

## Diradicaloids

## Equilibrium Formation of Stable All-Silicon Versions of 1,3-Cyclobutanediyl

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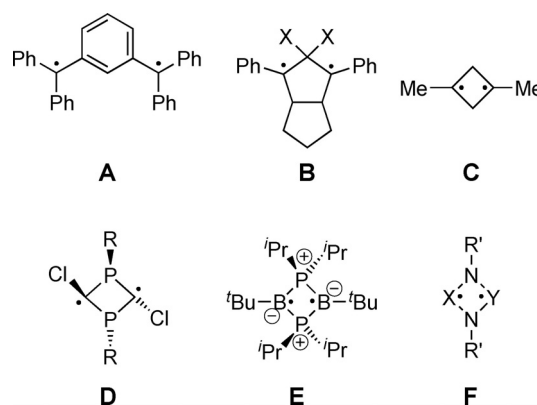
**Abstract:** Main group analogues of cyclobutane-1,3-diyls are fascinating due to their unique reactivity and electronic properties. So far only heteronuclear examples have been isolated. Here we report the isolation and characterization of all-silicon 1,3-cyclobutanediyls as stable closed-shell singlet species from the reversible reactions of cyclotrisilene  $c\text{-Si}_3\text{Tip}_4$  ( $\text{Tip} = 2,4,6\text{-triisopropylphenyl}$ ) with the  $N$ -heterocyclic silylenes  $c\text{-}[(\text{CR}_2\text{CH}_2)(\text{NtBu})_2]\text{Si}$ : ( $\text{R} = \text{H}$  or methyl) with saturated backbones. At elevated temperatures, tetrasilacyclobutenes are obtained from these equilibrium mixtures. The corresponding reaction with the unsaturated  $N$ -heterocyclic silylene  $c\text{-}(\text{CH})_2(\text{NtBu})_2\text{Si}$ : proceeds directly to the corresponding tetrasilacyclobutene without detection of the assumed 1,3-cyclobutanediyl intermediate.

Organic molecules with two unpaired electrons have attracted considerable interest ever since the importance of electron pairing for bonding and structure was recognized in the early 20<sup>th</sup> century.<sup>[1]</sup> Such diradicals assume a fundamental role in the understanding of electronic structure, bond formation and bond scission.<sup>[2]</sup> Due to spin-ordering based on the magnetic interaction of unpaired electrons, di- and polyradicalic systems also show considerable promise for applications in materials science.<sup>[3]</sup> Organic diradicals are typically short-lived and occur as reactive intermediates in numerous chemical reactions,<sup>[4]</sup> although more stable derivatives have been reported early on such as the Schlenk diradical **A** (Scheme 1).<sup>[5]</sup> Efforts to generate two or more unpaired electrons in closer proximity to each other have culminated in the generation of transient 1,3-diradicals **B** in which the spins are separated by a bridging unit with only one carbon atom.<sup>[6]</sup> In particular, cyclobutane-1,3-diyls **C** have

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**Scheme 1.** Selected examples of diradicals and diradicaloid heteroanalogues **A** to **F** (**B**:  $\text{X} = \text{F}, \text{OEt}$ ; **D**:  $\text{R} = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$ , **F**:  $\text{R}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ,  $\text{Si}(\text{SiMe}_3)_3$ ,  $\text{X}, \text{Y} = \text{P}, \text{As}$ ;  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ).

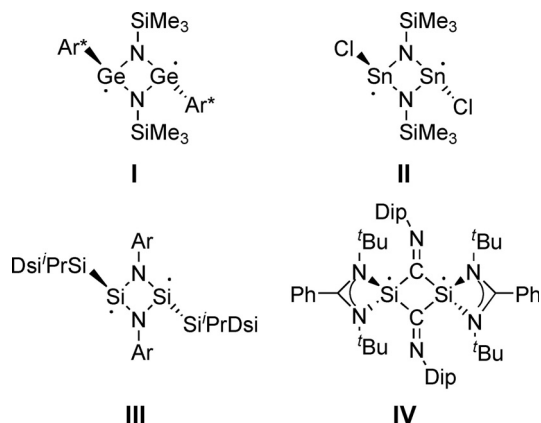
been studied in low temperature matrices.<sup>[7]</sup> The substituents  $\text{R}$  at the bridging moieties exert a strong influence on the nature of their electronic ground state.<sup>[8]</sup> Electron withdrawing groups such as  $\text{R} = \text{OEt}$  allow for substantial interaction between the formally unpaired electrons through energetically lowered  $\sigma^*$  orbitals and thus stabilize the singlet state in comparison to the triplet state by up to  $7.4 \text{ kcal mol}^{-1}$ .<sup>[9]</sup> Based on the inherently low-lying  $\sigma^*$  orbitals of heavier main group elements and thus on the same principle of stabilization, numerous stable analogues of 1,3-cyclobutanediyls of type **D** to **F** have been reported.<sup>[10]</sup> They are typically referred to as diradicaloids in order to account for the comparatively large singlet-triplet gap and the resulting closed-shell nature of their electronic ground state.<sup>[11]</sup>

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So far, all reported stable heavier Group 14 diradicaloids of the 1,3-cyclobutanediyl type contain heteronuclear bridging units (Scheme 2). In 2004, the groups of Lappert and Power isolated the Sn and Ge derivatives **I**<sup>[12]</sup> and **II**.<sup>[13]</sup> Sekiguchi et al. reported the first silicon derivative **III**,<sup>[14]</sup> followed by **IV**, an extensively delocalized diradicaloid prepared by So and co-workers.<sup>[15]</sup>



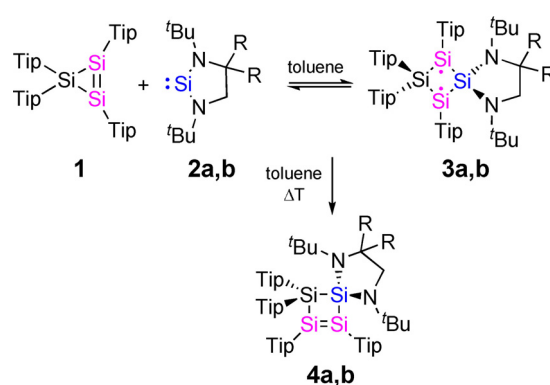
**Scheme 2.** Silicon-, germanium and tin-centered diradicaloids ( $Ar^* = 2,6\text{-Dip}_2\text{C}_6\text{H}_3$ ,  $\text{Dip} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ,  $\text{Dsi} = \text{CH}(\text{SiMe}_3)_2$ ).

Although tetrasilacyclobutane-1,3-diyls were proposed as intermediates in the thermal and photochemical interconversion of tetrasilacyclobutenes and tetrasilabicyclo[1.1.0]butane isomers,<sup>[16]</sup> the synthesis of homonuclear heavy analogues of cyclobutane-1,3-diyls remains elusive. Herein we report on the equilibrium formation and isolation of all-silicon versions.

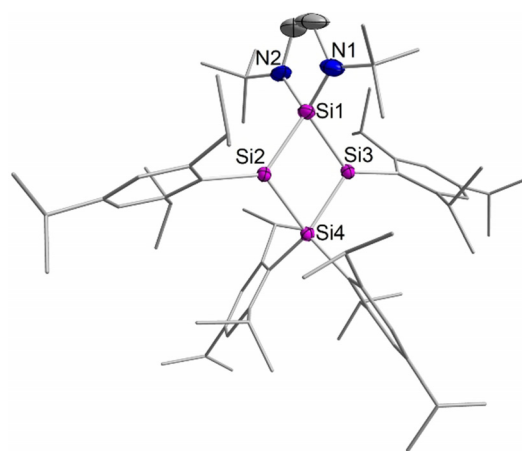
Cyclotrisilene **1**<sup>[17]</sup> readily undergoes ring expansion with isocyanides,<sup>[18]</sup> carbon monoxide<sup>[19]</sup> and the 2-phosphaethynolate anion.<sup>[20]</sup> Towards styrene and benzil, disilenylysilylene-like reactivity of **1** is observed.<sup>[21]</sup> Most notably, however, in the presence of an N-heterocyclic carbene it exists in equilibrium with the NHC-stabilized silicon version of a vinyl carbene.<sup>[22]</sup> These observations prompted us to investigate the reactivity of **1** toward N-heterocyclic silylenes (NHSi) as the heavier congeners of NHCs.<sup>[23]</sup>

Treatment of cyclotrisilene **1** with one equivalent of the N-heterocyclic silylene **2a** in toluene at room temperature affords a red-brown solution that gradually turns purple at lower temperature. The <sup>29</sup>Si NMR signals at +172.8, −14.4, and −64.6 ppm at 25°C show partial conversion into a new species alongside the starting materials. Storage of a concentrated solution in toluene, however, afforded dark-purple single crystals of **3a** in 63% yield (Scheme 3).

An X-ray diffraction study of the crystals revealed the structure of the homonuclear diradicaloid **3a** with a cyclic Si<sub>4</sub> subunit (Figure 1). The four-membered ring is essentially planar (sum of internal angles of 359.5°) with a strikingly long distance between the tri-coordinate silicon atoms (Si2...Si3: 2.871(1) Å), which is significantly longer than the most elongated Si–Si bond length ever reported (*t*Bu<sub>3</sub>Si–Si*t*Bu<sub>3</sub>: 2.697 Å),<sup>[24]</sup> suggesting a very weak interaction, if any. Even in previously reported systems with diradical character such



**Scheme 3.** Equilibrium reactions of cyclotrisilene **1** and N-heterocyclic silylenes **2a,b** with **3a,b** and syntheses of **4a,b** (Tip = 2,4,6-triisopropylphenyl, R = H for **2a/3a/4a** and R = methyl for **2b/3b/4b**).



**Figure 1.** Molecular structure of **3a** in the solid state.<sup>[27]</sup> Hydrogen atoms omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [Å]: Si1–N1 1.750(2), Si1–N2 1.743(2), Si1–Si2 2.326(1), Si1–Si3 2.315(1), Si2–Si4 2.328(1), Si3–Si4 2.330(1), Si2...Si3 2.871(1).

as Breher's pentasilapropellane<sup>[25]</sup> as well as hexasilabenzene isomers<sup>[26]</sup> the Si–Si distances are much shorter. Both, Si2 and Si3 exhibit trigonal planar coordination environments with sums of bond angles of 359.9° and 360.0°, respectively. The Si–Si bonds of the perimeter are slightly shorter than typical Si–Si single bonds (between 2.315(1) and 2.330(1) Å).

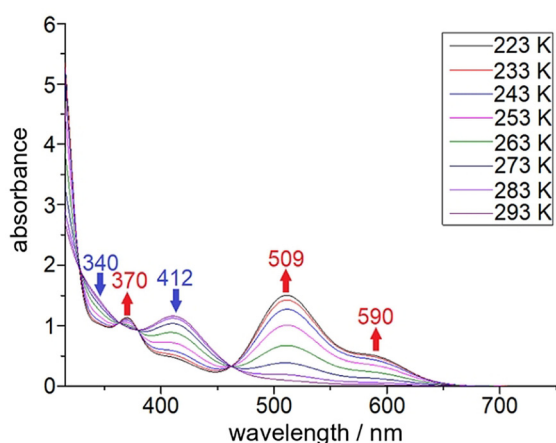
Dissolution of single crystals of **3a** re-establishes the equilibrium with **1** and **2a** (Scheme 3). In line with entropic considerations, cooling of the solution leads to an increase of the concentration of **3a** at the expense of **1** and **2a**; only very little of the starting materials remains at 193 K in [D<sub>8</sub>]toluene according to the <sup>29</sup>Si NMR with three dominant broad resonances in the intensity ration of 2:1:1. On the basis of the 2D <sup>29</sup>Si–<sup>1</sup>H correlation, the signal at −14.1 ppm is assigned to Si1 and the one at −63.1 ppm to Si4, whereas the downfield signal at +198.2 ppm is due to Si2 and Si3. In the solid state, CP-MAS <sup>29</sup>Si NMR signals at +203.0 and +198.4 ppm allow for the differentiation of two chemically inequivalent sites due to the low symmetry of the solid-state lattice. The <sup>29</sup>Si NMR chemical shifts calculated by DFT at the OLYP/6-

311G(d,p)/SCRF=toluene level of theory reproduce the experimental data reasonably well ( $\delta_{\text{calc}} = 232, -11$  and  $-61$  ppm).<sup>[28]</sup>

The experimentally observed Gibbs free energy difference for **3a** compared to **1** and **2a** (0.113 M in toluene) was estimated to  $\Delta\Delta G_{298} = -1.1$  kcal mol<sup>-1</sup> based on VT-NMR. The DFT calculated  $\Delta\Delta G_{298}$  of  $-5.6$  kcal mol<sup>-1</sup> at the B3LYP-D3(bj)/6-311G(d,p)/SCRF=toluene level of theory reasonably reproduces this value.<sup>[28]</sup> UV/Vis experiments at different concentrations of **2a** give a similar result of  $\Delta\Delta G_{298} = -2.6$  kcal mol<sup>-1</sup> (see Supporting Information for details). Additionally, VT-UV/Vis experiments for **3a** at a concentration of  $2.1 \times 10^{-3}$  M in hexane were performed. The isobestic points clearly demonstrate the full reversibility of the equilibrium with increasing concentrations of **3a** upon decreasing of temperature (293 K to 223 K, Figure 2). In line with entropic effects, the calculated free energy of **3a** decreases with temperature ( $\Delta\Delta G_{223} = -10.7$  kcal mol<sup>-1</sup>).<sup>[28]</sup> The increasing intensity of the absorbance bands at  $\lambda_{\text{max}} = 370, 509,$  and  $590$  nm with lower temperature or higher concentration thus allow for their unambiguous assignment to **3a**.

The singlet ground state of **3a** is confirmed by the well-resolved NMR spectra at low temperature as well as the absence of an EPR signal at RT, 193 K, and frozen state in toluene solution. This is confirmed by DFT calculations, which determine the singlet state of **3a** as 8.4 kcal mol<sup>-1</sup> lower energy than the triplet at the B3LYP-D3(bj)/6-311G(d,p)/SCRF=toluene level of theory.<sup>[28]</sup> The calculated HOMO-LUMO energy gap ( $\Delta E_{\text{H-L}}$ ) is 2.21 eV, the HOMO corresponding to a suspended  $\pi$ -bond (bond order 0.57) across the two silicon centers and the LUMO to the  $\pi^*$ -orbital for that bond resembling the bonding situation in **E**<sup>[10b]</sup> (Scheme 1). Fischer and Frenking et al. identified such  $\pi$ -bond unsupported by an underlying  $\sigma$ -bond in a cyclic Ge<sub>2</sub>Ga<sub>2</sub> diradicaloid as well.<sup>[10g]</sup>

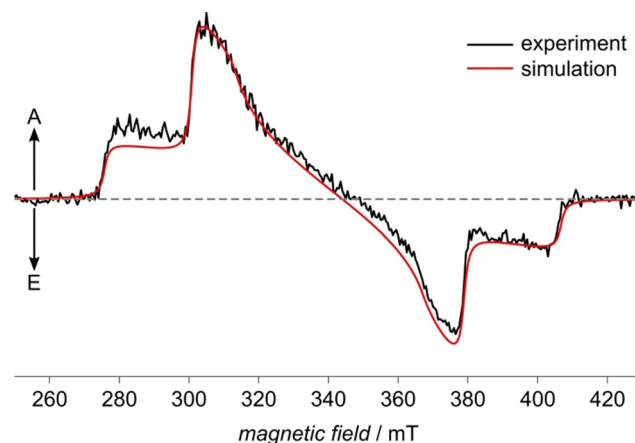
The nonetheless relatively low  $\Delta E_{\text{S-T}}$  and  $\Delta E_{\text{H-L}}$  values of **3a** prompted us to probe its photoexcitation by time-resolved



**Figure 2.** VT-UV/Vis spectrum of an equilibrium mixture of **1**, **2a** and **3a** in hexane at 10 K intervals from 223 K to 293 K (Concentration of **3a**:  $2.1 \times 10^{-3}$  mol L<sup>-1</sup>,  $\lambda_{\text{max}} = 370, 509,$  and  $590$  nm for **3a**,  $\lambda_{\text{max}} = 340$  and  $412$  nm for **1**).

electron paramagnetic resonance (TR-EPR) experiments. Figure 3 shows the TR-EPR spectrum recorded after pulse laser excitation of the complex in frozen solution at 80 K together with a spectral simulation.<sup>[29,30]</sup> A broad signal is observed centered at about 340 mT, a value that compares well with reported silicon-centered diradicals.<sup>[31]</sup> The width of the spectrum suggests that it arises from the dipolar coupling between two unpaired electrons in a triplet state. Moreover, its shape indicates that this triplet state is not at Boltzmann equilibrium, but rather spin-polarized. Spectra with these characteristics<sup>[32]</sup> indicate the formation of a triplet state by intersystem crossing from an excited singlet state following photoexcitation. On the basis of the simulations, the two characteristic parameters of the dipolar coupling can be estimated to  $|D| = (1842 \pm 5)$  MHz and  $|E| = (115 \pm 2)$  MHz (see Supporting Information for details). *D* has an inverse cubic dependence on the distance between the two unpaired electron spins, and hence gives information about the delocalization of the triplet exciton. Comparing the value of *D* with those obtained for naphthalene ( $D = 2982$  MHz) and anthracene ( $D = 2154$  MHz)<sup>[33]</sup> seems to indicate that the triplet exciton is more delocalized in **3a** although such comparisons are to be treated with caution as the even lower value of the thermally excited triplet state of  $(t\text{Bu}_2\text{MeSi})_2\text{Si}=\text{Si}(\text{SiMe}_t\text{Bu}_2)_2$  shows ( $D \approx 1340$  MHz).<sup>[32b]</sup> Excitation at different wavelengths within the absorption spectrum resulted in identical spectra, both in terms of their shape as well as in the overall intensity if normalized to the number of incident photons.

As the difference between bicyclo[1.1.0]butanes and 1,3-cyclobutanediyls can be subtle,<sup>[34]</sup> we decided to also investigate the addition of silylene **2b** with a modified backbone to the Si=Si unit of cyclotrisilene **1**. In contrast to **2a**, silylene **2b** does not cause any visible color change of the reaction mixture at room temperature (Scheme 3). Accordingly, multinuclear NMR spectra ( $[\text{D}_8]$ toluene, 300 K) show only the signals corresponding to free **1** and **2b**. In a similar fashion as



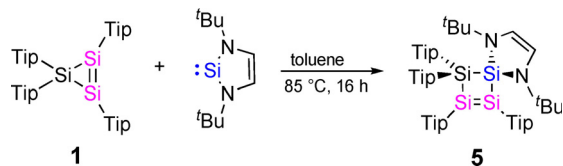
**Figure 3.** Time-resolved EPR spectrum after pulse laser excitation of **3a** at 590 nm in frozen solution at 80 K together with a spectral simulation. Simulation fitted to a slice at 500 ns after laser flash, averaged over 200 ns. Experimental parameters: microwave frequency 9.68964 GHz, microwave power 2.00 mW, 200 accumulations, 5 ns laser pulse length with 2 mJ per pulse, laser repetition rate of 20 Hz.

during the equilibrium formation of **3a**, however, cooling the reaction mixture leads to a gradual color change from orange to a deep violet at  $-80^{\circ}\text{C}$ . The  $^{29}\text{Si}$  VT-NMR spectrum at low temperature ( $[\text{D}_8]$ toluene, 210 K) shows three additional signals at +191.8 (broad),  $-10.4$ , and  $-62.1$  ppm assigned to diradicaloid **3b** on the basis of their similarity to those of **3a**. The relative concentration of **3b** at 210 K based on the integration of signals in  $^{29}\text{Si}$  VT-NMR is approximately 25%. Apparently, the buttressing effect of the additional methyl groups in the backbone of **2b** slightly disfavors the formation of **3b**.

Despite its lower formation tendency, crystallization from a concentrated hexane solution at  $-80^{\circ}\text{C}$  yielded a few purple crystals suitable for X-ray diffraction. The planarity of the four-membered  $\text{Si}_4$  ring system in **3b** is slightly less pronounced as manifest in the sum of the internal angles of  $357.0^{\circ}$  being somewhat less close to  $360^{\circ}$  than in case of **3a** ( $359.5^{\circ}$ ). The tricoordinate Si2 and Si3 atoms are almost ideally planar with the sum of the angles being  $359.5^{\circ}$  and  $360.0^{\circ}$ , respectively. The distance between the tricoordinate silicon centers in **3b** is determined to be  $0.047 \text{ \AA}$  shorter than that of **3a**. VT-UV/Vis spectra qualitatively show the same trends as in case of **3a**. Below 243 K, two additional broad bands appear at 518 and 601 nm, which become more intensive upon further cooling. Due to the lower concentrations of **3b** as well as the low intensities of the bands at 518 and 601 nm and partial overlap with the band of free **1** (412 nm) we were unable to calculate the exact concentration of **3b** at low temperatures.

Considering the putative role of tetrasilacyclobutane-1,3-diyls in the thermal conversion between tetrasilacyclobutenes and tetrasilabicyclo[1.1.0]butanes,<sup>[16]</sup> we were interested whether the weak cycloadducts **3a,b** could be converted into the isomeric cyclotetrasilenes. A clean reaction was indeed observed by a color change from red-brown to yellow after heating of a 0.1 M equilibrium solution of **3a** for 18 hours at  $65^{\circ}\text{C}$ . Unsurprisingly, the isolation of **3a** is entirely unnecessary and hence overnight heating of **1** and **2a** solution in a 1:1 ratio results in the direct formation of **4a** in 68% yield. Compound **4b** was obtained in a similar manner from **1** and **2b** although full conversion could not be achieved (see Supporting Information for details). Interestingly, although the silylene with an unsaturated C=C backbone does not form the corresponding tetrasilacyclobutane-1,3-diyl even at low temperature, the  $\sigma$  insertion product, tetrasilacyclobutene **5** was isolated after heating for 16 hours at  $85^{\circ}\text{C}$  (Scheme 4), which suggests that the formation **4a,b** may also proceed without the involvement of **3a,b** as intermediates.

The tetrasilacyclobutenes **4a,b** and **5** were characterized by  $^{29}\text{Si}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR and UV/Vis spectroscopy. The

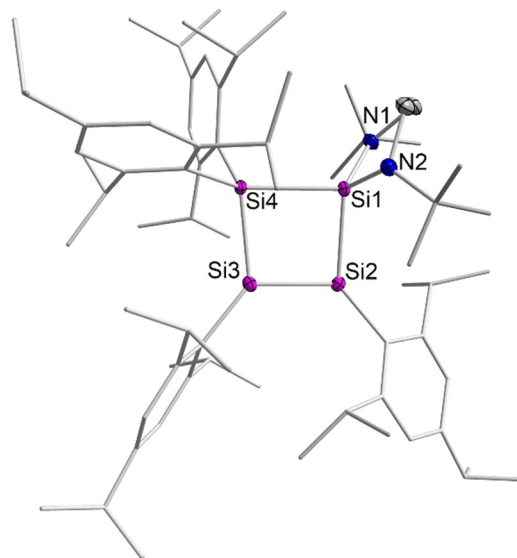


**Scheme 4.** Reactivity of cyclotrisilene **1** toward N-heterocyclic silylene with unsaturated backbone to directly yield tetrasilacyclobutene **5**.

$^{29}\text{Si}$  NMR spectra of **4a** and **5** in  $[\text{D}_6]$ benzene exhibit four distinct signals for each of the silicon centers. The downfield signals at +112.6, +95.6 ppm for **4a** and +122.5, +83.0 ppm for **5** are diagnostic of the  $\text{sp}^2$  hybridized Si2 and Si3 atoms; while the NHSi-Si centers (Si1) appear at +2.1 (**4a**) and +1.1 (**5**) ppm. The Si4 atoms of the  $\text{Tip}_2\text{Si}$  fragments show signals at  $-26.8$  for **4a** and  $-31.1$  ppm for **5**. As for **4b**, two sets of signals were observed as expected due to the formation of two rotamers. The  $\text{sp}^2$  hybridized Si2 and Si3 atoms are in the range of +122.3 to +93.3 ppm, two very close peaks at +2.1 and +1.5 ppm arise from Si1 of the NHSi moiety of **4b**. The two additional close upfield peaks at  $-22.7$  and  $-28.9$  ppm are assigned to Si4. The UV/Vis spectra of **4a** and **5** are similar, with maxima at  $\lambda_{\text{max}} = 383$  and 296 nm for **4a** and 394 and 326 nm for **5**.

The molecular structures of **4a,b** and **5** were confirmed by X-ray crystallography. The structure of **4a** is shown in an exemplary manner in Figure 4. The almost identical four-membered rings in **4a,b** and **5** are essentially planar (sum of internal angles:  $359.6^{\circ}$  (**4a**),  $359.5^{\circ}$  (**4b**),  $357.9^{\circ}$  (**5**)). The Si2–Si3 double bond lengths are  $2.170(1) \text{ \AA}$  (**4a**),  $2.174(1) \text{ \AA}$  (**4b**), and  $2.167(1) \text{ \AA}$  (**5**) and resemble the reported value of Kira's tetrasilacyclobutene.<sup>[16a]</sup> The Si1–Si4 single bond lengths of  $2.473(1) \text{ \AA}$  for **4a**,  $2.533(1) \text{ \AA}$  for **4b** and  $2.458(1) \text{ \AA}$  for **5** are significantly longer than typical silicon-silicon single bonds due to the steric hindrance of bulky Tip and *tert*-butyl substituents.

In conclusion, the equilibrium formation of homonuclear silicon based 1,3-cyclobutanediyl analogues (**3a** and **3b**) from reactions of saturated silylenes (**2a** and **2b**) with peraryl cyclotrisilene **1** sheds further light on the interplay of different low-valent species. Systems in which seemingly no reaction occurs may still form weakly bonded complexes at low temperatures. Such complexes are of considerable interest



**Figure 4.** Molecular structure of **4a** in the solid state.<sup>[27]</sup> Hydrogen atoms and co-crystallized toluene were omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [ $\text{\AA}$ ]: Si1–N1 1.755(2), Si1–N2 1.752(2), Si1–Si2 2.343(1), Si1–Si4 2.473(1), Si2–Si3 2.170(1), Si3–Si4 2.339(1).

within the context of bond activation and catalysis in particular in cases such as the recently reported cooperative effect between the two silylene centers of bridged silylenes.<sup>[35]</sup> It is worthy of note that the energetic value of such interactions may even be too small to experimentally detect them. The effect of equilibrium formation of 1,3-tetrasilabutenediyls on bond activation in small molecules is currently being investigated in our laboratories with special emphasis on the effect of light irradiation. The excitation of **3a** into the excited triplet state by laser pulses may entail considerable consequences for the reactivity. The synthesis of another example of a homonuclear tetrasila-1,3-cyclobutanediyl diradicaloid was published after the submission of our manuscript by Nukazawa and Iwamoto.<sup>[36]</sup> The two independent findings suggest that many more examples of this structural motif may be accessible.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** diradicaloids · low-valent species · silicon · small ring · synthesis

- [1] a) A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893; b) M. Abe, J. Ye, M. Mishima, *Chem. Soc. Rev.* **2012**, *41*, 3808–3820; c) T. Stuyver, B. Chen, T. Zeng, P. Geerlings, F. De Proft, R. Hoffmann, *Chem. Rev.* **2019**, *119*, 11291–11351.
- [2] M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.
- [3] a) I. Ratera, J. Veciana, *Chem. Soc. Rev.* **2012**, *41*, 303–349; b) Z. Zeng, X. Shi, C. Chi, J. T. López Navarrete, J. Casado, J. Wu, *Chem. Soc. Rev.* **2015**, *44*, 6578–6596; c) D. Yuan, *Chem* **2019**, *5*, 744–745.
- [4] a) M. Newcomb in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones Jr), Wiley, Hoboken, **2004**, Chapter 4; b) K. C. Mondal, S. Roy, H. W. Roesky, *Chem. Soc. Rev.* **2016**, *45*, 1080–1111.
- [5] W. Schlenk, M. Brauns, *Chem. Ber.* **1915**, *48*, 661–669.
- [6] a) W. Adam, W. T. Borden, C. Burda, H. Foster, T. Heidenfelder, M. Heubes, D. A. Hrovat, F. Kita, S. B. Lewis, D. Scheutzow, J. Wirz, *J. Am. Chem. Soc.* **1998**, *120*, 593–594; b) M. Abe, W. Adam, M. Hara, M. Hattori, T. Majima, M. Nojima, K. Tachibana, S. Tojo, *J. Am. Chem. Soc.* **2002**, *124*, 6540–6541.
- [7] R. Jain, M. B. Sponsler, F. D. Coms, D. A. Dougherty, *J. Am. Chem. Soc.* **1988**, *110*, 1356–1366.
- [8] D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88–94.
- [9] M. Abe, W. Adam, T. Heidenfelder, W. M. Nau, X. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 2019–2026.
- [10] a) E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 555–557; *Angew. Chem.* **1995**, *107*, 640–642; b) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880–1881; c) P. P. Power, *Chem. Rev.* **2003**, *103*, 789–810; d) T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2011**, *50*, 8974–8978; *Angew. Chem.* **2011**, *123*, 9136–9140; e) S. Demeshko, C. Godemann, R. Kuzora, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2013**, *52*, 2105–2108; *Angew. Chem.* **2013**, *125*, 2159–2162; f) S. González-Gallardo, F. Breher, in *Comprehensive Inorganic Chemistry II, Vol. 1*. Elsevier, Oxford, **2013**, pp. 413–455; g) A. Doddi, C. Gemel, M. Winter, R. A. Fischer, C. Goedecke, H. S. Rzepa, G. Frenking, *Angew. Chem. Int. Ed.* **2013**, *52*, 450–454; *Angew. Chem.* **2013**, *125*, 468–472; h) A. Hinz, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2015**, *54*, 668–672; *Angew. Chem.* **2015**, *127*, 678–682; i) A. Hinz, R. Kuzora, A. K. Rölke, A. Schulz, A. Villinger, R. Wustrack, *Eur. J. Inorg. Chem.* **2016**, 3611–3619.
- [11] a) G. Wittig, A. Klein, *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 2087–2097; b) F. Seel, *Naturwissenschaften* **1946**, *33*, 60–61; c) M. J. S. Dewar, E. F. Healy, *Chem. Phys. Lett.* **1987**, *141*, 521–524.
- [12] H. Cox, P. Hitchcock, M. Lappert, L. Pierssens, *Angew. Chem. Int. Ed.* **2004**, *43*, 4500–4504; *Angew. Chem.* **2004**, *116*, 4600–4604.
- [13] C. Cui, M. Brynda, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2004**, *126*, 6510–6511.
- [14] K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 12478–12481.
- [15] S. H. Zhang, H. W. Xi, K. H. Lim, Q. Meng, M. Huang, C. W. So, *Chem. Eur. J.* **2012**, *18*, 4258–4263.
- [16] a) M. Kira, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1996**, *118*, 10303–10304; b) T. Iwamoto, M. Kira, *Chem. Lett.* **1998**, *27*, 277–278; c) T. Iwamoto, M. Tamura, C. Kabuto, M. Kira, *Organometallics* **2011**, *30*, 2342–2344; d) M. Kira, *Proc. Jpn. Acad. Ser. B* **2012**, *88*, 167–191.
- [17] K. Leszczyńska, K. Abersfelder, A. Mix, B. Neumann, H.-G. Stammer, M. J. Cowley, P. Jutzi, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2012**, *51*, 6785–6788; *Angew. Chem.* **2012**, *124*, 6891–6895.
- [18] Y. Ohmori, M. Ichinohe, A. Sekiguchi, M. J. Cowley, V. Huch, D. Scheschkewitz, *Organometallics* **2013**, *32*, 1591–1594.
- [19] a) M. J. Cowley, Y. Ohmori, V. Huch, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2013**, *52*, 13247–13250; *Angew. Chem.* **2013**, *125*, 13489–13492; b) M. J. Cowley, V. Huch, D. Scheschkewitz, *Chem. Eur. J.* **2014**, *20*, 9221–9224.
- [20] T. P. Robinson, M. J. Cowley, D. Scheschkewitz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, *54*, 683–686; *Angew. Chem.* **2015**, *127*, 693–696.
- [21] H. Zhao, K. Leszczyńska, L. Klemmer, V. Huch, M. Zimmer, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2018**, *57*, 2445–2449; *Angew. Chem.* **2018**, *130*, 2470–2474.
- [22] M. J. Cowley, V. Huch, H. S. Rzepa, D. Scheschkewitz, *Nat. Chem.* **2013**, *5*, 876–879.
- [23] a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692; b) R. West, M. Denk, *Pure Appl. Chem.* **1996**, *68*, 785–788; c) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Chem. Soc. Chem. Commun.* **1995**, 1931–1932.
- [24] N. Wiberg, H. Schuster, A. Simon, K. Peters, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 79–80; *Angew. Chem.* **1986**, *98*, 100–101.
- [25] D. Nied, R. Koppe, W. Kloppe, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, *132*, 10264–10265.
- [26] a) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2011**, *50*, 7936–7939; *Angew. Chem.* **2011**, *123*, 8082–8086; b) P. Willmes, K. Leszczyńska, Y. Heider, K. Abersfelder, M. Zimmer, V. Huch, D.

- Scheschkewitz, *Angew. Chem. Int. Ed.* **2016**, *55*, 2907–2910; *Angew. Chem.* **2016**, *128*, 2959–2963.
- [27] Deposition numbers 1998729 (for **3a**), 1998730 (for **3b**), 1998728 (for **4a**), 1998731 (for **4b**), and 1998727 (for **5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
- [28] Primary FAIR data is available; C. B. Yildiz, K. I. Leszczyńska, S. Gallardo, M. Zimmer, A. Azizoglu, T. Biskup, C. W. M. Kay, V. Huch, H. S. Rzepa, D. Scheschkewitz, Imperial College Data Repository, **2020**, <https://doi.org/10.14469/hpc/6773> and sub-collections therein.
- [29] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42–55.
- [30] D. L. Meyer, F. Lombeck, S. Huettner, M. Sommer, T. Biskup, *J. Phys. Chem. Lett.* **2017**, *8*, 1677–1682.
- [31] a) T. Nozawa, M. Nagata, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 5773–5775; b) A. Kostenko, B. Tumanskii, M. Karni, S. Inoue, M. Ichinohe, A. Sekiguchi, Y. Apeloig, *Angew. Chem. Int. Ed.* **2015**, *54*, 12144–12148; *Angew. Chem.* **2015**, *127*, 12312–12316.
- [32] a) M. M. Roessler, E. Salvadori, *Chem. Soc. Rev.* **2018**, *47*, 2534–2553; b) T. Biskup, *Front. Chem.* **2019**, *7*, 10.
- [33] M. Schwoerer, H. C. Wolf, in *Organic Molecular Solids*, Wiley-VCH, Weinheim, **2007**
- [34] D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, *43*, 585–587; *Angew. Chem.* **2004**, *116*, 595–597.
- [35] a) Y. P. Zhou, S. Raoufmoghaddam, T. Szilvási, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 12868–12872; *Angew. Chem.* **2016**, *128*, 13060–13064; b) Y. Wang, A. Kostenko, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2017**, *139*, 13499–13506; c) Y. Wang, M. Karni, S. Yao, A. Kaushansky, Y. Apeloig, M. Driess, *J. Am. Chem. Soc.* **2019**, *141*, 12916–12927; d) Y. Xiong, S. Yao, T. Szilvási, A. Ruzicka, M. Driess, *Chem. Commun.* **2020**, *56*, 747–750.
- [36] T. Nukazawa, T. Iwamoto, *J. Am. Chem. Soc.* **2020**, *142*, 9920–9924.

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