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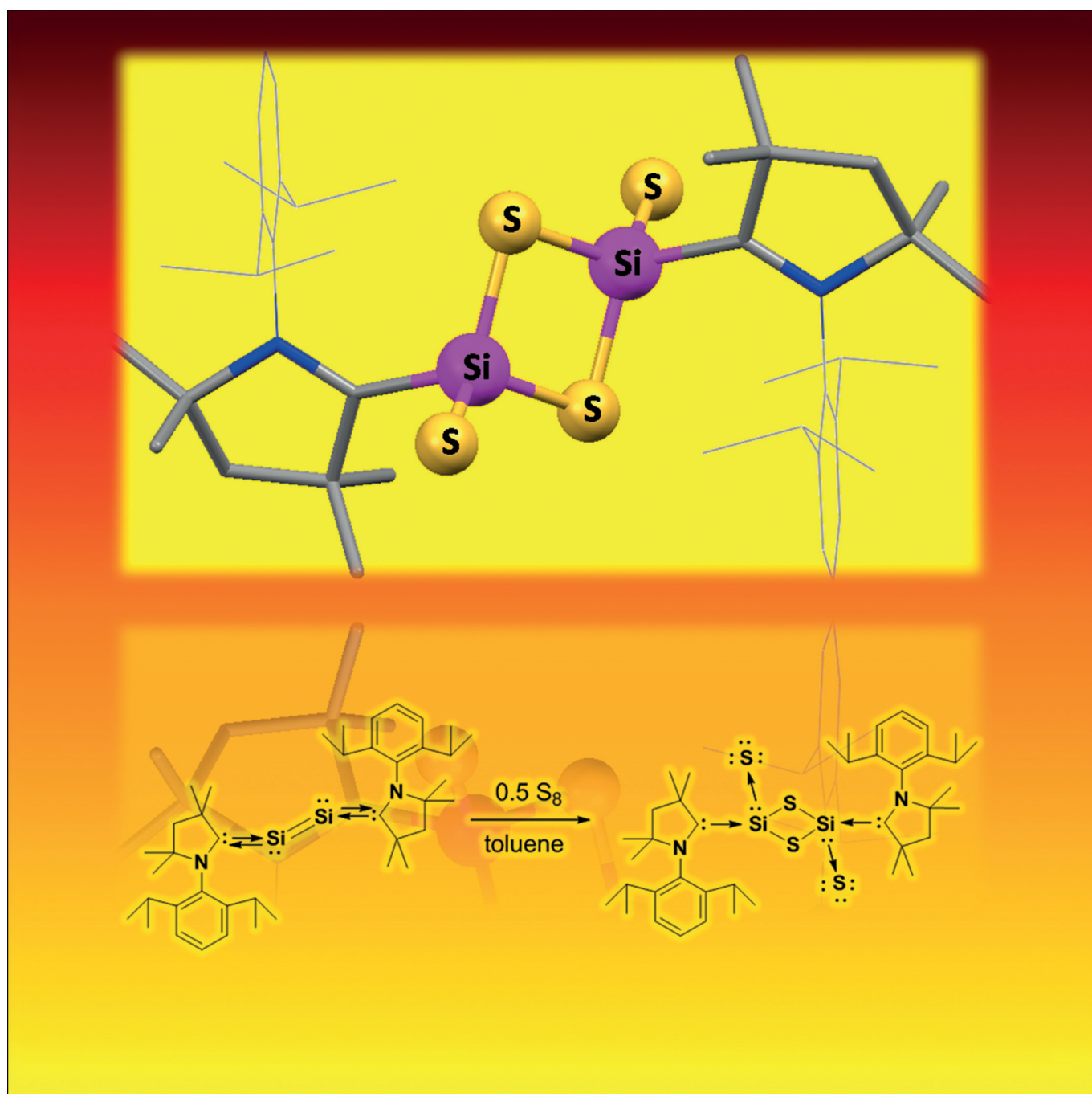
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■ Silicon–Sulfur Complex

A Stable Dimer of SiS₂ Arranged between Two Carbene Molecules

Chandrajeet Mohapatra,^[a] Kartik Chandra Mondal,^[a] Prinson P. Samuel,^[a] Helena Keil,^[a]
Benedikt Niepötter,^[a] Regine Herbst-Irmer,^[a] Dietmar Stalke,^{*,[a]} Sayan Dutta,^[b]
Debasis Koley,^{*,[b]} and Herbert W. Roesky^{*,[a]}

Dedicated to Professor Karl Otto Christe on the occasion of his 80th birthday



Abstract: The Me-cAAC-stabilized dimer of silicon disulfide (SiS_2) has been isolated in the molecular form as $(\text{Me-cAAC})_2\text{Si}_2\text{S}_4$ (**2**) at room temperature [Me-cAAC = cyclic alkyl(amino) carbene]. Compound **2** has been synthesized from the reaction of $(\text{Me-cAAC})_2\text{Si}_2$ with elemental sulfur in a 1:4 molar ratio under oxidative addition. This is the smallest molecular unit of silicon disulfide characterized by X-ray crystallography, electron ionization mass spectrometry, and NMR spectroscopy. Structures with three sulfur atoms arranged around a silicon atom are known; however, **2** is the first structurally characterized silicon-sulfur compound containing one terminal and two bridging sulfur atoms at each silicon atom. Compound **2** shows no decomposition after storing for three months in an inert atmosphere at ambient temperature. The bonding of **2** has been further studied by theoretical calculations.

Silicon is the second most abundant element in the earth's crust and the sister element of carbon. Even though silicon and carbon have remarkably different chemical characteristics in numerous cases, they share many properties in common due to their similar outer shell electronic configuration. Hence, the studies on the differences in bonding of carbon and silicon have become a challenging research area. Silicon compounds are attracting the interest of modern research and they are often compared to the similar carbon systems. The research on analogous compounds of carbon and silicon is very important from the point of view of bonding. The most prominent carbon sulfur compound is CS_2 , which has a linear structure. In 1935 Zintl and Loosen^[1] and Büssem et al.^[2] reported on the solid-state structure of the silicon congener as a fibrous structure in which the silicon atom is located at the center of a distorted tetrahedron formed by sulfur atoms. These tetrahedral units are connected by means of edge-sharing to form long chains. In 1965 Silverman and Soulen carried out a high pressure experiment for SiS_2 , which revealed a different structure in which the distorted tetrahedral units (SiS_4) are corner-sharing to generate a network.^[3] Recently, Evers and Schnöckel have discovered two new high-pressure phases of SiS_2 which possess both edge- and corner-sharing distorted SiS_4 tetrahedra.^[4] All the reported structures of SiS_2 are polymeric by nature. A monomeric form of SiS_2 was detected in a matrix at very low temperature by Schnöckel in 1989.^[5] Mück et al. reported the

first observation and characterization of a cyclic SiS_2 by utilizing both theoretical and microwave spectroscopic techniques.^[6] There are several theoretical studies that have been carried out to predict the geometries of small SiS_2 clusters,^[7] but till today they are not experimentally realized. Therefore, stabilization of small units of SiS_2 is an interesting challenge for chemists.

Silylenes are reported to produce several unexpected products by reactions with small molecules like P_4 ^[8] and NH_3 .^[9] Silylenes have also been known to activate elemental sulfur to form a $\text{Si}=\text{S}$ bond.^[10] The reactions of disilenes with elemental sulfur to generate ring compounds with bridging sulfur atoms between two silicon centers have also been documented.^[11] The theoretically optimized structure of dimeric SiS_2 possesses two bridging and two terminal sulfur atoms. The latter show double-bond character with the silicon atoms.^[7] With all the above background knowledge, we reasoned that $(\text{Me-cAAC})_2\text{Si}_2$ ^[12] should be a suitable silicon precursor as it contains both two silylene centers and a silicon-silicon double bond. Herein, we report on the synthesis to stabilize the first molecular dimer of SiS_2 at ambient temperature. During the preparation of this manuscript, Robinson et al. reported the synthesis of NHC-stabilized Si_2O_4 and Si_2O_3 species using $(\text{NHC})_2\text{Si}_2$ as precursor.^[13]

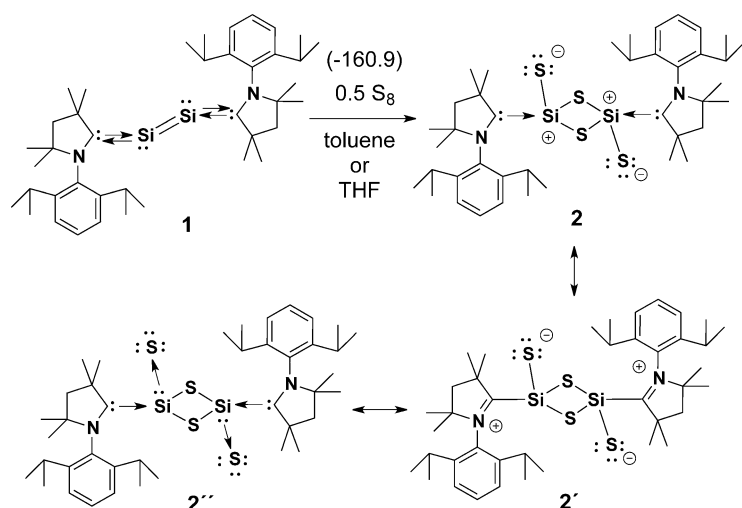
The reaction of $(\text{Me-cAAC})_2\text{Si}_2$ ^[12] with elemental sulfur in a 1:4 molar ratio yields $(\text{Me-cAAC})_2\text{Si}_2\text{S}_4$ (**2**) (Scheme 1). The reaction was conducted in toluene at -78°C , allowed to come to room temperature very slowly, and continued overnight to give a bright yellow-colored solution of **2**. When the reaction was carried out in THF instead of toluene, it was much faster and required only half an hour to go to completion.

Compound **2** is sparingly soluble in toluene and hexane but readily soluble in THF. The single crystals of **2** were grown from a mixture of solvents (THF and hexane) at ambient temperature. Compound **2** has also been characterized by electron ionization mass spectrometry and it shows the molecular ion of **2** (at m/z 754.4) (see Supporting Information). The experimental IR absorption bands are at 732 and 637 cm^{-1} . The calculated IR frequencies of $\text{Si}/\text{Si}^*-\text{S}/\text{S}^*$ are 668.5 and 696.4 cm^{-1} . Compound **2** shows absorption bands at 215, 270, 320, and 380 nm in THF. We have also studied TD-DFT calculations for UV/Vis spectroscopy of **2** as shown in Table S7 (373 and 392 nm). The calculated values are in good agreement with those of experimental values of **2** (see Supporting Information). The ^{29}Si NMR spectrum of **2** has been recorded in $[\text{D}_8]\text{THF}$ which exhibits a resonance at $\delta = -24.99\text{ ppm}$ with a large shift when compared with that of **1** ($\delta = 251.72\text{ ppm}$ in $[\text{D}_8]\text{THF}$). The ^{13}C NMR spectrum shows a resonance at $\delta = 213.9\text{ ppm}$ for the carbene carbon atom of **2**, which is upfield shifted when compared to that of **1** ($\delta = 236.7\text{ ppm}$). The compound **2** is stable in $[\text{D}_8]\text{THF}$ for five days as confirmed by NMR measurements, even though the solution was prepared in open air. On the contrary, **1** is sensitive to air and moisture. The dark powder of **1** degrades to a colorless solid within ten minutes of exposure to air. Compound **2** decomposes very slowly in CDCl_3 and produces H_2S and SiO_2 on exposure to air/moisture.

[a] Dr. C. Mohapatra, Dr. K. C. Mondal, Dr. P. P. Samuel, H. Keil, B. Niepötter, Dr. R. Herbst-Irmer, Prof. Dr. D. Stalke, Prof. Dr. H. W. Roesky
Institut für Anorganische Chemie, Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
E-mail: dstalke@chemie.uni-goettingen.de
hroesky@gwdg.de

[b] S. Dutta, Dr. D. Koley
Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246 (India)
E-mail: koley@iiserkol.ac.in

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Scheme 1. Synthesis of compound **2** from **1**. The energy term in parenthesis is ΔG (kcal mol⁻¹) at the R-M06-2X/TZVPP/SMD//M06-2X/SVP level of theory.

Compound **2** crystallizes in the monoclinic space group, $P2_1/n$. The asymmetric unit possesses one half of the molecule of **2** and one THF molecule. The X-ray single-crystal structure of **2** revealed a four-membered Si₂S₂ ring with two additional terminal sulfur atoms. Two carbene carbon atoms of Me-cAAC: are coordinated to two silicon atoms (Figure 1).

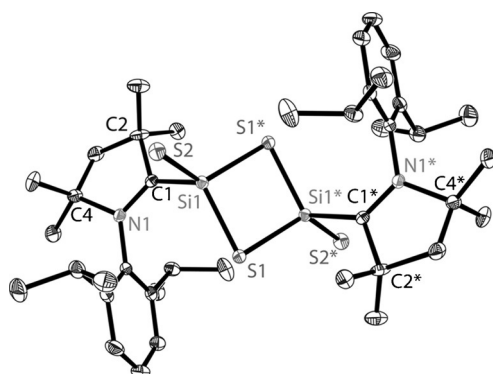


Figure 1. Molecular structure of compound **2**. Hydrogen atoms and solvent molecules are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental [calculated at the R-M06-2X/SVP level of theory for the singlet state] bond lengths [Å] and angles [°]: Si1–S1 2.1526(7) [2.170], Si1–S1* 2.1624(6) [2.176], Si1–S2 2.0110(5) [2.013], C1–Si1 1.9351(12) [1.945], C1–C2 1.527(6) [1.529], N1–C1 1.3079(16) [1.306], S1–Si1–S2 121.77(2) [122.59], C1–Si1–S1 112.94(4) [111.87].

The core structure shows a four-membered ring which possesses Si1, Si1*, S1, and S1* in a plane with angles Si1–S1–Si1* 84.54(2)° and S1–Si1–S1* 95.46(2)°. Due to the crystallographic inversion center the terminal bound sulfur atoms (S2 and S2*) are exactly oriented in a *trans*-position to each other exhibiting an angle of 121.77(2)° (S1–Si1–S2) with the plane of the four-membered ring. All the above observations indicate that the Si₂S₄ core is a very symmetric one with an inversion center (*i*) of the four-membered ring (Figure 2).

According to the theoretical optimization of the structure and geometry for small silicon sulfur clusters, the structure of

dimeric SiS₂ should be planar (Scheme 2, a).^[6,7] In the case of **2**, the dimer is not planar, because the terminal sulfur atoms (S2 and S2*) are displaced from the plane due to the coordination from the carbene carbon atoms of Me-cAAC: to both the silicon atoms (Figure 2 and Scheme 2, b). In compound **2**, both the silicon atoms are bound to three sulfur atoms (Si1 to S1, S1*, and S2; S1* to S1, S1*, and S2*) and one carbene carbon atom (Si1–C1; S1*–C1*) to form a distorted tetrahedral geometry around the silicon atoms (Figure 2). In all the reported polymeric structures of SiS₂, the silicon atoms have a distorted tetrahedral geometry surrounded by four sulfur atoms.^[1–4] In compound **2** one of the sulfur atoms present in the polymeric forms is re-

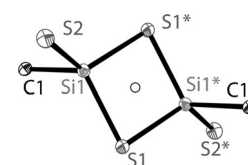
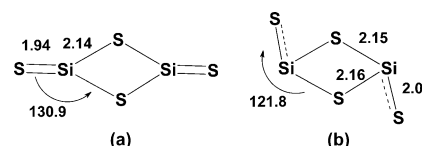


Figure 2. Si₂S₄ core of compound **2** (Inversion center is depicted as a black circle.).



Scheme 2. a) Theoretically optimized structure of dimeric SiS₂.^[6] b) Si₂S₄ core of compound **2**. Bond lengths [Å] and angle [°]: Si1–S2 2.0110(5), Si1–S1 2.1526(7), Si1–S1* 2.1625(6); S1–Si1–S2 121.77(2).

placed by a Me-cAAC: molecule. Hence in **2**, the polymerization is arrested by the carbene, which results in the isolation of a dimeric form of SiS₂. The Si₂S₄ core of compound **2** is geometrically very similar to the Si₂O₄ nucleus, recently reported by Robinson et al.^[13] The silicon–silicon bond lengths are slightly different since the sulfur atom is bigger than the oxygen atom.

When the Si₂S₄ core of **2** is compared with the optimized structure of dimeric SiS₂, the bond lengths of terminal silicon sulfur bonds are consequently quite different (calculated; 1.94 Å and **2**; Si1–S2, 2.0110 (5) Å; Scheme 2). The average distance between the bridging sulfur atoms (S1 and S1*) and silicon atom Si1 (2.1575(7) Å) is similar to the bond length in the optimized structure (Scheme 2). In compound **2**, the angle between the terminal and bridging sulfur atoms (S1–Si1–S2 121.77(2)°) is quite different from the theoretically calculated one (Scheme 2). In compound **2**, the Si1–S2 bond is a little longer than the reported Si=S bonds^[10c,d] but the average bond length between the bridging sulfur and silicon atoms is nearly the same as that for reported Si₂S₂^[11a,e] compounds.

DFT calculations were performed to illustrate the electronic structure and bonding nature of compound **2**. The optimized geometry at the M06-2X/SVP level of theory is in very good agreement with the data from the X-ray crystal structure of **2** (superimposed experimental/theoretical structures shown in Figure S5). The bonding scenario of **2** is represented by using

NBO analysis, implemented in Gaussian09 and QTAIM (Quantum Theory of Atoms in Molecules) calculations (see Computational Methods in the Supporting Information for further details). The NBO results reveal that the C1 is connected to the Si1 atom by a single bond and to the N1 atom with double bond. The C1–Si1 bonding electron occupancy is 1.944 e, which is highly polarized towards the C1 center (77%) due to the higher electronegativity of C1 than Si1. Furthermore, C1 becomes highly electron deficient during the 1→2 transformation, due to the inability of the Si1→C1 back donation (Figure 3a). Nonetheless the electron deficiency at C1 is reduced

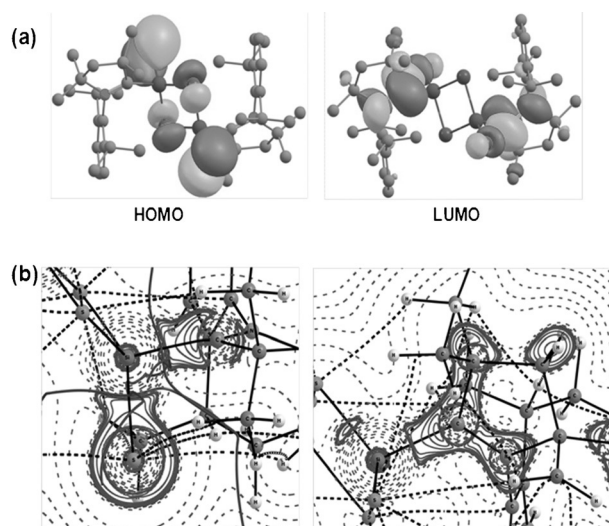


Figure 3. a) Computed Kohn–Sham (KS) MO of **2** at R-M06-2X/TZVPP//R-M06-2X/SVP level. Hydrogen atoms are omitted for clarity. b) Laplacian distribution [$\nabla^2\rho(r)$] in C1–Si1–S2 (left) and N1–C1–Si1 plane (right) of **2**. Solid lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). The range of contours of the Laplacian is -8×10^2 to $+8 \times 10^2$.

by the π -bonding interaction with N1, as evident from the significant shortening of the N1–C1 bond length in **2** (1.306 Å) from **1** (1.343 Å).^[12] However it is important to note that weak π -overlap between N1 and C1 does not satisfy the electron deficiency at the C1 center, since π -bonding electron densities are primarily localized at the N1 atom (74%, see NBO results in Tables S4 and S5 in the Supporting Information).

According to NBO results, there is a single bond observed between the Si1 and S2 atoms along with three lone pairs on S2 atoms (terminal sulfur). However, the Si1–S2 bond length (2.013 Å) is shorter than the single bond (2.159 Å in $\text{H}_3\text{Si–SH}$) and slightly longer than the double bond (1.942 Å in $\text{H}_2\text{Si=Si}$), which indicates to some extent the double-bond character. Additionally, the two bridging sulfur atoms (S1 and S1*) are bound to the Si1 center by a single bond. The bond lengths [$r_{\text{Si1–S1/S1*}} = 2.170/2.176$ Å] are comparable to the Si–S bond in $\text{H}_3\text{Si–SH}$.

To gain better insight into bonding scenario, we also performed topological and topographical analyses of compound **2**. Detailed results of AIMALL calculations are tabulated in the Supporting Information (Table S6). At the (3,–1) bond critical

point (BCP) the calculated electron density [$\rho(r)$] of C1–Si1 and Si1–S2 bonds are 0.100 and 0.119 and along with the respective Laplacian [$\nabla^2\rho(r)$; +0.190, +0.190, Figure 3b] these indicate a closed-shell interaction. Therefore, it is certain that Si1 is connected to C1 and S2 by a donor–acceptor type interaction. Interestingly the positive yet negligible Laplacian values for Si1–S1/S1* bonds (+0.081 and +0.076) do not guarantee a closed-shell interaction, rather they are highly polarized covalent bonds from the inherent electronegativity differences between the Si and S atoms.

In summary we have prepared the first carbene-stabilized Si_2S_4 molecule from the reaction of $(\text{Me-cAAC})_2\text{Si}_2$ (**2**) with elemental sulfur in a 1:4 molar ratio. This compound is stable at room temperature in an inert atmosphere for at least three months without any decomposition. Furthermore, this compound has one terminal and two bridging sulfur atoms at each silicon atom. The molecular structure of compound **2** was confirmed by X-ray single-crystal diffraction and EI mass spectrometry, and further characterized by NMR spectroscopy. Compound **2** was also studied by theoretical calculations which show very interesting bonding aspects (Scheme 2 and Figure 3). The strong σ -donation from the carbene to the silicon of the Si_2S_4 unit leads to acute differences in their bonding as shown in Scheme 2.

Experimental Section

Synthesis of $(\text{Me-cAAC})_2\text{Si}_2\text{S}_4$ (**2**)

Method 1: A mixture of **1**^[12] (100 mg; 0.159 mmol) and sulfur (20.4 mg; 0.637 mmol) was placed into a 100 mL round bottom flask, and toluene (50 mL) was added at -78°C . The dark violet reaction mixture was allowed to warm to room temperature very slowly (2.5 h) to give a light red solution. The reaction was then continued overnight resulting in a bright yellow-colored solution of compound **2**. The reaction mixture was filtered and the solvent was evaporated under high vacuum to afford the yellow-colored product **2** (84% yield). Elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{62}\text{N}_2\text{S}_4\text{Si}_2$: C 63.60, H 8.27, N 3.71, S 16.91; found: C 63.67, H 8.33, N 3.67, S 16.96; decomposes above 185°C , ^1H NMR (298 K, $[\text{D}_8]\text{THF}$, 500.133 MHz): $\delta = 7.31\text{--}7.22$ (m, 6H, Har), 2.82 (m, 4H, CHMe_2), 2.25 (s, 4H, CH_2), 1.43 (s, 12H, NCMe_2), 1.29 (s, 12H, CMe_2), 1.27–1.25 (d, 12H, CHMe_2), 1.19–1.17 ppm (d, 12H, CHMe_2); ^{13}C NMR (298 K, $[\text{D}_8]\text{THF}$, 126 MHz): $\delta = 213.9$ (C), 147.2, 133.9, 130.6, 129.6, 129.4, 128.9, 51.8, 33.9, 31.7, 30.2, 30.1, 30.0, 23.6, 21.5 ppm; ^{29}Si NMR (298 K, $[\text{D}_8]\text{THF}$, 99.38 MHz): $\delta = -24.99$ ppm; EI-MS: m/z (%): 754.4(90) [M^+], 755.4(70) [M^+], 756.4(35) [M^+], and 757.3(17) [M^+]; mass spectrometry was performed on solid sample of **2**; IR (KBr): $\tilde{\nu} = 2959(\text{m})$, 2952(m), 2866(w), 1494(w), 1456(s), 1386(w), 1371(w), 1322(m), 1260(s), 1189(m), 1132(m), 1094(m), 1019(m), 803(s), 732(m), 637(s) cm^{-1} .

Method 2: A mixture of **1**^[12] (100 mg; 0.159 mmol) and sulfur (20.4 mg; 0.637 mmol) was placed into a 100 mL round bottom flask and THF (50 mL) was added at -78°C . The reaction mixture was warmed to room temperature within 30–45 min and stirred for another 30 min to afford the bright yellow-colored solution of **2**. The volatiles were removed under vacuum to get the solid of **2** with similar yield as mentioned in *Method 1*. Single crystals of **2** were grown from a solution of a mixture of *n*-hexane and THF at room temperature.

Crystal structure analysis of 2

A suitable single crystal for X-ray structural analysis of **2** was mounted at low temperature in inert oil under an argon atmosphere by applying an X-Temp2 device.^[14] The data were collected on a Bruker D8 three-circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Ag microfocus source with INCOATEC Quazar mirror optics.^[15] Data reduction was performed with SAINT.^[16] A semi-empirical absorption correction was applied with SADABS.^[17] The structure was solved by direct methods (SHELXT2014)^[18] and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-2014/7).^[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 -carbon atoms and 1.2 times for all other carbon atoms. The disordered solvent and ligand molecules were refined by using 1,2 and 1,3 distance restraints as well as restraints for the atomic displacement parameters. The given bond lengths in the paper always refer to the main residue. For further information see the Supporting Information.

2: (Me-cAAC)₂Si₂S₄, $M = 899.54 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/n$, $a = 14.463(2)$, $b = 10.229(2)$, $c = 17.575(3) \text{ \AA}$, $\beta = 109.67(2)^\circ$, $V = 2448.4(8) \text{ \AA}^3$, $Z = 4$, $\mu(\text{Ag-K}\alpha) = 0.151 \text{ mm}^{-1}$, $T = 100(2) \text{ K}$, 64570 reflections measured, 6595 unique reflections, $R_{int} = 0.0471$, 427 parameters refined, R_1 (all data) = 0.0443, $R_1 [I > 2 \sigma(I)] = 0.0337$, wR_2 (all data) = 0.0877, $wR_2 [I > 2 \sigma(I)] = 0.0814$, GOF = 1.047, largest diff. peak and hole 0.671 and $-0.254 \text{ e \AA}^{-3}$.

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Keywords: density functional calculations • main group chemistry • silicon • silylene • sulfur activation

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