-hybridized silicon in silenes and is in good agreement with calculated NMR chemical shifts for substituted 2-silanaphthalenes (e.g., $\delta(^{29}Si) = 94.3$ for 2-phenyl-2-silanaphthalene in which the phenyl group is fixed in a perpendicular conformation to the plane of the silanaphthalene in analogy to the Tbt-residue in **4**). Unequivocally, **4** posseses a Si=C bond, a finding which is supported by the chemical reactivity of **4**, which is typical for silenes.

4

(a)

What can be learned about aromaticity in this compound? Is the Si=C bond localized, or is the π bond part of a delocalized system similar to naphthalene? An indication for a delocalized structure are the $^1J_{Si,C}$ coupling constants to both neighboring carbon atoms ($^1J_{Si,C1} = 92$ Hz and $^1J_{Si,C3} = 76$ Hz), which are both clearly larger than expected for a Si–C bond (about 50 Hz). The value of the coupling constant suggests double-bond character for both Si–C bonds, although the comparison with coupling constants in silenes is problematic due to the very limited number of comparative values ($^1J_{Si=C}$: 83–85 Hz in $(Me_3Si)_2Si{=}C(OSiMe_3)R$[2a] and 104 Hz in a 1-silaallene).[2b] A clear geometrical indication for the delocalized structure of 2-silanaphthalenes is provided by DFT calculations. The calculated SiC1 and SiC3 distances in 2-silanaphthalene are intermediate between the Si=C bond length in silene and the Si–C bond length in methylsilane. This implies a bond order between 1 and 2 for both SiC bonds in **4**. The calculation of the Nucleus Independent Chemical Shift (NICS)[9] for 2-silanaphthalene, a method invented by Schleyer and co-workers for the quantification of the aromaticity of a compound, support the experimental evidence for the aromaticity of 2-silanaphthalene. The NICS indicates the magnetic shielding in the center of a cyclic molecule. Characteristicly NICSs are negative for aromatic compounds: for benzene a shielding of −9.7 ppm is calculated. The NICS calculated for 2-silanaphthalene is only slightly larger than that for naphthalene (−8.9 ppm for 2-silanaphthalene and −9.9 ppm for naphthalene). The experimental and theoretical results show concurrently that the aromaticity of naphthalene is only marginally reduced by the replacement of a ring carbon by a silicon atom.

These results give rise to the next question: to what extent is conjugation between Si=Si bonds possible? Recent studies by Weidenbruch and co-workers give a preliminary answer. They synthesized in a fascinating, simple reaction sequence the first tetrasilabutadiene stable at room temperature (**7**)[10]. The key step to the synthesis of **7** is the metathesis reaction between a transitory disilene bromide **6** and a disilenyllithium compound **5**.



(b)

Tetrasilabutadiene **7** is kinetically exceptionally stabilized by six bulky 2,4,6-triisopropylphenyl (Tip) substituents. In the absence of air the compound melts without decomposition, and only at 267°C it is destroyed irreversibly! In the crystal **7** adopts a twisted s-*cis* conformation (C_2 symmetry) with a dihedral angle of 51° between the planes of the planar Si=Si bonds. Of interest are the SiSi distances in the molecule. The Si=Si bond lengths (217.5 pm) are 2–3 pm longer than isolated Si=Si bonds,[11] and the central Si–Si bond (232.1 pm) is relatively short, especially in view of the bulky Tip substituents. Due the limited published data, however, it is hard to distinguish whether this short central Si–Si bond is an indication of conjugation, as suggested by Weidenbruch et al. or is a result of the sp^2 hybridization of the silicon atoms in **7**. SiSi separations for $Si(sp^2)$–$Si(sp^3)$ bonds in disilenes scatter between 233.4 and 241.1 pm.[11] The UV spectra of a solution of **7** provides more clear evidence. The bathochromic shift of about 100 nm of the characteristic band of the π–π* transition in disilenes in **7** indicates the conjugation between the Si=Si bonds in **7** in solution. A similar red shift is also found by comparison of the UV absorption of ethene and of 1,3 dienes with s-*cis* conformation.[12] Further investigations of the bonding situation in **7** are, however, certainly desirable to determine more precisely the interaction between the two Si=Si bonds.

With the isolation and characterization of these two substances another two dream molecules of the organosilicon chemists became reality. What is next on the agenda? Certainly, the synthesis of other silaarenes up to hexasilabenzene and its valence isomers will give us further important insights in the nature of chemical bonding in main group chemistry. At the moment, however, the quest for compounds with dicoordinated silicon seems to be a hotter topic. While stable silylenes have already gained entry into text books, the evidence for molecules with triply bonded silicon is rather scarce. Possible synthetic approaches to silaalkynes, disilaalkynes, and also 2-silaallenes are currently under intensive investigation in several groups.[13–15] Theoretically oriented papers have been published, which suggest possible synthetic pathways to these also thermodynamically very unstable compounds.[13] Suitable precursors for the generation of 2-silaallenes have been recently synthesized,[14] and the doubly bridged isomer of the disilaalkyne has been indentified spectroscopically in the gas phase and in the matrix.[15] Further highlights from the chemistry of low-valent silicon might therefore be expected for the near future.

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