One-Electron-Mediated Rearrangements of 2,3-Disiladicarbene

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S *Supporting Information*

ABSTRACT: A disiladicarbene, $(Cy\text{-}cAAC)_2Si_2$ (**2**), was synthesized by reduction of Cy-cAAC:SiCl$_4$ adduct with KC$_8$. The dark-colored compound **2** is stable at room temperature for a year under an inert atmosphere. Moreover, it is stable up to 190 °C and also can be characterized by electron ionization mass spectrometry. Theoretical and Raman studies reveal the existence of a Si═Si double bond with a partial double bond between each carbene carbon atom and silicon atom. Cyclic voltammetry suggests that **2** can quasi-reversibly accept an electron to produce a very reactive radical anion, **2**$^{•-}$, as an intermediate species. Thus, reduction of **2** with potassium metal at room temperature led to the isolation of an isomeric neutral rearranged product and an anionic dimer of a potassium salt via the formation of **2**$^{•-}$.

In 2008, Robinson et al.[1] paved the way for N-heterocyclic carbene (NHC:)-stabilized diatomics with the L:→Si(0)═Si(0)←:L compound (**A**) (L: = NHC: = :C[N(2,6-iPr$_2$C$_6$H$_3$)-CH]$_2$), prepared by potassium graphite reduction of NHC:→SiCl$_4$. Since then, molecular species containing the elemental units Ge$_2$,[2] Sn$_2$,[3] P$_2$,[4,5] As$_2$,[6] and B$_2$[7] have been prepared in the presence of various NHCs, which have an enormous impact on the stabilization of compounds of zero-valence elements through strong σ-donation. When compound **A** was reacted with BH$_3$·THF, cleavage of the silicon−silicon double bond was observed, and two quite different "push−pull" stabilized products with borane- and carbene-coordinated silylene moieties were isolated.[8] Perhaps due to its unusual stability, reactivity studies of **A** are sparse.[1,8]

The carbene carbon atom of NHC: is bound to two σ-withdrawing and two π-donating N atoms. When the cyclic alkyl(amino) carbene (cAAC:) is used instead of the NHC:, one π-donating and σ-withdrawing N atom is replaced by one σ-donating quaternary C atom. Thus, the cAAC: becomes more nucleophilic but also more electrophilic when compared with NHC:.[9] Several radical species of main-group elements, such as PN$^{•+}$, P$_2$$^{•+}$, phosphinyl radical cation, H−B$^{•+}$, CO$^{•+}$, and ketene with biradical character, were stabilized with cAAC:.[10]

Both cAAC: and NHC: form stable adducts with SiCl$_4$.[11] In a recent review,[10] Bertrand et al. mentioned that an analogue of

Robinson's **A** with cAAC: might be expected as a biradical, and the possible formation of a radical anion or a radical cation can be studied from its redox chemistry. Herein we targeted the synthesis of a cAAC: analogue of **A**, $(Cy\text{-}cAAC)_2Si_2$ (**2**), and its cyclic voltammetry (CV) was investigated. CV shows that formation of the radical anion **2**$^{•-}$ from **2** is a quasi-reversible process. Utilizing this finding, unprecedented one-electron (from potassium metal)-mediated rearrangements of **2** are reported via the formation of a very reactive radical anion, **2**$^{•-}$, as an intermediate.

The Cy-cAAC: carbene readily forms the adduct Cy-cAAC:→SiCl$_4$ (**1**). Reduction of **1** with KC$_8$ in a molar ratio of 1:4 produces $(Cy\text{-}cAAC:)_2Si_2$ (**2**) in 54% yield (Scheme 1), which is

Scheme 1. Synthesis of Compound 2 from 1 under KC$_8$ Reduction
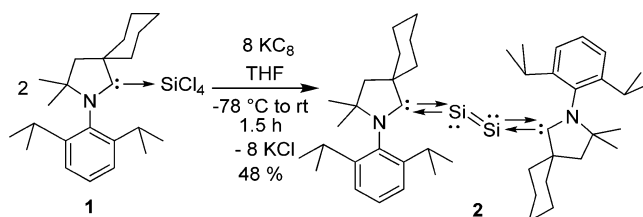
higher than that of NHC:Si═Si:NHC (**A**, 21%).[1] However, **2** is not obtained when Cy-cAAC: is directly reacted with NHC:Si═Si:NHC in THF at ambient temperature. When **2** was treated with 2 equiv of Cy-cAAC:, formation of $(Cy\text{-}cAAC:)_2Si$[12] was not observed.

Compound **2** melts in the range of 188−190 °C and was further characterized by electron ionization mass spectrometry (EI-MS, m/z (%) = 706.4 (100)) (see Supporting Information (SI)). The UV−vis spectrum of **2** recorded in *n*-hexane solution shows two absorption bands at 416 and 528 nm (see SI). The magnetic susceptibility measurements of **2** confirmed a singlet spin ground state (see SI). The ^{29}Si NMR spectrum of **2** was recorded in C$_6$D$_6$. It shows a single resonance at 249.1 ppm, which is more downfield shifted than that of **A** (δ = 224.5 ppm).[1] The ^{13}C NMR spectrum of **2** exhibits a resonance at 234.7 ppm,

which is more upfield shifted than that for Cy-cAAC:, 309.4 ppm, but more downfield shifted than that for $(Me_2\text{-cAAC})_2Si$, 210.0 ppm.[12]

Compound **2** crystallizes in the space group $P\bar{1}$ and does not possess a center of inversion like **A**. The asymmetric unit contains a complete molecule of **2** (Figure 1). The C_{cAAC}–Si
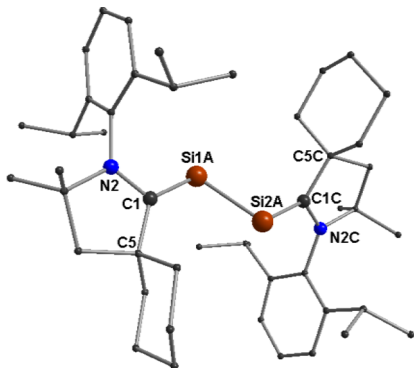

Figure 1. Molecular structure of compound **2**. H atoms are omitted for clarity. Selected experimental [calculated at BP86/TZVPP for the singlet state] bond lengths [Å] and angles [°] (as averages of two independent molecules): C1–Si1A 1.876(4) [1.871], C1C–Si2A 1.849(4) [1.869], Si1A–Si2A 2.254(3) [2.264]; C1–Si1A–Si2A 101.22(13) [106.0], C1C–Si2A–Si1A 105.14(13) [107.9].

bond lengths commonly range from 1.849(4) to 1.876(4) Å. The Si–C distance found for **2** (1.887(4) Å) is shorter than that in **A** (1.921(15) Å)[1] but is a little longer ($\sim$0.04 Å) than those of the previously reported biradical, $(Me_2\text{-cAAC}^\bullet)_2SiCl_2$ (1.8455(16) and 1.8482(17) Å),[13] although it is very close to those of typical Si–C (aryl) single bonds ($\sim$1.879 Å).[14]

The C–Si bond lengths of **2** are longer than Si=C double bonds (170.2–177.5 pm),[16] in particular that in *trans*-2,3-disila-1,3-butadiene (1.727 Å).[15] The experimental Si=Si bond distance of **2** (2.254(3) Å) is close to that of NHC:Si=Si:NHC in **A** (2.2294(11) Å).[1] The C–N bond length in **2** is 1.352(3) Å, which is close to those of 1.37–1.39 Å in the biradicaloid $(Me_2\text{-cAAC})_2Si$[12] and biradical $(Me_2\text{-cAAC}^\bullet)_2SiCl_2$,[12,13] suggesting significant back-donation from the silicon atoms to each carbene carbon atom. For **2**, the C–Si–Si angles range from 101.22(13) to 105.14(13)°, $\sim$10° wider than those of **A** (93.37(5)°).[1] The lone pairs of electrons on the two N atoms of NHC: in **A** are almost perpendicular to the π-orbital of the Si=Si double bond, while those of **2** are in conjugation with the Si=Si unit.

Compound **2** was further studied by theoretical calculations, and the results were corroborated with experimental Raman data (see SI). Despite a very complicated vibrational spectrum, we hoped to identify the νSi=Si vibration by its enhanced Raman intensity because the polarization of a Si atom is greater than that of a C atom. Normal coordinate analysis results show that the calculated Si=Si stretching mode for L'_2Si_2 (**2′**, L′ = :$C(CH_2)(CMe_2)_2NMe$) has a wavenumber of 475 cm^{-1} and is well localized, its contribution to PED reaching 68%. This is in contrast to the data of "normal" disilenes of the type $C_2Si=SiC_2$, where there is no normal mode characteristic to the Si=Si bond, because the Si=Si and Si–C internal stretching coordinates are heavily mixed and the degree of mixing depends on the particular substituents.[17] Their in-phase combination results in a Raman-active normal mode with wavenumber in the range of 460–550 cm^{-1}. In the experimental Raman spectrum of **2** (Figure S2),

there are several bands of enhanced intensity just in the region 450–500 cm^{-1}. One of them, most likely the strongest at 482 cm^{-1}, can be assigned to νSi=Si. This rather high frequency confirms that this band can be attributed to the double-bond stretch (νSi=Si). Inspection of the electronic structure of **2** gives clear evidence for the occurrence of a Si=Si double bond. The shape of the HOMO−1 of **2** (Figure 2) can unambiguously be
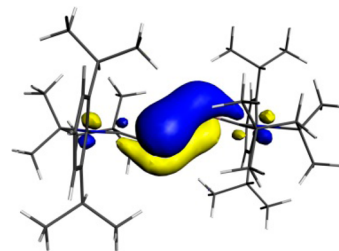

Figure 2. Plot of the HOMO−1 of **2**.

identified with the Si=Si π bond. The pattern of chemical bonding was further elucidated by QTAIM (Quantum Theory of Atoms in Molecules) calculations[18] on **2**. The molecular graphs of **2** (Figure S6) exhibit all expected bonds and ring critical points.

Topological parameters of important $(3,-1)$ bond critical points (BCPs) are presented in Table S9. The relationship between the electron density $\rho(\mathbf{r})$ value and its Laplacian $\nabla^2\rho(\mathbf{r})$ for the Si=Si bond shows that it is a covalent bond, and its high ellipticity ($\varepsilon = 0.36$ for **2** and 0.38 for **2′**) points to a significant double bond character. The same is demonstrated by the delocalization index (DI) value of $\delta(Si,Si)$, 1.25 (cf. DI = 1.33 for $H_2Si=SiH_2$.)[19] In the deformation electron density maps, the lone pairs on each Si atom are clearly seen; see projections in the C–Si–Si–C plane (Figure S7a), in a perpendicular plane (Figure S7b), and in the Si–C–N plane (Figure S7c).

The topological parameters of the Si–C BCPs (Table S9) correspond to the intermediate character of these interactions and are close to those in a $(Cy\text{-cAAC})_2Si$ molecule. In particular, for both molecules the DI values are significantly higher (av. 0.85) than that for an ordinary Si–C bond in H_3Si–CH_3 (0.55) and significantly lower than that for the double Si=C bond in $H_2Si=CH_2$ (1.17).[19] This means that, although the Si–C bonds in **2** are somewhat weaker than in $(Cy\text{-cAAC})_2Si$, both types of the Si–C bonds have a similar, partial double bond character; namely, they involve C→Si donation of σ-type and partial C←Si back-donation of π-type.

The CV of **2** was investigated, as suggested by Bertrand et al.[10] CV of a THF solution of **2**, containing 0.1 M $[n\text{-Bu}_4N]PF_6$ as an electrolyte, shows two oxidations and three reductions (see SI for complete CV). The quasi-reversible reduction at $E_{1/2} = -1.40$ V versus $Cp^*_2Fe/Cp^*_2Fe^+$ indicates the formation of a radical anion, $\mathbf{2}^{\bullet-}$ (Figure 3).

The purple color of the THF solution turned to red when **2** was reacted with metallic potassium at room temperature for 16 h. A similar transformation of color was observed during CV measurements. However, the formation of a pale yellow solution was easily observed around the surface of the piece of potassium when the reaction solution was examined with a close look at a static solution. Pale yellow rods of **3** were formed when the concentrated THF solution was stored at -32 °C in a freezer. X-ray single-crystal diffraction revealed a rearranged structure, which is shown in Scheme 2 and Figure 4. Compound **3** can be considered as an isomer of **2**.
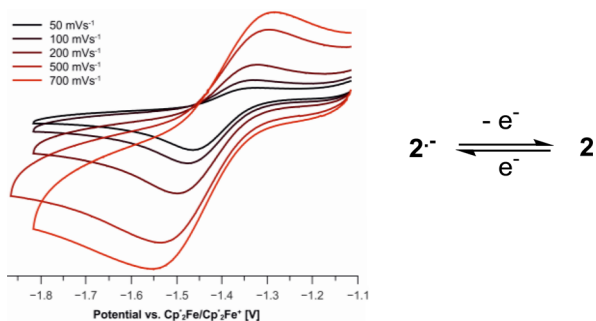
Figure 3. Cyclic voltammogram of a THF solution of **2**, containing 0.1 M [n-Bu$_4$N]PF$_6$ as electrolyte.

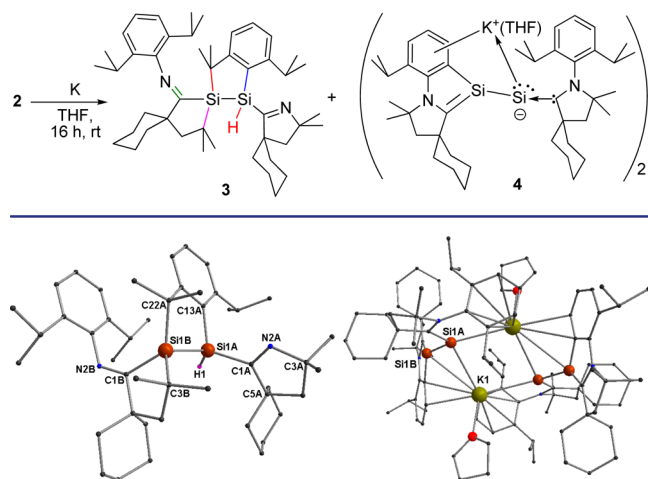**Scheme 2. Synthesis of Compounds 3 and 4**

Figure 4. Molecular structures of compounds **3** (left) and **4** (right). Hydrogen atoms (C−H) are removed for clarity. Selected experimental [calculated at BP86/SVP; **4** was calculated as monomer without K$^+$(THF)] bond lengths [Å] and angles [°]: For **3**, Si1B−C1B 1.9268(15) [1.960], Si1B−C3B 1.9011(15) [1.937], Si1B−C22A 1.9209(15) [1.952], Si1B−Si1A 2.3342(5) [2.367], C1B−Si1B−C3B 89.50 (6) [90.4], C22A−Si1B−Si1A 92.63(5) [91.9], C5B−C1B−N2B 117.53(13) [117.7]; Si1A−C1A 1.8987(15) [1.925], Si1A−C13A 1.8797(15) [1.909], C5A−C1A−N2A 116.30(13) [115.6], C1A−N2A−C3A 110.22(13) [111.0]. For **4**, Si1B−C1B 1.7815(18) [1.800], Si1B−C14B 1.8370(18) [1.867], Si1B−Si1A 2.3400(6) [2.373], C1B−N2B 1.413(2) [1.420], C13B−N2B 1.407(2) [1.409], C13B−C14B 1.446(2) [1.459], Si1B−K1 3.7811(6), C15B−K1 3.1079(16), C1B−Si1B−C14B 88.38(8) [87.7], N2B−C1B−C5B 111.15(14) [113.7], C1B−Si1B−Si1A 134.88(6) [130.6], C14B−Si1B−Si1A, 126.11(6) [132.5], C1B−Si1B−K1, 119.62(6), N2B−C1B−Si1B, 113.13(12) [113.7]; Si1A−K1 3.5543(6), Si1A−K1′ 3.3907(6), Si1A−C1A 1.8199(17) [1.841], C1A−N2A 1.408(2) [1.424], K1−K1′ 4.424.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$. X-ray single-crystal diffraction (Figure 4) revealed that **3** underwent multiple rearrangements when compared with **2**. Both of the silicon atoms of **3** adopt a distorted tetrahedral geometry. The Si1B center is bound to three carbons (C1B, C3B, C22A) and one silicon (Si1A) atom. Furthermore, Si1A is bound to two carbons (C1A, C13A), one hydrogen (H1), and one silicon (Si1B) atom. All four Si−C/H bonds are electron sharing σ bonds. Bond parameters are given in the caption of Figure 4. It is worth mentioning that both silicon atoms of **3** can be considered as chiral centers, where Si1B sits in the center of the two five-membered spiro rings.

After the fractional crystallization of **3**, the flask is rotated and the red mother liquor is again stored at −32 °C in the freezer to form small red blocks of **4**, which crystallize in the monoclinic space group $P2_1/c$. X-ray single-crystal diffraction (Scheme 2, Figure 4) revealed that **4** can be considered as a dimer of the monoanionic potassium salt, suggesting the radical anion **2**$^{•−}$ underwent elimination of a 2-propyl radical to produce an anion together with the potassium cation, which dimerizes through a silylone bridge to form **4**. Each potassium atom accepts π-chelation from two nearest aromatic rings.

A mechanism was proposed which is shown in Scheme 3. CV suggests the formation of the radical anion **2**$^{•−}$ (Figure 3) via a

Scheme 3. Proposed Reaction Pathway for the Formation of 3 from 2$^{•−}$ ^{a}
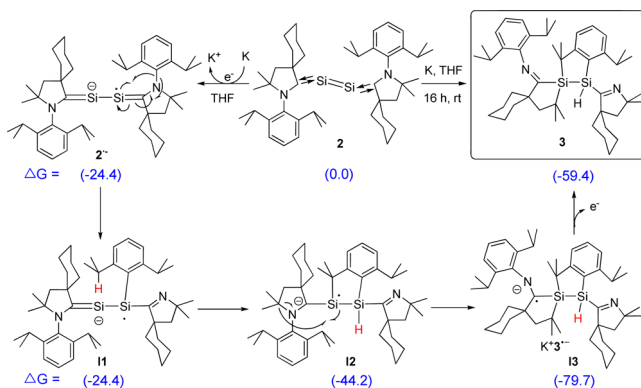

^{a}Relative free energies ΔG at BP86/SVP are given in kcal/mol.

quasi-reversible electron-transfer process between **2** and metallic potassium. Since **2**$^{•−}$ is not stable enough, as indicated by CV, it undergoes bond activation followed by rearrangements. The reaction proceeds in a cascade[20] fashion via the intermediates **I1**, **I2**, and **I3** through cleavage of C−N bond of **2**$^{•−}$, followed by migration of a 2,6-diisopropylphenyl (Dip) group from the nitrogen atom of a five-membered carbene ring, causing C−N bond breaking, C═N bond formation, and then C(sp^3)−H bond splitting across the silicon−silicon double bond. On the other end of the Cy-cAAC═Si unit, opening of the five-membered carbene ring via cleavage of the C$_{alkyl}$−N bond and migration of the tertiary alkyl part to the nearest silicon atom take place in a radical pathway. Finally, the electron is removed from **I3** at the end of the cycle to produce the neutral compound **3**.

Alternatively, **2**$^{•−}$ can undergo fragmentation via the elimination of a 2-propyl radical from one isopropyl group (Scheme 4), with the formation of a Si−C$_{aromatic}$ bond to form a five-membered biheteroaromatic ring, which can be considered as an N-substituted 3-silylindole. On the left side, the carbene−silicon bond in **4** converted into a double bond[16] (Si1B−C1B = 1.7815(18) Å), while on the right side, the negatively charged silicon atom is bound to one silicon atom and a carbene carbon atom and acts as a bridge between two potassium ions (Figure 4) since the negative charge is centered on this silicon atom (Si1B). Calculations at BP86/SVP of the free anions suggest that the reaction **2**$^−$ → 0.5 **4**$^−$ + 0.5 Me$_2$CHCHMe$_2$ is exergonic by −59.6 kcal/mol.

^{29}Si NMR spectra of **3** and **4** show resonances at −5.0, −58.2 and −50.0, −56.5 ppm, respectively, which are far upfield shifted when compared with those of **2** (249.1 ppm). Similarly, ^{13}C resonances of **3** are at 196.3, 186.6 ppm, which are also upfield shifted with respect to those of **2** (234.7 ppm, see Table S11).

Scheme 4. Proposed Reaction Pathway for the Formation of 4 from 2•⁻
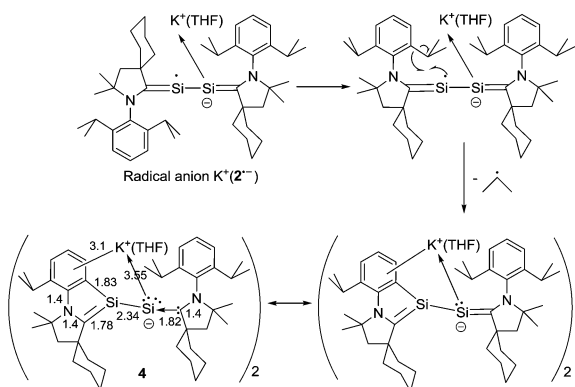
In conclusion, we have shown that disiladicarbene with the general formula $(Cy\text{-cAAC:})_2Si_2$ (**2**) can be synthesized via reduction of the adduct $(Cy\text{-cAAC:})SiCl_4$ (**1**) with KC_8. **2** is stable at room temperature for a year under an inert atmosphere and stable up to 190 °C. It is studied by Raman spectroscopy, and the nature of the C_{cAAC}-Si and Si≡Si bonds is corroborated with theoretical calculation. CV suggests that **2** can quasi-reversibly accept an electron to produce a very reactive radical anion, **2•⁻**, as an intermediate species. Consequently, reduction of **2** with potassium metal led to the isolation of the isomeric rearranged neutral product **3** and a dimer of potassium salt **4**.

The electron-mediated transformation of **2** into **3** via the formation **2•⁻** followed by unusual rearrangements proceeds in a cascade fashion. The energetics were studied by theoretical calculations which also suggest an alternative pathway to explain the formation of **4**. The rearrangements are energetically favorable. Until now, only the ring expansions of NHC-containing compounds (Si,[21] Be,[22a] B,[22b] Zn[22c]) were reported. To the best of our knowledge, this type of rearrangement has no precedence in silicon chemistry until today.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, UV and CV data, magnetic susceptibility, Raman spectrum, table of crystallographic data, and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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