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Low-Valent Silicon in Formally Antiaromatic Four-Membered Ring Systems**

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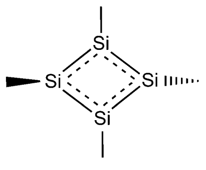
antiaromaticity · low-coordinate silicon · low-valent compounds · organosilicon compounds · silicon

During the past years, great progress has been made in the chemistry of low-valent and low-coordinate silicon. Several novel classes of organosilicon compounds have been discovered, mainly by using properly designed substituents for kinetic and thermodynamic stabilization[1,2] and by considering a fundamental recent discovery, the stabilization of highly reactive species such as Si_2, Si_2Cl_2, $SiHal_2$, and SiRHal (Hal = halide) in the form of their adducts with Arduengo-type N-heterocyclic carbenes (NHCs).[3] Such adducts are promising starting materials for the synthesis of other low-valent silicon species.

Comparable compounds of low-valent silicon and carbon very often differ in their structures and electronic properties, mainly owing to the fact that silicon, in contrast to carbon, forms only weak π bonds and does not profit energetically from hybridization.[4] Therefore, the discovery of novel classes of compounds in organosilicon chemistry is often connected with the introduction of novel bonding concepts.

The fundamental question of how silicon would handle antiaromaticity in four-membered ring systems has been tackled experimentally for the first time in two very recent publications: The group of Tamao and Matsuo has presented the synthesis of a tetrasilacyclobutadiene with a planar rhombic framework (**A**) using a novel aryl substituent for kinetic stabilization,[5] and the groups of Roesky and Frenking have described the preparation of a planar dimer of a silaisonitrile (**B**) stabilized by very bulky Power-type aryl substituents.[6]



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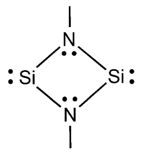

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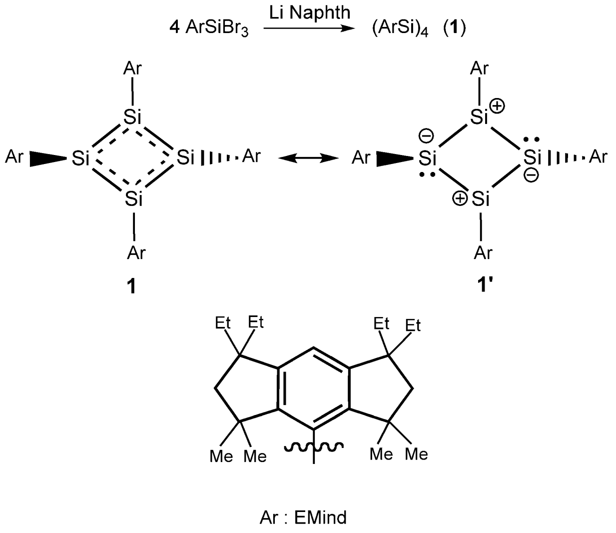

Scheme 1. Synthesis and structure of the tetrasilacyclobutadiene **1**.

The reaction of the aryl(tribromo)silane (EMind)$SiBr_3$ with three equivalents of lithium naphthalenide led to the air- and moisture-sensitive orange tetrasilacyclobutadiene Si_4Ar_4 (**1**, Scheme 1). Compound **1** decomposes at room temperature slowly in solution and even in the solid state. Nevertheless, it could be characterized by X-ray crystallography and NMR and UV/Vis spectroscopy. The molecular structure of **1** features a planar central Si_4 ring with nearly identical Si–Si distances (ca. 2.28 Å) intermediate between typical Si–Si single (2.34 Å) and double (2.14 Å) bonds. Thus, no bond alternation can be observed. Up to this point, **1** would fulfill the criteria for an antiaromatic system (four delocalized π electrons in a cyclic, planar compound), but the further observations speak against this classification: The silicon atoms exhibit two different coordination geometries; one set of diagonal silicon atoms (Si1 and Si3) shows a planar and the other set (Si2 and Si4) a pyramidal surrounding. The positions of the *ipso*-carbon atoms of the aryl groups at Si2 and Si4 deviate up and down from the plane of the Si_4 ring by approximately 34°. The presence of two types of silicon atoms is also manifested in the solid-state ^{29}Si NMR CP-MAS spectrum (CP = cross polarization, MAS = magic-angle spin-

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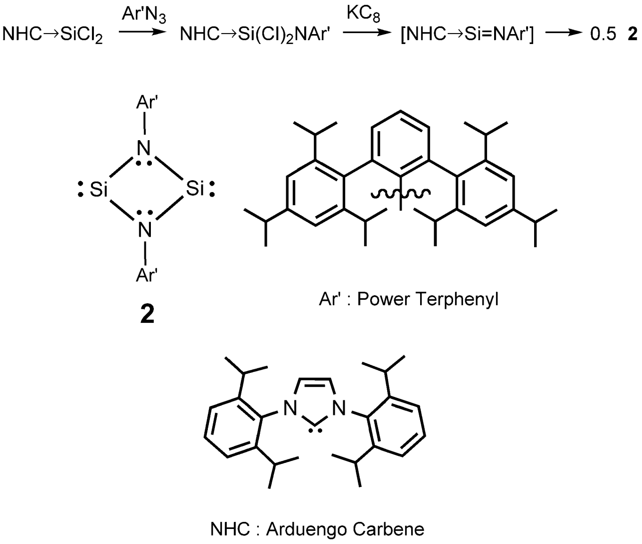
ning), which shows two sets of resonances, one in the higher field ($\delta = -52$, -50 ppm), the other in the lower field ($\delta = 300$, 308 ppm) region. The considerable chemical shift difference indicates the contribution of the resonance structure **1′** with charge separation on the silicon centers. Calculations at the B3LYP/6-31G(d,p) level also support the importance of the polar structure **1′**. A natural population analysis (NPA) reveals considerable charge differences for the two types of silicon atoms (Si1 +0.647, Si3 +0.637, Si2 +0.144, Si4 +0.167). A calculated nucleus-independent chemical shift value[7] (NICS(1)) of −0.9 indicates the lack of important contributions from a diatropic or paratropic ring current effected by π-electron delocalization.[8] Thus, the tetrasilacyclobutadiene **1** is "*neither aromatic nor antiaromatic, but nonaromatic*".[5] Interestingly, the NMR spectra (^{1}H, ^{13}C) of **1** in solution indicate a fluxional structure based on the rapid interconversion of the Si1,3 and Si2,4 positions (automerization).

Whereas the synthesis of the low-valent silicon compound **1** involved the reduction of a silicon(IV) compound, the synthesis of **2** was performed starting from a carbene-stabilized silicon(II) species. Reaction of the NHC–dichlorosilylene adduct (NHC: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with aryl azide (Ar′: 2,6-bis(2,4,6-triisopropylphenyl)phenyl) led to the corresponding NHC-stabilized dichlorosilaimine, which by reduction with KC_8 afforded the first member of a novel class of organosilicon compounds, the dimeric silaiosonitrile **2** (Scheme 2). The monomeric silaisonitrile is regarded as an intermediate, which is stabilized only insufficiently by the bulky aryl substituent and by the carbene.



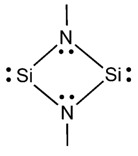
Scheme 2. Synthesis and structure of the dimeric silaisonitrile **2**.

Compound **2** is stable in solution and in the solid state. It has been characterized by X-ray crystallography and by NMR spectroscopy. Each of the silicon atoms is two-coordinate, and the four-membered Si_2N_2 ring is nearly planar, with endocyclic N-Si-N bond angles of 86.02(6)° and Si-N-Si bond angles of 94.02(9)°. The Si−N bond lengths (av. 1.755(1) Å) agree with those found for other heterocycles containing low-valent silicon atoms. Calculations were performed using density functional theory at the M05-2X/TZVPP level (Ar′ = phenyl). The calculated distances and angles agree well with the experimental values.

The question whether the novel ring system can be regarded as a delocalized four-π-electron antiaromatic species is of special interest. An natural bond orbital (NBO) analysis provides charges of −1.33 e for the N atoms and of +1.23 e for the Si atoms. The ^{29}Si chemical shift at rather low field ($\delta = 183.29$ ppm) is in accordance with positively charged silicon atoms. From this data it is concluded that the cyclic Si_2N_2 moiety in **2** exhibits rather strongly polarized $Si^{\delta+}{-}N^{\delta-}$ σ bonds. Only weak π-type back-bonding contributions from the N lone pairs into the vacant Si p orbitals take place. The calculated NICS(1) value (+0.91) is in accordance with this interpretation.[8] The structure **2** with π-type lone pairs at the nitrogen atoms and vacant π orbitals at the silicon atoms represents the dominating form. Further calculations will have to consider this interesting bonding situation in more detail.

Compound **2** is the first example of a disilylene containing two-coordinate silicon atoms. The Laplacian distributions nicely exhibit the charge concentrations of the electron lone pairs at the silicon atoms in the exocyclic positions of the planar ring system. The silicon lone pairs are effectively protected by the *N*-aryl substituents, but they are still accessible for further reactions. This reactivity is documented by the reaction with trimethylsilyl azide, which leads to the corresponding bis(silaimine).

In carbon chemistry, the parent species in the class of four-membered, four-π-electron systems is cyclobutadiene, C_4H_4. This highly reactive species is regarded as a key compound to study the consequences of antiaromaticity.[9,10] There is experimental and theoretical evidence that a Jahn–Teller distortion leads to a rectangular D_{2h} structure with alternating single and double bonds. This structure rapidly undergoes automerization. A cyclic carbon compound with two two-coordinate carbon atoms bridged by NR groups (type **C**), comparable to the silicon compound **2** of type **B**, has not been described in the literature to date. However, an isoelectronic compound of type **D**, featuring one two-coordinate carbon atom, two NR groups, and one BR group, is known and was described as a species with the four π electrons mostly distributed over the N-C-N fragment.[11]



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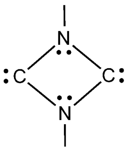

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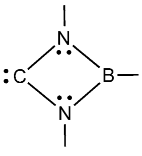

D

In silicon chemistry, the kinetically stabilized compounds **1**[12] and **2** provide valuable insight into how silicon handles antiaromaticity: For the Si_4 ring system, a novel type of Jahn–Teller distortion leads to the planar rhombic charge-separated tetrasilacyclobutadiene **1′** as the dominating form; for the Si_2N_2 ring system, a nearly quadratic structure with π-electron pairs mainly located at the nitrogen atoms is found, as represented by structure **2.** With these structural solutions, the formation of conjugated systems including Si=El π bonds (El = Si, N) is avoided. On the other hand, conjugation in a cyclic four-π-electron system is a prerequisite for antiaromaticity. Thus, the description of these novel types of organosilicon compounds as antiaromatic species is a rather formal one.

Recent calculations have shown that several isomers with similar ground-state energies exist in low-valent silicon compounds, including such isomers containing substituent-free low-coordinate silicon atoms.[3] The class of Si_nH_n compounds with $n = 4$ or 6 represents a good example.[13] Based on these results, the synthesis of further exciting compounds with unprecedented structural features can be anticipated. Future experimental work in this field will be dominated by the search for the ideal substituent and by the use of NHCs as stabilizing neutral ligands.

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