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Ring-Opening Protonolysis of Strained Silicon-Containing Rings: A New Approach to Ions with Silylium Character

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The existence of silylium ions $[R_3Si]^+$ has aroused a great deal of controversy and the earliest reported examples were subsequently shown to have their perchlorate “counteranion” covalently bound.[1−5] Silylium ions are much more reactive than carbocations, $[R_3C]^+$, and are generally solvated in solution. However, Lambert and co-workers have shown that $[Mes_3Si]^+$ is an almost completely isolated cation in the presence of a noncoordinating counterion such as the tetrakis(pentafluorophenyl)borate anion.[6] Silylium ions are interesting from a fundamental perspective, as reactive intermediates, and as synthetic reagents as a consequence of their Lewis acidity.[1−3,7] For example, tetracoordinate Si cations $[R_3SiL]^+$ have been postulated to be reactive intermediates in the cationic polymerization of hexamethylcyclotrisiloxane, $[Me_2SiO]_3$.[8]

There are currently two main routes for the formation of cations with high silylium character.[1−4] The first involves electrophilic abstraction of X^- from four-coordinate R_3SiX molecules and is driven by the insolubility of metal salts (e.g. eq 1a), or the formation of a strong C−H bond (e.g. eq 1b). The second route involves electrophilic addition of E^+ to an allyl substituent on Si, leading to elimination of $CH_2{=}CH{-}CH_2E$ (eq 2). In this paper, we present a novel ring-opening route to silylium ions that is free of byproducts.

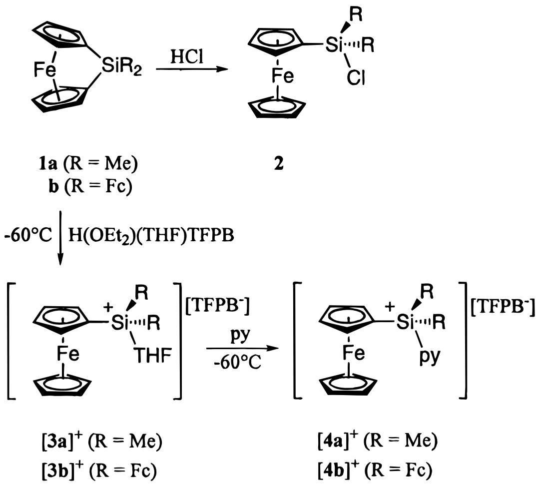
$$R_3SiCl + AgY \longrightarrow R_3Si^+Y^- + AgCl \qquad (1a)$$

$$R_3SiH + Ph_3C^+Y^- \longrightarrow R_3Si^+Y^- + Ph_3CH \qquad (1b)$$

(2)

We have recently shown that ring-opening addition of HCl to the strained Si−C bonds of [1]silaferrocenophanes (**1**) is a convenient and controlled route to ferrocenylchlorosilanes (**2**) (Scheme 1).[9] When **1b** was reacted with HBF_4 a mixture of ferrocenylfluorosilanes, such as Fc_3SiF and Fc_2SiF_2 (Fc = (η-C_5H_4)Fe(η-C_5H_5)), resulted, suggesting the presence of a highly reactive cationic silicon intermediate that could extract F^- from BF_4^-.[2,10] Coordination of an electron-rich iron atom from a ferrocenyl substituent might be expected to stabilize a silylium ion,[4b,11] in a manner similar to the carbonium ion $FcCPh_2^+$.[12] We report here that when an acid with a noncoordinating anion Y^- such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$)[13] is used, the ring-opening addition to [1]silaferrocenophanes, $fcSiR_2$ (fc = (η-C_5H_4)$_2$Fe) generates novel solvated Si cations.

Scheme 1



To investigate if solvated Si cations are formed in the reactions of **1a** and **1b** with $H(OEt_2)(THF)TFPB$, we characterized the products by low-temperature NMR spectroscopy (Figure 1). In the reaction of $H(OEt_2)(THF)TFPB$ with **1a** at ca. −60 °C, a new ^{29}Si NMR resonance was observed at 49.7 ppm, remarkably downfield from that of **1a** ($\delta = -3.0$ ppm in CD_2Cl_2).[14] The ^{29}Si NMR chemical shift of the product is consistent with similar ether-coordinated silylium species prepared by Sakurai and co-workers[15] (see Table 1) and suggested that the solvated Si cation [**3a**]$^+$ is formed at low temperature. The ^1H NMR spectrum at this temperature was consistent with this interpretation and showed sets of peaks assigned to ferrocenyl and $SiMe_2$ groups together with resonances characteristic of free diethyl ether and one set consistent with a coordinated THF molecule. This indicated that the four-coordinate silylium ion [**3a**]$^+$ had formed. The THF multiplets were shifted downfield ($\delta = 4.35$, 2.15 ppm) from the shifts expected for THF in CD_2Cl_2, as would be expected for ligation to a silicon center with significant cationic character. Some broadening of the coordinated THF resonances was observed, possibly indicative of coordinative exchange of the ligand.[15] In the ^{13}C NMR spectrum similar resonances for

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(12) (a) In crystalline $FcCPh_2^+$ the CPh_2 group is bent toward the Fe atom with an angle of 20.7° between the Cp−CPh_2 bond and the Cp plane. For further information see: Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89−98. (b) Fe stabilization of α-carbocation centers has been reviewed. See: Koridze, A. A. *Russ. Chem. Rev.* **1986**, *55*, 113−126.

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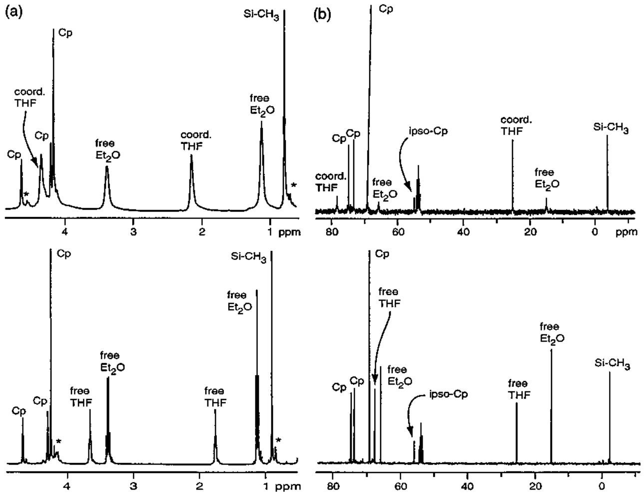

Figure 1. (a) ^{1}H and (b) ^{13}C NMR spectra at −60 °C in CD_2Cl_2 before (top) and after (bottom) addition of pyridine to the solvated silylium cation [**3a**]$^+$. Peaks marked with an asterisk indicate impurities and unreacted monomer **1a**.

Table 1. ^{29}Si NMR Shifts of Solvated Silylium Ions[a]

cation	*T* (°C)	^{29}Si (*δ*)[b]	ref
[$Me_3Si(OEt_2)$]$^+$	−70	66.9	15
[$Ph_2MeSi(OEt_2)$]$^+$	−40	38.0	15
[(2-thienyl)$_2$MeSi(OEt_2)]$^+$	−40	21.4	15
[**3a**]$^+$	−60	49.7	this work
[**4a**]$^+$	−60	33.3	this work
[**3b**]$^+$		*c*	this work
[**4b**]$^+$	25	25.2[d]	this work

[a] [TFPB]$^-$ salts. [b] In dichloromethane-*d*$_2$. [c] See ref 17. [d] In chloroform-*d*.

ferrocenyl and $SiMe_2$ groups, coordinated THF, and free ether molecules were observed. No other species, aside from the expected TFPB anion, were detected in any of the spectra,[16] indicating clean ring-opening protonolysis of the [1]silaferrocenophane. After the sample had reached room temperature, it became green, indicative of oxidation to Fe(III) species.

In a further experiment with **1a**, an aliquot of pyridine (py) was added at −60 °C after the formation of [**3a**]$^+$ had been confirmed by NMR. Upon addition of the pyridine, the solution changed from yellow to orange and the ^{29}Si NMR resonance moved upfield from 49.7 to 33.3 ppm. This was accompanied by changes to the ^{1}H and ^{13}C NMR spectra that were consistent with the replacement of coordinated THF with pyridine to afford [**4a**]$^+$ (Figure 1).[16] In particular, resonances consistent with free THF were then observed. In this case, when the sample was warmed to 25 °C, [**4a**]$^+$ proved to be stable.

We also investigated the addition of H(OEt_2)(THF)TFPB to the [1]ferrocenophane **1b** with two additional bulky ferrocenyl substituents. A methodology identical to that for the reaction between **1a** and H(OEt_2)(THF)TFPB was used. Again, the reaction was monitored in situ by ^{1}H and ^{13}C NMR at −60 °C.[16,17] Once again pyridine was added to the cooled sample of [**3b**]$^+$ and a similar change in the shifts of the THF molecules was detected by ^{1}H NMR spectroscopy that indicated the formation of [**4b**]$^+$.[16] To confirm the structure of [**4b**][TFPB], a single-crystal X-ray diffraction study was undertaken on crystals obtained from $CDCl_3$ at −50 °C.[16] Figure 2 shows the structure of [**4b**][TFPB], where three ferrocenyl moieties and pyridine are coordinated to the silicon atom.[16] The nearest approach of the anion to the Si atom is 3.93 Å. The Si−N bond length of 1.86 Å is in accord with other silylium species coordinated by pyridine such as [Me_3Si(py)][X] (X = Br, I).[18] From the bond length, we calculated that the Pauling bond order is 0.61,[19] characteristic of a mainly covalent interaction. The sum of the three C−Si−C bond angles in the cation is 337.7°, intermediate between that expected for a trigonal planar 3-coordinate Si cation and a tetrahedral species.

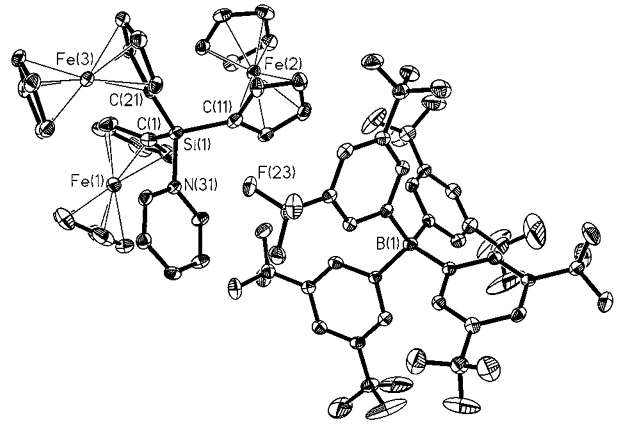

Figure 2. Molecular structure of [Fc_3Si(py)][TFPB] ([**4b**][TFPB]) with thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [deg]: Si(1)−N(31) 1.858(5), Si(1)−C(1) 1.832(6), Si(1)−C(11) 1.833(6), Si(1)−C(21) 1.843(6), C(1)−Si(1)−C(11) 114.9(3), C(1)−Si(1)−C(21) 115.0(3), C(11)−Si(1)−C(21) 107.8(3), C(1)−Si(1)−N(31) 106.8(2), C(11)−Si(1)−N(31) 104.3(2), C(21)−Si(1)−N(31) 107.2(2).

In summary, we report a new, convenient route to solvated Si cations with ferrocenyl substituents. Low-temperature NMR studies indicate that addition of H(OEt_2)(THF)TFPB to [1]ferrocenophanes generates cationic species with silylium character. The methodology described should be transferable to other strained silicon-containing heterocycles such as silacyclobutanes and also to rings containing other Group 14 elements.

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Supporting Information Available: Experimental details and NMR data for new compounds; Crystallographic details, tables of bond lengths, bond angles, and atomic coordinates for [**4b**][TFPB] (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) See Supporting Information for details.

(17) In this case, we were unable to obtain a ^{29}Si NMR signal at low temperature due to the long relaxation time of the Si center and difficulty using a DEPT sequence (lack of α-protons).

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