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An NMR Study of the Formation of N-Silylacetonitrilium Ions by Using Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as Counteranion[1)]

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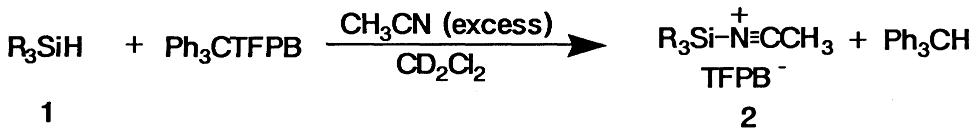
The formation of adducts of silicenium ions with acetonitrile (N-silylacetonitrilium ions) was elucidated by means of NMR spectroscopy during the hydride abstraction from hydrosilanes by trityl TFPB in CD_2Cl_2 in the presence of excess acetonitrile. The results indicate that acetonitrile is not a non-nucleophilic solvent suitable for formation of free silicenium ions, but stabilizes the ions by complexation giving tetracoordinate silicon species in solution.

We have recently demonstrated that adducts of silicenium ions with weak bases like ether[2)] and ketone[3)] are formed by the hydride abstraction from hydrosilanes by trityl tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (TFPB) in CD_2Cl_2 in the presence of the bases. The use of TFPB as a counteranion is crucial for the formation of these adducts; silyl perchlorates show no significant interaction with ethers. In view of these findings, we were intrigued by the reports of Lambert et al.[4)] that the complexation between acetonitrile and silicenium perchlorates is negligible and therefore, acetonitrile is a non-nucleophilic solvent suitable for production of free silicenium ions. We report herein an NMR study of the formation of N-silylacetonitrilium ions (**2**) by the reactions of the hydrosilanes with trityl TFPB in CD_2Cl_2 and discuss the structure on the basis of the results of ab initio MO calculations.



$$\underset{\mathbf{1}}{R_3SiH} + Ph_3CTFPB \xrightarrow[CD_2Cl_2]{CH_3CN\ (excess)} \underset{\mathbf{2}}{\underset{TFPB^-}{R_3Si\text{-}\overset{+}{N}{\equiv}CCH_3}} + Ph_3CH \quad (1)$$

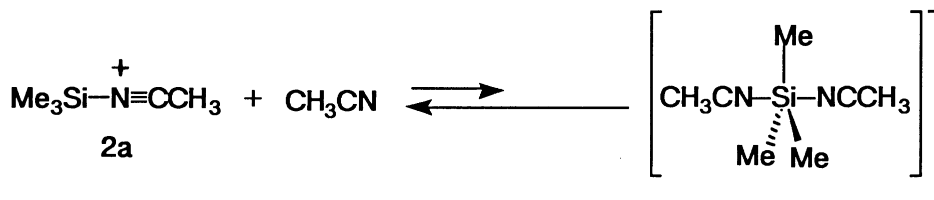
a, $R_3Si = Me_3Si$; **b**, $R_3Si = Ph_2MeSi$; **c**, $R_3Si = (2\text{-Thienyl})_2MeSi$;
d, $R_3Si = (3,5\text{-Di-t-butylphenyl})_3Si$.

In a typical experiment, trimethylsilane and excess acetonitrile were introduced to a frozen CD_2Cl_2 solution of trityl TFPB, which was pregenerated as a yellow solution by the reaction of trityl chloride with NaTFPB[5)] at room temperature followed by filtration of NaCl. After being sealed in an NMR tube, the mixture was allowed to react at -30 °C. Quantitative formation of triphenylmethane as well as formation of an apparently single species having trimethylsilyl moiety was observed by the ^1H, ^{13}C, and ^{29}Si NMR spectroscopy of the mixture; the molar ratio of acetonitrile to the silyl moiety (CN/Si) was determined to be

27/1 by ^{1}H NMR spectroscopy. The ^{1}H and ^{13}C resonances for the methyl of acetonitrile were somewhat broadened but showed almost the same chemical shifts with those of free acetonitrile in CD_2Cl_2 (Entry 5 in Table 1). The sole ^{29}Si resonance was observed at δ 28.4. As shown in Table 1, the ^{1}H, ^{13}C, and ^{29}Si resonances for both acetonitrile and trimethylsilyl moieties depended significantly on the experimental conditions. Thus, among Entries 1 - 4, the ^{1}H and ^{13}C resonances for the acetonitrile methyl and the ^{29}Si resonance for trimethylsilyl varied by about 0.4 , 1.5, and 10.1 ppm, respectively. Existence of the free silicenium ion under these conditions should be excluded, because the ^{29}Si resonance for a *free* trimethylsilicenium ion has been predicted to be at lower field than 200 ppm by various methods.[6,7] We have recently shown by NMR spectroscopy that a similar reaction in the absence of any base gave a mixture of Me_3SiX (X = F and Cl) instead of the corresponding silicenium TFPB.[2] Although many factors would be responsible for the variation of the resonances (*vide infra*), these features are indicative of significant interaction between acetonitrile and trimethylsilicenium ion, *i.e.* the formation of a stable N-trimethylsilylacetonitrilium TFPB in solution.

At the low CN/Si ratios (Entries 3 and 4 in Table 1), the ^{29}Si NMR resonances appeared at around 38 ppm. The resonances would be close to that for tetracoordinate N-trimethylsilylacetonitrilium ion **2a**; the ^{29}Si resonances for the related trimethylsilylaminium ions, $(Me_3Si)Et_3N^+$ and $Me_3SiC_5H_5N^+$, have been reported to be 46.0 and 42.3 ppm, respectively.[8] The higher ^{29}Si resonance for **2a** than those for diethyl(trimethylsilyl)oxonium ions (66.9 ppm)[2] and trimethylsiloxydiphenylcarbenium ion (52.3 ppm)[3] may suggest that the positive charge on **2a** is delocalized significantly onto the nitrile carbon.

The ^{29}Si resonance for **2a** appears to shift to higher field with increasing the CN/Si ratio. It is suggested that there is minor but significant contribution of a pentacoordinate silicon species in the equilibrium shown in Eq. 2, especially when the CN/Si ratio is high. In this context, it should be noted that dimethylsilyl triflate has been reported to form adducts with pyridine, 4-dimethylaminopyridine, and N-methylimidazole to give the corresponding five-coordinate species (2:1 adducts), whose ^{29}Si NMR resonances appear at δ -44, -52, and -82, respectively, while the formation of pentacoordinate silicon species with these bases is prevented in more hindered silyl triflates such as trimethylsilyl triflate.[9] Acetonitrile may be assumed to be small enough to make pentacoordinate silicon species even with **2a**. On the other hand, the reason why the ^{29}Si NMR resonance for diethyl(trimethylsilyl)oxonium ion is insensitive to the excess diethyl ether[2] may be attributed to the steric hindrance which prevents the formation of the corresponding pentacoordinate silicon species.



(2)

Similar hydride abstraction reactions from diphenylmethylsilane, di(2-thienyl)methylsilane, and tris(3,5-di-t-butylphenyl)silane in the presence of excess acetonitrile gave also the evidence for the formation of the corresponding N-silylacetonitrilium TFPB, whose ^{29}Si NMR resonances varied depending on the CN/Si ratios and appeared at 10.5 (1/1), -9.9 (10/1) and -2.8 ppm (10/1), respectively (the ratio of CN/Si is shown in parenthesis). The ^{29}Si resonances for **2a** - **d** are observed at ca. 20 - 30 ppm lower field than those of the

Table 1. NMR Chemical Shifts (δ) for N-trimethylsilylacetonitrilium TFPB under Various Conditions in CD_2Cl_2

Entry	Conditions		CH_3CN			Me_3Si		
	CN/Si[a]	Temp/K	^1H	$^{13}C(CH_3)$	$^{13}C(CN)$	^1H	^{13}C	^{29}Si
1	—[b]	263	1.96	1.3	118.5	0.63	-1.3	31.7
2	27/1	213	1.99	1.3	117.2	0.52	-1.8	28.4
3	1.9/1	263	2.32	2.4	120.4	0.62	-1.5	38.5
4	1.7/1	243	2.42	2.8	121.4	0.63	-1.9	36.7
5	—[c]	243	1.96	2.0	117.2	—	—	—

a) Molar ratio of acetonitrile to trimethylsilyl moiety determined by ^1H NMR spectroscopy.
b) In CD_3CN solvent. c) Free CH_3CN in CD_2Cl_2.

corresponding hydrosilanes.

Concerning the interaction between acetonitrile and silyl perchlorates, Lambert et al. have reported that when 1 equiv of [^{15}N]acetonitrile was added to a solution of triphenylsilyl perchlorate in CD_2Cl_2, the ^{15}N resonance for CH_3CN is found at 245.7 ppm, which value is essentially unchanged from that of free CH_3CN (244.2 ppm), while ^{15}N resonance for N-triphenylsilylpyridinium perchlorate appeared at about 100 ppm lower field than that for free pyridine in CD_2Cl_2 (314.0 ppm). On the basis of this and some other findings, Lambert et al. have concluded4) that silyl perchlorates undergo ionization in a highly dilute acetonitrile solution and the silicenium ions do not show significant interaction with acetonitrile. Alternatively, our present results indicate that silyl perchlorates do not undergo ionization even in a highly dilute acetonitrile solution, since acetonitrile is not nucleophilic enough to substitute the perchlorate group in covalent silyl perchlorates.

Finally, we discuss the structure of N-silylacetonitrilium ion [$(H_3SiNCCH_3)^+$] (3) fully optimized by ab initio MO calculations using 6-31G* basis set.10) The bond lengths (pm) of Si-N, C-N, and C-C for the geometry of 3 were 186.2, 113.1, and 146.6, respectively, and the bond angle of Si-N-C was 180°. These bond lengths are compared with the corresponding values for the related ions whose geometry was optimized using 6-31G* basis (pm); 113.5 (C-N) and 146.8 (C-C) for acetonitrile and 112.5 [C(nitrile)-N], 145.5 [C(methyl)-N], and 146.8 [C(methyl)-C(nitrile)] for N-methylacetonitrilium ion. Although geometrical parameters for acetonitrile were not seriously changed by complexation giving 3, the Mulliken charge on the nitrile carbon increased from 0.296 for acetonitrile to 0.571 for 3. The calculated Si-N bond length for 3 (186.2 pm) is in good agreement with that for trimethylsilylpyridinium ion (186 pm, X-ray crystallography)12) but significantly longer than that for trimethylsilyldimethylamine (171 pm, electron diffraction).13)

The energy for the formation of 3 by the reaction of silicenium ion with acetonitrile was calculated as -71.3 kcal/mol by using the total energies of silicenium ion,14) acetonitrile, and 3 calculated by 6-31G* basis (Eq. 6). Stabilization of silicenium ion by complexation with acetonitrile is rather comparable with the related reaction energy for formation of N-methylacetonitrilium ion (-85.2 kcal/mol).

$$\mathrm{H_3Si^+} + \mathrm{CH_3CN} \longrightarrow \mathrm{H_3Si{-}\overset{+}{N}{\equiv}CCH_3} \qquad (3)$$

$$\Delta E = -71.3\ \mathrm{kcal\ /\ mol}$$

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