Dalton Transactions

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry

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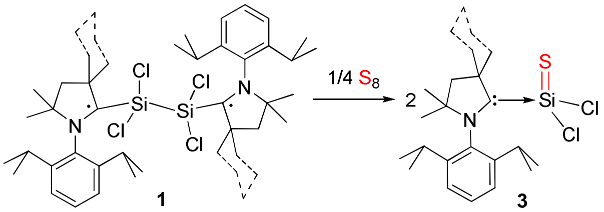
TOC

The cAAC-ligand stabilized monomeric siliconthiodichloride (cAAC)$SiSCl_2$ (**3**) is prepared via reaction of $(cAAC\cdot)_2Si_2Cl_4$ (**1**) or $(cAAC)_2Si_2Cl_2$ (**2**) with elemental sulfur (S_8).



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ARTICLE

Monomeric Siliconthiodichloride Trapped by a Lewis Base †

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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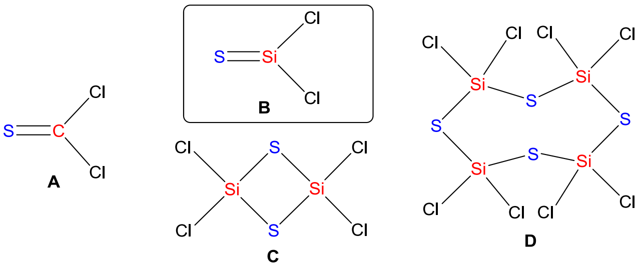
Thiophosgene ($CSCl_2$), a chemical reagent used in numerous organic syntheses, exists in the monomeric form while its heavier silicon analogue [siliconthiodichloride ($SiSCl_2$)] is isolated so far as a dimer at room temperature and tetramer at 180 °C. Herein, we report on the first synthesis, isolation, and characterization of cyclic alkyl(amino) carbene (cAAC) stabilized siliconthiodichloride (cAAC)$SiSCl_2$ (**3**) in the neutral monomeric form. **3** is synthesized via reaction of $(cAAC\cdot)_2Si_2Cl_4$ (**1**) or $(cAAC)_2Si_2Cl_2$ (**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.

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 are prone to undergo dimerization, oligomerization, or polymerization. In contrast, the carbon analogues are stable and isolable as monomeric species.[2] For example, the heavier analogue of thiophosgene ($CSCl_2$)[3] (Scheme 1, **A**) is siliconthiodichloride (**B**) [4] which exists in dimeric (**C**) [5] at room temperature and tetrameric forms (**D**) [6] at 180 °C. Thiophosgene ($CSCl_2$) (**A**) is quite stable, accessible, and utilized as 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 temperature.[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.



Scheme 1. Selected carbon- and silicon- sulfur species.

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 Si(0)=Si(0), Si(Cl)–Si(Cl), and $SiCl_2$ molecules are not stable at ambient condition 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)Si(0)=Si(0)(NHC),[11a] (NHC)Si(Cl)–Si(Cl)(NHC), [11a] and (NHC)$SiCl_2$ [11b] are stable and isolable at ambient condition. 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 ($C_{NHC}\rightarrow Si$) is a coordinate σ-bond in (NHC)Si(0)=Si(0)(NHC), (NHC)Si(Cl)–Si(Cl)(NHC), and (NHC)$SiCl_2$.[11a-b] The C_{cAAC}–Si bonds in (cAAC)Si(0)=Si(0)(cAAC) and (cAAC)Si(Cl)–Si(Cl)(cAAC) are partial double bonds since cAACs are better π-acceptors.[13a-b]

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† Electronic Supplementary Information (ESI) available: [Syntheses, NMR, UV-vis, Raman spectra, crystallographic table, and theoretical details are given in the Supporting Information]. See DOI: 10.1039/x0xx00000x

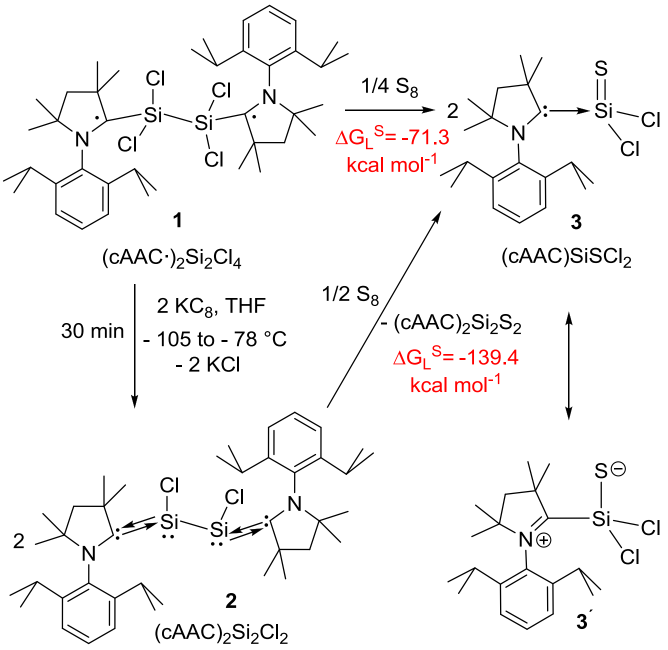
cAAC gains strong π-back donation from the silicon atom to the carbene carbon atom (C_{cAAC}←Si) inducing radical character in the cAAC containing compounds.[13a-b] Each cAAC–Si bond in diradical (cAAC·)Si(Cl_2)–Si(Cl_2)(cAAC·) is an electron sharing single bond with a radical electron on each carbene carbon atom of a cAAC.[13c-d]

The NHC stabilized bis-silylene (NHC)Si(Cl)–Si(Cl)(NHC) has been isolated in 6.1% yield with a small amount of side product (NHC)Si(0)=Si(0)(NHC) when (NHC)$SiCl_4$ is reduced with six equivalents of KC_8 in *n*-hexane.[11a] The yield of the cAAC analogue, (cAAC)Si(Cl)–Si(Cl)(cAAC) is eight times higher.[13b] We carried out the reduction of (NHC/cAAC)$SiCl_4$ adduct with KC_8. A large amount of free NHC is recovered when (NHC)$SiCl_4$ is reduced with three equivalents of KC_8 suggesting the formation of NHC during the reduction process. Note, that the LUMO is higher [14] in energy for (NHC)$SiCl_4$ than that of (cAAC)$SiCl_4$ and hence during the reduction process the electron transfer from KC_8 to the LUMO of (NHC)$SiCl_4$ is possibly less efficient than that of (cAAC)$SiCl_4$.[15] This also rationalizes the lower yield of (NHC)Si(Cl)–Si(Cl)(NHC) [11a] which leads to a limitation in the development of the reactivity of this extremely interesting compound.

The red colored $(cAAC\cdot)_2Si_2Cl_4$ (**1**) [13c] and green colored $(cAAC)_2Si_2Cl_2$ (**2**) [13b] are produced in good yields when (cAAC)$SiCl_4$ is reduced with two and three equivalents of KC_8, respectively in THF. The reaction of **1** or **2** with one fourth or equivalent of S_8 leads to the isolation of (cAAC)$SiSCl_2$ (**3**). Herein, we report on the synthesis, characterization, and theoretical calculation of **3**.

Result 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.



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

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 (cAAC)$SiSCl_2$ (**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 $(cAAC)_2Si_2Cl_2$ (**2**) was reacted with sulfur powder (Scheme 2) under identical reaction condition. Compound **2** was dissolved in THF to obtain a dark red solution (at -78 °C) which was passed into another flask containing sulfur powder (**2**: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 to 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 (NHC)$SiCl_2$ was reacted with S_8 rather NHC=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 $(cAAC)_2Si_2S_2$/$(cAAC)_2Si_2S_4$ was confirmed by mass spectrometry (see SI).

The crystals of **3** are air and moisture and the THF solution slowly looses their color when exposed to air. Yellow powders of decomposes above 160 °C. The UV-vis spectrum of compounds was recorded in THF solution which shows absorption band at 273 nm (250-300 nm) and 360 nm (300-440 nm; $LP_{S1}\rightarrow\pi^*_{C1-N1}$ excitation; Figure S3) (see SI). 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 $LP_{S1}\rightarrow\pi^*_{C1-N1}$ excitation (Figure S3). The infrared (IR) spectrum of **3** (measured in the range of 400-4000 cm^{-1}) showed a sharp absorption bands at 671.5 and 693.1 cm^{-1}. Theoretically calculated IR bands are (υ_{Si1-S1}) 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** shows a resonance at -156.0 ppm (3-bond coupling with ^{1}H at 1.48 ppm of CH_2 and 0.85 ppm of $NCMe_2$ of five-membered carbene ring of the cAAC) which is close to that of (cAAC)→$SiCl_4$ (-164.1 ppm) but down field shifted when compared with that of **2** (-208.5 ppm). This suggests that σ-bond C_{cAAC}→Si in **3** is stronger than that of (cAAC)→$SiCl_4$.

Compound **3** crystallized in the space group *Pbca*. The molecular structure of **3** has been shown in Figure 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 C_{cAAC}–Si bond length of **3** is 1.936 (3) Å which is almost the same to 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 C_{cAAC}–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 $(R_2SiS)\leftarrow NR^1_3$ (2.013(3) Å)[9l] and R_2R_3SiS (1.948(4) Å).[9k] The bond parameters suggest that the bond between the carbene carbon atom and silicon atom is a coordinate σ-bond ($C_{cAAC}\rightarrow Si$), 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 Figure 1.

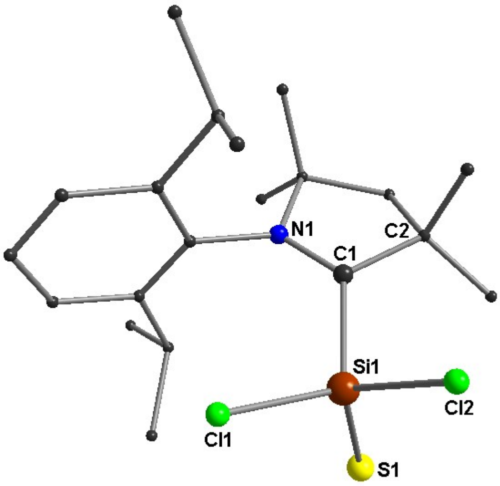
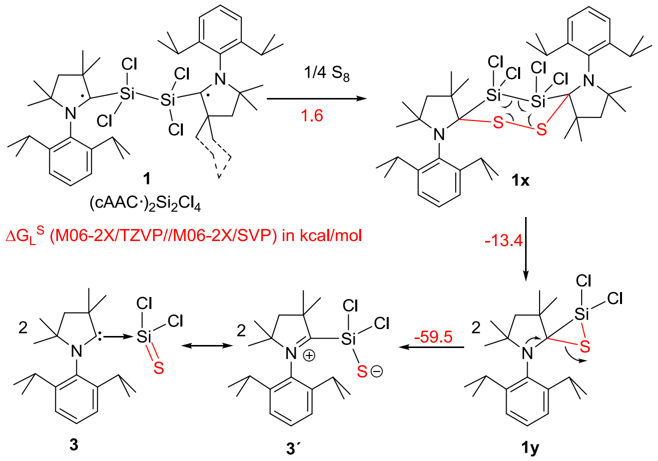


Figure 1. Molecular Molecular structure of compound **3**. H atoms are omitted for clarity. Selected experimental [calculated at R-M06-2X/SVP for the singlet state] bond lengths [Å] and angles [°] (as averages of two independent molecules): C1–Si1 1.936(3) [1.943], Si1–S1 1.9895(10) [1.984], Si1–Cl1 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].

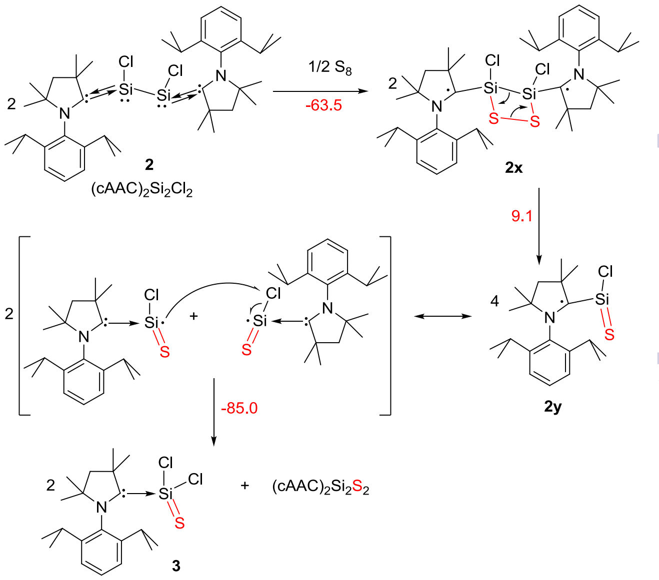
The possible path ways for the formation of **3** from the reaction of elemental sulfur with (cAAC·)$_2$Si$_2$Cl$_4$ (**1**) and (cAAC)$_2$Si$_2$Cl$_2$ (**2**) are proposed in Schemes 3-4 and the energetic are theoretically calculated.



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

The diradical **1** reacts with S_8 to produce the intermediate **1x** having a six-embered ring $C_2S_2Si_2$ which is slightly endothermic by +1.6 kcal mol^{-1}. The intermediate undergoes further transformation to form **1y** containing 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 dark red solution of (cAAC)$_2$Si$_2$Cl$_2$ (**2**) is reacted with sulfur powder an intermediate dark green color (compound **1** has the similar color) is observed. This intermediate species is believed to be (cAAC·)$_2$Si$_2$S$_2$Cl$_2$ (**2x**) possessing a cyclic four-membered ring Si$_2$S$_2$. The conversation 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 side product (cAAC)$_2$Si$_2$S$_2$. This reaction is computed to be exothermic by -85.0 kcal mol^{-1}. The (cAAC)$_2$Si$_2$S$_2$ reacts with sulfur powder to produce (cAAC)$_2$Si$_2$S$_4$.[9m] An alternative pathway of formation of **3** from **2** is also proposed and comparable energies are given in the SI (Scheme S1).



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

To understand the electronic structure and bonding scenario, geometry optimization of **3** was accomplished at M06-2X/SVP level of theory (see Computational Details). Optimization of both the singlet and triplet states reveals that the singlet state is more stable than triplet state by 45.6 kcal mol^{-1} (M06-2X/TZVP//M06-2X/SVP level). The bond parameters of **3** are in good agreement with those of 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 to triplet geometry, the optimized singlet state shows good agreement with the X-ray crystal structure as visualized from the alignments and superposition plot. (Figure 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 single bond occupancy and N1 atom via double bond with occupancies of 1.979 e and 1.970 e respectively (Figure S2 and Table S2, S3). The C1 atom mainly contributes electron density (~76%) towards the C1–Si1 bond formation, indicating polar character. This result is further supported by AIM (atoms in molecules) calculation at the bond critical point (BCP). The electron density [ρ(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 covalent interaction in former two bonds and closed-shell interaction in last one (Table S4). In consonance with 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 (~63%) because of higher electronegativity of S1 atom than Si1. Additionally, NBO locates three lone pairs on 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 S1 atom can be encountered as some sort of donor-acceptor type interaction with Si1 atom, leading to shortening of bond distance. The strength of these delocalization interactions are estimated by second-order perturbation theory analysis of Fock matrix in NBO basis. The electron donation from three lone pairs on the S1 atom to the anti-bonding orbital of Si1 atom (donor→acceptor) leads to the stabilization energies of 6.2, 8.0 and 8.2 kcal/mol, 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 $H_3Si–SH$ and $H_2Si=S$ respectively) and calculated high Wiberg bond indices (WBI of Si–S = 1.43, Table S2) indicates significant double bond character. The above results are further supported by the Laplacian of (3,-3) critical point, called valence-shell charge concentration (VSCC), displayed in Figure 2.

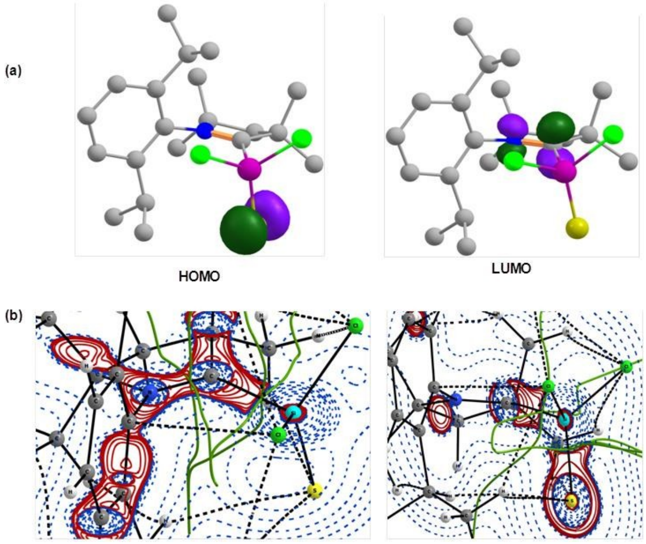


Figure 2. (a) Computed KS-MOs of **3** at M06-2X/TZVP//M06-2X/SVP level. Hydrogen atoms are omitted for clarity. (b) Laplacian distribution [$\nabla^2\rho$(r)] in N1–C1–Si1 (left) and C1–Si1–S1 plane (right) of 2. Solid lines indicate the areas of charge concentration ($\nabla^2\rho$(r) < 0) while dotted lines mean the charge depletion ($\nabla^2\rho$(r) > 0). The range of contours of the Laplacian is -8×10^2 to +8×10^2. Solid lines connecting atomic nuclei (black) are the bond paths and those lines (green) separating the atomic basins indicates 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 Me_2-cAAC, $(cAAC\cdot)_2Si_2Cl_4$ (**1**) and $(cAAC)_2Si_2Cl_2$ (**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 Na/K alloy followed by distillation in 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 a Büchi B-540 melting point apparatus.

Method A: Compound $(cAAC\cdot)_2Si_2Cl_4$ (**1**) (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 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 °C in a freezer to form yellow needles of $(cAAC)SiSCl_2$ (**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 °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 °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 °C in a freezer to form small yellow needles of **3** in 35% yield.

Elemental analysis found in % (calcd) for $C_{20}H_{31}NSiSCl_2$: C, 56.50 (57.67); H, 7.61 (7.50); N, 3.32 (3.36). **3** decomposes above 160 °C, 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 at 671.5 and 693.1 cm^{-1} for υ_{Si1-S1}.

^{1}H NMR of **3** (300 MHz, 298 K, C_6D_6, ppm) δ: 7.13-6.8 (m, 3 H_{Ar}), 2.68 (m, 2H, CH_2), 1.84 (s, 6H, CMe_2), 1.51 (d, 6H, J = 6 Hz, $CHMe_2$), 1.48 (s, 2H), 1.38 (d, 6H, J = 6 Hz, $CHMe_2$), 0.85 (s, 6H, $NCMe_2$). ^{13}C NMR (75 MHz, 298 K, C_6D_6, 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. ^{15}N-HMBC (50.709 MHz, 298 K, C_6D_6, ppm) δ: -155.0 (3-bond coupling with ^{1}H at 1.48 ppm of CH_2 and 0.85 ppm of $NCMe_2$).

^{29}Si NMR (99 MHz, 298 K, C_6D_6, ppm) δ: +3.8.

See SI for X-ray single crystal structure determination.

Conclusions

In conclusion, we have developed synthesis routes for cAAC ligand stabilized monomeric siliconthiodichloride (cAAC)$SiSCl_2$ (**3**) which was prepared via reaction of $(cAAC\cdot)_2Si_2Cl_4$ (**1**) or $(cAAC)_2Si_2Cl_2$ (**2**) with elemental sulfur (S_8). The mechanism of reaction pathayws were studied by theoretical calculations. The energetics were found to be favourable. The NHC analogue of **3** was not isolated possibly due to 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 $SiSCl_2$ 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.

Acknowledgements

Dedicated to Professor Alan H.Cowley for his outstanding contributions in chemistry. H. W. R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/64-I) for financial support. T.M. thanks CSIR for SRF fellowship, and D.K. to IISER-Kolkata acknowledges IISER-Kolkata and CSIR project fund (01(2770)/13/EMR-II) for financial support. Parts of this research were carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). We would like to thank Saravanan Panneerselvam for assistance in using beamline PX11.

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