Formation of a 1,4-Diamino-2,3-disila-1,3-butadiene Derivative

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S Supporting Information

ABSTRACT: A 1,4-diamino-2,3-disila-1,3-butadiene derivative of composition $(Me_2\text{-cAAC})_2(Si_2Cl_2)$ (Me_2-cAAC = :C(CMe$_2$)$_2$(CH$_2$)N-2,6-iPr$_2$C$_6$H$_3$) was synthesized by reduction of the Me_2-cAAC:SiCl$_4$ adduct with KC$_8$. This compound is stable at 0 °C for 3 months in an inert atmosphere. Theoretical studies reveal that the silicon atoms exhibit pyramidal coordination, where the Cl−Si−Si−Cl dihedral angle is twisted by 43.3° (calcd 45.9°). The two silicon−carbon bonds are intermediates between single and double Si−C bonds due to twisting of the C−Si−Si−C dihedral angle (163.6°).

Silicon chemistry, with Si as the sister element of carbon, has seen a number of exciting developments in recent years. Among the unsaturated compounds the disilynes RSi≡SiR of Sekiguchi et al. and Wiberg et al. were highlights in this field,[1] whereas a compound with a C≡Si triple bond was characterized by Baceiredo et al.,[2] although the latter is only stable up to −30 °C. Apeloig, Schwarz, and co-workers[3] characterized small silynes HC≡SiX in the gas phase. The first compounds with Si=C and Si=Si double bonds were already reported 30 years ago,[4] followed by a hexaaryltetrasilabuta-1,3-diene in 1997.[5] In recent years, N-heterocyclic carbenes (NHC) and cyclic alkyl(amino) carbenes (cAAC) have been used for the stabilization of silylenes.[6,7] In the former, the carbene carbon atom is bound to two σ-withdrawing and π-donating N-atoms. However, in the case of cAAC one of the σ-withdrawing and π-donating N-atoms is replaced by one σ-donating quaternary C-atom. Thus, the cAAC becomes more nucleophilic but also more electrophilic when compared with that of NHC.[8] Thus, the electronic properties of analogous compounds of NHC and cAAC may change dramatically. For example, Robinson et al. have shown[9a] that NHC:-stabilized P$_2$ allotrope can have two canonical forms; NHC:→P−P←:CHN and NHC=P−P=CHN. The former conformer[9a] was stated as the predominant product based on the chemical shift values of ^{31}P NMR, while the latter one[9b] was shown to be the only conformer for the cAAC: analogue.[9] Furthermore, it was observed that two radical centers could be easily generated just next to the SiCl$_2$ unit by replacing one NHC of NHC:SiCl$_2$ by two cAAC due to their better π-accepting ability and the lower singlet−triplet gap than that of NHC.[7] This explains the dramatic change from a donor−acceptor bond in NHC→SiCl$_2$ to electron-sharing bonds in cAAC−SiCl$_2$−cAAC, with a singlet biradical spin ground state.[7a]

This chemical behavior of cAAC has no precedence with NHC which is due to the small HOMO−LUMO gap of the former. However, in common both cAAC[10] and NHC form a stable adduct with SiCl$_4$. The NHC:SiCl$_4$ adduct was reduced to a base-stabilized singlet bis-silylene (NHC:Si(:)Cl)$_2$ (**A**) and NHC:Si=Si:NHC (**B**) utilizing KC$_8$ as a reducing reagent.[11] In a recent review,[12] Bertrand et al. mentioned that an analogue of Robinson's **B** with cAAC carbene might be expected to form a biradical. To investigate this further we targeted the synthesis of the cAAC analogue of **A**.

The three-electron reduction of Me_2-cAAC:SiCl$_4$ (**1**)[10] with KC$_8$ in a molar ratio of 1:3 in THF resulted in (Me_2-cAAC)$_2$(Si$_2$Cl$_2$) (**2**). The reaction proceeds already at −78 °C; it took 30 min to obtain a green solution (Supporting Information). The temperature was slowly raised, and stirring was continued at room temperature for 3 h to obtain a red solution of (Me_2-cAAC)$_2$(Si$_2$Cl$_2$) (**2**) (Scheme 1). Compound

Scheme 1. Synthesis of Compound 2 from 1 under KC$_8$ Reduction
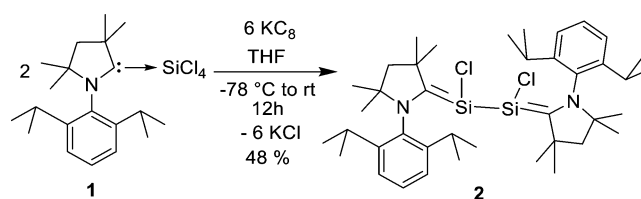
2 was extracted with n-hexane and crystallized as a red solid in 48% yield. The X-ray single-crystal structure analysis of **2** revealed a unprecedented formation of a C=Si−Si=C chain (Scheme 1) instead of the monomeric silylene radical of composition (Me_2-cAAC·)−Si(:)Cl. To the best of our knowledge, a mixed carbon and silicon-centered chain of a stable and isolable 1,4-diamino-2,3-disila-1,3-butadiene has not been reported before.

Compounds **1** and **2** are isolated and colorless and rose-red solid, respectively. Compound **2** is soluble in toluene, benzene, n-hexane, and THF, whereas **1** is only soluble in THF due to its

zwitterionic nature. Compound **2** is stable in an inert atmosphere for 3 months at −32 to 0 °C, but it slowly decomposes to a colorless solid after one week upon storage at room temperature and loses its color completely in 3−4 weeks.

Compound **2** decomposes above 109 °C and turns to darker red, above 128 °C adopts a brown red and finally melts to form a black brown liquid at 200 °C. Compound **2** is stable in solution in an inert atmosphere but immediately hydrolyzes to the Me_2-cAAC:H^+Cl^- salt upon exposure to air.

The UV−Vis spectrum of compound **2** was recorded in *n*-hexane, which exhibited absorption bands at 615, 526, 438, 349, 254 nm (Supporting Information). The biradical (Me_2-cAAC)$_2$SiCl$_2$ and the biradicaloid siladicarbene (Me_2-cAAC)$_2$Si show absorptions at higher values (569,[7a] 569 and 611 nm).[7b] The ^{29}Si NMR spectrum of **2** exhibits a resonance at δ = +25.62 ppm which is downfield shifted with respect to that of the precursor **1** (δ = −103.5 ppm,[10] Supporting Information) but upfield shifted (δ = +38.4 ppm) when compared with (NHC:Si(:)Cl)$_2$ (**A**).[11]

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two molecules of **2**. Each of the silicon atoms adopts a distorted trigonal pyramidal geometry (Figure 1). It is well-known that the Si−Cl bond distances
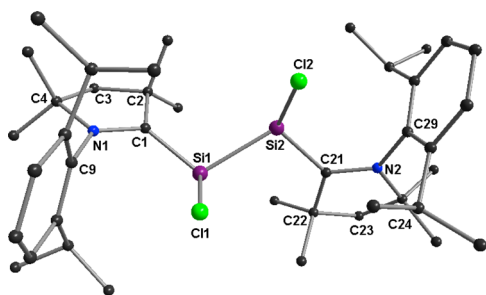

Figure 1. Molecular structure of compound **2**. H-atoms and isopropyl groups are omitted for clarity. Selected experimental (calculated at BP86/TZVPP for the singlet state) bond lengths (pm) and angles (deg) (as averages of two independent molecules): Si1−C1/Si2−C21 182.3(3)/182.6(3) (185.9), Si1−Cl1/Si2−Cl2 210.27(18)/209.10(13) (214.6/214.7), C1−N1/C21−N2 133.6(3)/133.7(2) (136.0), Si1−Si2 230.58(13) (236.8), N1−C9/N2−C29 143.8(2)/143.7(2) (145.1), N1−C1−C2/N2−C21−C22 107.85(17)/107.95(17) (108.1), C1−Si1−Si2/C21−Si1−Si2 110.40(8)/110.85(8) (108.0/108.1), C1−Si1−Cl1/C21−Si2−Cl2 110.95(8)/110.85(8) (111.2/111.4), Cl1−Si1−Si2/Cl2−Si2−Si1 106.62(4)/107.30(6) (107.9/108.0), Cl1−Si1−Si2−Cl2 43.31 (45.9), C1−Si1−Si2−C21 163.56 (165.0).

depend on the coordination number and formal oxidation state of the silicon atom. The Si−C1 bond distances are in the range of 205.81(9) to 219.64(10) pm for the precursor (**1**)[10] and 203.96(4) to 206.48(4) pm for the biradical (Me_2-cAAC·)$_2$SiCl$_2$.[7a] The experimentally observed Si−Cl and Si−C$_{carbene}$ bond distances in **2** are 209.10(13)−210.27(18) and 182.3(3)−182.6(3) pm. The Si−C$_{carbene}$ bond length is 194.4(2) pm in the precursor **1**.[10]

It is noteworthy that the Si−C distances in **2** are longer than Si═C double bonds (170.2−177.5 pm).[13] The longer silicon−carbon bonds in **2** are likely caused by the twisted C−Si−Si−C unit and particularly by the pyramidal coordination at the silicon atoms. This becomes obvious from the dihedral angle Cl1−Si1−Si2−Cl2 of 43.31° which deviates significantly from a planar arrangement. Two of the silicon−carbon bonds are

intermediates between single and double Si−C bonds which are 10 pm shorter than the values (193.9(6)−192.9(7) pm) reported for (NHC:Si(:)Cl)$_2$ (**A**).[11] The Si−Si bond distance in **2** is 230.58(13) pm and therefore ∼9 pm shorter than the Si−Si single bond (239.3(3) pm) of (NHC:Si(:)Cl)$_2$ (**A**) but ∼7 pm longer than the Si═Si double bond length of NHC:Si═Si:NHC (**B**).[11] The above-mentioned comparison suggests that there might be some additional bonding between the two silicon atoms. The C$_{carbene}$−N bond lengths of **2** are slightly different (133.6(3)−133.7(2) pm) and are a little shorter than in the biradical (Me_2-cAAC)$_2$SiCl$_2$[7a] (139.94(19) pm), however, longer (∼ 3 pm) than that (130.6(3) pm) observed for the zwitterionic precursor **1**. Moreover, the N−C$_{carbene}$−C angles in **2** (107.85(17)−107.95(17)°) are slightly sharper when compared with that of **1** (111.15(13)°). The C−Si−Cl bond angles of **2** are in the range of 110.95(8)−110.85(8)° which are more acute (∼9−10°) than those (100.7(2)−101.2(2)°) of (NHC:Si(:)Cl)$_2$ (**A**).[11] The Cl−Si−Si bond angles in **2** are in the range of 106.62(4)−107.30(6)° which are close to the values (107.96(11)−108.75(11)°) reported for **A**. The C−Si−Si bond angles in **2** are 110.40(8)−110.85(8)° which are wider by ∼9−11° than those of **A** (98.76(19)−98.7(2)°).[11] The sum of the bond angles around Si1 and Si2 in **2** is 327.96° and 325.34°, respectively. The distances from each of the silicon atoms to the C−Cl−Si planes are 68.8 and 71.6 pm, suggesting that the bond between the two silicon atoms is not a complete double bond. The X-ray single-crystal structural bond parameters and the valency of the two carbene carbon atoms and of the two silicon atoms indicate an interesting bonding situation.

A comparison of compound **A**[11] with compound **2** clearly shows that both C−Si bonds as well as the Si−Si bond in **2** are significantly shorter (Scheme 2). An explanation for the

Scheme 2. Bonding Situation and Comparison of Bond Lengths of Compound A[11] with Compound 2
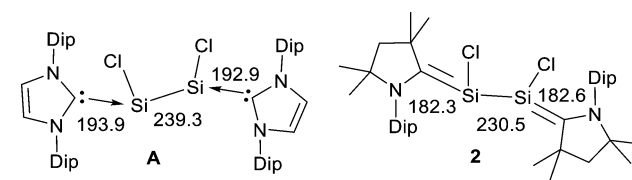
different structures can be given in terms of the bonding situations of the molecules which are sketched in Scheme 2. Molecule **A** has NHC→(SiCl)$_2$←NHC donor−acceptor bonds while **2** possesses cAAC−(SiCl)$_2$−cAAC electron-sharing bonds. A similar change in the bonding situation was recently reported for NHC→SiCl$_2$ and cAAC−SiCl$_2$−cAAC.[7a]

The C−Si−Si−C fragment in **2** could be compared with a distorted *trans*-2,3-disila-1,3-butadiene which carries terminal amino groups. This interpretation agrees with the available experimental and theoretical data. The Si−Si distance in **2** (230.5 pm) concurs very well with the calculated value for *trans*-2,3,-disila-1,3-butadiene (229.9 pm)[15] The π-conjugation in **2** is not fully effective because the C−Si−Si−C fragment is not planar but has a dihedral angle of 163.6° while the Cl−Si−Si−Cl moiety has a torsion angle of 43.3°. This explains why the C−Si distance in **2** (182.3/182.6 pm) is significantly longer than in *trans*-2,3,-disila-1,3-butadiene (172.7 pm).[15] The distortion from π-conjugation comes clearly to the fore when the shapes of the two highest lying occupied orbitals are

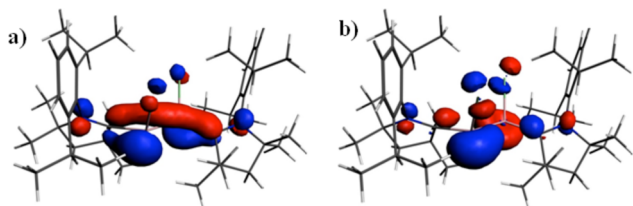considered (Figure 2). The HOMO shows some C—Si and Si—Si π conjugation, but the HOMO-1 (Figure 2) denotes two

Figure 2. (a) HOMO and (b) HOMO-1 of compound **2**.

weakly bonding electrons at the silicon atoms. Thus, while compound **2** may be considered as substituted *trans*-2,3-disila-1,3-butadiene, it becomes obvious that the substituents exert a strong distortion on the π-conjugation in the parent system.[16]

Quantum chemical calculations at the BP86/TZVPP level predict a singlet ground state for **2** which is 27.9 kcal/mol lower than the triplet state and 54.8 kcal/mol lower than the quintet state. The caption of Figure 1 provides that the optimized bond distances and angles are in very good agreement with the experiment. The silicon atoms exhibit a pyramidal coordination where the Cl—Si—Si—Cl dihedral angle (calcd 45.9°, expt 43.3°) is even more twisted than the C—Si—Si—C angle (calcd 165.0°, expt 163.6°).

In conclusion, we have synthesized $(Me_2\text{-}cAAC)_2(Si_2Cl_2)$ (**2**) through a controlled reduction of the zwitterionic adduct $Me_2\text{-}cAAC$:$SiCl_4$ (**1**) with KC_8 in THF. Compound **2** can be regarded as a 1,4-diamino-2,3-disila-1,3-butadiene derivative. Theoretical calculation revealed that the twisted conformation about the C—Si—Si—C fragment, which is possibly caused by steric interactions of the bulky substituents, leads to longer silicon—carbon bond lengths in **2**.[17] To the best of our knowledge the preparation of such species has not been reported before.

Previously the NHC:$SiCl_4$ adduct was reduced to bis-silylene (NHC:Si(:)Cl)$_2$ (**A**) with KC_8. The cAAC analogue of **A** can be better described as 2,3-disila-1,3-butadiene derivative (**2**). It possesses a singlet ground state and is isolable and stable between 0° and −32 °C for at least 3 months, but after one week **2** slowly loses its color if stored at room temperature. The bond between the silicon and the carbene carbon atom changes its nature from a coordinate bond in **1** to a covalent electron-sharing double bond in **2**.

Synthesis of Compound $(Me_2\text{-}cAAC)_2(Si_2Cl_2)$ (2). The 1:3 molar solid mixture of $Me_2\text{-}cAAC$:$SiCl_4$ (**1**) (3.3 mmol) and KC_8 (10.0 mmol) and THF (80 mL) were separately cooled to −78 °C, and then THF was added through a cannula. The reaction mixture was stirred at −78 °C for 30 min to produce a light green solution and black residue of graphite. Then the reaction solution was slowly warmed to room temperature and stirred for 2−3 h. During this period, the color of the solution changed from light green to red. The black residue was separated by filtration, dried under vacuum, and extracted with *n*-hexane (80 mL). The volume of *n*-hexane solution was decreased to 10−15 mL. Transparent needles of **2** were formed after 1 day either at room temperature or at 0 °C in a refrigerator. Compound **2** was separated by filtration and dried under vacuum. C, H, and N analysis found (calcd) for $C_{40}H_{62}Cl_2N_2Si_2$: C 68.52 (68.83), H 8.85 (8.95), N 4.08 (4.01). Decomposes above 109 °C. NMR data of **2** are given in the Supporting Information. UV−visible bands: 615, 526, 438, 349,

and 254 nm. ^{1}H NMR (500.133 MHz, C_6D_6, 298 K, δ ppm): 7.09−7.03 (m, 3H, H_{ar}), 3.11 (m, 2H, CHMe$_2$), 1.903 (s, 6H, NCMe$_2$), 1.69 (s, 2H, CH$_2$), 1.65 (d, 6H, CHMe$_2$), 1.22 (d, 6H, CHMe$_2$), 1.01 (s, 6H, CMe$_2$). ^{13}C NMR (δ ppm): 148.6, 129.2, 128.3, 124.7, 71.9, 55.8, 50.6, 33.1, 31.8, 30.9, 30.7, 29.0, 27.6, 24.6, 22.9. ^{29}Si NMR (δ ppm): +25.62. Compound **5** should not be dried under vacuum at room temperature for long since it slowly decomposes and slowly loses its color.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Synthesis, UV, crystallographic table, and theoretical details. This information is available free of charge via the Internet at http://pubs.acs.org. CCDC 928147 contains the supplementary crystallographic data of compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(16) The distortion is mainly caused by electronic effects rather than steric interactions. Geometry optimization at BP86/TZVPP of $(NH_2)HC$=$Si(Cl)$−$Si(Cl)$=$CH(NH_2)$ show that the equilibrium geometry has strongly pyramidal coordinated silicon atoms with a dihedral angle Cl−Si−Si−Cl of 36.6° while the parent systems H_2C=$Si(Cl)$−$Si(Cl)$=CH_2 is planar.

(17) Calculations with less bulky amino substituents gave also strongly twisted conformations which suggest that the twisting of the structure occurs due to electronic interactions. Holzmann, N. Ph.D. Thesis, Marburg, 2013.