Trapping a Silicon(I) Radical with Carbenes: A Cationic cAAC–Silicon(I) Radical and an NHC–Parent-Silyliumylidene Cation

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Abstract: *The trapping of a silicon(I) radical with N-hetero-cyclic carbenes is described. The reaction of the cyclic (alkyl)-(amino) carbene [$cAAC_{Me}$] ($cAAC_{Me} =$:$C(CMe_2)_2(CH_2)NAr$, $Ar = 2,6\text{-}iPr_2C_6H_3$) with H_2SiI_2 in a 3:1 molar ratio in DME afforded a mixture of the separated ion pair [($cAAC_{Me})_2Si$·]$^+I^-$ (**1**), which features a cationic cAAC–silicon(I) radical, and [$cAAC_{Me}-H$]$^+I^-$. In addition, the reaction of the NHC–iodosilicon(I) dimer [$I_{Ar}(I)Si$·]$_2$ ($I_{Ar} =$:$C\{N(Ar)CH\}_2$) with 4 equiv of I_{Me} (:$C\{N(Me)CMe\}_2$), which proceeded through the formation of a silicon(I) radical intermediate, afforded [($I_{Me})_2SiH$]$^+I^-$ (**2**) comprising the first NHC–parent-silyliumylidene cation. Its further reaction with fluorobenzene afforded the $C_{Ar}-H$ bond activation product [1-F-2-I_{Me}-C_6H_4]$^+I^-$ (**3**). The isolation of **2** and **3** confirmed the reaction mechanism for the formation of **1**. Compounds **1–3** were analyzed by EPR and NMR spectroscopy, DFT calculations, and X-ray crystal-lography.*

Silyl radicals are important intermediates in chemistry[1] but their isolation requires the thoughtful design of synthetic strategies. They have beneficial applications in building more complex molecules and in electrochemistry.[1,2] Their low-valent analogues, which have silicon atoms in low formal oxidation states (0, I, II), display the amphiphilic character of a low-valent silicon atom and the properties of a radical. Owing to these electronic properties, low-valent silicon radicals show extraordinary synthetic potential. However, the high reactivity hampers their isolation, for example, the first persistent silylene radical anion **A** (Scheme 1) had a lifetime of about 20 min at room temperature.[3] In addition, the persistent radical anion intermediate **B**,[4] which features

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Scheme 1. Charged radicals of low-valent silicon derivatives.

a low-valent silicon atom, was observed in the reduction of the cAAC–silicon(0) complex [($cAAC_{Me})_2Si$] (cAAC = cyclic (alkyl)(amino) carbene; $cAAC_{Me} =$:$C(CMe_2)_2(CH_2)NAr$, $Ar = 2,6\text{-}iPr_2C_6H_3$)[5] with potassium to afford the C−H bond activation product.[4] With the aid of suitable thermodynamic and/or kinetic stabilization, a handful of stable charged radicals of silylenes, such as the silylene radical anion **C**[6] and the NHC-stabilized silylene radical cation **D**,[7] have been synthesized.

Other spectacular low-valent silicon radicals are silicon(I) radicals, [R−Si·]·, and their separated ion pair derivatives [·Si·]$^+R^-$ (R = supporting ligands). Compared with [R−Si·]·, [·Si·]$^+R^-$ compounds are more reactive owing to the enhanced electrophilicity of the silicon centers. They should be worth-while synthetic targets, but are currently still unknown. In the past few years, several research groups attempted to synthe-size silicon(I) radical derivatives through the reduction of trihalosilanes [$RSiX_3$] (X = Cl, Br, I) with an alkali metal, but no attempt was successful. Only silicon(I) dimers of the composition [RSi·]$_2$ were obtained.[8] These results illustrate that silicon(I) radicals are reactive and readily undergo dimerization. Although unprecedented silicon radicals can be stabilized in the form of adducts with N-heterocyclic carbenes (NHCs), the reduction of the NHC–tetrahalosilane complexes [(I_{Ar})$SiCl_4$] ($I_{Ar} =$:$C\{N(Ar)CH\}_2$) or [($cAAC_{Me}$)SiX_4] (X = Cl, I) with alkali metal did not afford any NHC–silicon(I) radical complexes; instead, the dimeric derivatives, namely the NHC–silicon(I) dimer [$I_{Ar}(Cl)Si$·]$_2$ or 2,3-disiladihalobutadiene [$cAAC_{Me}$=Si(X)]$_2$ were formed, respectively.[8c,9] It seems that the isolation of silicon(I) radical derivatives is a formidable synthetic challenge and cannot be achieved by conventional reduction strategies.

On the other hand, NHCs are able to reduce halosilanes to afford silylene derivatives by the elimination of imidazo-lium salts [NHC−H]$^+Cl^-$.[10a–d] They are also capable of inducing disproportionation reactions of halodisilanes, along with cleavage of the Si−Si bond, to form NHC−silylene adducts.[10e] We were interested in exploring these synthetic strategies to isolate a stable silicon(I) radical. Herein, we report the reaction of NHCs with H_2SiI_2 and a silicon(I) dimer to form a cationic cAAC–silicon(I) radical and an NHC–parent-silyliumylidene cation, respectively.[11]

In the first experiment, the reaction of the cAAC [cAAC$_{Me}$] with H$_2$SiI$_2$ in a 2:1 molar ratio in THF initially gave a purple mixture, which then turned into a white suspension within a few minutes. This observation prompted us to employ a higher 3:1 molar ratio of cAAC$_{Me}$/H$_2$SiI$_2$ in the reaction in THF, which afforded a sustainable dark purple-red suspension, and then a colorless crystalline solid of [cAAC$_{Me}$−H]$^+$I$^−$ (see the Supporting Information, Figure S9) was gradually formed. After filtration of [cAAC$_{Me}$−H]$^+$I$^−$, the separated ion pair [(cAAC$_{Me}$)$_2$Si$^•$]$^+$I$^−$ (**1**) featuring a cationic cAAC–silicon(I) radical complex was isolated as purple crystals in 5% yield (Scheme 2).[12a,b] In addition, the 2,3-
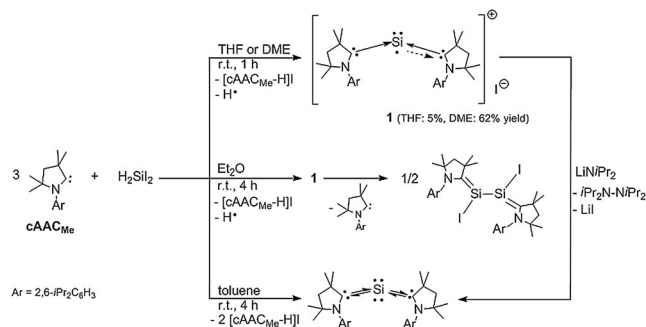

Scheme 2. Synthesis of **1**.[13]

disiladiiodobutadiene derivative [cAAC$_{Me}$=Si(I)]$_2$ was not observed in this reaction.[9] In the second experiment, when the solvent was changed to Et$_2$O, the reaction of cAAC$_{Me}$ and H$_2$SiI$_2$ in a 3:1 molar ratio afforded a mixture of crystals of **1** (a few pieces of crystals), [cAAC$_{Me}$−H]$^+$I$^−$ (major product), and [cAAC$_{Me}$=Si(I)]$_2$ (major product, 22% yield).[9] These results show that **1** is formed in Et$_2$O, but is unstable and dimerizes to form [cAAC$_{Me}$=Si(I)]$_2$.[9] In the third experiment, when toluene was used as the solvent for the reaction of cAAC$_{Me}$ and H$_2$SiI$_2$ in a 3:1 molar ratio, **1** was not afforded; instead a mixture of the cAAC–silicon(0) complex [(cAAC$_{Me}$)$_2$Si] (32% yield) and [cAAC$_{Me}$−H]$^+$I$^−$ as the sole products was afforded.[5] In the last experiment, cAAC$_{Me}$ was reacted with H$_2$SiI$_2$ in a 3:1 molar ratio in dimethoxyethane (DME) to afford **1** in high yield (62%). Similarly, [cAAC$_{Me}$=Si(I)]$_2$ was not observed.[9] Using a higher 4:1 molar ratio of cAAC$_{Me}$ and H$_2$SiI$_2$ in DME did not improve the yield of **1**. These results illustrate that compound **1** cannot be formed in non-ethereal solvents because cAAC$_{Me}$ undergoes a double dehydroiodination.

The following mechanism for the formation of stable and isolable **1** is proposed (Scheme S1). Two molecules of cAAC$_{Me}$ simultaneously undergo dehydroiodination and coordination with H$_2$SiI$_2$ to form [cAAC$_{Me}$−H]$^+$I$^−$ and a cAAC–iodosilylene intermediate, "(cAAC$_{Me}$)Si(I)H". Subsequently, the latter reacts with another molecule of cAAC$_{Me}$, along with displacement of the I$^−$ anion, to form a cAAC–parent-silyliumylidene iodide intermediate, "{(cAAC$_{Me}$)$_2$SiH}$^+$I$^−$". This intermediate displaces a H$^•$ radical by reacting with ethereal solvents to form **1**, in which the resulting Si^I radical is stabilized by one cAAC$_{Me}$ ligand (see below).[13] On the basis of the experimental results, the

displacement of a H$^•$ radical is favored in DME as DME is able to undergo radical reactions via homoleptic cleavage of the central C−C bond in CH$_3$OCH$_2$−CH$_2$OCH$_3$.[14] This mechanism is further supported by the following facts: 1) The yield did not improve when cAAC$_{Me}$ and H$_2$SiI$_2$ were reacted in a 4:1 molar ratio, indicating that cAAC$_{Me}$ cannot abstract a H$^•$ radical from the {(cAAC$_{Me}$)$_2$SiH}$^+$I$^−$ intermediate. 2) H$_2$ gas was not observed in the abovementioned reactions. 3) Results derived from the formation and reactivity of compound **2** (see below).

Compound **1** is the first example of a separated ion pair of a base-stabilized silicon(I) radical, following a previous report on the only example of a neutral germanium(I) radical, [HC{C(tBu)N(Ar)}$_2$Ge$^•$]$^•$.[15] Purple crystals of complex **1** are air- and moisture-sensitive but stable under an inert atmosphere for one month. They are soluble in THF and DME, but only marginally soluble in toluene.

The X-ray crystal structure of **1** (Figure 1) shows that the Si1 atom adopts a bent geometry, and is coordinated to the C1 and C21 atoms of cAAC$_{Me}$. The Si1 atom lies on the same plane as the N1-C1-C2 skeleton while it is displaced from the N2-C21-C22 least-squares plane by 0.564 Å. The cAAC$_{Me}$ rings are tilted with respect to each other (C1-N1-C21-N2 = 133.37°). The C1-Si1-C21 bond angle (122.96(15)°) is significantly wider than that of the cAAC–silicon(0) complex [(cAAC$_{Me}$)$_2$Si] (117.70(8)°).[5] The two C−Si1 bonds do not have the same lengths (C1–Si1 1.896(4) Å, C21–Si1 1.867(3) Å) but both are slightly longer than the donor–acceptor Si−C double bonds in [(cAAC$_{Me}$)$_2$Si] (1.8411(18), 1.8417(17) Å).[5] They are comparable to the donor–acceptor Si−C$_{cAAC}$ single bond in the NHC–cAAC–iodosilyliumylidene iodide [cAAC$_{Me}$(SiI)I$_{iPrMe}$]$^+$I$^−$ (1.878(5) Å).[16] Simultane-
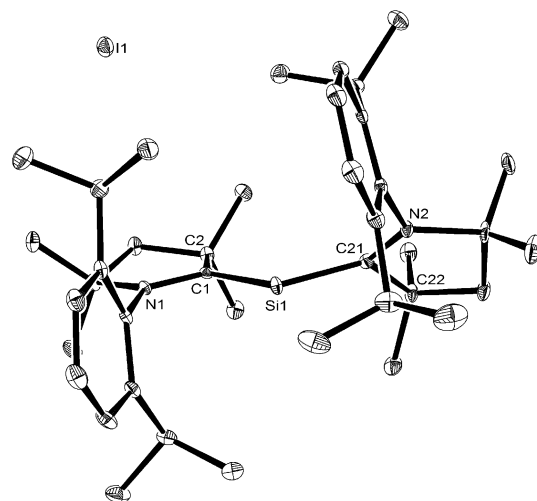
Figure 1. Molecular structure of **1**. Ellipsoids set at 30% probability. Solvent molecule and hydrogen atoms are omitted for clarity. The calculated geometrical parameters at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths [Å] and angles [°]: C1–N1 1.319(4) [1.345], C1–Si1 1.896(4) [1.945], C21–N2 1.332(4) [1.352], C21–Si1 1.867(3) [1.930]; N1-C1-C2 109.9(3) [109.0], C2-C1-Si1 134.0(2) [130.6], N2-C21-C22 109.1(3) [108.9], C22-C21-Si1 127.0(2) [136.9], N2-C21-Si1 120.5(3) [113.9], C1-Si1-C21 122.96(15) [115.4].

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ously, the C1−N1 (1.319(4) Å) and C21−N2 bonds (1.332-(4) Å) are shorter than those of the C$_{cAAC}$-centered radical [cAAC$_{Me}$•−Si(Cl)$_2$−cAAC$_{Me}$•] (1.395(2)–1.3994(19) Å)[17] and the cAAC–silicon(0) complex [(cAAC$_{Me}$)$_2$Si] (1.378(2) Å).[5]

A purple solution of **1** in 1:1 toluene/THF solvent was characterized by continuous wave (CW) EPR spectroscopy.[12a] The 298 K EPR spectrum (Figure 2a) shows a three-
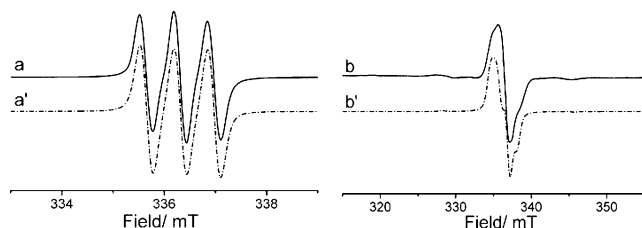
Figure 2. CW EPR (X-band) spectra of **1** in toluene/THF solution recorded at a) 298 K and b) 115 K. The corresponding simulations are shown in a′ and b′.

line hyperfine multiplet pattern with $a(^{14}N)_{iso} = 18.5$ MHz, suggestive of about 1% s-orbital electron spin density localized on a single ^{14}N nucleus. This characteristic splitting pattern suggests that the radical delocalizes to one of the cAAC ligands only, which is consistent with the calculated spin densities of **1** (see below). In addition, the 115 K EPR spectrum (Figure 2b) shows an intense signal at $B \approx 336$ mT, which has some evidence for a small degree of anisotropy. Although the ^{14}N hyperfine coupling is only poorly resolved in the frozen-solution spectrum, a pair of weak satellite features can be observed with $a(^{29}Si) \approx 212$ MHz, which likely arises from coupling to the low-abundant nuclear-spin-active ^{29}Si nuclei, consistent with about 5% s-orbital electron spin density localized on the silicon nucleus. The experimental spin-Hamiltonian parameters for **1** are listed in Table 1, and are in good agreement with DFT-calculated hyperfine coupling values based on the crystal structure, performed in ORCA 3.0.3[18] using the hybrid PBE0 functional and a basis set consisting of EPR-II on C, H, and N[19] and def2-TZVP on Si.[20] The deviation of the ^{29}Si EPR data arises from some disorder in the frozen solution, which is not reflected in the crystal structure from which the DFT output was calculated. In this context, the EPR spectroscopic data suggest that **1** is a separated ion pair of a base-stabilized silicon(I) radical complex with the unpaired electron localized in a p-orbital on the Si atom.

In support of the experimental observations, DFT calculations of **1** were performed at the M06/def2-TZVPP//BP86/

Table 1: Spin Hamiltonian parameters for compound **1**.

g_{iso}			
expt.[a]	2.0037		
DFT	2.0078		

a_{iso} [MHz]	^{14}N1	^{14}N2	^{29}Si
expt.[b]	–	10.67	212.00
DFT	5.52	11.32	102.00

[a] ±0.0001; [b] ±5 MHz.

def2-SVP level of theory (Figure S12).[12a] The MO analysis indicates that the SOMO is mainly a π-type p-orbital localized on the Si atom with little back-donation to the C−N π*-MO of one of the cAAC$_{Me}$ fragments (Figure 3a). In addition, the

(a) SOMO (-7.95)   (b) HOMO-1 (-8.68)   (c)
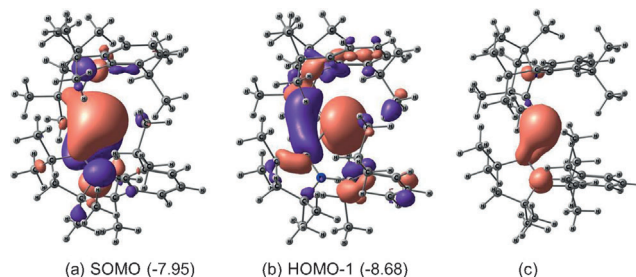
Figure 3. Plots of a) the SOMO, b) the lone pair on the Si atom (HOMO-1; isosurface value 0.03), and c) the spin density calculated by natural population analysis (isosurface value 0.008) of **1** at the M06/def2-TZVPP//BP86/def2-SVP level of theory. Eigenvalues in eV are given in parentheses.

orientations of the two cAAC$_{Me}$ rings prevent simultaneous back-donation of the unpaired electron on the Si atom into two C−N π*-MOs of the cAAC$_{Me}$ ligands. Accordingly, in the calculations, one cAAC$_{Me}$ ligand has a longer C21−N2 bond (1.352 Å) and a shorter C21−Si1 bond (1.930 Å) than the other cAAC$_{Me}$ ligand (calculated C1−N1 1.345 Å, C1−Si1 1.945 Å). This back-donation is also consistent with the lower occupancy of the π-type p-orbital on the Si atom (0.67 e, Table S3). The HOMO-1 is a σ-type lone-pair orbital (Figure 3b) on the Si atom with greater s-character (α- and β-type s-orbitals from NBO analysis: 77.3 and 73.2%).

The plot of the natural spin density also corroborates well with the MO and geometrical data that the unpaired electron is mainly localized on the Si atom (0.52 e) with a little delocalization to one of the cAAC$_{Me}$ ligands (Figure 3c and Table S4). This is in line with the EPR spectroscopic data.

The nature of the bonding interaction between the [:Si•]$^+$ (^{2}P; $3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC$_{Me}$ fragments in **1** was further analyzed by the EDA-NOCV approach (Table S5). In the Si−C$_{cAACMe}$ bonds, the covalent interaction ($\Delta E_{orb} = 55.8\%$) has a higher energy contribution than the electrostatic interaction, in which the energy corresponding to σ-donation from the cAAC$_{Me}$ ligands to the [:Si•]$^+$ center (Figure S15 and Scheme S3; $\Delta E_{\sigma(++)} + \Delta E_{\sigma(+-)} = -221.6$ kcal mol^{-1}) is significantly higher than that of the π-back-donation from the unpaired electron in the π-type p-orbital on the [:Si•]$^+$ center to one of the C−N π*-MOs of the cAAC$_{Me}$ ligands ($\Delta E_\pi = -38.1$ kcal mol^{-1}).

Thus, on the basis of these experimental and theoretical results, compound **1** is a separated ion pair featuring a cationic cAAC–silicon(I) radical complex with two donor–acceptor σ-bonds between the [:Si•]$^+$ (^{2}P; $3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC$_{Me}$ moieties, one σ-type lone-pair orbital, and one unpaired electron on the p-type orbital on the Si center.
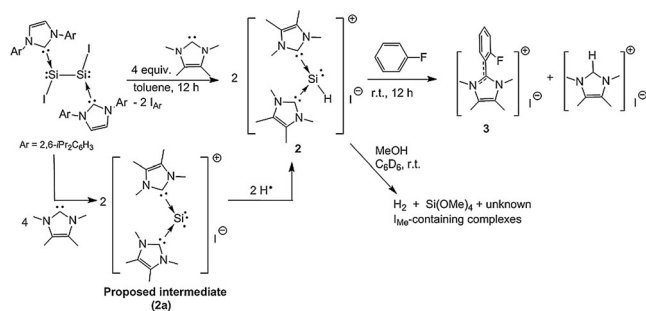
Following complete characterization of **1**, its reactivity was preliminarily investigated. It can undergo a one-electron reduction with LiNiPr$_2$ in toluene to form a mixture of the

cAAC–silicon(0) complex [(cAAC$_{Me}$)$_2$Si], iPr$_2$N–NiPr$_2$, and LiI (Scheme 2).

The mechanism for the formation of **1** was also studied. It is proposed that the cAAC–parent-silyliumylidene intermediate "{(cAAC$_{Me}$)$_2$SiH}$^+$I$^-$" is the key intermediate in the reaction of cAAC$_{Me}$ and H$_2$SiI$_2$, which displaces a H$^\cdot$ radical with ethereal solvents to form **1**. As such, the feasibility of a base-stabilized parent-silyliumylidene cation and its reactivity toward solvents were studied. The formation of **1** inspired us towards an opposite idea, namely that if there is an unstable silicon(I) radical, it could abstract a H$^\cdot$ radical from the solvent to form a stable parent-silyliumylidene cation "{:SiH}$^+$". In this context, we investigated the cleavage of the Si–Si bond in a silicon(I) dimer with NHCs to generate an NHC–silicon(I) radical intermediate, which then rearranges to form an NHC–parent-silyliumylidene cation complex. After numerous attempts,[21] the reaction of the NHC–iodosilicon(I) dimer [I$_{Ar}$(I)Si:]$_2$ (I$_{Ar}$ = :C{N(Ar)CH}$_2$)[22] with four equiv of I$_{Me}$ (:C{N(Me)CMe}$_2$) in toluene afforded the first NHC–parent-silyliumylidene iodide [(I$_{Me}$)$_2$SiH]$^+$I$^-$ (**2**; Scheme 3).[12a] It is proposed that the I$_{Me}$ ligands displace the

Scheme 3. Synthesis of compounds **2** and **3**. The proposed mechanism for the formation of **2** via the silicon(I) radical intermediate **2a** is also shown.

I$_{Ar}$ ligands and iodide ions in [I$_{Ar}$(I)Si:]$_2$, along with homoleptic cleavage of the Si–Si bond, to afford the separated ion pair **2a** with a cationic NHC–silicon(I) radical intermediate, which then abstracts a H$^\cdot$ radical from toluene to form **2** (Scheme 3).[23]

Orange crystals of **2** were isolated from a concentrated solution in fluorobenzene after two hours (see below). They are quite stable under an inert atmosphere for two months but they are highly unstable in solution. They instantaneously decompose in THF and CHCl$_3$ and slowly decompose in fluorobenzene (see below) and pyridine over three days. The ^{1}H NMR spectrum shows one set of resonances that is due to the I$_{Me}$ ligands and another one arising from the Si–H proton ($\delta = 9.73$ ppm). The latter is downfield-shifted in comparison with that in the NHC–hydridosilylene complexes [I$_{Me}$→:SiH-(SitBu$_3$)] ($\delta = 3.17$ ppm) and [I$_{Me}$→:SiH(Ter)] (Ter = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$, $\delta = 4.00$ ppm) owing to the presence of an electron-withdrawing cationic Si^{II} center.[24] The ^{29}Si NMR signal of **2** ($\delta -77.9$ ppm, $J_{Si,H} = 283$ Hz) is an intermediate value between that of the NHC–iodosilyliumylidene iodide [(I$_{Ar}$)(I$_{iPrMe}$)SiI]$^+$I$^-$ (I$_{iPrMe}$ = :C{N(iPr)CMe}$_2$,

$\delta -55.3$ ppm)[25] and [I$_{Me}$→:SiH(SitBu$_3$)] ($\delta -137.8$ ppm).[24b] The Si–H chemical shift is further evidenced by its disappearance when compound **2** reacted with MeOH in C$_6$D$_6$ to afford a mixture of hydrogen gas, Si(OMe)$_4$, and I$_{Me}$-containing compounds (Scheme 3 and Figure S4).
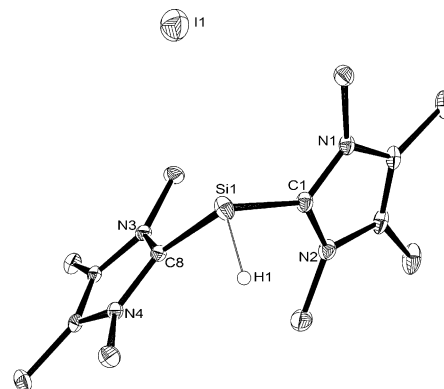
The X-ray crystal structure of **2** shows a separated ion pair with a Si···I distance (10.013 Å) that is longer than the sum of their van der Waals radii (ca. 4.08 Å; Figure 4). The Si atom

Figure 4. X-ray crystal structure of **2**. Ellipsoids set at 30% probability. Hydrogen atoms except the H1 atom are omitted for clarity. The geometrical parameters calculated at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths [Å] and angles [°]: Si1–H 1.455 [1.529], Si1–C1 1.932(3) [1.977], Si1–C8 1.931(3) [1.949]; C1-Si1-C8 96.63(12) [100.7], C1-Si1-H1 100.07 [96.0], C8-Si1-H1 95.49 [94.6].

adopts a trigonal-pyramidal geometry. The sum of the bond angles at the Si atom (292.19°) indicates the presence of a stereoactive lone pair at the silicon atom. The Si–C bond lengths of 1.932(3) and 1.931(3) Å are intermediate values between those in the NHC–iodosilyliumylidene iodide [(I$_{Ar}$)-(I$_{iPrMe}$)SiI]$^+$I$^-$ (1.947(2), 1.967(2) Å) and the NHC–silicon(II) dication [(I$_{Me}$)$_3$Si]$^{2+}$ (1.917(3)–1.909(3) Å).[25] The hydrogen atom bound to the Si1 atom was located in the electron difference map and refined isotropically to the expected Si–H bond length of 1.455 Å.[26]

When the recrystallization of compound **2** in fluorobenzene was prolonged, orange crystals of compound **2** cannot be isolated. Instead [I$_{Me}$–H]$^+$I$^-$ and yellow crystals of [1-F-2-I$_{Me}$-C$_6$H$_4$]$^+$I$^-$ (**3**; Scheme 3 and Figure S10) were obtained. These results show that compound **2** further reacts with fluorobenzene. As such, the reaction of the NHC–iodosilicon(I) dimer [I$_{Ar}$(I)Si:]$_2$ and I$_{Me}$ was performed in fluorobenzene, which directly afforded a mixture of [I$_{Me}$–H]$^+$I$^-$ and **3**. Although the mechanism for the formation of **3** is unknown as yet, the reaction appears to proceed through an electrophilic aromatic substitution at the *ortho* position of fluorobenzene with **2** (Scheme S2). Thus the formation of **2** and **3**, along with the reactivity of **2** towards MeOH, supports our hypothesis for the reaction of [cAAC$_{Me}$] with H$_2$SiI$_2$ that the Si–H bond in the "{(cAAC$_{Me}$)$_2$SiH}$^+$I$^-$" intermediate can react with ethereal solvents to form **1**.

In support of the feasibility of intermediate **2a** and its high reactivity to abstract a H$^\cdot$ radical from toluene to form **2**,[23]

DFT calculations of **2a** were performed. Its HOMO-1 (Figure S13) is a lone-pair orbital on the Si center (79.2 and 75.9 % α- and β-type s-orbitals). Moreover, the SOMO (Figure S13) mainly consists of the π-type p-orbital localized on the Si center, along with the contribution from the C−N π*-MO of I_{Me}. In addition, EDA-NOCV analysis (Table S5 and Figure S16) showed that the energy corresponding to the π-back-donation from the unpaired electron on the [:Si·]⁺ moiety to one C−N π*-MO of I_{Me} ($\Delta E_\pi = -28.1$ kcal mol⁻¹) is smaller than that in **1** ($\Delta E_\pi = -38.1$ kcal mol⁻¹). Accordingly, the group charge analysis indicates a lower positive charge for the Si atom (0.43 e, Table S2) in **2a** than that in **1** (0.83 e). These studies are in line with the poor π-acidity of I_{Me} compared to $cAAC_{Me}$.[27] In this context, these results indicate that the unpaired electron in **2a** (0.74 e; Figure S13 and Table S4) is more active than that in **1**, which accounts for the instability of **2a** and the abstraction of a H· radical from toluene to form **2**.

The bonding analysis of **2** shows that its HOMO is a lone-pair orbital on the Si atom with 58.6 % s-character (Figure S14). The EDA-NOCV analysis (Table S5 and Figure S17) suggests that the best bonding description is a donor–acceptor interaction between the Si⁺(H) and two I_{Me} moieties. The Si−C_{IMe} bonds have almost equal contributions from covalent ($\Delta E_{orb} = 51.7$ %) and electrostatic interactions. The energy for the donor–acceptor interaction between two I_{Me} ligands and Si⁺(H) fragment is −185.2 kcal mol⁻¹.

Thus, on the basis of the experimental and theoretical results, compound **2** is a separated ion pair of the NHC–parent-silyliumylidene complex, which has one lone-pair orbital on the Si atom and two donor–acceptor σ-bonds between the Si⁺(H) and two I_{Me} moieties.

In conclusion, the first separated ion pair of a cAAC–silicon(I) radical [(cAAC_{Me})₂Si·]⁺I⁻ (**1**) has been prepared by a simple procedure. It has a lone pair of electrons and a radical on the silicon center. The radical is stabilized by delocalization onto one of the $cAAC_{Me}$ ligands. Compound **1** is prepared by the dehydroiodination of H_2SiI_2 by $cAAC_{Me}$ to form the cAAC–parent-silyliumylidene iodide intermediate "{(cAAC_{Me})₂SiH}⁺I⁻", which then displaces a H· radical by reacting with DME to form **1**. The feasibility of the "{(cAAC_{Me})₂SiH}⁺I⁻" intermediate is supported by the isolation of the first NHC–parent-silyliumylidene iodide [(I_{Me})₂SiH]⁺I⁻ (**2**). The reactivity of **2** towards solvents supports our hypothesis that the reactive Si−H bond in the "{(cAAC_{Me})₂SiH}⁺I⁻" intermediate can react with DME to form the stable compound **1**.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenes · cations · low-valent homologues · radicals · silicon

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[11] The reaction of I_{Ar} and H_2SiCl_2 resulting in the formation of the adduct [(I_{Ar})₂Si(H)₂Cl₂] has been reported; see: A. P. Singh, R. S. Ghadwal, H. W. Roesky, J. J. Holstein, B. Dittrich, J.-P. Demers, V. Chevelkov, A. Lange, *Chem. Commun.* **2012**, *48*, 7574–7576.

[12] a) For details of the experimental procedures, spectroscopic data, and theoretical studies, see the Supporting Information; b) the yield of **1** is low because **1** could further be involved in the radical-mediated ring-opening polymerization of THF. This hypothesis is supported by the presence of a ring-opening polymerization product with repeating units of THF in the reaction mixture, which was confirmed by LC-MS analysis (see the Supporting Information).

[13] In Scheme 2, the dashed arrow in compound **1** depicts the Si^I radical being stabilized by partial back-donation to the C−N π*-MO of one of the $cAAC_{Me}$ fragments.

[14] For radical reactions of DME, see: L. F. Loucks, K. J. Laidler, *Can. J. Chem.* **1967**, *45*, 2785–2792. It is proposed that the displacement of a H· radical in "{(cAAC_{Me})₂SiH}⁺I⁻" is favored in DME as DME is able to abstract a H· radical to form dimethyl

ether (CH_3OCH_3) via cleavage of the C−C bond in CH_3OCH_2−CH_2OCH_3. To prove this hypothesis, the reaction mixture was analyzed by LC-MS, which showed a peak at m/z 46.81 corresponding to a $[MeOMe]^+$ fragment (see the Supporting Information). However, the peak may also be due to the presence of DME. In this context, the formation of MeOMe in the reaction is not conclusive.

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[21] a) The reaction of $[I_{Ar}(I)Si\colon]_2$ with 4 equiv of I_{Me} (:C{N-(Me)CMe}$_2$) in other solvents such as hexane or ethereal solvents did not afford **2a** or **2**; instead a mixture of unidentified products was isolated; b) the reaction of $[I_{Ar}(I)Si\colon]_2$ with 4 equiv of cAAC$_{Me}$ afforded the 2,3-disiladiiodobutadiene derivative $[cAAC_{Me}=Si(I)]_2$; c) there is no reaction between the amidinato silicon(I) dimer with cAAC$_{Me}$ and I_{Me}.

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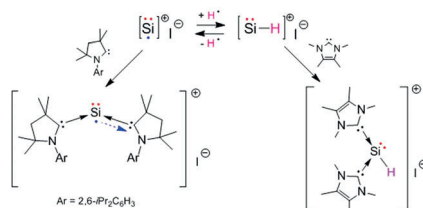[27] D. Martin, Y. Canac, V. Lavallo, G. Bertrand, *J. Am. Chem. Soc.* **2014**, *136*, 5023 – 5030.

Communications

Silicon Radicals

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Trapping a Silicon(I) Radical with
Carbenes: A Cationic cAAC–Silicon(I)
Radical and an NHC–Parent-
Silyliumylidene Cation

Ar = 2,6-*i*Pr₂C₆H₃

Unusual intermediates: The reaction of a cyclic (alkyl)(amino) carbene with H_2SiI_2 afforded a separated ion pair containing a cationic cAAC–silicon(I) radical complex (see scheme, left). On the other hand, treatment of the NHC–iodosilicon(I) dimer $[I_{Ar}(I)Si:]_2$ with a different NHC led to an NHC–parent-silyliumylidene cation (right).