Disilenes

Formation of a Stable, Lattice-Framework Disilene: A Strategy for the Construction of Bulky Substituents**

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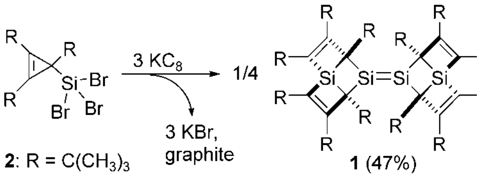
Although multiple-bonded species of carbon such as olefins and acetylenes are very common compounds, it was thought that their heavier homologues, such as Si–Si double-bonded species (disilenes), could not be isolated owing to their high reactivity. However, the steric protection with bulky substituents has been found to be an effective means of isolating labile compounds.[1] To date, trisila- and tristanna-allene derivatives[2,3] as well as the heavier analogues of acetylene[4,5] have been isolated by using various bulky substituents. Evidently, the bulkier a substituent, the higher its protecting ability. However, very bulky substituents cannot be introduced to the target species and their precursors. Herein we show a novel conceptual method for the introduction of such bulky substituents. In the study described herein, we have employed a tri(*tert*-butyl)cyclopropenyl group,[6–9] which becomes an extremely bulky substituent and a good protecting group. The growth is primarily attributed to a spontaneous transformation and combination. This strategy was used to isolate a unique lattice-framework disilene with C_2 symmetry.

Tri(*tert*-butyl)cyclopropenyltribromosilane (**2**)[8,10] was reduced with potassium graphite (KC_8) in 2-MeTHF at approximately −120°C; the reaction yielded red-orange crystals of the unexpected lattice-framework disilene **1**, which was readily isolated in 47% yield by recrystallization from hexane [Eq. (1)].



2: R = $C(CH_3)_3$ **1** (47%) (1)

The structure of **1** was established by using mass spectrometry and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and was confirmed by X-ray crystallography. As shown in Figure 1, **1** was highly strained; however, it was found to be thermally stable up to 257°C. The disilene **1** could be manipulated even in air in the crystal form, but gradually oxidized in solution.[11] A solution of **1** in benzene under an oxygen atmosphere was stirred at room temperature for a week to yield the 1,3-disila-2,4-dioxetane derivative **3**, which consists of seven four-membered rings [Eq. (2)].[10]

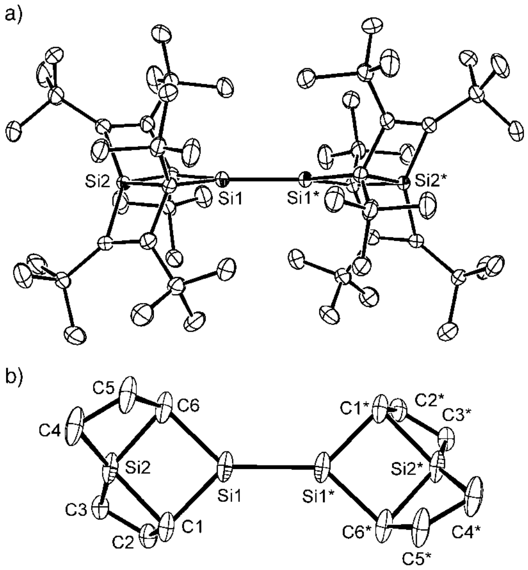
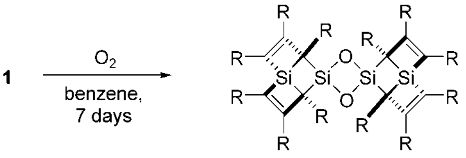


Figure 1. a) Side and b) top ORTEP views of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (a and b) and *tert*-butyl groups (b) were omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si1* 2.2621(15), C1–Si2 1.894(3), C1–Si1 1.958(3), C6–Si2 1.894(3), C6–Si1 1.976(3), C1–C2 1.573(4), C5–C6 1.581(4), C2-C1-Si1 113.07(18), Si2-C1-Si1 88.22(13), C5-C6-Si1 114.9(2), Si2-C6-Si1 87.71(14), C1-Si1-C6 89.77(12), C1-Si1-Si1* 133.97(10), C6-Si1-Si1* 136.26(11), C4-Si2-C3 147.40(12), C1-Si2-C6 94.22(13), C1-Si1-Si1*-C6* 12.08(15).



3: R = $C(CH_3)_3$ (2)

Recently, the reversible tetramerization of a diaminosilylene was reported;[12] **1** is a formal tetramer of tri(*tert*-butyl)cyclopropenylsilylyne. Although the formation pathway of **1** remains uncertain, multistep reactions include the reduction of the silicon–bromine bonds, isomerization,[6,7,13] and condensation to build silylene **4**, which undergoes dimerization to give **1** (Scheme 1).

Compound **1** is the first disilene that has C_2-symmetric chirality through the silicon–silicon double bond, although it was obtained as a racemic mixture of (*S*,*S*,*S*,*S*)-**1** and (*R*,*R*,*R*,*R*)-**1** (Scheme 1). The component silylene **4** is also

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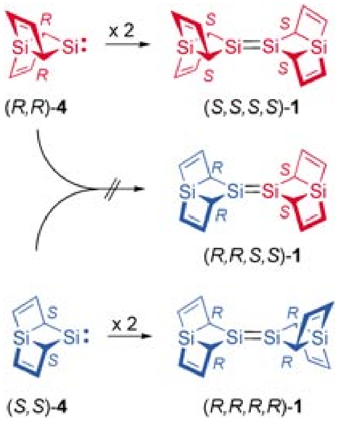

Scheme 1. Dimerization of chiral silylene **4** to chiral disilene **1**. *tert*-Butyl groups are omitted for clarity. The absolute configurations of the stereogenic carbon atoms of **4** are formally changed during the dimerization.

chiral with absolute configurations *R*,*R* and *S*,*S*; (*R*,*S*)-**4** was excluded as a possible structure of **4** because of its large ring strain. The *meso* isomer of the disilene (*R*,*R*,*S*,*S*)-**1** that can be formed by the combination of (*R*,*R*)-**4** and (*S*,*S*)-**4** was not observed, probably as a result of the larger steric repulsion between the heterochiral silylene pair. In other words, the recognition of chirality by the steric hindrance is observed in this system.

The silicon–silicon double-bond length of **1** is 2.26 Å, which is the longest of all the reported carbon-substituted disilenes.[1] Carbon-substituted disilenes generally adopt *trans* bent structures;[14] however, the structure of **1** around the disilene moiety is not bent, but slightly twisted. The unsaturated silicon atom Si1 is not pyramidized and the bent angle defined by Si1* = Si1–Si2 is 177.8°. The central 1,3-disilacyclobutane rings (Si1-C1-Si2-C6) are almost planar (within 0.018 Å from their least-squares plane) and twisted together: the C1-Si1-Si1*-C6* dihedral angle is 12.1°. Notably, the energy levels of the C1–C2 and C5–C6 σ-bonds are raised by the ring strain and the σ bonds are fixed almost perpendicular to the Si=Si bond; the Si1*-Si1-C1-C2 and Si1*-Si1-C6-C5 torsion angles are 96.7 and 102.9°, respectively. Accordingly, the stereoelectronic interactions between the strained C–C σ bonds and the Si–Si π bond become effective.[15]

The UV/Vis absorption maximum of the $\pi\rightarrow\pi^*$ transition of **1** occurs at 493 nm. This value indicates that the transition is red-shifted relative to the typical values for the tetraalkyldisilenes: 350 nm for tetramethyldisilene[16] and 393 nm for tetrakis[bis(trimethylsilyl)methyl]disilene.[17] This remarkable red shift is mainly due to the lengthened and twisted Si=Si bond. Also, the stereoelectronic interactions are important.

Theoretical calculations successfully revealed the importance of the stereoelectronic interactions.[18] DFT calculations at the B3LYP/6-311 + G(d,p) level were carried out for model compound **5**, in which all the *tert*-butyl groups of **1** were replaced by hydrogen atoms. The optimized structure of **5** did not reproduce the experimental structure of **1**; thus the skeletal structure of **5** was fixed to that of **1**. As shown in Figure 2, the HOMO of **5** consisted not only of the Si–Si π orbitals, but also of the C–C σ orbitals of the strained C1–C2 and C5–C6 bonds. Moreover, we found a substantial contribution from the C–C π orbitals of C2–C3 and the C4–C5 double bonds to the LUMO. The $\pi\rightarrow\pi^*$ transition wavelength of **5** was calculated to be 484 nm by using the TDDFT method[19] and was in good agreement with the observed value of **1** (493 nm).

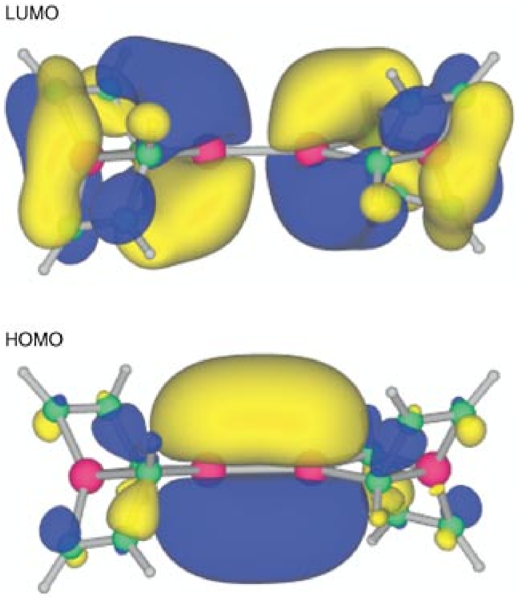

Figure 2. Frontier molecular orbitals of **5** at the B3LYP/6-311 + G(d,p) level.

In summary, the one-pot reduction of tri(*tert*-butyl)cyclopropenyltribromosilane with potassium graphite yields a unique lattice-framework disilene **1**, which is a formal tetramer of tri(*tert*-butyl)cyclopropenylsilylyne. We are now applying this strategy to other compounds.

Experimental Section

1: Dry 2-MeTHF (4 mL) was added to a mixture of **2** (98 mg, 0.21 mmol) and KC_8 (92 mg, 0.68 mmol) at −196 °C. After stirring at −120 to −130 °C for 6 h, the resulting mixture was concentrated under reduced pressure at room temperature. Dry hexane (10 mL) was added, and the resulting salt and graphite were removed by decantation. Evaporation of the solvents in vacuo gave a dark red solid. Recrystallization from dry hexane gave **1** (23 mg, 0.024 mmol, 47 %). Red-orange crystals; mp 257.5–260 °C (decomp.); ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS): $\delta = 1.43$ (s, 36 H), 1.48 (s, 36 H), 1.64 ppm (s, 36 H); ^{13}C NMR (75 MHz, [D6]benzene, TMS): $\delta = 34.3$, 34.5, 35.7, 36.0, 36.7, 38.7, 74.3, 164.3, 165.6 ppm; ^{29}Si NMR (59 MHz, [D$_6$]benzene, TMS): $\delta = -36.7$, 102.5 ppm; MS (14 eV): *m*/*z* (%): 941 (9) [M^+], 471 (37), 207 (100); UV/Vis (hexane): λ_{max} (ε) = 359 (6500), 419 (3800), 493 (11 600); Raman (crystals): $\nu_{Si=Si} = 548\ cm^{-1}$; elemental analysis: calcd for $C_{60}H_{108}Si_4$ (%): C 76.52, H 11.56; found: C 76.30, H 11.54. Crystal data: $M_w = 941.82$; $T = 123$ K; red-orange plate; orthorhombic; *Pcca*, $a = 28.034(5)$ Å, $b = 19.327(3)$ Å, $c = 10.7343(19)$ Å, $V = 5816.0(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.076\ Mg\,m^{-3}$; 0.21 × 0.18 × 0.10 mm^3; independent reflections = 5719; parameters = 307; GOF = 1.027; final $R1 = 0.0618$ [$I > 2\sigma(I)$], $wR2 = 0.1730$ (all data). Intensity data were collected on a Bruker SMART 1000 CCD system with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data integration was carried out with the SAINT program. An empirical method was employed for absorption correction with the SADABS program. Subsequent calculations were carried out with the SHELXTL system. CCDC-232428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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