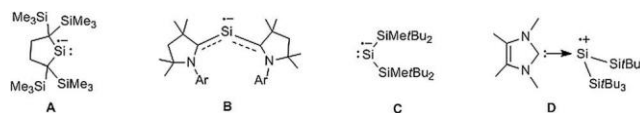


Trapping a Silicon(I) Radical with Carbenes: A Cationic cAAC–Silicon(I) Radical and an NHC–Parent-Silyliumylidene Cation

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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} = DC(CMe₂)₂(CH₂)NAr, Ar = 2,6-iPr₂C₆H₃) with H₂SiI₂ in a 3:1 molar ratio in DME afforded a mixture of the separated ion pair [(cAAC_{Me})₂SiDC]⁺1[⊖] (1), which features a cationic cAAC–silicon(I) radical, and [cAAC_{Me}@H]⁺1[⊖]. In addition, the reaction of the NHC–iodosilicon(I) dimer [I_{Ar}(I)SiD]₂ (I_{Ar} = DC{N(Ar)CH}₂) with 4 equiv of I_{Me} (DC{N(Me)CMe₂}), which proceeded through the formation of a silicon(I) radical intermediate, afforded [(I_{Me})₂SiH]⁺1[⊖] (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}-C₆H₄]⁺1[⊖] (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 crystallography.

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



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} = DC(CMe₂)₂(CH₂)NAr, Ar = 2,6-iPr₂C₆H₃)^[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@SiD]C, and their separated ion pair derivatives [CSiD]⁺R[⊖] (R = supporting ligands). Compared with [R@SiD]C, [CSiD]⁺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 synthesize silicon(I) radical derivatives through the reduction of trihalosilanes [RSiX₃] (X = Cl, Br, I) with an alkali metal, but no attempt was successful. Only silicon(I) dimers of the composition [RSiD]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})SiCl₄] (I_{Ar} = DC{N(Ar)CH}₂) or [(cAAC_{Me})SiX₄] (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)SiD]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 imidazolium 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 H₂SiI₂ and a silicon(I) dimer to form a cationic cAAC–silicon(I) radical and an NHC–parent-silyliumylidene cation, respectively.^[11]

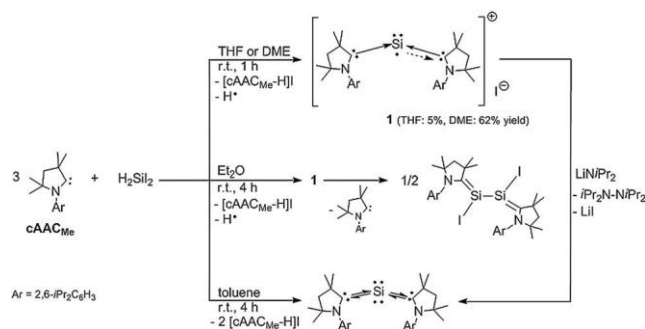
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In the first experiment, the reaction of the cAAC [cAAC_{Me}] with H₂SiI₂ in a 2:1 molar ratio in THF initially gave a purple mixture, which then turned into a white suspension within a few minutes. This observation prompted us to employ a higher 3:1 molar ratio of cAAC_{Me}/H₂SiI₂ 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})₂SiDC]⁺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 Et₂O, the reaction of cAAC_{Me} and H₂SiI₂ 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 Et₂O, 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 H₂SiI₂ in a 3:1 molar ratio, 1 was not afforded; instead a mixture of the cAAC–silicon(0) complex [(cAAC_{Me})₂Si] (32% yield) and [cAAC_{Me}@H]⁺I[⊖] as the sole products was afforded.^[5] In the last experiment, cAAC_{Me} was reacted with H₂SiI₂ 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 H₂SiI₂ in DME did not improve the yield of 1. These results illustrate that compound 1 cannot be formed in non-etheral 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 H₂SiI₂ to form [cAAC_{Me}@H]⁺I[⊖] and a cAAC–iodosilylene intermediate, “(cAAC_{Me})Si(I)H”. Sub-sequently, the latter reacts with another molecule of cAAC_{Me}, along with displacement of the I[⊖] anion, to form a cAAC–parent-silyliumylidene intermediate, “{(cAAC_{Me})₂SiH}⁺I[⊖]”. This intermediate displaces a HC radical by reacting with etheral 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 HC radical is favored in DME as DME is able to undergo radical reactions via homoleptic cleavage of the central C@C bond in CH₃OCH₂@CH₂OCH₃.^[14] This mechanism is further supported by the following facts: 1) The yield did not improve when cAAC_{Me} and H₂SiI₂ were reacted in a 4:1 molar ratio, indicating that cAAC_{Me} cannot abstract a HC radical from the {(cAAC_{Me})₂SiH}⁺I[⊖] intermediate. 2) H₂ 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)}₂GeD]C.^[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 = 133.378). The C1-Si1-C21 bond angle (122.96(15)°) is significantly wider than that of the cAAC–silicon(0) complex [(cAAC_{Me})₂Si] (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})₂Si] (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)IiPrMe]⁺I[⊖] (1.878(5) Å).^[16] Simultane-

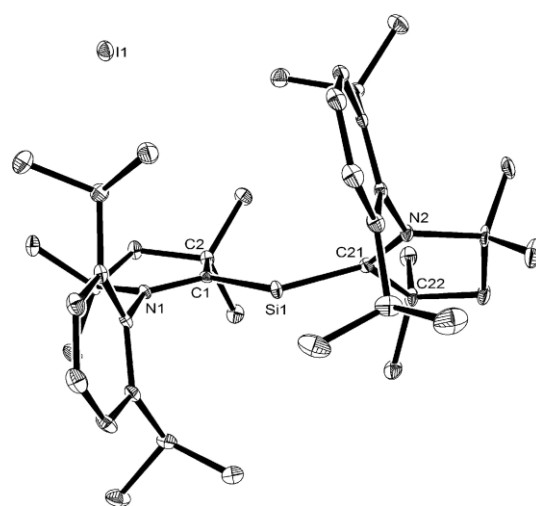


Figure 1. Molecular structure of 1. Ellipsoids set at 30 % probability. Solvent molecule and hydrogen atoms are omitted for clarity. The calculated geometrical parameters at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths [Å] and angles [°]: C1–N1 1.319(4) [1.345], 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], N1-C1-Si1 115.9(3) [115.6], 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].

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}C@Si(Cl)₂@cAAC_{Me}C] (1.395(2)–1.3994(19) Å)^[17] and
the cAAC–silicon(0) complex [(cAAC_{Me})₂Si] (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 2 a) shows a three-

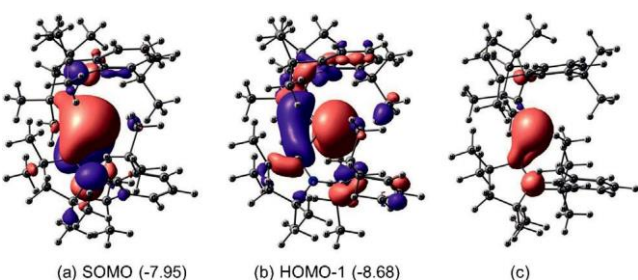


Figure 2. CW EPR (X-band) spectra of 1 in toluene/THF solution recorded at a) 298 K and b) 115 K. The corresponding simulations are shown in a' and b'.

line hyperfine multiplet pattern with $a(^{14}\text{N})_{\text{iso}} = 18.5$ 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 2 b) shows an intense signal at B 336 mT, which has some evidence for a small degree of anisotropy.

Table 1: Spin Hamiltonian parameters for compound 1.

g_{iso}	
expt. ^[a]	2.0037
DFT	2.0078
a_{iso} [MHz]	$^{14}\text{N1}$
expt. ^[b]	–
DFT	5.52

[a] :0.0001; [b] :5 MHz.

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

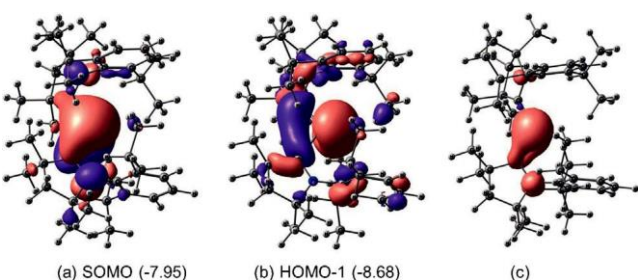


Figure 3. Plots of a) the SOMO, b) the lone pair on the Si atom (HOMO-1; isosurface value 0.03), and c) the spin density calculated by natural population analysis (isosurface value 0.008) of 1 at the M06/def2-TZVPP//BP86/def2-SVP level of theory. Eigenvalues in eV are given in parentheses.

orientations of the two cAAC_{Me} rings prevent simultaneous back-donation of the unpaired electron on the Si atom into two C@N p*-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 p-type p-orbital on the Si atom (0.67 e,

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) 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/

	$^{14}\text{N}_2$	^{29}Si
	10.67	212.00
	11.32	102.00

Table S3). The HOMO-1 is a s-type lone-pair orbital (Figure 3 b) on the Si atom with greater s-character (a- and b-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 3 c and Table S4). This is in line with the EPR spectroscopic data.

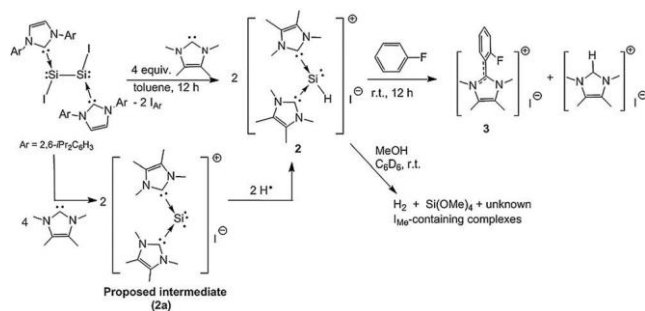
The nature of the bonding interaction between the [DSiC]⁺ ($^2\text{P}; 3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC_{Me} fragments in **1** was further analyzed by the EDA-NOCV approach (Table S5). In the Si@cAAC_{Me} bonds, the covalent interaction ($DE_{\text{orb}} = 55.8\%$) has a higher energy contribution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

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 s-bonds between the [DSiC]⁺ ($^2\text{P}; 3s^2 3p_x^0 3p_y^0 3p_z^1$) and cAAC_{Me} moieties, one s-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 LiNiPr₂ in toluene to form a mixture of the

cAAC–silicon(0) complex [(cAAC_{Me})₂Si], iPr₂N@NiPr₂, and Lil (Scheme 2).

The mechanism for the formation of 1 was also studied. It is proposed that the cAAC–parent-silyliumylidene intermediate “{(cAAC_{Me})₂SiH}⁺” is the key intermediate in the reaction of cAAC_{Me} and H₂Si₂, which displaces a HC 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 HC radical from the solvent to form a stable parent-silyliumylidene cation “{DSiH}⁺”. 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 rear-ranges to form an NHC–parent-silyliumylidene cation complex. After numerous attempts,^[21] the reaction of the NHC–iodosilicon(I) dimer [I_{Ar}(I)SiD]₂ (I_{Ar} = DC(N(Ar)CH)₂)^[22] with four equiv of I_{Me} (DC(N(Me)CMe)₂) in toluene afforded the first NHC–parent-silyliumylidene iodide [(I_{Me})₂SiH]⁺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 2 a is also shown.

I_{Ar} ligands and iodide ions in [I_{Ar}(I)SiD]₂, along with homoleptic cleavage of the Si@Si bond, to afford the separated ion pair 2 a with a cationic NHC–silicon(I) radical intermediate, which then abstracts a HC 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 CHCl₃ and slowly decompose in fluorobenzene (see below) and pyridine over three days. The ¹H NMR spectrum shows one set of resonances that is due to the I_{Me} ligands and another one arising from the Si@H proton (d = 9.73 ppm). The latter is downfield-shifted in comparison with that in the NHC–hydrosilylene complexes [I_{Me}@DSiH-(SitBu₃)] (d = 3.17 ppm) and [I_{Me}@DSiH(Ter)] (Ter = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂, d = 4.00 ppm) owing to the presence of an electron-withdrawing cationic Si^{II} center.^[24] The ²⁹Si NMR signal of 2 (d@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} = DC(N(iPr)CMe)₂,

d@55.3 ppm)^[25] and [I_{Me}@DSiH(SitBu₃)] (d@137.8 ppm).^[24b] The Si@H chemical shift is further evidenced by its disappearance when compound 2 reacted with MeOH in C₆D₆ 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

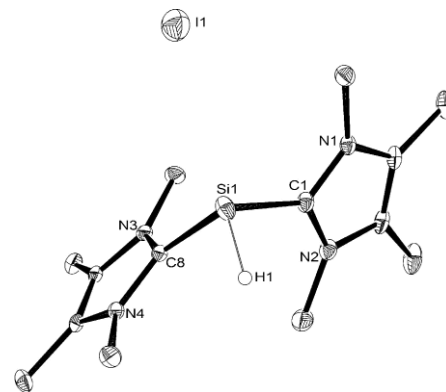


Figure 4. X-ray crystal structure of 2. Ellipsoids set at 30% probability. Hydrogen atoms except the H1 atom are omitted for clarity. The geometrical parameters calculated at the BP86/def2-SVP level of theory are given in square brackets. Selected bond lengths [Å] and angles [°]: Si1–H 1.455 [1.529], 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 (292.198) 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})₃Si]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}-C₆H₄]⁺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)SiD]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 H₂Si₂ that the Si@H bond in the “{(cAAC_{Me})₂SiH}⁺” intermediate can react with ethereal solvents to form 1.

In support of the feasibility of intermediate 2 a and its high reactivity to abstract a HC radical from toluene to form 2,^[23]

DFT calculations of **2** were performed. Its HOMO-1 (Figure S13) is a lone-pair orbital on the Si center (79.2 and 75.9% a- and b-type s-orbitals). Moreover, the SOMO (Figure S13) mainly consists of the p-type p-orbital localized on the Si center, along with the contribution from the C@N p*-MO of I_{Me} . In addition, EDA-NOCV analysis (Table S5 and Figure S16) showed that the energy corresponding to the p-back-donation from the unpaired electron on the $[DSiC]^+$ moiety to one C@N p*-MO of I_{Me} ($DE_p = @28.1 \text{ kcal mol}^{-1}$) is smaller than that in **1** ($DE_p = @38.1 \text{ kcal mol}^{-1}$). Accordingly, the group charge analysis indicates a lower positive charge for the Si atom (0.43 e, Table S2) in **2** than that in **1** (0.83 e). These studies are in line with the poor p-acidity of I_{Me} compared to $cAAC_{Me}$.^[27] In this context, these results indicate that the unpaired electron in **2** (0.74 e; Figure S13 and Table S4) is more active than that in **1**, which accounts for the instability of **2** and the abstraction of a HC 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 $Si@C_{I_{Me}}$ bonds have almost equal contributions from covalent ($DE_{orb} = 51.7\%$) 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 s-bonds between the $Si^+(H)$ and two I_{Me} moieties.

In conclusion, the first separated ion pair of a $cAAC$ -silicon(I) radical $[(cAAC_{Me})_2SiDC]^+1^{\ominus}$ (**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 $\{[(cAAC_{Me})_2SiH]^+I^{\ominus}\}$, which then displaces a HC radical by reacting with DME to form **1**. The feasibility of the $\{[(cAAC_{Me})_2SiH]^+I^{\ominus}\}$ intermediate is supported by the isolation of the first NHC-parent-silyliumylidene iodide $[(I_{Me})_2SiH]^+I^{\ominus}$ (**2**). The reactivity of **2** towards solvents supports our hypothesis that the reactive $Si@H$ bond in the $\{[(cAAC_{Me})_2SiH]^+I^{\ominus}\}$ intermediate can react with DME to form the stable compound **1**.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

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

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- [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^{\cdot} radical being stabilized by partial back-donation to the C@N p*-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 HC radical in $\{[(cAAC_{Me})_2SiH]^+I^{\ominus}\}$ is favored in DME as DME is able to abstract a HC radical to form dimethyl

ether (CH₃OCH₃) via cleavage of the C@C bond in CH₃OCH₂@CH₂OCH₃. 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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