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Monomeric siliconthiodichloride trapped by a Lewis base†

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Thiophosgene (CSiCl_2), a chemical reagent used in numerous organic syntheses, exists in the monomeric form while its heavier silicon analogue [siliconthiodichloride (SiSiCl_2)] has been isolated so far as a dimer at room temperature and as a tetramer at 180 °C. Herein, we report on the first synthesis, isolation, and characterization of cyclic alkyl(amino) carbene (cAAC) stabilized siliconthiodichloride (cAAC) SiSiCl_2 (**3**) in the neutral monomeric form. **3** is synthesized *via* reaction of (cAAC) $_2\text{Si}_2\text{Cl}_4$ (**1**) or (cAAC) $_2\text{Si}_2\text{Cl}_2$ (**2**) with S_8 in the temperature range of –78 to 20 °C. An NHC [NHC = N-heterocyclic carbene] analogue of **3** is not isolated when (NHC) SiCl_2 is reacted with S_8 . The bright yellow colored compound **3** is soluble in polar organic solvents. It is stable at room temperature for a month under an inert atmosphere. **3** decomposes above 160 °C. The monomeric molecular structure of **3** has been unambiguously confirmed by X-ray single crystal diffraction. **3** is also characterized by NMR, UV-vis, and IR spectroscopy. The bonding and electron density distributions of **3** have been further studied by theoretical calculations.

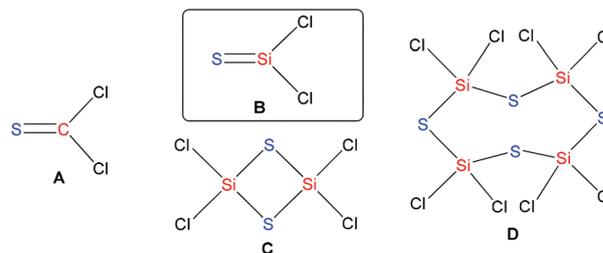
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Introduction

Silicon is the sister element of carbon. The chemistry of silicon is often quite different. The bonding in silicon compounds is unlike that in carbon, since the 3s and 3p orbitals of silicon are more diffuse.¹ Thus, it is challenging to stabilize silicon analogues of carbon containing multiple bonds.² Compounds with Si–X multiple bonds tend to undergo dimerization, oligomerization, or polymerization. In contrast, carbon analogues are stable and isolable as monomeric species.² For example, the heavier analogue of thiophosgene (CSiCl_2)³ (Scheme 1, **A**) is siliconthiodichloride (**B**)⁴ which exists in the dimeric form (**C**)⁵ at room temperature and in the tetrameric form (**D**)⁶ at 180 °C. Thiophosgene (CSiCl_2) (**A**) is quite stable and accessible, and utilized as a laboratory reagent for crucial chemical transformations (such as Corey–Winter olefin synthesis).⁷ Siliconthiodichloride (**B**) has not been stabilized in its monomeric form till now. **B** was only studied by matrix isolation at low tempera-



Scheme 1 Selected carbon- and silicon-sulfur species.

tures.⁸ The silathionium [ClSiS]⁺ cation chelated by a nitrogen donating bis(iminophosphorane) ligand has been reported so far.^{9a} Although some compounds containing Si=S double bonds have been previously reported,^{9b–k} compounds with Si=S stabilized by neutral ligands^{9l–m} have rarely been reported.

Over the last one decade N-heterocyclic carbenes (NHCs) have been utilized as strong and efficient σ -donor ligands for the stabilization of several unstable species of main group elements.^{10–12} The $\text{Si}(0)=\text{Si}(0)$, $\text{Si}(\text{Cl})-\text{Si}(\text{Cl})$, and SiCl_2 molecules are not stable under ambient conditions and thus they readily undergo dimerization or polymerization. Low-oxidation state silicon halides (such as Si_2Cl_6) are also prone to disproportionation to produce SiCl_4 and SiCl_2 both of which were trapped by NHC too.^{10c} However, these compounds are prevented from undergoing further transformation when NHCs are employed as σ -donor ligands. NHC supported (NHC)- $\text{Si}(0)=\text{Si}(0)(\text{NHC})$,^{11a} (NHC) $\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{NHC})$,^{11a} and (NHC)-

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SiCl_2^{11b} are stable and isolable under ambient conditions. We have shown that the bonding and electron density distributions of the cAAC analogues of the above mentioned compounds differ significantly.^{11a,b,13} The bond between a carbene carbon atom and a silicon atom ($\text{C}_{\text{NHC}} \rightarrow \text{Si}$) is a coordinate σ -bond in $(\text{NHC})\text{Si}(0)=\text{Si}(0)(\text{NHC})$, $(\text{NHC})\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{NHC})$, and $(\text{NHC})\text{SiCl}_2$.^{11a,b} The $\text{C}_{\text{cAAC}}-\text{Si}$ bonds in $(\text{cAAC})\text{Si}(0)=\text{Si}(0)-(\text{cAAC})$ and $(\text{cAAC})\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{cAAC})$ are partial double bonds since cAACs are better π -acceptors.^{13a,b} cAAC gains strong π -back donation from the silicon atom to the carbene carbon atom ($\text{C}_{\text{cAAC}} \leftarrow \text{Si}$) inducing a radical character in the cAAC containing compounds.^{13a,b} Each cAAC-Si bond in diradical $(\text{cAAC}^{\cdot})\text{Si}(\text{Cl}_2)-\text{Si}(\text{Cl}_2)(\text{cAAC}^{\cdot})$ is an electron sharing single bond with a radical electron on each carbene carbon atom of a cAAC.^{13c,d}

The NHC stabilized bis-silylene $(\text{NHC})\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{NHC})$ has been isolated in 6.1% yield with a small amount of the side product $(\text{NHC})\text{Si}(0)=\text{Si}(0)(\text{NHC})$ when $(\text{NHC})\text{SiCl}_4$ is reduced with six equivalents of KC_8 in *n*-hexane.^{11a} The yield of the cAAC analogue, $(\text{cAAC})\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{cAAC})$, is eight times higher.^{13b} We carried out the reduction of the $(\text{NHC}/\text{cAAC})-\text{SiCl}_4$ adduct with KC_8 . A large amount of free NHC is recovered when $(\text{NHC})\text{SiCl}_4$ is reduced with three equivalents of KC_8 suggesting the formation of NHC during the reduction process. Note that the LUMO is higher¹⁴ in energy for $(\text{NHC})-\text{SiCl}_4$ than that of $(\text{cAAC})\text{SiCl}_4$ and hence during the reduction process the electron transfer from KC_8 to the LUMO of $(\text{NHC})-\text{SiCl}_4$ is possibly less efficient than that of $(\text{cAAC})\text{SiCl}_4$.¹⁵ This also rationalizes the lower yield of $(\text{NHC})\text{Si}(\text{Cl})-\text{Si}(\text{Cl})(\text{NHC})$ ^{11a} which leads to a limitation in the development of the reactivity of this extremely interesting compound.

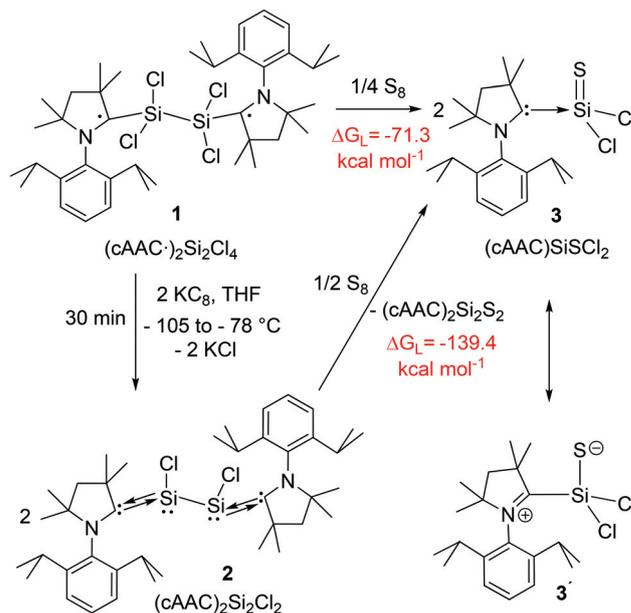
The red colored $(\text{cAAC}^{\cdot})_2\text{Si}_2\text{Cl}_4$ (**1**)^{13c} and green colored $(\text{cAAC})_2\text{Si}_2\text{Cl}_2$ (**2**)^{13b} are produced in good yields when $(\text{cAAC})-\text{SiCl}_4$ is reduced with two and three equivalents of KC_8 , respectively in THF. The reaction of **1** or **2** with one fourth or equivalent amount of S_8 leads to the isolation of $(\text{cAAC})\text{SiSCL}_2$ (**3**). Herein, we report on the synthesis, characterization, and theoretical calculation of **3**.

Results and discussion

Compound **1** and S_8 (4 : 1) were placed in two separate round bottomed flasks. The pre-cooled THF (at -78°C) was added to the flask containing **1**. Sulfur was dissolved in toluene (5 mL) at rt and subsequently cooled to -20°C .

The dark green THF solution of **1** was added to the toluene solution of sulfur and stirred at -78°C for 5 min. The color of the solution (at -10°C) changes from dark green to faded green upon stirring the solution for 15 min. A bright yellow solution of $(\text{cAAC})\text{SiSCL}_2$ (**3**) (Scheme 2) is obtained. Yellow needles of **3** were formed at -32°C in a freezer in 61% yield.

Compound **3** was also obtained when $(\text{cAAC})_2\text{Si}_2\text{Cl}_2$ (**2**) was reacted with sulfur powder (Scheme 2) under identical reaction conditions. Compound **2** was dissolved in THF to obtain a dark red solution (at -78°C) which was passed into another



Scheme 2 Synthesis of compound **3** from **1** and **2**.

flask containing sulfur powder ($2 : \text{S}_8 = 4 : 1$ molar ratio). The temperature of the reaction solution was slowly raised over 15 min to obtain a lighter red solution which turned light green after a short time. Finally a yellow colored solution was obtained after 30 min of total stirring. The concentrated bright yellow solution was stored at -32°C in a freezer to form small yellow needles of **3** in 35% yield. An NHC analogue of **3** is not obtained when $(\text{NHC})\text{SiCl}_2$ was reacted with S_8 rather $\text{NHC}=\text{S}$ was isolated. cAAC is a stronger σ -donor and better π -acceptor than NHC which might be the reason why the employment of cAAC is necessary to isolate the desired product **3**. The formation of byproducts $(\text{cAAC})_2\text{Si}_2\text{S}_2/(\text{cAAC})_2\text{Si}_2\text{S}_4$ was confirmed by mass spectrometry (see the ESI[†]).

The crystals of **3** are air and moisture sensitive and the THF solution slowly loses its color when exposed to air. The yellow powders decompose above 160°C . The UV-vis spectrum of compound **3** was recorded in THF solution which shows absorption bands at 273 nm (250–300 nm) and 360 nm (300–440 nm; $\text{LP}_{\text{S}_1} \rightarrow \pi_{\text{C}_1-\text{N}_1}^*$ excitation; Fig. S3) (see the ESI[†]). The TDDFT treatment on **3** (B3LYP/TZVP//M06-2X/SVP) shows the signature peak at 380.2 nm with an oscillator strength of 0.10, designating the $\text{LP}_{\text{S}_1} \rightarrow \pi_{\text{C}_1-\text{N}_1}^*$ excitation (Fig. S3[†]). The infrared (IR) spectrum of **3** (obtained in the range of $400\text{--}4000 \text{ cm}^{-1}$) showed sharp absorption bands at 671.5 and 693.1 cm^{-1} . Theoretically calculated IR bands are found ($\nu_{\text{Si}_1-\text{S}_1}$) at 707.0 and 724.8 cm^{-1} . Compound **3** was studied by NMR measurements. ^{29}Si NMR resonance is observed at +3.8 ppm which is close to the theoretically calculated (at M06-2X/TZVP//M06-2X/SVP level) value of +5.7 ppm. The ^{13}C NMR spectrum shows a resonance at 209.6 ppm (C_{cAAC}) which is close to that of **2** (207.1 ppm) but upfield shifted when compared with that of free cAAC (304.2 ppm). The ^{15}N -HMBC NMR spectrum of **3**

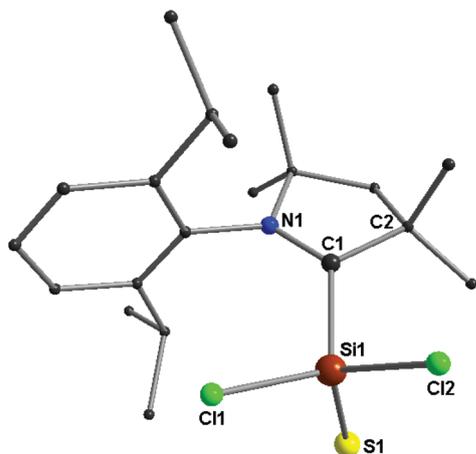


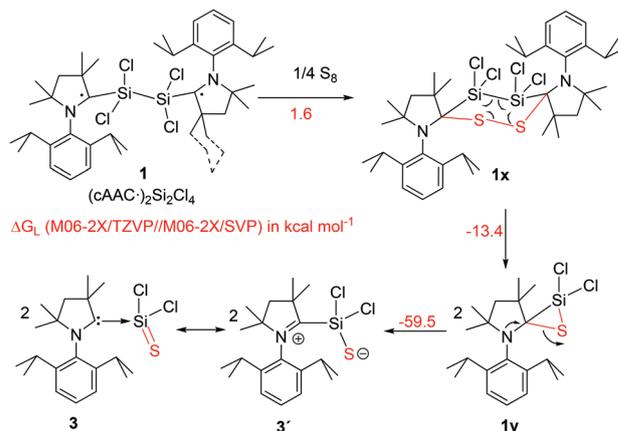
Fig. 1 Molecular structure of compound **3**. H atoms are omitted for clarity. Selected experimental [calculated at R-M06-2X/SVP for the singlet state] bond lengths [Å] and angles [°] (as averages of two independent molecules): C1–Si1 1.936(3) [1.943], Si1–S1 1.9895(10) [1.984], Si1–Cl1 2.0904(11) [2.089], Si1–Cl2 2.0806(11) [2.099], C1–N1 1.298(3) [1.303]; C2–C1–N1 109.6(2) [109.9], C1–Si1–S1 103.58(8) [102.0], C1–Si1–Cl1 113.07(8) [110.1], C1–Si1–Cl2 104.55(8) [102.3], Cl1–Si1–S1 115.89(4) [119.0], Cl1–Si1–Cl2 100.79(5) [101.5], Cl2–Si1–S1 118.79(5) [120.6].

shows a resonance at -156.0 ppm (3-bond coupling with ^1H at 1.48 ppm of CH_2 and 0.85 ppm of NCMe_2 of the five-membered carbene ring of the cAAC) which is close to that of (cAAC) \rightarrow SiCl_4 (-164.1 ppm) but downfield shifted when compared with that of **2** (-208.5 ppm). This suggests that σ -bond $\text{C}_{\text{cAAC}} \rightarrow \text{Si}$ in **3** is stronger than (cAAC) \rightarrow SiCl_4 .

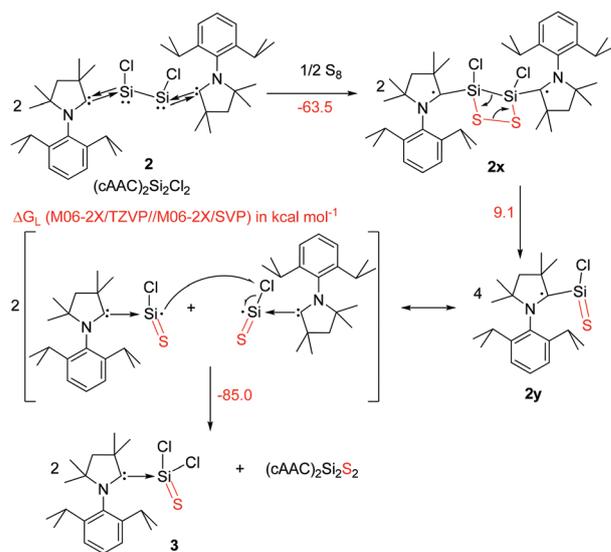
Compound **3** crystallized in the space group *Pbca*. The molecular structure of **3** is shown in Fig. 1. The silicon atom is bound to one sulfur, two chlorine atoms, and one carbene carbon atom of cAAC to adopt a four coordinate distorted tetrahedral geometry. The $\text{C}_{\text{cAAC}}\text{--Si}$ bond length of **3** is 1.936 (3) Å which is almost the same as that of (cAAC) SiCl_4 (1.944 (2) Å)¹⁵ but significantly longer than those in **1** (1.846(5) Å)^{13c} and **2** (182.3(3)–182.6(3) Å).^{13b} The $\text{C}_{\text{cAAC}}\text{--N}$ bond length of **3** is 1.298(3) Å which is close to that of (cAAC) SiCl_4 (1.306(3) Å) and shorter than that of **1** (1.376(6) Å).^{13b,c} The Si1–S1 bond length of **3** is 1.9895(10) Å which is in between those of (R_2SiS) \leftarrow NR_3^1 (2.013(3) Å)^{9l} and $\text{R}_2\text{R}_3\text{SiS}$ (1.948(4) Å).^{9k} The bond parameters suggest that the bond between the carbene carbon atom and the silicon atom is a coordinate σ -bond ($\text{C}_{\text{cAAC}} \rightarrow \text{Si}$), rather than an electron sharing covalent single bond in **1**^{13c} or a donor–acceptor partial double bond in **2**^{13b} as illustrated in Scheme 2. Selected bond lengths and bond angles are given in the caption of Fig. 1.

The possible pathways for the formation of **3** from the reaction of elemental sulfur with (cAAC) $_2\text{Si}_2\text{Cl}_4$ (**1**) and (cAAC) $_2\text{Si}_2\text{Cl}_2$ (**2**) are proposed in Schemes 3 and 4 and the energetics are theoretically calculated.

The diradical **1** reacts with S_8 to produce the intermediate **1x** having a six-membered ring $\text{C}_2\text{S}_2\text{Si}_2$ which is slightly



Scheme 3 Proposed mechanism for the formation of **3** from **1** reacting with sulfur.



Scheme 4 Proposed mechanism for the formation of **3** from **2** reacting with sulfur.

endothermic by $+1.6$ kcal mol $^{-1}$. The intermediate undergoes further transformation to form **1y** containing a three-membered ring CSSi . This step is exothermic by -13.4 kcal mol $^{-1}$. Finally **1y** rearranges to product **3/3'** which is highly exothermic by -59.5 kcal mol $^{-1}$ (Scheme 3).

When a dark red solution of (cAAC) $_2\text{Si}_2\text{Cl}_2$ (**2**) is reacted with sulfur powder an intermediate of dark green color (compound **1** has a similar color) is observed. This intermediate species is believed to be (cAAC) $_2\text{Si}_2\text{S}_2\text{Cl}_2$ (**2x**) possessing a cyclic four-membered ring Si_2S_2 . The conversion from **2** to **2x** is highly exothermic by -63.5 kcal mol $^{-1}$. The intermediate **2x** dissociates into two symmetrical radical intermediates **2y**. This is an endothermic process ($+9.1$ kcal mol $^{-1}$). Two molecules of **2y** further react with each other to produce product **3** and the side product (cAAC) $_2\text{Si}_2\text{S}_2$. This reaction is computed to be

exothermic by $-85.0 \text{ kcal mol}^{-1}$. The $(\text{cAAC})_2\text{Si}_2\text{S}_2$ reacts with sulfur powder to produce $(\text{cAAC})_2\text{Si}_2\text{S}_4$.^{9m} An alternative pathway of formation of **3** from **2** is also proposed and comparable energies are given in the ESI (Scheme S1†).

To understand the electronic structure and bonding scenario, geometry optimization of **3** was accomplished at the M06-2X/SVP level of theory (for Computational details, see ESI†). Optimization of both the singlet and triplet states reveals that the singlet state is more stable than the triplet state by $45.6 \text{ kcal mol}^{-1}$ (M06-2X/TZVP//M06-2X/SVP level). The bond parameters of **3** are in good agreement with those of the singlet. Moreover for further validation, CASSCF(2,2)/SVP calculation was carried out at the M06-2X/SVP optimized structure. The calculated coefficient values are 1.0, 0.0 and 0.0 for the corresponding (2,0), (1,1) and (0,2) states respectively, ensuring the closed-shell singlet state to be the electronic ground state of **3**. In comparison with triplet geometry, the optimized singlet state shows good agreement with the X-ray crystal structure as visualized from the alignments and superposition plot. (Fig. S1 and Table S1†). NBO population analysis of **3** entails that the C1 atom is connected with Si1 (1.945 e) and C2 (1.958 e) *via* the single bond occupancy and the N1 atom *via* a double bond with occupancies of 1.979 e and 1.970 e, respectively (Fig. S2 and Tables S2 and S3†). The C1 atom mainly contributes an electron density ($\sim 76\%$) towards the C1–Si1 bond formation, indicating its polar character. This result is further supported by the AIM (atoms in molecules) calculation at the bond critical point (BCP). The electron density $[\rho(r)]$ at the BCP of C1–N1 [0.347], C1–C2 [0.246] and Si1–C1 [0.097] bonds along with the respective Laplacian $[\nabla^2\rho(r)]$; -0.615 , -0.598 and $+0.241$ indicates the covalent interaction in the former two bonds and the closed-shell interaction in the last one (Table S4†). In consonance with the NBO results, there is a single bond noticed between Si1 and S1 atoms with 1.958 e occupancy, which is slightly more polarized towards the S1 centre ($\sim 63\%$) because of the higher electronegativity of the S1 atom than Si1. Additionally, NBO located three lone pairs on the S1 atom with occupancies of 1.971, 1.780 and 1.722 e (Table S3†). Surprisingly, the lowering in the occupancy of the last two lone pairs on the S1 atom can be encountered as some sort of donor–acceptor type interaction with the Si1 atom, leading to shortening of the bond distance. The strength of these delocalization interactions is estimated by second-order perturbation theory analysis of the Fock matrix in the NBO basis. The electron donation from three lone pairs on the S1 atom to the anti-bonding orbital of the Si1 atom (donor \rightarrow acceptor) leads to stabilization energies of 6.2, 8.0 and 8.2 kcal mol^{-1} , respectively (Table S5†). However, NBO exhibits a single bond occupancy, but the shorter Si1–S1 distance (1.984 Å) compared to the single bond length (2.159 Å and 1.942 Å in $\text{H}_3\text{Si-SH}$ and $\text{H}_2\text{Si=S}$, respectively) and the calculated high Wiberg bond indices (WBI of Si–S = 1.43, Table S2†) indicate a significant double bond character. The above results are further supported by the Laplacian of the (3,–3) critical point, called the valence-shell charge concentration (VSCC), displayed in Fig. 2.

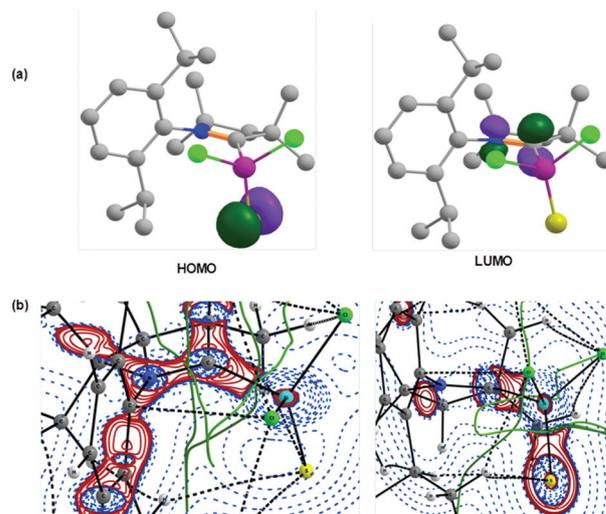


Fig. 2 (a) Computed KS-MOs of **3** at the M06-2X/TZVP//M06-2X/SVP level. Hydrogen atoms are omitted for clarity. (b) Laplacian distribution $[\nabla^2\rho(r)]$ in the N1–C1–Si1 (left) and C1–Si1–S1 plane (right) of **2**. Solid lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). The range of contours of the Laplacian is -8×10^2 to $+8 \times 10^2$. Solid lines connecting atomic nuclei (black) are the bond paths and those lines (green) separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

Experimental section

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. Ligand $\text{Me}_2\text{-cAAC}$, $(\text{cAAC}^*)_2\text{Si}_2\text{Cl}_4$ (**1**) and $(\text{cAAC}^*)_2\text{Si}_2\text{Cl}_2$ (**2**) were prepared according to literature methods.^{13b,c} Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C_6D_6 was dried by stirring for 2 days over a Na/K alloy followed by distillation in a vacuum and degassed. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on Büchi B-540 melting point apparatus.

Method A

Compound **1** $(\text{cAAC}^*)_2\text{Si}_2\text{Cl}_4$ (0.5 mmol; 384 mg) and S_8 (0.125 mmol; 32 mg) were placed in two separate round bottomed flasks. The pre-cooled (at -78°C) THF (40 mL) was added to a flask containing **1**. Sulfur was dissolved in toluene (5 mL) at rt and subsequently cooled to -20°C . The dark green THF solution of **1** was added to the toluene solution of sulfur and stirred at -78°C for 5 min. The temperature of the solution was slowly raised to -10°C . The color of the solution changed from dark green to faded green upon stirring the solution for 15 min at this temperature. A bright yellow

solution of **3** was obtained which was concentrated under vacuum and stored at $-32\text{ }^{\circ}\text{C}$ in a freezer to form yellow needles of (cAAC)SiSCl₂ (**3**) in 61% yield.

Method B

Compound **2** (0.5 mmol; 349 mg) was dissolved in THF to obtain a dark red solution which was cooled to $-78\text{ }^{\circ}\text{C}$ using a frozen solvent bath. The cold solution of **2** was passed into another flask containing sulfur powder (0.125 mmol; 32 mg). The mixture was stirred for 5 min at $-78\text{ }^{\circ}\text{C}$. The temperature of the reaction solution was slowly raised over 15 min during which the color of the solution slowly changed from dark red to lighter red. The color of the solution changed further from faint red to light green after a short time. Finally a yellow colored solution was obtained after 30 min of total stirring. The volume of the THF solution was reduced (1–2 mL) under vacuum. The bright yellow solution was stored at $-32\text{ }^{\circ}\text{C}$ in a freezer to form small yellow needles of **3** in 35% yield.

Elemental analysis found in % (calcd) for C₂₀H₃₁NSiSCl₂: C, 56.50 (57.67); H, 7.61 (7.50); N, 3.32 (3.36). **3** decomposes above 160 °C, and shows UV-visible bands at 273, and 360 nm. The needles of **3** are sensitive to air and moisture. They slowly lose their color from yellow to colorless when exposed to air. IR bands were observed at 671.5 and 693.1 cm⁻¹ for $\nu_{\text{Si1-S1}}$.

¹H NMR of **3** (300 MHz, 298 K, C₆D₆, ppm) δ : 7.13–6.8 (m, 3 H_{Ar}), 2.68 (m, 2H, CH₂), 1.84 (s, 6H, CMe₂), 1.51 (d, 6H, $J = 6\text{ Hz}$, CHMe₂), 1.48 (s, 2H), 1.38 (d, 6H, $J = 6\text{ Hz}$, CHMe₂), 0.85 (s, 6H, NCMe₂). ¹³C NMR (75 MHz, 298 K, C₆D₆, ppm) δ : 209.6 (C_{cAAC}), 144.41, 130.89, 127.73, 124.95, 124.57, 123.41, 79.93, 53.65, 49.50, 30.24, 28.21, 28.02, 27.56, 26.8, 25.6, 23.50, 22.08. ¹⁵N-HMBC (50.709 MHz, 298 K, C₆D₆, ppm) δ : -155.0 (3-bond coupling with ¹H at 1.48 ppm of CH₂ and 0.85 ppm of NCMe₂).

²⁹Si NMR (99 MHz, 298 K, C₆D₆, ppm) δ : +3.8.

See the ESI† for X-ray single crystal structure determination.

Conclusions

In conclusion, we have developed synthesis routes for cAAC ligand stabilized monomeric siliconthiodichloride (cAAC)SiSCl₂ (**3**) which was prepared *via* reaction of (cAAC')₂Si₂Cl₄ (**1**) or (cAAC)₂Si₂Cl₂ (**2**) with elemental sulfur (S₈). The mechanism of reaction was studied by theoretical calculations. The energetics were found to be favourable. The NHC analogue of **3** was not isolated possibly due to the weaker σ -donor and π -acceptor properties of NHC than those of cAAC. The stronger σ -donor property of cAAC is beneficial for an effective anchoring of cAAC to the SiSCl₂ unit. The bright yellow powder of compound **3** is soluble in polar organic solvents. **3** is stable at rt for a month under an inert atmosphere and thermally stable up to 160 °C. The monomeric molecular structure of **3** has been confirmed by X-ray single crystal diffraction and it was characterized by NMR, UV-vis, and IR spectroscopy. The bonding and electron density distributions of **3** have been studied by theoretical calculations.

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Notes and references

- Silicon Chemistry; From atom to extended systems*, ed. P. Jutzi and U. Schubert, Wiley-VCH, 2003.
- T. Iwamoto and S. Ishida, Multiple bonds with silicon: Recent Advances in synthesis, structure, and functions of stable disilenes, in *Functional Molecular Silicon Compounds II: Low Oxidation States*, Springer, 2014, pp. 125–202.
- (a) G. M. Dyson, *Org. Synth.*, 1926, **6**, 86; (b) S. Sharma, *Synthesis*, 1978, 803.
- M. Blix and W. Wirbelauer, *Chem. Ber.*, 1903, **36**, 4220.
- Y. Etienne, *Bull. Soc. Chim. Fr.*, 1953, 791.
- W. C. Schumb and W. J. Bernhard, *J. Am. Chem. Soc.*, 1955, **77**, 862.
- E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, 1963, **85**, 2677.
- H. Schnöckel, H. J. Gocke and R. Koppe, *Z. Anorg. Allg. Chem.*, 1989, **578**, 159.
- (a) Y. Xiong, S. Yao, S. Inoue, E. Irran and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 10074, (*Angew. Chem.*, 2012, **124**, 10221); (b) S.-H. Zhang, H.-X. Yeong and C.-W. So, *Chem. – Eur. J.*, 2011, **17**, 3490; (c) S. Yao, Y. Xiong and M. Driess, *Chem. – Eur. J.*, 2010, **16**, 1281; (d) T. Iwamoto, K. Sato, S. Ishida, C. Kabuto and M. Kira, *J. Am. Chem. Soc.*, 2006, **128**, 16914; (e) Y. Xiong, S. Yao, S. Inoue, E. Irran and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 10074; (f) S. Khan, R. Michel, D. Koley, H. W. Roesky and D. Stalke, *Inorg. Chem.*, 2011, **50**, 10878; (g) R. West, D. J. D. Young and K. J. Haller, *J. Am. Chem. Soc.*, 1985, **107**, 4942; (h) J. E. Mangette, D. R. Powell and R. West, *Organometallics*, 1995, **14**, 3551; (i) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase and M. Goto, *J. Am. Chem. Soc.*, 1998, **120**, 11096; (j) N. Wiberg, W. Niedermayer, K. Polborn and P. Mayer, *Chem. – Eur. J.*, 2002, **8**, 2730; (k) H. Suzuki, N. Tokitoh, S. Nagase and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11578; (l) P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot and C. Priou, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1016; (m) C. Mohapatra, K. C. Mondal, P. P. Samuel, H. Keil, B. Niepötter, R. Herbst-Irmer, D. Stalke, S. Dutta, D. Koley and H. W. Roesky, *Chem. – Eur. J.*, 2015, **21**, 12572–12576.

- 10 (a) Y. Wang and G. H. Robinson, *Dalton Trans.*, 2012, **41**, 337; (b) R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444; (c) G. Tavčar, S. S. Sen, R. Azhakar, A. Thorn and H. W. Roesky, *Inorg. Chem.*, 2010, **49**, 10199.
- 11 (a) Y. Wang, Y. Xie, P. Wie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069; (b) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem., Int. Ed.*, 2009, **48**, 5683, (*Angew. Chem.*, 2009, **121**, 5793); (c) A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2013, **52**, 6974, (*Angew. Chem.*, 2013, **125**, 7112).
- 12 (a) Y. Wang, Y. Xie, P. Wie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 14970; (b) Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2013, **135**, 19139.
- 13 (a) K. C. Mondal, P. P. Samuel, H. W. Roesky, R. R. Aysin, L. A. Leites, S. Neudeck, J. Lübber, B. Dittrich, M. Hermann and G. Frenking, *J. Am. Chem. Soc.*, 2014, **136**, 8919; (b) K. C. Mondal, H. W. Roesky, B. Dittrich, N. Holzmann, M. Hermann, G. Frenking and A. Meents, *J. Am. Chem. Soc.*, 2013, **135**, 15990; (c) K. C. Mondal, B. Dittrich, B. Maity, D. Koley and H. W. Roesky, *J. Am. Chem. Soc.*, 2014, **136**, 9568; (d) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter and D. Stalke, *Angew. Chem., Int. Ed.*, 2013, **52**, 1801, (*Angew. Chem.*, 2013, **125**, 1845).
- 14 (a) D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2011, **2**, 389; (b) D. Martin, M. Melaimi, M. Soleilhavoup and G. Bertrand, *Organometallics*, 2011, **30**, 5304.
- 15 K. C. Mondal, H. W. Roesky, A. C. Stückl, F. Ihret, W. Kaim, B. Dittrich, B. Maity and D. Koley, *Angew. Chem., Int. Ed.*, 2013, **52**, 11804, (*Angew. Chem.*, 2013, **125**, 12020).