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Synthesis of cAAC stabilized biradical of "Me_2Si" and "Me_2SiCl" monoradical from Me_2SiCl_2 – an important feedstock material†

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The cyclic alkyl(amino) carbene (cAAC) coordinated biradical of dimethylsilicon was isolated as $(cAAC)_2Me_2Si$ (1), (cAAC = $C(CH_2)(CMe_2)_2N$-2,6-i-$Pr_2C_6H_3$), synthesized from the reduction of Me_2SiCl_2 using two equivalents of KC_8 in the presence of two equivalents of cAAC. The reduction of Me_2SiCl_2 by one equivalent of KC_8 in the presence of one equivalent of cAAC resulted in the stable dimethylsiliconchloride monoradical $(cAAC)Me_2SiCl$ (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-diphenyl-benzyl 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 $(cAAC)_2SiCl_2$ (**I**)[8] (Chart 1) from the reaction of NHC → $SiCl_2$ (NHC = N-heterocyclic carbene) with a cyclic alkyl(amino) carbene. Furthermore, our group successfully synthesized cAAC stabilized SiX_2 (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_2 bridged biradical $(cAAC)_2SiF_2$ (**III**) (Chart 1) was synthesized from the reduction of $(cAAC)SiF_4$ by using two equivalents of KC_8 in the presence of one equivalent of cAAC.[9] While, $(cAAC)_2SiH_2$ (**IV**) (Chart 1) was prepared from the reduction of H_2SiI_2 with two equivalents of KC_8, in the presence of two equivalents of cAAC.[10] After the successful isolation of cAAC stabilized SiX_2 (X = H, Cl, F) bridged 1,3-biradicals, the isolation of $SiMe_2$ analogues $(cAAC)_2Me_2Si$ (**1**) was a prominent missing link in this class of compounds. Dimethyl silicon is not stable at room temperature and polymerises to $(SiMe_2)_n$. In our earlier synthetic route, we tried to isolate **1**, by the reaction of $(cAAC)_2SiCl_2$ 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] Me_2SiCl_2 is the most important feedstock material in the industry for the preparation of silicones.[13] We envisaged an

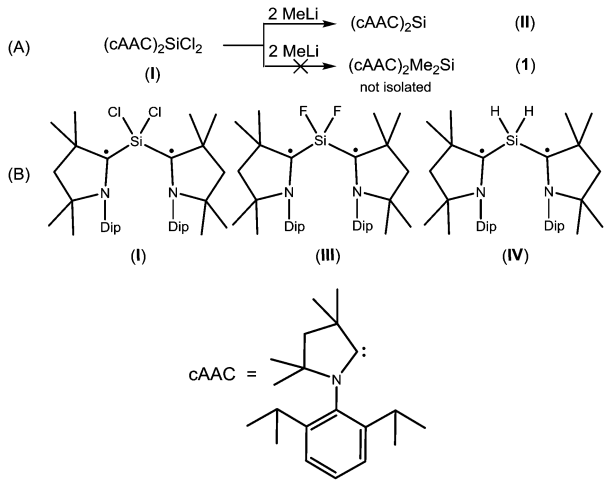

Chart 1 (A) The unsuccessful attempted synthesis of $(cAAC)_2Me_2Si$ (**1**); (B) structurally characterized stable biradicals containing SiX_2 (X = Cl, F, H) moiety[8–10]

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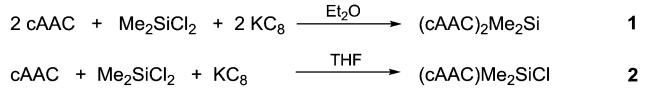

Scheme 1 Synthesis of **1** and **2**.

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 $(cAAC)_2Me_2Si$ (**1**) and monoradical $(cAAC)Me_2SiCl$ (**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†). ^{1}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 °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 $[M]^+$. 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 $(cAAC)Me_2SiCl$ (**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 *C*2/*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 C_{cAAC}–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)°) is widened due to the steric hindrance of the bulky cAAC ligands, but nevertheless smaller than in the silylone $(cAAC)_2Si$ of 119.10(**1**).[12b]

2 crystallizes in the orthorhombic space group *Pbca*. The molecular structure (Fig. 2) reveals the silicon atom to be tetracoordinated with three carbon and one chlorine atom. The Si–Cl bond length (2.1228(5) Å) is longer than those in $(^{Me}cAAC)SiCl_3$ (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 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).

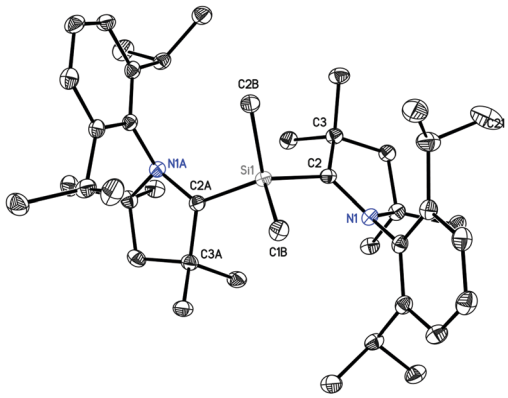

Fig. 1 Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [°]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C2B, 1.8768(13) [1.891], Si1–C1B, 1.8800(13) [1.891]; Si1–C2; 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].

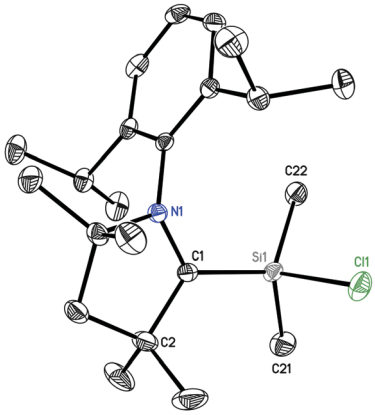

Fig. 2 Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plot is drawn at 50% probability. Selected experimental bond lengths [Å] and angles [°]. Calculated values at BP86/def2-TZVP are given in brackets: Si1–C1, 1.8323(12) [1.841]; Si1–C22, 1.8633(13) [1.878]; Si1–C21, 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].

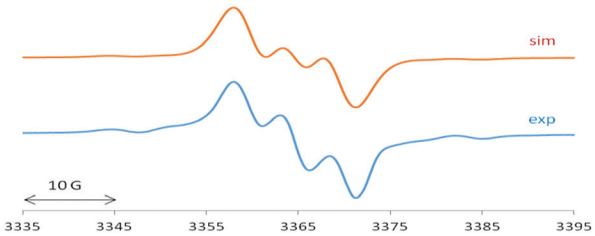

Fig. 3 EPR spectrum of **1** with computer simulation (top). For parameters see main text.

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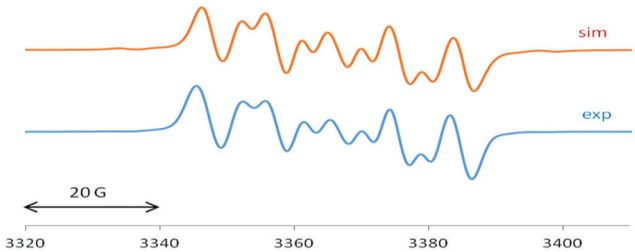

Fig. 4 EPR spectrum of **2** with computer simulation (top). For parameters see main text.

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 level[23] 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 $SiMe_2$ moiety in the triplet state. For compound **2** we took the cAAC ligand in the triplet state and the $SiMe_2Cl$ 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 $\Delta E_{orb(1)}$ and $\Delta E_{orb(2)}$ in compound **1** and one dominant term $\Delta E_{orb(1)}$ 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 $\Delta E_{orb(1)}$ in compound **1** is due to the interaction between the singly occupied σ orbital (SOMO) of $SiMe_2$ with the in-phase (+, +) combination of the π-type[26] SOMO of $(cAAC)_2$, where the net charge flow is from $SiMe_2$ → $(cAAC)_2$. The stabilization energy $\Delta E_{orb(2)}$ in compound **1** comes from the interaction of the π SOMO of $SiMe_2$ with the out-of-phase (+, −) combination of the σ-type[26] SOMO of $(cAAC)_2$. The dominant orbital interaction $\Delta E_{orb(1)}$ in compound **2** is due to the interaction between the σ SOMO of $SiClMe_2$ 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 NBO[27] method. The computed charges q at the BP86/def2-TZVP level are $q(SiMe_2)$ = +0.82 e for **1** and $q(SiClMe_2)$ = +0.36 e for **2**. Thus, the cAAC ligand in **1** and **2** acts as an acceptor rather than donor.

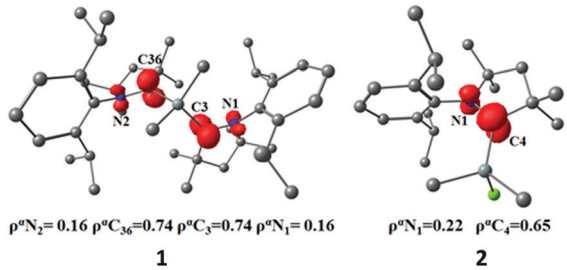

Fig. 5 Spin density at the of compounds **1** and **2** at the BP86/def2-TZVP level.

In summary, we report on the synthesis of 1,3-biradical containing Me_2Si moiety using cAAC as ligand. Moreover we isolated the monoradical $(cAAC)Me_2SiCl$. 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, λ = 0.71073 Å) and smart APEX II detector. They were integrated with SAINT.[17] A multi-scan absorption correction and a 3λ correction[18] 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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Conflicts of interest

There are no conflicts to declare.

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