The First Cyclic π-Conjugated Silylium Ion: The Silatropylium Ion Annelated with Rigid σ-Frameworks

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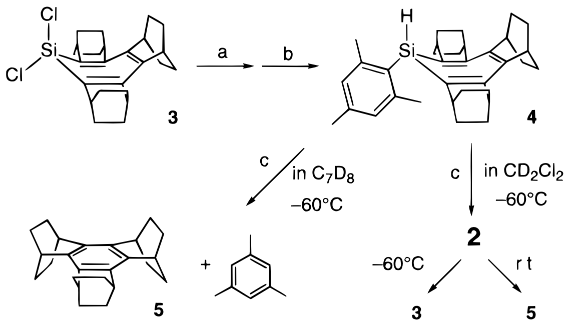
Studies on silylium ion in condensed phases have attracted much attention,[1] particularly following the X-ray structural analyses made by Lambert's[2] and Reed's[3] groups. Nevertheless, only a few types of compounds having a silylium-ion character have been reported so far,[2−7] because in many cases the silylium ion forms a strong coordinate bond with the solvent or counteranion.[1e−j] As one of the representative π-conjugated silylium ions, the silatropylium ion (**1**) is of great interest from the viewpoints of its aromaticity, structure, and reactivity. However, its presence in solution has been highly questioned.[8] Even in the gas phase, the recent suggestion of **1** as one of the $C_6H_7Si^+$ isomers observed in a FT ICR mass spectrum[9] was disproved by a subsequent experimental study showing that it was rearranged isomer $C_6H_6{\cdot}SiH^+$.[10] Theoretical studies have indicated that **1** is less stable than "silabenzyl cation" by 9 kcal mol^{-1}.[11] Thus, the synthesis of the silatropylium ion remains as a major challenge in organosilicon chemistry. For its realization, we designed a modification of the seven-membered ring with rigid σ-frameworks which involves annelation with bicyclo[2.2.2]octene (BCO) units. In our previous study, such structural modification was found to be the most effective in stabilizing the carbon analogue, tropylium ion, in terms of the thermodynamic criterion.[12] Here we report the first example of the generation and NMR characterization of the silatropylium ion **2** stabilized by such a structural modification together with the placement of a bulky substituent on the silylium center.

Scheme 1[a]



[a] (a) Mesityllithium, THF, rt; (b) LiAlH$_4$, THF, 40 °C; (c) trityl TPFPB.

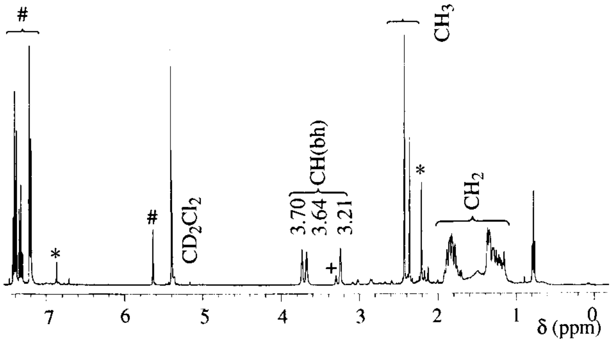
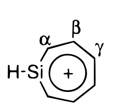


Figure 1. ^{1}H NMR spectrum (400 MHz) for **2** at −50 °C in CD_2Cl_2. The signals marked with +, *, and # corresponds to those for **5**, mesitylene, and triphenylmethane, respectively. A signal for the two mesityl ring protons of **2** is overlapped with signals for triphenylmethane.



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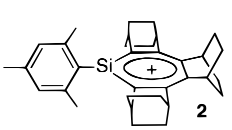

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The precursor silepin **4** having a mesityl (Mes) group on silicon was prepared from dichlorosilepin **3**[13] in 40% yield as shown in Scheme 1. When the first attempt was made to generate **2** by hydride abstraction from **4** with an equivalent of trityl tetrakis-(pentafluorophenyl)borate (TPFPB) in toluene-d_8 (C_7D_8) under vacuum at −50 °C, a ring contraction occurred to show the ^{1}H NMR signals for benzene derivative **5** and mesitylene, possibly via a nonclassical ion **5**$\cdot$Mes-Si^+ which corresponds to $C_6H_6{\cdot}SiH^+$ observed in the gas phase.[10] On the other hand, when the reaction was conducted in dichloromethane-d_2 (CD_2Cl_2) at −50 °C, the ^{1}H and ^{13}C NMR signals corresponding to silatropylium ion **2** were observed[14] as shown in Figure 1 and Table 1. Apparently, C_7D_8 with its lower polarity and a larger molecular size could not stabilize the cationic species by coordination,[1i−j,15] while CD_2Cl_2 with its medium polarity is small in size for

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(14) As to the hydride abstraction reaction, ∼0.5 equiv trityl cation was not consumed and about 6% of **5** and mesitylene were also formed. The fate of the possible species such as Mes−Si^+ generated on the ring contraction of **2** is not known, but such a species and its degradation products would also work to abstract hydride from **4**.

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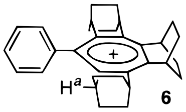
Table 1. ^{13}C NMR Chemical Shifts for **2** at −50 °C in CD_2Cl_2

C(sp^2)		C(sp^3)		
tropyl	aryl	CH	CH$_2$	CH$_3$
175.9	144.8	36.8	25.1	25.9
153.2	143.8	35.1	24.2	21.4
149.7	128.0	34.9	23.9	
	118.7			

approaching the silylium-ion center to coordinate to it. Cation **2** is stable at temperatures below −50 °C, but it slowly abstracts the chloride ion from CD_2Cl_2 to furnish dichlorosilepin **3** at −50 °C ($t_{1/2} \approx 6$ h).[16] Such an abstraction of the chloride ion from CH_2Cl_2 by the silylium ion has been previously reported.[3,17] When the temperature was raised, **2** decomposed to give **5** as was observed in C_7D_8 at low temperature.

The ^{29}Si NMR signal of **2** was observed at δ 142.9 ppm in CD_2Cl_2, which is 192.2 ppm downfield-shifted compared with the precursor silepin **4** (δ −49.3). This is taken as the clear evidence for the silylium-ion character of **2**. The observed ^{29}Si chemical shift is also in fair agreement with the value calculated for the mother compound **1** (δ 158.1).[18,19] This method of calculation is known to reproduce the experimental value observed for the trimesitylsilylium ion.[20] This ^{29}Si chemical shift of **2** is 28 ppm downfield-shifted compared with the solid-state NMR chemical shift (δ 115) of *i*-Pr_3Si^+ $(Cl_6{-}CB_{11}H_6)^-$ which was shown to have some interaction between the silylium-ion center and the chlorine atom of the counterion.[6c] Thus, the interaction between the silylium-ion center of **2** and CD_2Cl_2 should be smaller than the case for *i*-Pr_3Si^+ $(Cl_6{-}CB_{11}H_6)^-$: the ion **2** may be considered as a nearly free silylium ion.

The chemical shift of the BCO's bridgehead (bh) protons is useful for judging the presence of diamagnetic ring current because they are rigidly fixed on the same plane as the silatropylium-ion ring.[21] As shown in Figure 1, the signals for these protons were observed at δ 3.70, 3.64, and 3.21[22] ppm, which were about 1 ppm downfield-shifted compared with those for the neutral precursor **4** (δ_{bh} 2.81 (4H), 2.61 (2H)). This is taken as the experimental proof for the aromatic ring current in **2**. Similar downfield shifts were observed in the corresponding phenyltropylium ion **6** upon going from the neutral precursor (δ_{bh} 2.88 (2H), 2.67 (4H)) to the ion (δ_{bh} 4.09, 4.06, 3.17).[12c] Also the nucleus independent chemical shift[23] at 1 Å above the ring (NICS(1))[24,26] and magnetic susceptibility exaltation (Λ)[25,26] calculated for the mother compound **1** (NICS(1) = −7.3, Λ = −15.6) showed that the aromaticity of **1** approaches that of the tropylium ion (NICS(1) = −10.7, Λ = −20.1).



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The ^{13}C NMR signals (Table 1) for the sp^2 carbons of **2** in CD_2Cl_2 (δ 175.9, 153.2, 149.7 ppm) showed downfield shifts compared with **4** (δ 152.0, 145.5, 141.8), indicating considerable positive-charge delocalization in the seven-membered ring. The most downfield-shifted signal (δ 175.9) is assigned to the β-carbon judging from the calculated chemical shifts for **1** (α, 136.5; β, 167.6; γ, 141.0).[18] These results imply that a contribution of the sila-allylic resonance structure is important for the positive-charge delocalization.

To estimate the degree of interaction between the silatropylium ion and the solvent molecule, the optimized structure and its energy for $\mathbf{1}\cdot CH_2Cl_2$ were calculated at the B3LYP/6-31G* level. The Si−Cl distance (2.735 Å) for $\mathbf{1}\cdot CH_2Cl_2$ was found to be considerably longer than that for $Me_3Si{-}Cl$ (2.11 Å) as a model compound for the covalent molecule. This Si−Cl distance for $\mathbf{1}\cdot CH_2Cl_2$ was still 0.33 Å longer than that for $Me_3Si^+\cdot CH_2Cl_2$ (2.41 Å), indicating that the cyclic conjugation of the silatropylium ion reduces the interaction between the silylium ion and CH_2Cl_2. Furthermore, although some stabilization energy is present for $\mathbf{1}\cdot CH_2Cl_2$ (7.7 kcal mol^{-1}) as estimated from the energy difference between $\mathbf{1}\cdot CH_2Cl_2$ and the sum of **1** and CH_2Cl_2, it is smaller due to the cyclic π-delocalization than the case for $Me_3Si^+\cdot CH_2Cl_2$ (18.2 kcal mol^{-1}). In addition, the bulky sustituent on silicon of **2** should have prevented the solvent molecule to approach the silylium-ion center.

In summary, we have succeeded in the first NMR observation of the silatropylium ion with the aid of annelation with rigid BCO frameworks and a bulky substituent on silicon. This study revealed not only that the silatropylium ion is aromatic but that the aromatic stabilization is effective for reducing the interaction between a solvent and silylium ion. Efforts aiming at the synthesis of a solvent-free isolable silatropylium ion are now under way.

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Note Added in Proof: A homoconjugated silylium ion, the homocyclotrisilenylium ion, was recently synthesized by Sekiguchi's group.[27]

Supporting Information Available: Experimental details describing the synthesis and characterization of compound **4** and the generation of **2**, and ^{1}H, ^{13}C, and ^{29}Si NMR spectra for **2** in CD_2Cl_2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The possible mechanism is considered as follows: the produced chloromethyl cation exerts an electrophilic aromatic substitution on the mesityl ring of the generated mesitylchlorosilepin to cleave the Si−Mes bond, and the second chloride abstraction by the chlorosilatropylium ion from the (chloromethyl)mesitylene furnishes dichlorosilepin **3**. The formation of tetramethylbenzene-*d*$_2$ ($C_{10}H_{12}D_2$) was confirmed by GC−MS analysis.

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(22) This signal resonates at a relatively high field because it would correspond to the proton (H^a) that sticks out in the shielding zone of mesityl ring as in the case of one of the bh protons (H^a) in the phenyltropylium ion annelated with BCO units: 12c.

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(25) Calculated at HF/CSGT/6-31+G*//B3LYP/6-31G*.

(26) For the method of calculations see Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Organometallics* **1997**, *16*, 2362−2369.

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