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 20th century. Such diradicals assume a fundamental role in the understanding of electronic structure, bond formation and bond scission. 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. Organic diradicals are typically short-lived and occur as reactive intermediates in numerous chemical reactions, although more stable derivatives have been reported early on such as the Schlenk diradical A (Scheme 1). 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. In particular, cyclobutane-1,3-diyls C have been studied in low temperature matrices. The substituents R at the bridging moieties exert a strong influence on the nature of their electronic ground state. Electron withdrawing groups such as R = OEt allow for substantial interaction between the formally unpaired electrons through energetically lowered σ* orbitals and thus stabilize the singlet state in comparison to the triplet state by up to 7.4 kcal mol$^{-1}$. Based on the inherently low-lying σ* 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. 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.

**Equilibrium Formation of Stable All-Silicon Versions of 1,3-Cyclobutane-1,3-diyls**

**Cem B. Yildiz, Kinga I. Leszczyńska, Sandra González-Gallardo, Michael Zimmer, Akin Azizoglu, Till Biskup, Christopher W. M. Kay, Volker Huch, Henry S. Rzepa, and David Scheschkewitz**

**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-Si$_3$Tip$_4$ (Tip = 2,4,6-trisopropylphenyl) with the N-heterocyclic silylenes c-[(CR$_2$CH$_2$)(NtBu)$_2$]Si: (R = 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-(CH)$_2$(NtBu)$_2$Si: proceeds directly to the corresponding tetrasilacyclobutene without detection of the assumed 1,3-cyclobutanediyl intermediate.

**Scheme 1.** Selected examples of diradicals and diradicaloid heteroanalogues A to F (B: X = F, OEt; D: R = 2,4,6-iBu$_3$C$_6$H$_2$, F: R = 2,6-Mes$_2$C$_6$H$_4$, Si(SiMes)$_3$), X, Y = P, As; Mes = 2,4,6-Me$_3$C$_6$H$_2$).

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So far, all reported stable heavier Group 14 diradicaloids of the 1,3-cyclobutane-1,3-diyl type contain heteronuclear bridging units (Scheme 2). In 2004, the groups of Lappert and Power isolated the Sn and Ge derivatives I \[^{[22]}\] and II \[^{[23]}\]. Sekiguchi et al. reported the first silicon derivative III \[^{[24]}\] followed by IV, an extensively delocalized diradicaloid prepared by So and co-workers.\[^{[25]}\]

Although tetrasilacyclobutane-1,3-diyls were proposed as intermediates in the thermal and photochemical interconversion of tetrasilacyclobutenes and tetrasilabicyclo[1.1.0]-butane isomers,\[^{[16]}\] 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 I \[^{[17]}\] readily undergoes ring expansion with isocyanides,\[^{[18]}\] carbon monoxide\[^{[19]}\] and the 2-phosphaethynolate anion.\[^{[20]}\] Towards styrene and benzil, disilenylsilylene \[^{[21]}\] affords a red-brown solution that gradually turns purple at lower temperature. The \[^{[21]}\] activity of I is observed.\[^{[22]}\] 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.\[^{[23]}\] These observations prompted us to investigate the reactivity of I toward N-heterocyclic silylenes (NHSi) as the heavier congeners of NHCs.\[^{[24]}\]

Treatment of cyclotrisilene I 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 \[^{[21]}\] 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 Si4 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 (iBu,Si–Si–Bu3, 2.697 Å),\[^{[26]}\] suggesting a very weak interaction, if any. Even in previously reported systems with diradical character such as Breher’s pentasilapropellane\[^{[22]}\] as well as hexasilabenene isomers,\[^{[26]}\] the Si–Si distances are much shorter. Both, Si2 and Si3 exhibit trigonal planar coordination environments with the 2D \[^{[21]}\] resonance identified in the intensity ratio of 2:1:1. On the basis of the 29Si NMR with three dominant broad resonances in the intensity ratio of 2:1:1. On the basis of the 2D \[^{[21]}\] correlation, the signal at +198.4 ppm is due to Si2 and Si3. In the solid state, CP-MAS \[^{[21]}\] NMR signals at +203.0 and +198.4 ppm allow the differentiation of two chemically inequivalent sites due to the low symmetry of the solid-state lattice. The \[^{[21]}\] NMR chemical shifts calculated by DFT at the OLYP/6-
The experimentally observed Gibbs free energy difference for 3a compared to 1 and 2a (0.113 m in toluene) was estimated to $\Delta G_{298} = -1.1$ kcal mol$^{-1}$ based on VT-NMR. The DFT calculated $\Delta G_{298}$ of $-5.6$ kcal mol$^{-1}$ at the B3LYP-D3(bj)/6-311G(d,p)/SCRF = toluene level of theory reasonably reproduces this value.\[28\] UV/Vis experiments at different concentrations of 2a give a similar result of $\Delta G_{298} = -2.6$ kcal mol$^{-1}$ (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 isosbestic 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 ($\Delta G_{298} = -10.7$ kcal mol$^{-1}$).\[28\] 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 in hexane at $10^3$ ppm.\[28\] Additionally, VT-UV/Vis experiments for 3a in hexane were performed. The isosbestic 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 ($\Delta G_{298} = -10.7$ kcal mol$^{-1}$).\[28\] 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.

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The nonetheless relatively low $\Delta E_{\text{S,T}}$ and $\Delta E_{\text{T,E}}$ values of 3a prompted us to probe its photoexcitation by time-resolved 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.\[29,30\] A broad signal is observed centered at about 340 mT, a value that compares well with reported silicon-centered diradicals.\[31\] 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\[32\] 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)\[33\] 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 $(\text{Bu}_2\text{MeSi})_2\text{Si} = \text{Si}(\text{SiMe}_3\text{Bu}_3)_2$ shows ($D \approx 1340$ MHz).\[32b\] 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-cyclobutadienyls can be subtle,\[34\] 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, multi-nuclear NMR spectra ([D$_8$]toluene, 300 K) show only the signals corresponding to free 1 and 2b. In a similar fashion as

![Figure 2](image-url)  
**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: $2.1 \times 10^{-3}$ m L$^{-1}$, $\lambda_{\text{max}} = 370, 509,$ and 590 nm for 3a, $\lambda_{\text{max}} = 340$ and 412 nm for 1).

![Figure 3](image-url)  
**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°C. The 29Si VT-NMR spectrum at low temperature ([D8]toluene, 210 K) shows three additional signals at +191.8 (broad), -10.4, and -62.1 ppm assigned to diradical 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 29Si VT-NMR is approximately 25%. Apparently, the butressing 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°C yielded a few purple crystals suitable for X-ray diffraction. The planarity of the four-membered Si2 ring system in 3b is slightly less pronounced as manifest in the sum of the internal angles of 357.0° being somewhat less close to 360° than in case of 3a (359.5°). The tricoordinate Si2 and Si3 atoms are almost ideally planar with the sum of the angles being 359.5° and 360.0°, respectively. The distance between the tricoordinate silicon centers in 3b is determined to be 0.047 Å 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 intense 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 tetrasilacylobutenes and tetrasilacyclo[1.1.0]butanes,[16] we were interested whether the weak cycloaducts 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°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-diyil even at low temperature, the o insertion product, tetrasilacylobutene 5 was isolated after heating for 16 hours at 85°C (Scheme 4), which suggests that the formation 4a,b may also proceed without the involvement of 3a,b as intermediates.

The tetrasilacylobutenes 4a,b and 5 were characterized by 29Si, 1H, and 13C NMR and UV/Vis spectroscopy. The 29Si NMR spectra of 4a and 5 in [D8]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 sp3 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 Tip2Si 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 sp3 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 λmax = 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° (4a), 359.5° (4b), 357.9° (5). The Si2–Si3 double bond lengths are 2.170(1) Å (4a), 2.174(1) Å (4b), and 2.167(1) Å (5) and resemble the reported value of Kira’s tetrasilacyclobutene.[16a] The Si1–Si4 single bond lengths of 2.473(1) Å for 4a, 2.533(1) Å for 4b and 2.458(1) Å 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 cycloisilene 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.

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

![Scheme 4](image-url)

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**Figure 4.** Molecular structure of 4a in the solid state.29Si Hydrogen atoms and co-crystallized toluene were omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths (Å): 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.[35] 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-tetrasilabuta-"tanediyls 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-cyclobutaneidyl diradicoid was published after the submission of our manuscript by Nakazawa and Iwamoto.[36] 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

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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.

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Stable homonuclear tetrasila-1,3-cyclobutanediyl analogues are obtained from the equilibrium reactions of a cyclotrisilene and saturated N-heterocyclic silylenes (c-[(CR₂CH₂)(NtBu)₂]Si: (R = H, Me)). Solid state structures show essentially planar four-membered Si₄ ring systems. Despite the long distance between the formal radical centers calculations suggest an unsupported π-bond between them.