Generation and aromaticity of 2-silaimidazolium ion, a new π-conjugated silylium ion†

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A novel cationic silaaromatic, 2-silaimidazolium cation (5), was synthesized by chloride abstraction from the corresponding chlorosilane (4) with [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate); cation 5 exists as a free silylium cation in solution due to bulky substituents on the five-membered ring.

Properties of cationic species of silicon or other higher group-14 elements are quite different from those of carbocations because of their decreased electronegativity, larger atom sizes, and lower bonding energies.[1,2] Particularly, the silylium ion, which is free from any interaction with a solvent or a counteranion, has attracted much attention, and has been realized by the combined use of specific substituents on silicon, non-coordinating counter-anions, and unusual synthetic methods.[2–5] However, examples of silylium ions incorporated into π-conjugated systems in condensed phases are still quite limited. Recently Sekiguchi's and our groups reported cyclotetrasilenylium 1[3,4] and silacycloheptatrienylium (silatropylium) ion 2,[5] which have 2π homoaromatic and 6π aromatic character, respectively. Since imidazolium ion is known as a typical stable heterocyclic cation, we wondered if it was possible to generate the corresponding silicon analogue, a 2-silaimidazolium (1,3-diaza-2-silacyclopentenylium) ion. Here we report the generation of such a cation and its aromaticity.


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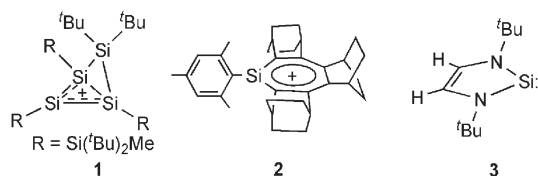
First, an attempt was made to directly convert cyclic diaminosilylene 3[6] to a 2-silaimidazolium ion by electrophilic addition of trityl cation. However, the reaction conducted in toluene at low temperature only resulted in the formation of an intractable mixture, probably due to the migration of the substituents on 3. In our next attempt, chlorosilane 4 having a bulky bis(trimethylsilyl)methyl (Dis) group on the silicon atom was designed as a precursor to reduce interaction between silylium ion and nucleophiles. Synthesis of 4 was conducted by the insertion of stable silylene 3[6] into bis(trimethylsilyl)methyl chloride.[7,8] Then, a chloride-ion abstraction from 4 was conducted by treatment with

1 equivalent of [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate)[3,9] in CD$_2$Cl$_2$ or in toluene-d_8 in a vacuum-sealed NMR tube at low temperature (Scheme 1).[10,11] Generation of 2-silaimidazolium ion 5 was clearly demonstrated by ^{29}Si NMR spectroscopy. A set of signals was observed at 53.0 and 4.3 ppm in CD$_2$Cl$_2$, and 53.2 and 4.0 ppm in toluene-d_8, together with signals of chlorotriethylsilane and an unidentified product[12] derived from triethylsilylium cation (Fig. 1). The signal for the central silicon atom is shifted 70 ppm downfield from that of chlorosilane 4 and is close to that of 5 predicted by GIAO calculation at B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level (60.0 ppm). No signal of the starting material was observed, suggesting that the reaction proceeds quantitatively. The fact that the chemical shift of the silylium center is insensitive to the solvents indicates that the complexation of the silylium center with these solvents is effectively inhibited by the bulky substituents. 2-Silaimidazolium ion 5 is stable at temperatures below −10 °C, but at higher temperatures 5 underwent decomposition to give a complex mixture which did not allow its isolation. Cation 5 was trapped by n-Bu$_4$NBr and gave the corresponding bromosilane 6 in 27% yield.[13]

Selected ^{13}C and ^{1}H NMR signals of 4 and 5 at −60 °C in CD$_2$Cl$_2$ are summarized in Table 1. Due to the severe steric congestion between tert-butyl and trimethylsilyl groups, the rotation around the Si$_{ring}$–Dis bond is restricted at lower temperatures, and therefore two (tert-Bu)NCH moieties in the five-membered ring are not equivalent on the NMR timescale.[14] Both the carbon and proton NMR signals of 5 are generally downfield shifted compared to those of 4, and are in fair agreement with those calculated for 5.

The signal of the methine proton in the Dis group in 5 is observed at 1.39 ppm, which is 1.06 ppm downfield shifted compared to that in 4. In the optimized structure of 5, the methine proton is positioned almost at the plane of the 2-silaimidazolium ring (the dihedral angle of H–C–Si–N is 177.8° and −7.2°), and therefore the proton nucleus is strongly affected by a diamagnetic ring current. A downfield shift of similar extent (0.9 ppm) has been observed for the bridgehead protons of the bicyclic frameworks in

4   5·TPFPB$^-$
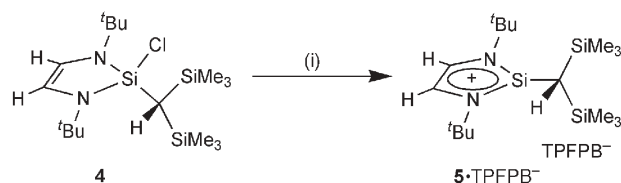
Scheme 1 *Reagents and conditions*: (i) [Et$_3$Si(benzene)]$^+$·TPFPB$^-$, CD$_2$Cl$_2$ or C$_7$D$_8$, −60 °C.

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† Electronic supplementary information (ESI) available: NMR spectra of 4 and 5, and the details of experiments and theoretical calculations. See http://www.rsc.org/suppdata/cc/b4/b415783d/
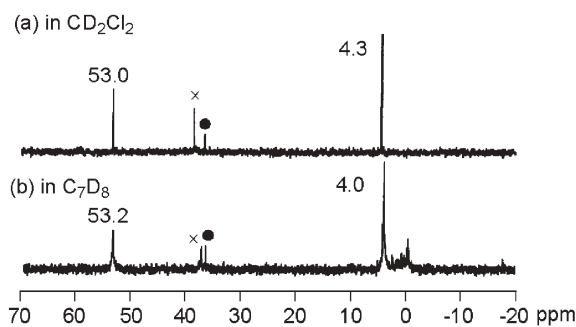*komatsu@scl.kyoto-u.ac.jp

(a) in CD_2Cl_2
53.0
4.3

(b) in C_7D_8
53.2
4.0

70 60 50 40 30 20 10 0 -10 -20 ppm

Fig. 1 ^{29}Si NMR spectra of a reaction mixture of **4** with [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ at -60 °C (a) in CD_2Cl_2, and (b) in C_7D_8. × : chlorotriethylsilane, ● : unidentified product.[12]

**Table 1** Selected NMR chemical shifts of **4** and **5**[a]

4: X = Cl
5: X = +

Compd	C1,3[b]	C4,5	C6	C7[c]	H4,5	H6	H7[c]
4	51.9	111.9	12.7	1.9	5.69	0.33	0.07
	52.0	112.5		2.9	5.75		0.16
5	57.1	118.2	8.9	2.7	6.70	1.39	0.34
	57.7	119.1			6.74		
5$_{calcd}$[d]	67.6 (av.)	124.8 (av.)	17.5	3.7 (av.)	7.05 (av.)	1.55	0.04 (av.)

[a] In CD_2Cl_2, -60 °C. [b] CMe_3. [c] $SiMe_3$. [d] GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d).
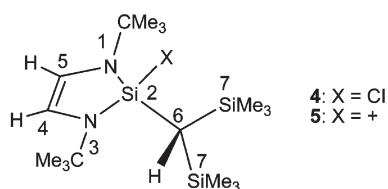
the case of silatropylium ion **2**.[5] Whereas two signals (both C and H) are observed for trimethylsilyl groups in **4**, only one signal is observed in **5**, suggesting that **5** has a planar five-membered ring containing a silicon atom. These spectroscopic features show the presence of aromaticity in 2-silaimidazolium ion **5**.

Theoretical calculations of 1,2,3-trimethyl-2-silaimidazolium (**7**) and 1,2,3-trimethylimidazolium (**8**) cations as model compounds were carried out to evaluate the aromaticity in 2-silaimidazolium ion.[15] In the optimized structure of **7**, the π-system is planar and the unsaturated silicon atom has an almost tricoordinated planar geometry. The sum of the interior angles of the silaimidazolium ring and the angles around the silicon atom of **7** are 540.2° and 359.9°, respectively. The NICS(1)[16] values of the optimized **7** and **8** were calculated to be -6.5 and -10.9 ppm, respectively. Aromatic stabilization energy (ASE) evaluated by a homodesmic reaction shown in equation (1) is 5.6 kcal mol^{-1} for **7** and 17.3 kcal mol^{-1} for **8**. These results support the presence of aromaticity in 2-silaimidazolium cation in agreement with the ^{1}H NMR data, although its extent is smaller than that of the carbon analogue. This can be ascribed to the greater polarization and length of the silicon–nitrogen bond compared to the carbon–nitrogen bond, in addition to less effective 3p–2p overlap than 2p–2p, resulting in less delocalization of positive charge over the 2-silaimidazolium ring.
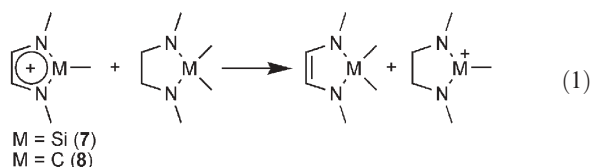
M = Si (**7**)
M = C (**8**)

(1)

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Notes and references

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8 Spectral data for chlorosilane **4**: mp 93–94 °C; ^{1}H NMR (298 K, CD_2Cl_2) δ 0.19 (brs, 18 H), 0.41 (s, 1 H), 1.33 (s, 18 H), 5.75 (s, 2 H); ^{13}C NMR (298 K, CD_2Cl_2) δ 3.2 (SiMe_3), 14.3 (>CH−), 31.1 (CH_3), 52.7 (>C<), 113.1 (=CH−); ^{29}Si NMR (298 K, CD_2Cl_2) δ -17.7 (SiCl), 3.1 (SiMe_3); MS (EI, 70 eV) m/z (%) 390 (M$^+$, 72), 278 (100). Anal. Calcd for $C_{17}H_{39}N_2ClSi_3$: C, 52.19; H, 10.05; N, 7.16%. Found: C, 52.18; H, 10.01; N, 7.40%. NMR signals of **4** significantly depend on the temperature. VT-NMR spectra of **4** are shown in the ESI.

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11 In a 5 mm NMR tube, carefully dried chlorosilane **4** and [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ were placed, and dry CD_2Cl_2 was introduced

by vacuum transfer. After being sealed, the tube was gently shaken in a cold methanol bath to mix the reactants thoroughly. The color of the solution turned to intense yellow. When toluene-d_8 was used as a solvent, the mixture separated into two layers and the lower layer was measured by NMR spectroscopy. Due to the viscosity of this layer, ^{1}H and ^{13}C NMR spectra only showed broad signals.

12 Since this signal was observed in the mixture of chlorotriethylsilane and [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ (1 : 1) without **4**, it is not related to silylium cation **5**.

13 Bromosilane **6** was obtained as a mixture with chlorosilane **4** and the corresponding fluorosilane probably due to halogen abstraction from solvent or counteranion. Identification and determination of the yield of **6** were made by MS and NMR spectroscopy; see ESI.

14 The rotational barrier of Si$_{ring}$–Dis in **4** is estimated to be 13.7 kcal mol^{-1} from the coalescence temperature (0 °C) of the olefinic proton signals. Although the steric congestion is expected to be smaller in **5**, the corresponding rotational barrier is estimated to be much higher than 14.0 kcal mol^{-1} from the coalescence temperature of the olefinic proton signals, which is apparently much higher than 0 °C. This may be ascribed to an interaction between the vacant 3p orbital on cationic silicon and the σ(Si–C) orbital in the Dis group, *i.e.*, "β-silyl hyperconjugation".

15 Geometry optimizations, NICS calculations, and estimation of ASEs were carried out at the B3LYP/6-31+G(d,p), B3LYP/6-311+G(2d,p), and MP2/6-31+G(d,p)+ZPE level, respectively.

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