Silicon Compounds

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An Extensive n, π, σ-Electron Delocalized Si_4 Ring**

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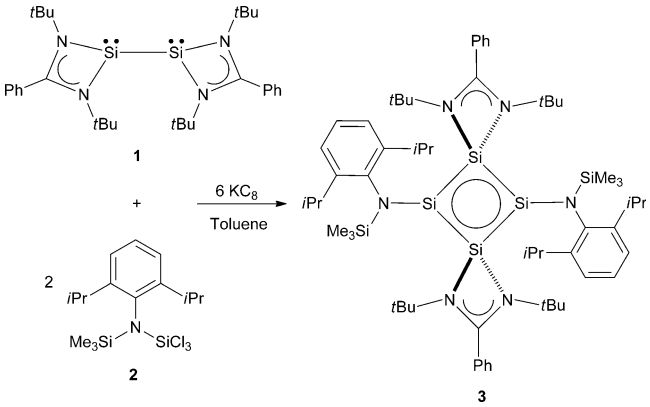
According to the Hückel rules, annulenes, which have $4n\pi$ electrons, are highly reactive owing to their antiaromaticity. One of the well-studied examples is cyclobutadiene, which is the smallest annulene containing conjugated double bonds (4π electrons).[1] Its existence in solution is shown by various trapping reactions to form Diels–Alder adducts.[2] Moreover, cyclobutadiene derivatives that are stable at room temperature, in which the carbon atoms are incorporated with sterically hindered substituents, have been synthesized and structurally characterized.[3] Recently, several research groups have demonstrated that the introduction of main-group elements into a formal 4π-electron four-membered ring has enabled the tuning of its stability and electronic structures by the perturbation of π-electron delocalization.[4] For example, Tamao et al. reported that the tetrasilacyclobutadiene $[(EMind)_4Si_4]$ (EMind = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacen-4-yl) comprises a planar rhombic Si_4 ring in which the diagonal silicon atoms adopt a trigonal-pyramidal geometry. This leads to a charge-separated structure and disfavors 4π-electron delocalization.[4b] Research groups of Roesky and Driess independently reported that the amidinate-stabilized 2,4-disila-1,3-diphosphacyclobutadiene has very weak, almost negligible antiaromaticity because the amidinate ligands attached to the Si atoms stabilize the conjugated 4π-electron system by increasing the energy difference between the occupied and unoccupied π molecular orbitals.[4h,i] Recently, we reported a base-stabilized germatrisilacyclobutadiene, in which the Si_3Ge four-membered ring is puckered and features a ylide structure with considerable electron delocalization.[4j] Moreover, research groups of Driess and Wu reported that the tetrasilacyclobutadiene dication does not have a conjugated π ring system because the lone-pair electrons on the diagonal silicon atoms lean out of the Si_4 ring. This leads to a charge localized structure with some 2π-electron delocalization.[4k,l] The results illustrate that the geometric and electronic structure of a 4π-electron four-membered ring system containing main-group elements are governed by main-group elements and supporting substituents. However, the electronic properties of the above examples are mainly elucidated by theoretical studies. No reactivity has been reported to understand these interesting 4π-electron four-membered ring systems. In this context, we are interested in exploring the reactivity of 4π-electron four-membered ring systems containing heavier Group 14 elements.

Herein, we demonstrate the introduction of four silicon atoms into a formal 4π-electron four-membered ring system. The reactivity and theoretical studies of the resulting compound illustrate the cyclic and extensive delocalization of n, π, σ electrons in the Si_4 ring, which cannot be found in the aforementioned examples.

The reaction of the amidinate silicon(I) dimer $[LSi:]_2$ (**1**, L = $PhC(NtBu)_2$),[5] two equivalents of the amido trichlorosilane $[L'SiCl_3]$[6] (**2**, L′ = 2,6-*i*$Pr_2C_6H_3NSiMe_3$), and 6 equivalents of KC_8 in toluene afforded $[LSi(\mu\text{-}SiL')_2SiL]$ (**3**, Scheme 1).[7] It was isolated as a highly air- and moisture-sensitive brown crystalline solid in very low yield (5.0%). Although the mechanism for the formation of **3** is unknown as yet, on the basis of experimental results, we propose that the reaction appears to proceed through the reduction of **2** with KC_8 to form an amido silicon(I) radical [L′Si•]. It then inserts into **1** to form a silicon(I) dimer intermediate [LSi–SiL′], which dimerizes to form **3**.



Scheme 1. Synthesis of **3**.

The ^1H NMR spectrum shows resonances that are due to the amidinate and amido ligands. The $^{29}Si\{^1H\}$ NMR spectrum shows two sharp singlets (δ −70.8, 32.2 ppm) that are attributable to the three-coordinate and four-coordinate silicon atoms in the Si_4 ring, respectively. The difference in chemical shift suggests that there is a contribution of a canonical form **3 A** (Scheme 2). The difference is significantly smaller than the ^{29}Si solid-state NMR resonances of $[(EMind)_4Si_4]$ (δ −52, 50, 300, 308 ppm, $\Delta\delta > 350$ ppm)[4b] and the ^{29}Si NMR signals of the tetrasilacyclobutadiene

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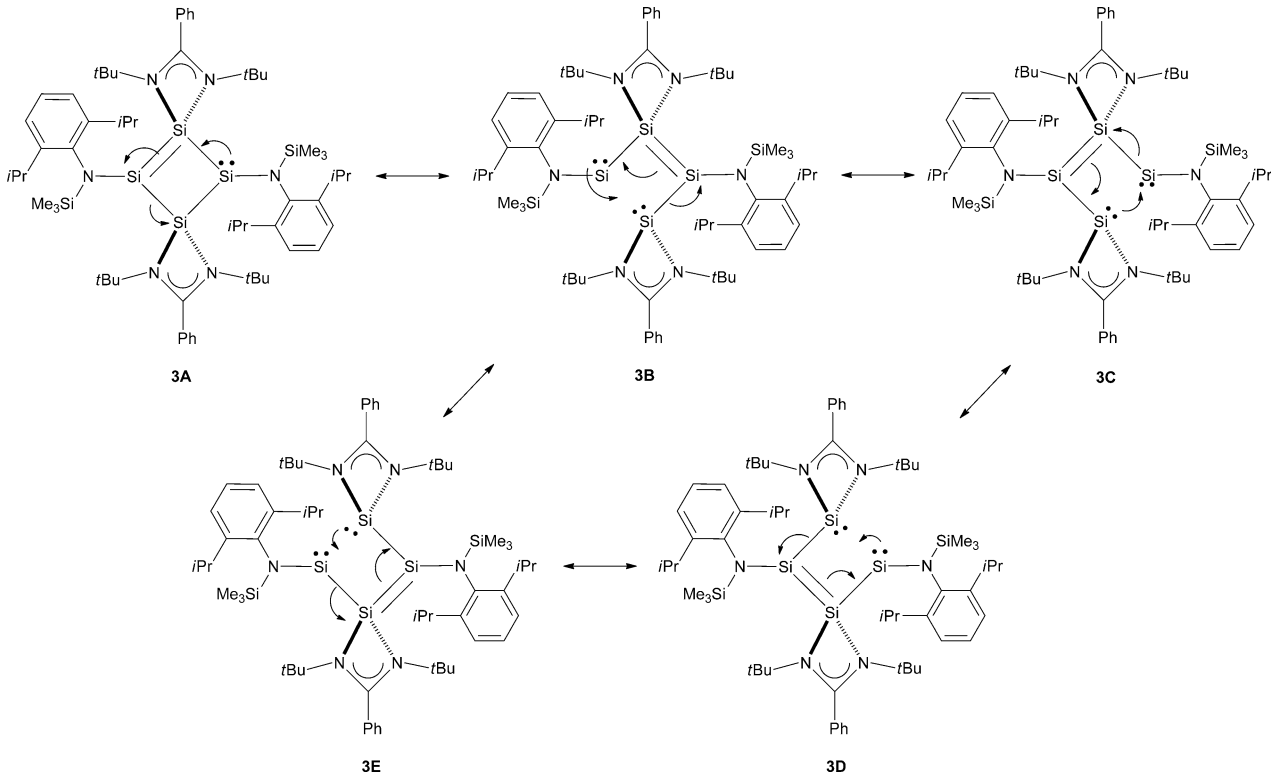


Scheme 2. The delocalization of two π, two σ, and two lone-pair electrons in canonical forms of **3**.

dication (δ −128.7, 53.5 ppm, $\Delta\delta = 182.2$ ppm).[4k] Moreover, the $^{29}Si\{^1H\}$ NMR spectrum shows a sharp singlet at δ 1.41 ppm that is attributable to the $SiMe_3$ substituent. The UV/Vis spectrum in toluene at room temperature shows an absorption band at 395 nm in the visible-light region. According to the time-dependent DFT (TD-DFT) calculations of **3**, the absorption maximum at 395 nm is assigned to the HOMO−1→LUMO transition (Supporting Information, Figure S2).

The molecular structure of **3** (Figure 1) shows that the Si_4 ring is planar and rhombic. The Si1-Si2-Si1A and Si2A-Si1-Si2 angles are 80.68(14)° and 99.32(14)°, respectively. The sum of the internal bond angles is 360.0°. The amidinate ligands are bidentate bonded to the Si1 and Si1A atoms, which adopt a distorted tetrahedral geometry. The Si2 and Si2A atoms are bonded with an amido substituent, which adopt a trigonal pyramidal geometry (the sum of bond angles around the Si atoms is 331.48°). The Si–Si bond lengths (2.322(4), 2.329(4) Å) are equal. They are comparable with those in the tetrasilacyclobutadiene dication (2.321(2), 2.331(2) Å),[4k] the tetrasilacyclobutadiene dianion (average 2.3292 Å)[8] and the dismutational aromatic Si_4 ring in the tricyclic isomer of hexasilabenzene (2.3275(5), 2.3034(8) Å).[9] Moreover, by comparison with the Si–Si bonds in **4** (Si4–Si: 2.414(1), 2.404(2) Å), the results indicate that there is an electron delocalization in the Si_4 ring.

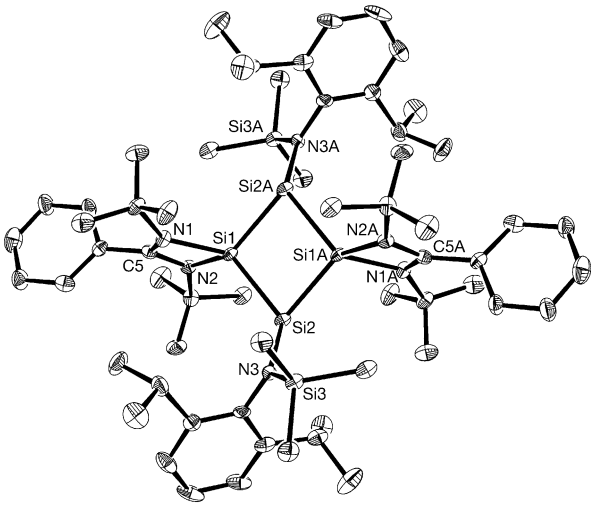


Figure 1. Molecular structure of **3** with ellipsoids set at 30% probability; hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.322(4), Si1–Si2A 2.329(4), Si2–N3 1.827(9), Si1–N1 1.901(9), Si1–N2 1.882(9), N1–C5 1.370(13), N2–C5 1.306(13); Si1-Si2-Si1A 80.68(14), Si2-Si1-Si2A 99.32(14), Si1-Si2-N3 124.8(3), Si1A-Si2-N3 126.0(3), N1-Si1-N2 68.9(4), N1-Si1-Si2 133.6(3), N1-Si1-Si2A 113.4(3), N2-Si1-Si2 112.6(3), N2-Si1-Si2A 131.6(3), Si1-N1-C5 91.1(6), Si1-N2-C5 93.9(6), N1-C5-N2 106.1(9).

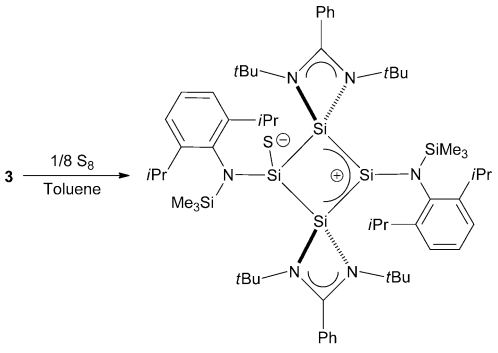
To understand the bonding nature in compound **3**, it was investigated by means of density functional calculations.[10] The optimized geometry of **3** (UB3PW91/6-31 + G(d) level; Supporting Information, Figure S1) is in good agreement with the X-ray crystallographic data. The CASSCF(4,4) calculations show that it has no biradicaloid character. The highest occupied molecular orbitals, HOMO, HOMO−1, and HOMO−3 are cyclically delocalized around the Si_4 ring (Supporting Information, Figure S2). The HOMO and

HOMO−1 show that there is precisely one lone-pair orbital and one π orbital on the Si_4 ring. Moreover, the HOMO−3 shows primarily that a σ orbital is involved in the delocalization. Furthermore, the HOMO−7 shows a donor–acceptor interaction between the $Si_{amidinate}$ and Si_{amido} atoms.

These frontier molecular orbitals illustrate that two π, two σ, and two lone-pair electrons are cyclically delocalized in the Si_4 ring in the canonical forms **3A**–**E** (Scheme 2). The delocalization is very similar to the dismutational aromaticity found in the Si_4 ring in the tricyclic isomer of hexasilabenzene,[9] which is a double intramolecular dismutational derivative of a Hückel aromatic compound comprising silicon atoms in three formal oxidation states (+2, +1, 0). However, compound **3** is not a Hückel aromatic compound and all of the silicon atoms are formally in the same oxidation state (+1) in the canonical forms **3A**–**E**. Moreover, the delocalization in compound **3** is different from the 2π-electron delocalization in the tetrasilacyclobutadiene dication.[4k,l]

The electron delocalization of **3** can also be illustrated by the nucleus-independent chemical shift (NICS).[11] The NICS(1) (−10.07 ppm) and NICS(0) (−15.71 ppm) values of **3** are comparable with that of benzene (NICS(0) = −8.08, NICS(1) = −10.23 ppm) and more negative than that of the 2,4-disila-1,3-diphosphacyclobutadiene (NICS(0) = −5.58, NICS(1) = −2.05 ppm) and the tetrasilacyclobutadiene dication (NICS(0) = −4.7, NICS(1) = −3.8 ppm).[4h,i,k] Thus, the significant negative NICS values of **3** suggest that it is aromatic. As the NICS values may also include shielding effects from the σ framework, the NICS of a simple derivative of the hydrogenation product **3h** (Supporting Information, Scheme S1), in which the delocalization is sequestered, was calculated to evaluate the effect. The results (NICS(0): 1.94, NICS(1): −0.45 ppm) suggest that the shielding effect from the Si_4 σ framework in **3** is negligible.

The electron delocalization in the Si_4 ring of **3** can be demonstrated by its reaction with elemental sulfur in toluene to form the allylic zwitterionic cyclic compound [(LSi)$_2$(μ-SiL′)(μ-Si(S)L′)] (**4**; Scheme 3), which was isolated as a highly air- and moisture-sensitive yellow crystalline solid in low yield (22.4%). The results show that the n, π, σ-electron delocalization is interrupted by sequestering the lone-pair electrons on the Si_{amido} atom with elemental sulfur, which results in a 2π-electron delocalization along the Si_3 skeleton in **4**. The results



4

Scheme 3. Synthesis of **4**.

are also consistent with theoretical studies that two lone-pair electrons on the Si_{amido} atom constitute the HOMO.

The ^{1}H and ^{13}C{^{1}H} NMR spectra display resonances that are due to the amidinate ligand and non-equivalent amido substituents. The ^{29}Si{^{1}H} NMR spectrum shows five singlets at δ −18.90, −17.56, 4.25, 6.87, and 9.02 ppm for the non-equivalent silicon atoms.

The molecular structure of **4** (Figure 2) shows that the Si_4 ring is puckered. The Si4–S1 bond (2.0514(14) Å) is com-

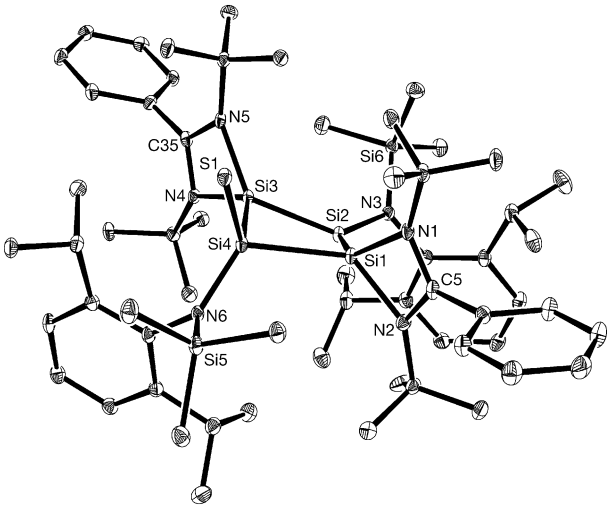


Figure 2. Molecular structure of **4** with ellipsoids set at 30% probability; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.2578(14), Si2–Si3 2.2558(13), Si3–Si4 2.4044(15), Si1–Si4 2.4141(13), Si1–N1 1.866(3), Si1–N2 1.867(3), N1–C5 1.339(5), N2–C5 1.336(5), Si2–N3 1.769(3), Si4–S1 2.0514(14), Si4–N6 1.786(3); Si1-Si2-Si3 89.07(5), Si2-Si3-Si4 92.51(5), Si3-Si4-Si1 82.14(5), Si4-Si1-Si2 92.21(5), N1-Si1-Si2 135.62(11), N1-Si1-Si4 117.22(11), N1-Si1-N2 70.17(14), N2-Si1-Si2 117.92(11), N2-Si1-Si4 128.50(11), Si1-N1-C5 91.4(2), Si1-N2-C5 91.5(2), N1-C5-N2 106.7(3), Si1-Si2-N3 131.26(11), N3-Si2-Si3 129.72(11), Si3-Si4-S1 110.48(6), Si3-Si4-N6 112.91(11), Si1-Si4-S1 110.08(5), Si1-Si4-N6 117.21(11), S1-Si4-N6 110.87(12).

parable with those in base-stabilized silanethione complexes (2.006(1)–2.013(3) Å) and it is shorter than the Si–S single bonds in the dithiodisiletanes (average 2.134 Å).[12] Thus, the Si4–S1 bond could have double-bond character or zwitterionic Si^+–S^- bonding character. The Si3–Si4 and Si1–Si4 bonds are typical single bonds and are significantly longer than those in **3**. The Si1–Si2 and Si2–Si3 bond lengths (2.2578(14), 2.2558(13) Å) are equal and intermediate between typical Si–Si single (2.34 Å) and double bonds (2.14 Å). They are also comparable with those in the homocyclotrisilenylium (average 2.242 Å) and cyclotetrasilenylium ions (average 2.223 Å), which show a 2π-electron homoaromaticity and an allylic cation structure, respectively.[13] These indicate that there is an electron delocalization along the Si3-Si2-Si1 skeleton, while no electron delocalizes along the Si3-Si4-Si1 skeleton.

In conclusion, [LSi(μ-SiL′)$_2$SiL] (**3**) consists of an aromatic silicon-containing four-membered ring in which two π, two σ, and two lone-pair electrons are cyclically delocalized.

Moreover, the aromaticity can be evidenced by its reaction with elemental sulfur, leading to the interruption of electron delocalization.

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