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# Synthesis of cAAC stabilized biradical of “Me<sub>2</sub>Si” and “Me<sub>2</sub>SiCl” monoradical from Me<sub>2</sub>SiCl<sub>2</sub> – an important feedstock material†

Soumen Sinhababu,<sup>a</sup> Subrata Kundu,<sup>a</sup> Mujahuddin M. Siddiqui,<sup>a</sup> Alexander N. Paesch,<sup>a</sup> Regine Herbst-Irmer,<sup>a</sup> Brigitte Schwederski,<sup>b</sup> Pinaki Saha,<sup>c</sup> Lili Zhao,<sup>c</sup> Gernot Frenking,<sup>d</sup> Wolfgang Kaim,<sup>\*c,d</sup> Dietmar Stalke<sup>ib,\*a</sup> and Herbert W. Roesky<sup>ib,\*a</sup>

The cyclic alkyl(amino) carbene (cAAC) coordinated biradical of dimethylsilicon was isolated as (cAAC)<sub>2</sub>Me<sub>2</sub>Si (**1**), (cAAC = C(CH<sub>2</sub>)(CMe<sub>2</sub>)<sub>2</sub>N-2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), synthesized from the reduction of Me<sub>2</sub>SiCl<sub>2</sub> using two equivalents of KC<sub>8</sub> in the presence of two equivalents of cAAC. The reduction of Me<sub>2</sub>SiCl<sub>2</sub> by one equivalent of KC<sub>8</sub> in the presence of one equivalent of cAAC resulted in the stable dimethylsiliconchloride monoradical (cAAC)Me<sub>2</sub>SiCl (**2**).

Radicals and biradicals have attracted considerable attention in chemistry and material science due to their unique optical, magnetic and electronic properties.<sup>1</sup> In 1915 Schlenk isolated the first paramagnetic biradical from the reaction of bis-diphenylbenzyl dichloride with a copper–tin alloy.<sup>2a</sup> Most of the radicals are unstable and are short-lived.<sup>2b–d</sup> However, they can be isolated and stored at room temperature in a pure form using either thermodynamic or kinetic stabilization.<sup>3,4</sup> Several stable carbon and silicon centered biradicals are known.<sup>5</sup> Carbon centered 1,3-biradicals are proposed to be key reactive intermediates in certain chemical reactions.<sup>6</sup> Limited examples of four-membered heterocyclic 1,3-biradicals of cyclobutane type were reported.<sup>7</sup> Recently, we have synthesized air stable carbon centered 1,3-biradical (cAAC)<sub>2</sub>SiCl<sub>2</sub> (**I**)<sup>8</sup> (Chart 1) from the reaction of NHC → SiCl<sub>2</sub> (NHC = N-heterocyclic carbene) with a cyclic alkyl(amino) carbene. Furthermore, our group successfully synthesized cAAC stabilized SiX<sub>2</sub> (X = H, F) (Chart 1) bridged 1,3-biradicals, which are stable at room temperature for more than three months under inert atmosphere. The elusive SiF<sub>2</sub> bridged biradical (cAAC)<sub>2</sub>SiF<sub>2</sub> (**III**) (Chart 1) was synthesized from the reduction of (cAAC)SiF<sub>4</sub> by using two equivalents of KC<sub>8</sub> in the presence of one equivalent of cAAC.<sup>9</sup> While, (cAAC)<sub>2</sub>SiH<sub>2</sub> (**IV**) (Chart 1) was prepared from the reduction of H<sub>2</sub>SiI<sub>2</sub> with two equivalents of KC<sub>8</sub>, in the presence of two equivalents of cAAC.<sup>10</sup> After the successful isolation of cAAC stabilized SiX<sub>2</sub> (X = H, Cl, F) bridged 1,3-biradicals, the isolation of SiMe<sub>2</sub> analogues (cAAC)<sub>2</sub>Me<sub>2</sub>Si (**1**) was a prominent missing link in this class of compounds. Dimethyl silicon is not stable at room temperature and polymerises to (SiMe<sub>2</sub>)<sub>n</sub>. In our earlier synthetic route, we tried to isolate **1**, by the reaction of (cAAC)<sub>2</sub>SiCl<sub>2</sub> with 2 equivalents of MeLi by the nucleophilic substitution method.<sup>11</sup> To our surprise, MeLi functioned as a reducing agent leading to the isolation of dehalogenated biradicaloid (cAAC)<sub>2</sub>Si (**II**).<sup>12</sup> Me<sub>2</sub>SiCl<sub>2</sub> is the most important feedstock material in the industry for the preparation of silicones.<sup>13</sup> We envisaged an

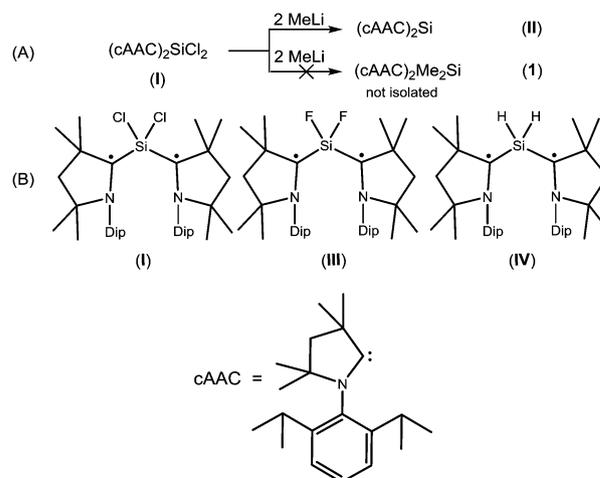


Chart 1 (A) The unsuccessful attempted synthesis of (cAAC)<sub>2</sub>Me<sub>2</sub>Si (**1**); (B) structurally characterized stable biradicals containing SiX<sub>2</sub> (X = Cl, F, H) moiety<sup>8–10</sup>

<sup>a</sup> Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany. E-mail: hroesky@gwdg.de, dstalke@chemie.uni-goettingen.de

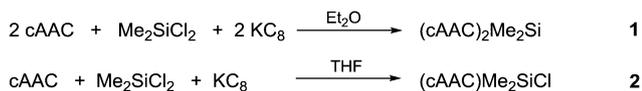
<sup>b</sup> Universität Stuttgart, Institut für Anorganische Chemie, 70569 Stuttgart, Germany. E-mail: kaim@iac.uni-stuttgart.de

<sup>c</sup> Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China

<sup>d</sup> Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Strasse, 35032 Marburg, Germany

† Electronic supplementary information (ESI) available: Including experimental section, computational details and details of X-ray structural analysis. CCDC 1894458 (**1**) and 1894459 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc01448a



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

alternative route to the isolation of **1** by the reduction of commercially available  $\text{Me}_2\text{SiCl}_2$ . 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  $\text{Me}_2\text{SiCl}_2$  with  $\text{KC}_8$ .

Both the compounds **1** and **2** were fully characterized by X-ray crystallography and EPR spectroscopy. Compound **1** was prepared by reduction of  $\text{Me}_2\text{SiCl}_2$  using  $\text{KC}_8$  in a 1:2 molar ratio in the presence of two equivalents of cAAC (Scheme 1; for details, see ESI†).  $^1\text{H}$  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  $148^\circ\text{C}$ . 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  $-26^\circ\text{C}$ .

A stable radical containing the  $\text{Me}_2\text{SiCl}$  group has not been reported so far. Equivalent amounts of cAAC,  $\text{Me}_2\text{SiCl}_2$  and  $\text{KC}_8$ , respectively, treated in THF at  $-90^\circ\text{C}$  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  $\text{C}_{\text{cAAC}}\text{–Si}$  distances [1.8814(13) and 1.8829(13) Å] and to the distances reported in the literature.<sup>10,14</sup> 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  $119.10(1)^\circ$ .<sup>12b</sup>

**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).<sup>15</sup>

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  $^{14}\text{N}$  atom ( $I = 1$ ). This splitting<sup>9,10,15</sup> suggests localized spin at only one of the two equivalent cAAC groups

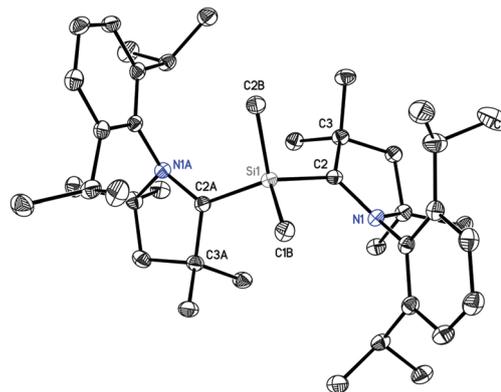


Fig. 1 Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [ $^\circ$ ]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C2B, 1.8768(13) [1.891], Si1–C1B, 1.8800(13) [1.891]; 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].

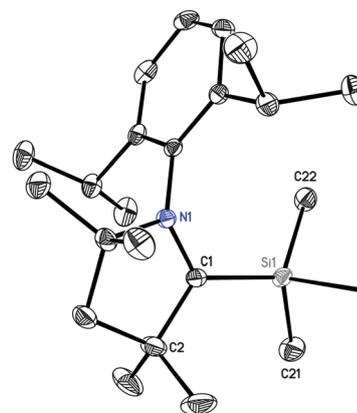


Fig. 2 Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [ $^\circ$ ]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C1, 1.8323(12) [1.841]; Si1–C22, 1.8633(13) [1.878]; 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].

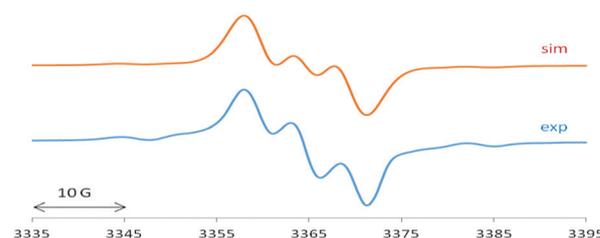


Fig. 3 EPR spectrum of **1** with computer simulation (top). For parameters see main text.

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



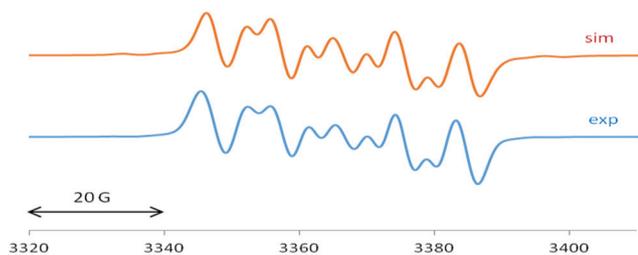


Fig. 4 EPR spectrum of **2** with computer simulation (top). For parameters see main text.

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

We carried out quantum chemical calculations using density functional theory at the BP86/def2-TZVP level<sup>23</sup> 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.<sup>24</sup> Table S1 (ESI<sup>†</sup>) 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)<sub>2</sub> ligand, and the SiMe<sub>2</sub> moiety in the triplet state. For compound **2** we took the cAAC ligand in the triplet state and the SiMe<sub>2</sub>Cl 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  $\Delta E_{\text{orb}}$  (see Tables S2 and S3 in ESI<sup>†</sup>). It has been shown in previous studies that the orbital values  $\Delta E_{\text{orb}}$  are a probe for the choice of the best fragments.<sup>25</sup>

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

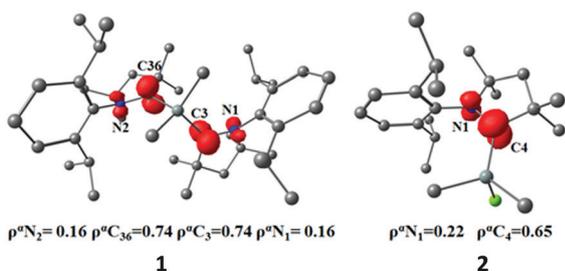


Fig. 5 Spin density at the of compounds **1** and **2** at the BP86/def2-TZVP level.

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<sup>†</sup>) 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<sup>†</sup>. It becomes obvious that  $\Delta E_{\text{orb}(1)}$  in compound **1** is due to the interaction between the singly occupied  $\sigma$  orbital (SOMO) of SiMe<sub>2</sub> with the in-phase (+, +) combination of the  $\pi$ -type<sup>26</sup> SOMO of (cAAC)<sub>2</sub>, where the net charge flow is from SiMe<sub>2</sub> → (cAAC)<sub>2</sub>. The stabilization energy  $\Delta E_{\text{orb}(2)}$  in compound **1** comes from the interaction of the  $\pi$  SOMO of SiMe<sub>2</sub> with the out-of-phase (+, –) combination of the  $\sigma$ -type<sup>26</sup> SOMO of (cAAC)<sub>2</sub>. The dominant orbital interaction  $\Delta E_{\text{orb}(1)}$  in compound **2** is due to the interaction between the  $\sigma$  SOMO of SiClMe<sub>2</sub> with the  $\sigma$  SOMO of cAAC. The direction of the charge flow between the ligands is in agreement with the calculated partial charges by the NBO<sup>27</sup> 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 Me<sub>2</sub>Si moiety using cAAC as ligand. Moreover we isolated the monoradical (cAAC)Me<sub>2</sub>SiCl. 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.<sup>16</sup> An appropriate crystal was selected using a polarize microscope, mounted on the tip of a MiTeGen<sup>®</sup> 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 $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) and smart APEX II detector. They were integrated with SAINT.<sup>17</sup> A multi-scan absorption correction and a  $3\lambda$  correction<sup>18</sup> was applied using SADABS.<sup>19</sup> The structure were solved by direct methods (SHELXT)<sup>20</sup> and refined by full-matrix least-squares methods against  $F^2$  (SHELXL)<sup>21</sup> in the graphical user interface ShelXle.<sup>22</sup> CCDC 1894458 (**1**) and 1894459 (**2**).<sup>†</sup>

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## Conflicts of interest

There are no conflicts to declare.

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