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Synthesis of cAAC stabilized biradical of “Me₂Si” and “Me₂SiCl” monoradical from Me₂SiCl₂ – an important feedstock material†

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The cyclic alkyl(amino) carbene (cAAC) coordinated biradical of dimethylsilicon was isolated as (cAAC)₂Me₂Si (**1**), (cAAC = C(CH₂)(CMe₂)₂N-2,6-i-Pr₂C₆H₃), synthesized from the reduction of Me₂SiCl₂ using two equivalents of KC₈ in the presence of two equivalents of cAAC. The reduction of Me₂SiCl₂ by one equivalent of KC₈ in the presence of one equivalent of cAAC resulted in the stable dimethylsiliconchloride monoradical (cAAC)Me₂SiCl (**2**).

Radicals and biradicals have attracted considerable attention in chemistry and material science due to their unique optical, magnetic and electronic properties.¹ In 1915 Schlenk isolated the first paramagnetic biradical from the reaction of bis-diphenylbenzyl dichloride with a copper–tin alloy.^{2a} Most of the radicals are unstable and are short-lived.^{2b–d} However, they can be isolated and stored at room temperature in a pure form using either thermodynamic or kinetic stabilization.^{3,4} Several stable carbon and silicon centered biradicals are known.⁵ Carbon centered 1,3-biradicals are proposed to be key reactive intermediates in certain chemical reactions.⁶ Limited examples of four-membered heterocyclic 1,3-biradicals of cyclobutane type were reported.⁷ Recently, we have synthesized air stable carbon centered 1,3-biradical (cAAC)₂SiCl₂ (**I**)⁸ (Chart 1) from the reaction of NHC → SiCl₂ (NHC = N-heterocyclic carbene) with a cyclic alkyl(amino) carbene. Furthermore, our group successfully synthesized cAAC stabilized SiX₂ (X = H, F) (Chart 1) bridged

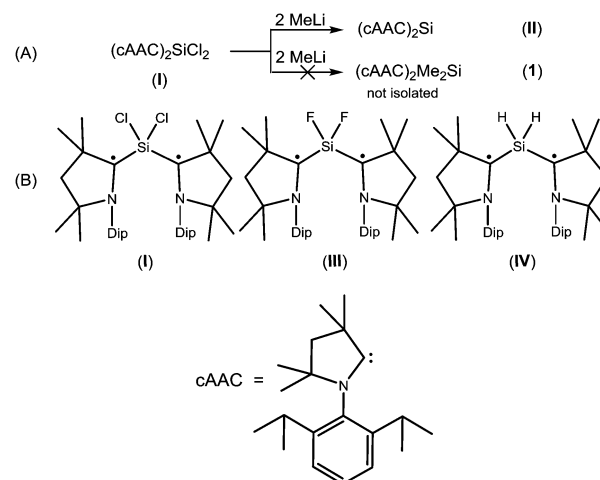


Chart 1 (A) The unsuccessful attempted synthesis of (cAAC)₂Me₂Si (**1**); (B) structurally characterized stable biradicals containing SiX₂ (X = Cl, F, H) moiety^{8–10}

1,3-biradicals, which are stable at room temperature for more than three months under inert atmosphere. The elusive SiF₂ bridged biradical (cAAC)₂SiF₂ (**III**) (Chart 1) was synthesized from the reduction of (cAAC)SiF₄ by using two equivalents of KC₈ in the presence of one equivalent of cAAC.⁹ While, (cAAC)₂SiH₂ (**IV**) (Chart 1) was prepared from the reduction of H₂SiI₂ with two equivalents of KC₈, in the presence of two equivalents of cAAC.¹⁰ After the successful isolation of cAAC stabilized SiX₂ (X = H, Cl, F) bridged 1,3-biradicals, the isolation of SiMe₂ analogues (cAAC)₂Me₂Si (**1**) was a prominent missing link in this class of compounds. Dimethyl silicon is not stable at room temperature and polymerises to (SiMe₂)_n. In our earlier synthetic route, we tried to isolate **1**, by the reaction of (cAAC)₂SiCl₂ with 2 equivalents of MeLi by the nucleophilic substitution method.¹¹ To our surprise, MeLi functioned as a reducing agent leading to the isolation of dehalogenated biradicaloid (cAAC)₂Si (**II**).¹² Me₂SiCl₂ is the most important feedstock material in the industry for the preparation of silicones.¹³ We envisaged an

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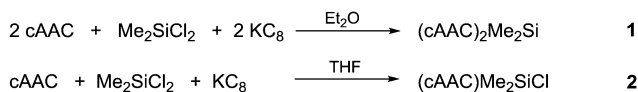
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Scheme 1 Synthesis of **1** and **2**.

alternative route to the isolation of **1** by the reduction of commercially available Me_2SiCl_2 . Herein, we report a one step synthesis of the biradical $(\text{cAAC})_2\text{Me}_2\text{Si}$ (**1**) and monoradical $(\text{cAAC})\text{Me}_2\text{SiCl}$ (**2**) by the reduction of Me_2SiCl_2 with KC_8 .

Both the compounds **1** and **2** were fully characterized by X-ray crystallography and EPR spectroscopy. Compound **1** was prepared by reduction of Me_2SiCl_2 using KC_8 in a 1:2 molar ratio in the presence of two equivalents of cAAC (Scheme 1; for details, see ESI†). ^1H NMR spectrum of compound **1** shows broad resonance indicating the radical nature. **1** has been characterized by EPR spectroscopy, LIFDI mass spectrometry, elemental analysis and single crystal structure analysis. **1** is stable in an inert atmosphere for more than 6 months in the solid state. It is thermally stable at room temperature and decomposes at 148°C . The UV/Vis spectrum of **1** in a hexane solution shows an absorption band at 575 nm. The LIFDI mass spectrum in toluene exhibits a peak at 629.6 m/z for $[\text{M}]^+$. Single crystals of **1** suitable for X-ray diffraction analysis were grown from hexane solution at -26°C .

A stable radical containing the Me_2SiCl group has not been reported so far. Equivalent amounts of cAAC, Me_2SiCl_2 and KC_8 , respectively, treated in THF at -90°C resulted in the desired monoradical product $(\text{cAAC})\text{Me}_2\text{SiCl}$ (**2**) as orange coloured crystals in 68% yield (Scheme 1).

2 was characterized by EPR spectroscopy, LIFDI mass spectrometry, elemental analysis and single crystal structure analysis. The LIFDI mass spectrum in toluene exhibits a molecular ion peak at 378.2 m/z . The UV/Vis spectrum of **2** in hexane shows an absorption band at 435 nm. The EPR spectra of compounds **1** and **2** were recorded in hexane solution at room temperature. It must be mentioned that efforts to isolate such type of radical species with NHC were not successful.

1 crystallizes in the monoclinic space group $C2/c$. The molecular structure of **1** (Fig. 1) reveals the central Si atom to be distorted tetrahedrally coordinated by four carbon atoms. The Si–Me bond lengths [1.8768(13) and 1.8800(13) Å] are similar to the $\text{C}_{\text{AAC}}\text{–Si}$ distances [1.8814(13) and 1.8829(13) Å] and to the distances reported in the literature.^{10,14} The C2–Si1–C2A bond angle ($116.86(5)^\circ$) is widened due to the steric hindrance of the bulky cAAC ligands, but nevertheless smaller than in the silylone $(\text{cAAC})_2\text{Si}$ of $119.10(1)^\circ$.^{12b}

2 crystallizes in the orthorhombic space group $Pbca$. The molecular structure (Fig. 2) reveals the silicon atom to be tetra-coordinated with three carbon and one chlorine atom. The Si–Cl bond length (2.1228(5) Å) is longer than those in $(^{\text{Me}}\text{cAAC})\text{SiCl}_3$ (2.0396(4)–2.0864(3) Å).¹⁵

The EPR spectrum of **1** is dominated by a 1:1:1 triplet of 4.65 G (Fig. 3), attributed to the coupling of the unpaired electron with one ^{14}N atom ($I = 1$). This splitting^{9,10,15} suggests localized spin at only one of the two equivalent cAAC groups

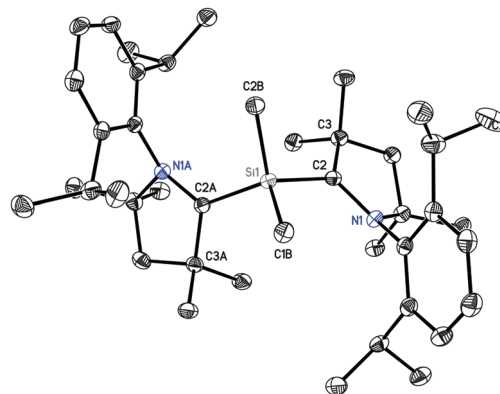


Fig. 1 Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [$^\circ$]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C2B, 1.8768(13) [1.891]; Si1–C1B, 1.8800(13) [1.891]; Si1–C2, 1.8814(13) [1.886]; Si1–C2A, 1.8829(13) [1.886]; C2B–Si1–C1B, $106.55(6)$ [106.6]; C2B–Si1–C2, $108.33(6)$ [108.7]; C1B–Si1–C2, $107.98(6)$ [108.9]; C2B–Si1–C2A, $108.40(6)$ [108.7]; C1B–Si1–C2A, $108.27(6)$ [108.7]; C2–Si1–C2A, $116.86(5)$ [114.9].

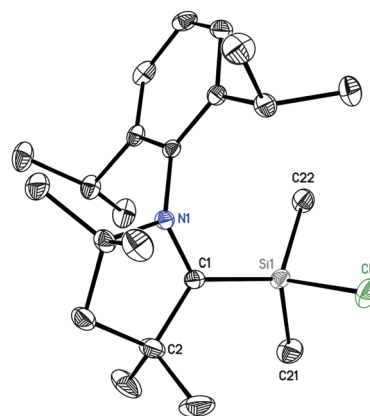


Fig. 2 Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [$^\circ$]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C1, 1.8323(12) [1.841]; Si1–C22, 1.8633(13) [1.878]; Si1–C21, 1.8645(13) [1.876]; Si1–Cl1, 2.1228(5) [2.138]; C1–Si1–C22, $117.67(6)$; C1–Si1–C21, $113.16(6)$; C22–Si1–C21, $108.22(6)$; C1–Si1–Cl1, $108.56(4)$ [108.1]; C22–Si1–Cl1, $104.05(4)$ [104.5]; C21–Si1–Cl1, $103.91(5)$ [105.0].

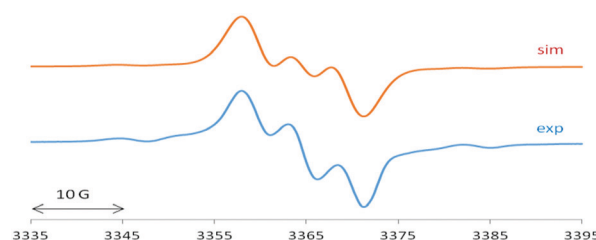


Fig. 3 EPR spectrum of **1** with computer simulation (top). For parameters see main text.

connected to the silicon atom which exhibits a typically ^{29}Si isotope coupling^{9,10,15} of 27.5 G (^{29}Si : $I = 1/2$, 4.7% nat. abundance).



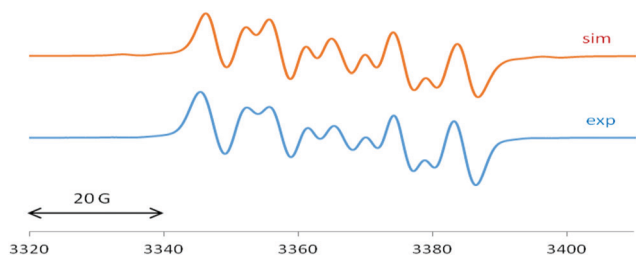


Fig. 4 EPR spectrum of **2** with computer simulation (top). For parameters see main text.

2 exhibits an EPR spectrum (Fig. 4) with similar ^{14}N and ^{29}Si values of 5.4 G and 25 G, respectively, in addition to a sizeable chlorine splitting from the isotopes ^{35}Cl ($I = 3/2$, 75.8% nat. abundance: 8.9 G) and ^{37}Cl ($I = 3/2$, 24.2%: 7.4 G). Such Cl(Si) coupling has been noted before for related silicon radicals.¹⁵

We carried out quantum chemical calculations using density functional theory at the BP86/def2-TZVP level²³ in order to analyze the electronic structure of compounds **1** and **2**. Fig. 1 and 2 shows also the computed bond lengths and angles of the optimized geometries of the two molecules, which are in excellent agreement with the experimental data. The calculations suggest that **1** has an electronic triplet ground state whereas **2** is a doublet, which concurs with the EPR results. Fig. 5 shows the spin density distribution of the two molecules. The unpaired electrons in **1** and **2** are mainly located at the nitrogen atoms and the carbene carbon atoms of the cAAC moieties.

We further analyzed the nature of the cAAC–Si bonds in **1** and **2** with the EDA-NOCV method.²⁴ Table S1 (ESI[†]) shows the numerical results. The calculations for **1** were carried out using the cAAC fragments in the electronic triplet state, which gives an overall quintet state for the (cAAC)₂ ligand, and the SiMe₂ moiety in the triplet state. For compound **2** we took the cAAC ligand in the triplet state and the SiMe₂Cl fragment in the doublet state. The choice of the open-shell fragments corresponds to electron-sharing single bonds. Comparative calculations using an electronic singlet state spin for the cAAC ligands, which correspond to dative bonds cAAC → Si, gave significantly larger orbital values ΔE_{orb} (see Tables S2 and S3 in ESI[†]). It has been shown in previous studies that the orbital values ΔE_{orb} are a probe for the choice of the best fragments.²⁵

The data in Table S1 (ESI[†]) show that the covalent orbital interactions ΔE_{orb} have nearly equal strength as the Coulomb attraction. There are two major orbital contributions $\Delta E_{\text{orb}(1)}$

and $\Delta E_{\text{orb}(2)}$ in compound **1** and one dominant term $\Delta E_{\text{orb}(1)}$ in **2**, which come from pairwise orbital interactions between the chosen fragments. Fig. S5 (ESI[†]) shows the plots of the associated deformation densities $\Delta\rho$, which illustrate the charge flow that is connected to the orbital interactions. The color code of the charge flow indicates the direction red → blue. The complete list of the deformation densities $\Delta\rho$ and the connected fragment orbitals are shown in Fig. S3 and S4 of ESI[†]. It becomes obvious that $\Delta E_{\text{orb}(1)}$ in compound **1** is due to the interaction between the singly occupied σ orbital (SOMO) of SiMe₂ with the in-phase (+, +) combination of the π -type²⁶ SOMO of (cAAC)₂, where the net charge flow is from SiMe₂ → (cAAC)₂. The stabilization energy $\Delta E_{\text{orb}(2)}$ in compound **1** comes from the interaction of the π SOMO of SiMe₂ with the out-of-phase (+, –) combination of the σ -type²⁶ SOMO of (cAAC)₂. The dominant orbital interaction $\Delta E_{\text{orb}(1)}$ in compound **2** is due to the interaction between the σ SOMO of SiClMe₂ with the σ SOMO of cAAC. The direction of the charge flow between the ligands is in agreement with the calculated partial charges by the NBO²⁷ method. The computed charges q at the BP86/def2-TZVP level are $q(\text{SiMe}_2) = +0.82 e$ for **1** and $q(\text{SiClMe}_2) = +0.36 e$ for **2**. Thus, the cAAC ligand in **1** and **2** acts as an acceptor rather than donor.

In summary, we report on the synthesis of 1,3-biradical containing Me₂Si moiety using cAAC as ligand. Moreover we isolated the monoradical (cAAC)Me₂SiCl. Theoretical investigations and EPR spectra of both compounds have been reported. The calculations suggest that **1** has an electronic triplet ground state whereas **2** is a doublet.

Crystal structure determination. Single crystals were selected and covered with perfluorinated polyether oil on a microscope slide.¹⁶ An appropriate crystal was selected using a polarize microscope, mounted on the tip of a MiTeGen[®] MicroMount, fixed to a goniometer head and shock cooled by the crystal cooling device. The data of **1** and **2** were collected from shock-cooled crystals at 100(2) K on a BRUKER D8 three circle diffractometer equipped with an INCOATEC Mo microsource with mirror optics (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) and smart APEX II detector. They were integrated with SAINT.¹⁷ A multi-scan absorption correction and a 3λ correction¹⁸ was applied using SADABS.¹⁹ The structure were solved by direct methods (SHELXT)²⁰ and refined by full-matrix least-squares methods against F^2 (SHELXL)²¹ in the graphical user interface ShelXle.²² CCDC 1894458 (**1**) and 1894459 (**2**).[†]

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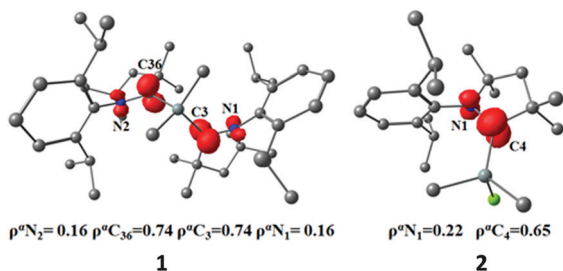


Fig. 5 Spin density at the of compounds **1** and **2** at the BP86/def2-TZVP level.



Conflicts of interest

There are no conflicts to declare.

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