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Stable Silylnitrilium Ions

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Abstract: Trityl tetrakis[bis(3,5-trifluoromethyl)phenyl]borate, $Ph_3C^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$, abstracts hydride from hydridosilanes, producing Ph_3CH. Use of a weakly coordinating solvent (i.e., CH_2Cl_2) results in near-quantitative conversion of a trialkylsilane to the fluorosilane. When a more strongly coordinating solvent, e.g., butyronitrile, is used, a nitrile-stabilized silicenium ion (silylnitrilium ion), $R_3Si(NCC_3H_7)^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$, is formed. This salt was characterized by NMR (^1H, ^{13}C, ^{11}B, ^{19}F, ^{29}Si) spectroscopy as well as IR spectroscopy and conductivity measurements. The reactions of this species with simple nucleophiles are also reported.

Introduction

Several studies have demonstrated the ability of strong nucleophiles (e.g., amines and amides) to form four-coordinate salts with organosilanes bearing a highly electronegative substituent (eq 1).[1] Crystal structures have verified the formation of 1:1 adducts of pyridine with Me_3SiBr and Me_3SiI.[2] However,

$$Me_3SiX + Nu \rightleftharpoons [Me_3SiNu]^+X^- \qquad (1)$$

$$Nu = HMPT, DMF, Ph_3PO, DMSO, amines$$

$$X = OSO_2CF_3^-, ClO_4^-, I^-, Br^-$$

the nature of the interaction of weaker nucleophiles, such as nitriles, with functionalized organosilanes is less clear. Studies probing acetonitrile interaction with Me_3SiX (X = Cl, Br, I, OSO_2CF_3)[3] did not generate evidence to support significant nitrile–silicon coordination. Lambert and co-workers[4] have claimed that silyl perchlorates are ionized in acetonitrile solvent by means of cryoscopic molecular weight measurements, conductivity, and ^1H, ^{13}C, and ^{15}N NMR spectroscopy. However, Olah et al.[5] have refuted these claims, concluding that the silyl perchlorates are covalent esters. Generation of $[R_3Si(NCCH_3)_n]^+$ species has been claimed on the basis of a comparative cyclic voltammetric study of Ph_3C^+ with R_3E^+ generated electrochemically from a series of compounds of the general formula, $R_3E–ER_3$, where E = Si, Ge.[6] Half-wave potentials are given to support the claim. To date, the only spectroscopic evidence for silylnitrilium ions has been provided by Olah's group in the form of ^1H and ^{13}C NMR data which suggest the presence of the equilibrium shown in eq 2.[7,8]

$$CH_3CN + Me_3SiI \overset{\text{acetone}}{\rightleftharpoons} [Me_3Si(NCCH_3)]^+I^- \qquad (2)$$

Although the tetraphenylborate anion is less reactive toward some electrophilic cationic compounds than other widely used counterions (i.e., ClO_4^-, BF_4^-, PF_6^-),[9] it still suffers from facile degradation and a tendency to π-coordinate through one of its phenyl groups.[10] We performed hydride abstractions on silanes with triphenylcarbenium tetraphenylborate[11] in attempts to generate silicenium ions, but observed only ambiguous results. We recently reported the synthesis of a new hydride abstraction reagent, $Ph_3C^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ (trityl TFPB), which gives cleaner reactions than triphenylcarbenium tetraphenylborate.[12] An independent study by Kira, Sakurai, and co-workers has shown the utility of trityl TFPB in the generation of silyloxonium ions.[13] In this article, we present chemical and spectroscopic evidence in support of stable silylnitrilium ions in nitrile solvents. These species were generated in high yields by the treatment of a hydridosilane with trityl tetrakis[bis(3,5-trifluoromethyl)phenyl]borate (trityl TFPB).

Results and Discussion

Generation and NMR Characterization of Silylnitrilium Ions. Treatment of a silane with 1 equiv of trityl TFPB in a nitrile solvent (acetonitrile, butyronitrile, isobutyronitrile, or trimethylacetonitrile) results in high yields of Ph_3CH and a stable silicon-containing species. We propose that the initially formed silicenium ion that results after hydride abstraction from the silane is stabilized by the nitrile solvent to produce silylnitrilium TFPB

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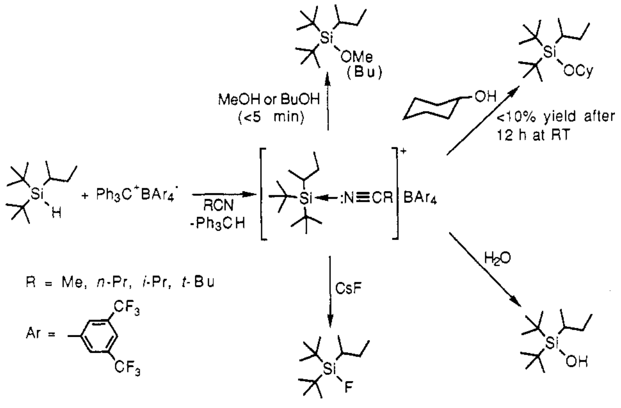

Scheme I. Production of the Silylnitrilium TFPB Species, $[t\text{-Bu}_2(s\text{-Bu})\text{Si(NCR)}]^+\text{TFPB}^-$, and Its Reactions with Simple Nucleophiles

(Scheme I). However, we cannot rule out the possibility of nucleophile-assisted hydride abstraction. Complete consumption of the silane takes from a few seconds to about 7–10 h for the more sterically hindered silanes, $t\text{-Bu}_2(s\text{-Bu})\text{SiH}$ and $t\text{-Bu}_2\text{SiH}_2$. For $t\text{-Bu}_2\text{SiH}_2$, abstraction of only one hydride was observed. Tables I and II list the ^{1}H, ^{13}C, and ^{29}Si NMR data of the silylnitrilium TFPB species studied thus far. Typically, formation of the silylnitrilium species is greater than 90%, with a small amount of hydrolysis (5–10%) to the silanol or disiloxane, as determined by ^{1}H NMR spectroscopy. ^{1}H and ^{13}C NMR chemical shifts of the TFPB anion, for all of the silylnitrilium species, are nearly identical (±0.02 ppm) to its sodium and trityl salts. The ^{11}B and ^{19}F NMR shifts, at least for $[(t\text{-Bu})_2(s\text{-Bu})\text{Si(NCCD}_3)]^+\text{TFPB}^-$, are each within ±0.1 ppm of trityl TFPB. This shows that the TFPB anion remains intact throughout the reaction.

A nitrile solution of silylnitrilium TFPB persists as a clear, light yellow mixture and is reasonably stable for several days, the main decomposition product being the silanol or disiloxane. For example, the species $[t\text{-Bu}_2(s\text{-Bu})\text{Si(NCPr)}]^+\text{TFPB}^-$ (Pr = $n\text{-C}_3\text{H}_7$) in butyronitrile predominantly showed silylnitrilium TFPB and $t\text{-Bu}_2(s\text{-Bu})\text{SiOH}$ along with a small amount of $t\text{-Bu}_2(s\text{-Bu})\text{SiF}$ after 7 days, as could be seen by ^{29}Si NMR spectroscopy. Attempts to isolate several silylnitrilium TFPB species have thus far proved unsuccessful. Removal of the butyronitrile from $[\text{Ph}_2\text{MeSi(NCPr)}]^+\text{TFPB}^-$ by vacuum or high dilution (50:1) with a noncoordinating solvent (i.e., toluene) causes decomposition to several products, of which only Ph_2MeSiF (<10%) could be unambiguously identified by GC–MS.

Addition of water to any of the silylnitrilium TFPB species produced the expected silanol or disiloxane (Scheme I). Addition of CsF gave immediate conversion to the fluorosilane. Treatment of $[t\text{-Bu}_2(s\text{-Bu})\text{Si(NCPr)}]^+\text{TFPB}^-$ with 1 equiv of methanol or butanol produced the alkoxysilane within a few minutes, but the more sterically hindered cyclohexanol gave <10% of the alkoxysilane after several hours. The addition of 1 equiv of Ph_3P to $[\text{Ph}_2\text{MeSi(NCPr)}]^+\text{TFPB}^-$ gave no evidence of phosphine coordination since the ^{29}Si NMR spectrum remained unchanged. Addition of 5 equiv of pyridine to $[t\text{-Bu}_2(s\text{-Bu})\text{Si(NCPr)}]^+\text{TFPB}^-$ produced a new ^{29}Si NMR resonance at δ 33.26 with complete disappearance of the silylnitrilium ion peak. This new resonance has been tentatively assigned to the silylpyridinium ion, and addition of water to this solution gives the expected silanol, $t\text{-Bu}_2(s\text{-Bu})\text{SiOH}$.

Table I lists the ^{1}H and ^{13}C NMR data for the silylnitrilium TFPB species. The ^{1}H and ^{13}C NMR shifts are, for the most part, not unusual for four-coordinate organosilicon compounds. This suggests that a significant portion of the positive charge of the silylnitrilium species is localized on the nitrile nitrogen. One can then view a silylnitrilium ion as a typical four-coordinate organosilicon compound possessing an electronegative group. ^{1}H and ^{13}C NMR chemical shifts of the silylnitrilium species appear to correlate roughly to the corresponding halosilane. For example, the silylnitrilium species, $[(t\text{-Bu})_2\text{SiH(NCCD}_3)]^+\text{TFPB}^-$, displays a ^{1}H NMR signal for the SiH proton at δ 4.286, which is similar to the signal of the chlorinated derivative, $t\text{-Bu}_2\text{SiHCl}$ (δ 4.24).

^{1}H and ^{13}C NMR shifts for the coordinated nitrile were not seen. This is not surprising since the majority of CD_3CN is free solvent and the coordinated CD_3CN would need to have significantly different ^{13}C NMR shifts to be visible. Also, if fast exchange of the nitrile group with bulk solvent is taking place as shown in Scheme II by either path a or path b, ^{13}C NMR chemical shifts for both carbons of CD_3CN would be averaged between free nitrile and coordinated nitrile on the NMR time scale. Since an averaged chemical shift caused by rapid equilibration between two species is dependent on the concentrations of the two species, the fast equilibria shown in Scheme II would result in an averaged shift virtually unchanged from that of the CD_3CN solvent due to the large concentration of free CD_3CN.

^{29}Si NMR data for silylnitrilium ions are given in Table II. Low-temperature ^{29}Si NMR of $[t\text{-Bu}_2(s\text{-Bu})\text{Si(NCPr)}]^+\text{TFPB}^-$ in butyronitrile gave no evidence of Si–F interaction down to −60 °C. The peak width corresponding to the silylnitrilium ion remained constant (6–7 Hz) down to −60 °C and underwent a slight upfield chemical shift change to δ 28.4. If the stable silicon species were free silicenium ions, chemical shifts should appear significantly downfield from the values listed. ^{29}Si chemical shifts for free silicenium ions have been predicted to appear 100–275 ppm downfield of tetramethylsilane.[14] Tilley's base-free silylene complex, $\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}[\text{S}(p\text{-tol})]_2\text{NCMe}\}^+\text{BPh}_4^-$,[15] can be viewed as an example of a ruthenium-stabilized silicenium ion. This complex has a room-temperature ^{29}Si chemical shift of δ 250.6. The acetonitrile-coordinated complex has a ^{29}Si NMR shift at δ 58.30, which is almost 200 ppm upfield of the base-free complex. With this in mind, the ^{29}Si NMR shift values listed in Table II are reasonable for silylnitrilium ions. As was the case in comparing the ^{1}H NMR chemical shifts of $[(t\text{-Bu})_2\text{SiH(NCCD}_3)]^+\text{TFPB}^-$ and $t\text{-Bu}_2\text{SiHCl}$, the ^{29}Si NMR chemical shifts are also somewhat similar at δ 19.3 and δ 27.1, respectively. The values of their respective ^{29}Si–^{1}H coupling constants ($^1J_{\text{SiH}}$) are 242 and 228 Hz. These values once again support a view that the silylnitrilium species generated in this study are similar to organosilicon compounds possessing an electronegative substituent. The ^{29}Si chemical shift of δ −94.9 for the silatrane derivative, $[(\text{PrCN})\text{Si(OCH}_2\text{CH}_2)_3\text{N}]^+\text{TFPB}^-$ is fairly typical of the shifts of other silatrane compounds.

Since data for coordinated nitrile cannot be obtained by ^{1}H NMR spectroscopy, the question of whether there are one, two, or possibly even three nitrile groups coordinated to the silicenium ion cannot be answered directly. It was previously stated that ^{1}H, ^{13}C, and ^{29}Si NMR chemical shift data support four-coordinate silylnitrilium ions; however, the following factors can also be considered: (1) For the silylnitrilium species $\{t\text{-Bu}_2(s\text{-Bu})\text{Si}[\text{NC}(t\text{-Bu})]\}^+\text{TFPB}^-$ in trimethylacetonitrile solvent, large steric consequences would have to be overcome for coordination of two trimethylacetonitrile groups to the already very sterically hindered $t\text{-Bu}_2(s\text{-Bu})\text{Si}$ moiety. (2) The ^{29}Si NMR shifts are generally independent of the coordinated nitrile (±0.5 ppm with respect to the silylacetonitrilium species), strongly indicative that all of the silylnitrilium species are of the same type (four-, five-, or six-coordinate).

All of the ^{29}Si NMR shifts for the alkylated or phenylated silylnitrilium ions are consistently 12–30 ppm downfield of that of the starting hydrosilane. Considering the possibility that perhaps only one nitrile group is coordinating with the bulky $t\text{-Bu}_2(s\text{-Bu})\text{Si}$ moiety but that two or three nitrile groups may

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Table I. ^{1}H and ^{13}C NMR Data of Silylnitrilium Ions in CD_3CN

species generated	^{1}H (δ)	^{13}C (δ)
$[t\text{-}Bu_2(s\text{-}Bu)Si(NCCD_3)]^+TFPB^-$	1.020 (t, J = 7.5 Hz, CH_3), 1.185 (s, 18 H, *t*-Bu), 1.211 (d, J = 7.5 Hz, CH_3), 1.35 (m, *s*-Bu), 1.85 (m, 1 H, *s*-Bu)[a]	13.70, 14.19, 22.13, 25.44 (*s*-Bu), 20.74 ($C(CH_3)_3$), 28.22 ($C(CH_3)_3$)
$[t\text{-}BuMe_2Si(NCCD_3)]^+TFPB^-$	0.544 (s, 6 H, CH_3), 1.047 (s, 9 H, *t*-Bu)	−5.26 ($SiCH_3$), 18.12 ($C(CH_3)_3$), 24.95 ($C(CH_3)_3$)
$[Et_3Si(NCCD_3)]^+TFPB^-$	1.07 (m, 15 H, Et)	4.28, 6.22 (Et)
$[Ph_2MeSi(NCCD_3)]^+TFPB^-$	1.190 (s, 3 H, CH_3), 7.2–7.8 (m, Ph)	−2.99 (CH_3), 129.9, 133.7, 135.8 (Ph)
$[(t\text{-}Bu)_2SiH(NCCD_3)]^+TFPB^-$	1.138 (s, 18 H, *t*-Bu), 4.286 (s, 1 H, SiH)	19.99 ($C(CH_3)_3$), 26.56 ($C(CH_3)_3$)
$[(CD_3CN)Si(OCH_2CH_2)_3N]^+TFPB^-$	3.216 (t, J = 5.9 Hz, 6 H, NCH_2), 3.956 (t, J = 5.9 Hz, 6 H, OCH_2)	52.76, 59.48
$[(EtO)_3Si(NCCD_3)]^+TFPB^-$	1.19 (t, J = 6.0 Hz, 9 H, CH_3), 3.82 (q, J = 6.0 Hz, 6 H, CH_3)	18.40 (CH_3), 59.99 (CH_2)

[a] Due to the presence of impurities, peak assignments are tentative for the *s*-Bu group.

Scheme II. Possible Routes of Nitrile Exchange for Silylnitrilium Ions

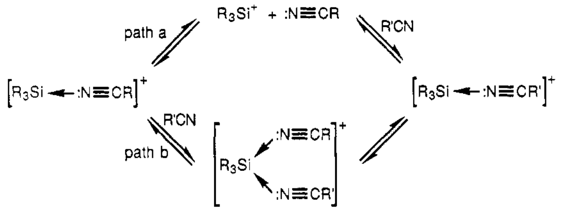


Table II. ^{29}Si NMR Data and ν(CN) Stretching Frequencies for Silylnitrilium Species

species generated	^{29}Si (δ)[a]	ν(CN) (cm^{-1})[b]
$[t\text{-}Bu_2(s\text{-}Bu)Si(NCPr)]^+TFPB^-$	30.39	2301
$[t\text{-}BuMe_2Si(NCPr)]^+TFPB^-$	36.50	2309
$[Et_3Si(NCPr)]^+TFPB^-$	37.01	2310
$[Ph_2MeSi(NCR)]^+TFPB^-$	4.23	2310
$[(t\text{-}Bu)_2SiH(NCR)]^+TFPB^-$	19.3 (d, J_{SiH} = 242 Hz)	2306
$[(PrCN)Si(OCH_2CH_2)_3N]^+TFPB^-$	−94.9	2331
$[(EtO)_3Si(NCPr)]^+TFPB^-$	*c*	2389

[a] All ^{29}Si NMR spectra were done in butyronitrile except Ph_2MeSiH and $t\text{-}Bu_2SiH_2$, which were done in CD_3CN. [b] In butyronitrile. [c] Unable to be determined.

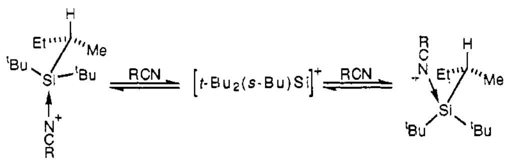
coordinate with the less bulky silyl moieties (Et_3Si, Ph_2MeSi, $t\text{-}BuMe_2Si$), the ^{29}Si NMR shifts for the five- or six-coordinate silicon species would be expected to be farther upfield than what is observed.[16] Of course, five- or six-coordinate species could coincidentally possess similar ^{29}Si NMR shifts to the four-coordinate $[t\text{-}Bu_2(s\text{-}Bu)Si(NCR)]^+$ cation. In our opinion, the silylnitrilium ions generated in this study are four-coordinate, with stabilization resulting from only one nitrile group.

Another question that needs to be addressed is whether or not fast exchange of nitrile is taking place (Scheme II). We feel that path b is unlikely for reasons presented in the previous two paragraphs. Evidence for the equilibrium shown as path a has recently been published by Tilley for the complex, $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]^+OTf^-$.[17] Low-temperature ^{1}H NMR showed the exchange of coordinated nitrile with free nitrile via a dissociative mechanism.

Although a similar study with the silylnitrilium species is not possible with the large excess of nitrile solvent, other evidence suggests that coordinated nitrile is exchanging. When equal amounts of equal molar solutions of $[t\text{-}Bu_2(s\text{-}Bu)Si(NCPr)]^+TFPB^-$ in butyronitrile (^{29}Si NMR δ 30.39 relative to internal TMS at room temperature) and $\{t\text{-}Bu_2(s\text{-}Bu)Si[NC(t\text{-}Bu)]\}^+TFPB^-$ in trimethylacetonitrile (^{29}Si NMR δ 31.07) are mixed, only one ^{29}Si NMR signal is observed at δ 30.46. If no exchange of nitrile had taken place, two signals would have been observed. A ^{29}Si NMR signal at δ 30.73 should have been measured if the mixture consisted of equal amounts of silylbutyronitrilium TFPB and silyltrimethylacetonitrilium TFPB in rapid equilibrium with each other. The new signal at δ 30.46 could be interpreted as an averaged ^{29}Si signal between the two silylnitrilium species with the butyronitrile-coordinated species predominating. An estimated ratio of butyronitrilium TFPB to silyltrimethylacetonitrilium TFPB of 90:10 can be inferred from the ^{29}Si chemical shifts. This ratio is consistent with the view that butyronitrile has fewer steric requirements as compared to trimethylacetonitrile and should be expected to coordinate with the sterically hindered $t\text{-}Bu_2(s\text{-}Bu)Si^+$ species with greater ease.

These results are based on the assumption that the dielectric constant of trimethylacetonitrile is not significantly different from that of butyronitrile. This should be a valid assumption since the measured dielectric constants of butyronitrile (ϵ = 20.3) and isobutyronitrile (ϵ = 20.4) are nearly identical.[18] Also, the ^{29}Si chemical shift of $[t\text{-}Bu_2(s\text{-}Bu)Si(NCCD_3)]^+TFPB^-$ in acetonitrile-d_3 (δ 30.42) is not significantly different from those of the PrCN-coordinated (δ 30.39) and *i*-PrCN-coordinated (δ 30.32) species, even though the dielectric constant of CH_3CN (ϵ = 37.5) is considerably greater than those of the other nitriles.

The diastereotopic *t*-Bu groups of $[t\text{-}Bu_2(s\text{-}Bu)Si(NCCD_3)]^+TFPB^-$ do not appear to be diastereotopic by ^{1}H and ^{13}C NMR spectroscopy. One explanation is fast exchange of nitrile on the NMR time scale via a dissociative mechanism, causing the *t*-Bu groups to become equivalent (eq 3). Of course the diastereotopic *t*-Bu groups may coincidentally have the same ^{1}H and ^{13}C NMR chemical shifts. It should be noted that the diastereotopic *t*-Bu groups have different ^{1}H and ^{13}C NMR shifts for similar compounds, $t\text{-}Bu_2(s\text{-}Bu)SiH$, $t\text{-}Bu_2(s\text{-}Bu)SiF$, and $t\text{-}Bu_2(s\text{-}Bu)SiOH$.



(3)

IR Spectroscopy. Use of infrared spectroscopy to determine the presence of coordinated nitrile is well documented.[19] The infrared spectra of the silylnitrilium TFPB solutions provide evidence for nitrile coordination. An IR spectrum of a 0.30 M trityl TFPB solution in butyronitrile shows a spectrum nearly identical to that of pure butyronitrile except for a shoulder on the ν(CN) stretching frequency for free butyronitrile. This shoulder might be explained by weak coordination of nitrile with the trityl cation. Addition of 1 equiv of Ph_2MeSiH to trityl TFPB in

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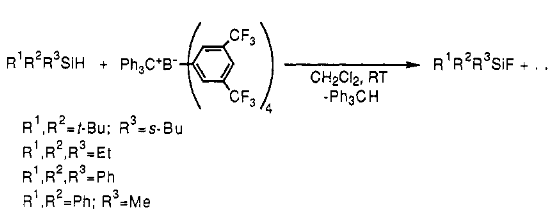
butyronitrile shows a new ν(CN) stretching band at 2310 cm^{-1} associated with the silylnitrilium ion. This stretching frequency is 61 cm^{-1} higher than the ν(CN) stretch for free butyronitrile (2249 cm^{-1}). Treatment of this solution with water resulted in complete disappearance of the 2310 cm^{-1} band. An increase in the ν(CN) stretching frequency for coordinated nitriles is due to an increase in the force constant of the CN bond.[20] The effective electronegativity of the nitrile nitrogen is increased, which results in a strengthening of the CN σ-bond. For comparison, an IR spectrum of $BF_3{\cdot}OEt_2$ in butyronitrile displayed the ν(CN) stretching frequency at 2340 cm^{-1} for the boron trifluoride species, $F_3B(NCPr)$. This ν(CN) stretch is 91 cm^{-1} greater than that of free butyronitrile and compares well with the acetonitrile adduct $F_3B(NCCH_3)$, which is 100 cm^{-1} greater than free CH_3CN.[21]

The IR data measured in butyronitrile for other silylnitrilium ions are given in Table II. The alkylated or phenylated species all have a ν(CN) stretch 50–60 cm^{-1} higher than that of free butyronitrile, while the silatrane derivative, $[(PrCN)Si(OCH_2CH_2)_3N]^+TFPB^-$, and $[(EtO)_3Si(NCPr)]^+TFPB^-$ possess much higher ν(CN) stretches of 2331 and 2389 cm^{-1}, respectively. These higher ν(CN) stretching frequencies correspond to a stronger coordination of butyronitrile to the silicenium ion due to the presence of the electron-withdrawing alkoxy groups. The coordinated nitrile ν(CN) stretching frequency for the silatrane derivative is 58 cm^{-1} lower than the (triethoxysilyl)nitrilium species, showing the significant intramolecular Si–N bonding interaction in the silatrane. However, this intramolecular Si–N bonding is not enough to prevent nitrile coordination. Solutions (0.30 M) of Me_3SiI and Me_3SiOTf in butyronitrile did not show any coordinated ν(CN) stretch.

$Ph_2MeSiOClO_3$, made by combining Ph_2MeSiH and $Ph_3C^+ClO_4^-$ in butyronitrile,[4] did show a weak band at 2280 cm^{-1}, which is significantly different from the 2310 cm^{-1} band for $[Ph_2MeSi(NCPr)]^+TFPB^-$. Also, the ^{29}Si NMR shift for $Ph_2MeSiOClO_3$ (0.18 M) in butyronitrile appears at δ 17.0 as compared to δ 4.23 for $[Ph_2MeSi(NCPr)]^+TFPB^-$. The most reasonable conclusion we can draw is that weak nitrile coordination is present. However, the perchlorate still possesses a significant interaction with the silicon.

Conductivity Data. Additional evidence for the formation of silylnitrilium ions is provided by conductivity data. The conductivity of a 0.090 M solution of trityl TFPB decreases only slightly with the addition of 1 equiv of Ph_2MeSiH and then remains unchanged at 2230 $\mu\Omega^{-1}$ cm^{-1} with excess silane. If the newly formed species were covalent, a much more dramatic decrease in conductivity would have been expected. A slight increase in conductivity associated with initial additions of silane is probably due to some hydrolysis of the silylnitrilium species formed. Addition of 0.5 equiv of water caused a large increase in conductivity to 2650 $\mu\Omega^{-1}$ cm^{-1}.

Reaction of Trityl TFPB and Hydridosilanes in Noncoordinating Solvent. The reaction between trityl TFPB and a trialkyl- or triarylsilane in a solvent with very poor coordinating ability (i.e., CH_2Cl_2) results in formation of Ph_3CH and the fluorosilane as the major (>90% by GC) silicon-containing product (eq 4). Numerous byproducts prevent trityl TFPB from being a viable fluorination reagent. Complete consumption of the hydridosilane took from a few minutes (Et_3SiH, Ph_2MeSiH, Ph_3SiH) to several hours (t-Bu_2(s-Bu)SiH).



(4)

Fluorosilane formation probably arises through initial hydride abstraction from the silane, producing a silicenium ion intermediate. The extremely reactive silicenium ion then abstracts fluoride from a CF_3 group of the TFPB anion. There are several examples where generation of a silicenium ion intermediate via hydride abstraction from a hydridosilane has been proposed.[22] However, the existence of long-lived silicenium ions in solution has been a highly debated subject.[4,5]

An attempt to detect an intermediate silicenium ion by ^{29}Si NMR for the sterically hindered silane, t-Bu_2(s-Bu)SiH, showed only starting silane and a doublet corresponding to the fluorosilane. If the silicenium ion is formed, it must be short-lived on the ^{29}Si NMR time scale or is not present in high enough concentration. An intermediate in which fluoride transfer to the t-Bu_2(s-Bu)Si moiety occurs at the same time as hydride abstraction cannot be eliminated. However, serious steric consequences would have to be overcome for this to occur. Attempts to generate the silylnitrilium species at room temperature in methylene chloride solvent with only 5 equiv of CH_3CN present gave results nearly identical to pure CH_2Cl_2 with the fluorosilane being produced as the major product. These reaction conditions are similar to those in which a butyronitrile solution of $[Ph_2MeSi(NCPr)]^+TFPB^-$ was diluted (>50:1) with toluene, leading to the decomposition of the silylnitrilium species to several products. Among these, Ph_2MeSiF was identified by GC–MS (<10% yield).

One-Pot Synthesis of the New Bulky Silanes, *t*-Bu$_2$(*s*-Bu)SiH and *t*-Bu$_2$(Cy)SiH. The new bulky silane, *sec*-butyldi-*tert*-butylsilane, was synthesized by a convenient one-pot procedure using in situ generated 1,1-di-*tert*-butyl-*trans*-2,3-dimethylsilacyclopropane (**1**) (Scheme III).[23] Treatment of a freshly prepared THF solution of silirane **1** with $LiAlH_4$ followed by addition of water gives the net result of hydrogenolysis of one of the Si–C bonds of the silacyclopropane ring. The *sec*-butyl group of t-Bu_2(s-Bu)SiH possesses a chiral carbon next to the silicon, which causes the *tert*-butyl groups to be diastereotopic as seen in its ^1H and ^{13}C NMR spectra. In a similar fashion, treatment of in situ generated silirane **2**[24] with $LiAlH_4$ and water gives a 48% yield of cyclohexyldi-*tert*-butylsilane (t-Bu_2(Cy)SiH). In comparing these two new bulky silanes in their reactions with trityl TFPB in methylene chloride, the Si–H bond in t-Bu_2(s-Bu)SiH appears to be more sterically hindered than that in t-Bu_2(Cy)SiH since t-Bu_2(s-Bu)SiH is consumed in about 7 h where t-Bu_2(Cy)SiH reacts completely in about 15 min.

Conclusions

Use of the nonnucleophilic anion, tetrakis[bis(3,5-trifluoromethyl)phenyl]borate, permits the observation of stable silylnitrilium species in nitrile solvents. Solutions of silylnitrilium TFPB are reasonably stable for days at room temperature under a nitrogen atmosphere. Treatment of these solutions with nucleophiles (H_2O, MeOH, BuOH, F^-) yields the expected products (silanols, disiloxanes, alkoxysilanes, fluorosilanes, respectively). Infrared spectroscopy clearly indicates the presence of coordinated nitrile, and a conductivity study of $[Ph_2MeSi(NCPr)]^+TFPB^-$ shows conductance similar to that of trityl TFPB. At similar concentrations (0.18 M), the silyl perchlorate, $Ph_2MeSiOClO_3$,

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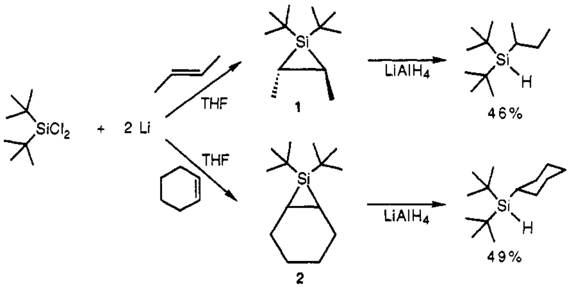
Scheme III. One-Pot Procedure for the Synthesis of *t*-Bu_2(*s*-Bu)SiH and *t*-Bu_2(Cy)SiH



gives different IR and ^{29}Si NMR data from the silylnitrilium complex, $[Ph_2MeSi(NCPr)]^+TFPB^-$, the former showing significant interaction of the perchlorate anion with the silicon.

Experimental Section

Materials and General Procedures. Trityl tetrakis[bis(3,5-trifluoromethyl)phenyl]borate (trityl TFPB) was synthesized from trityl triflate and sodium TFPB.[11] Di-*tert*-butyldichlorosilane was synthesized by chlorination of commercially available (Aldrich) di-*tert*-butylchlorosilane using benzoyl peroxide in CCl_4. Hydridosilanes were obtained commercially or produced by reduction of the corresponding chlorosilane with $LiAlH_4$. $HSi(OCH_2CH_2)_3N$ was synthesized by a literature method.[25] Butyronitrile, isobutyronitrile, and trimethylacetonitrile were dried by distillation twice from P_2O_5 and storage over 4-Å molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl just prior to use. CH_2Cl_2 was distilled from P_2O_5 immediately before use. Hexane was stirred over H_2SO_4 and distilled. Benzene was shaken with H_2SO_4, dried by azeotropic removal of water, and distilled into a storage bottle with 4-Å molecular sieves. All experiments were performed under a dry nitrogen atmosphere, and air-sensitive compounds were transferred in an argon-filled glovebox.

^{1}H (270.17 or 399.78 MHz), ^{13}C (67.94 or 100.53 MHz), and ^{29}Si (53.67 or 79.43 MHz) NMR spectra were obtained on a JEOL GSX270 or JEOL GSX400 spectrometer. ^{29}Si NMR spectra were acquired by using either a refocused INEPT pulse sequence[26] or by standard acquisition (>1000 transients, pulse width = 45°, pulse delay = 30 s). ^{11}B (128.3 MHz) and ^{19}F (376.1 MHz) NMR spectra were obtained on a JEOL GSX400 spectrometer with chemical shifts reported relative to external $BF_3{\cdot}OEt_2$ in $CDCl_3$ (0 ppm) and $CFCl_3$ in $CDCl_3$ (0 ppm), respectively. Infrared spectra of nitrile solutions were accomplished through use of a CaF cell (0.1 mm path length) and were recorded on a Mattson Cygnus 25 FT-IR. Elemental analyses were performed by Desert Analytics in Tucson, AZ. Mass spectra were obtained on a Hewlett-Packard 5988A mass spectrometer at 70 eV. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Conductivity data were obtained with a Cole-Parmer Model 1481-60 conductivity meter with dip cell.

***sec*-Butyldi-*tert*-butylsilane.** 1,1-Di-*tert*-butyl-*trans*-2,3-dimethylsilacyclopropane was prepared in solution by combining Li dispersion (0.45 g, 65 mmol), *trans*-2-butene (5 g), *t*-Bu_2SiCl_2 (3.0 g, 14 mmol), and 10 mL of THF using previously reported procedures.[23,27] $LiAlH_4$ (0.45 g, 12 mmol) was added through a neck of the flask in small portions over a 15-min period followed by stirring for 30 min. Water (3 mL) was added *very slowly* by syringe, followed by the addition of 20 mL of hexane. The orange solution was decanted away from the unreacted lithium and $LiAlH_4$. The hexane and THF were removed by vacuum, and the remaining liquid was distilled by molecular distillation (45 °C, 2 Torr), giving 1.3 g (46% yield) of *sec*-butyldi-*tert*-butylsilane (99% pure by GC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (m, 1 H, CH), 0.98 (t, J = 7.5 Hz, 3 H, CH_3), 1.062 (s, 9 H, *t*-Bu), 1.069 (s, 9 H, *t*-Bu), 1.16 (d, J = 7.5 Hz, 3 H, CH_3), 1.39 (m, 1 H, CH_2), 1.78 (m, 1 H, CH_2), 3.32 (s, 1 H, SiH); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 13.96, 16.16, 19.77, 27.30 (*s*-Bu), 19.77 (CCH_3), 29.44, 29.55 ($C\mathit{C}H_3$); ^{29}Si NMR (79.43 MHz, $CDCl_3$) δ 17.8 (d, J_{SiH} = 180 Hz); IR (neat) 2086 cm^{-1} (ν(SiH)); MS (EI) 200 (4.0, M^+), 143 (26, $M^+ - C_4H_9$), 57 (100, $C_4H_9^+$). Anal. Calcd for $C_{12}H_{28}Si$: C, 71.91; H, 14.08. Found: C, 71.82; H, 13.86.

Cyclohexyldi-*tert*-butylsilane. Li dispersion (0.45 g, 65 mmol), cyclohexene (10 mL, 99 mmol), and 20 mL of THF were combined in a 100-mL 2-necked flask fitted with a condenser/N_2 inlet and rubber septum. Di-*tert*-butyldichlorosilane (3.0 g, 14.1 mmol) was added by syringe and the contents were sonicated using a bath sonicator for 8 h, producing 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane.[24] $LiAlH_4$ (0.45 g, 12 mmol) was added through a flask neck over a 5-min period and sonication continued for 15 min. H_2O (3 mL) was added *very slowly* to dispose of any leftover Li and $LiAlH_4$, followed by the addition of another 20 mL of water. This was poured into 50 mL of ether and the entire mixture was gravity filtered. The ether layer was separated, and the aqueous layer was extracted with another 50-mL portion of ether. Combination of the ether portions, drying over $MgSO_4$, and removal of ether by vacuum gave a clear, yellow liquid, which was purified by molecular distillation (60 °C, 0.3 Torr) giving 1.56 g (49% yield) of cyclohexyldi-*tert*-butylsilane (>98% pure by GC): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.01 (m, 1 H, Cy), 1.07 (s, 18 H, *t*-Bu), 1.25 (m, 3 H, Cy), 1.48 (m, 2 H, Cy), 1.74 (m, 3 H, Cy), 1.85 (m, 2 H, Cy), 3.20 (s, 1 H, SiH); ^{13}C NMR (67.94 MHz, $CDCl_3$) δ 19.79 ($(CH_3)_3\mathit{C}$), 29.46 ($(\mathit{C}H_3)_3C$), 24.83, 26.86, 28.70, 30.32 (Cy); ^{29}Si NMR (53.67 MHz, $CDCl_3$) δ 14.4 (d, J_{SiH} = 176 Hz); IR (neat) 2091 cm^{-1} (ν(SiH)); MS (EI) 226 (3.7, M^+), 169 (33, $M^+ - C_4H_9$), 87 (100). Anal. Calcd for $C_{14}H_{30}Si$: C, 74.24; H, 13.35. Found: C, 73.88; H, 13.55.

General Procedure for Generation of Silylnitrilium TFPB. Trityl tetrakis[bis(3,5-trifluoromethyl)phenyl]borate (trityl TFPB) (100 mg, 0.090 mmol) and 0.5 mL of CD_3CN were mixed in a 5-mm NMR tube, giving an orange-yellow solution, and sealed with a rubber septum. Hydridosilane (0.090 mmol) was introduced by syringe through the septum, and the contents were shaken vigorously for 30 s. Monitoring the reaction progress by GC showed that *t*-Bu_2(*s*-Bu)SiH and *t*-Bu_2SiH_2 took 7–10 h to react completely, while all other silanes were consumed within minutes producing a clear, light yellow solution. Ph_3CH, identified by comparison of its ^{1}H and ^{13}C NMR signals as well as its GC–MS data with an authentic sample, was produced in quantitative yield as determined by integration of its ^{1}H NMR signals relative to those signals corresponding to the borate and silylnitrilium ions. Due to a trace amount of water in the nitrile solvent, 5–10% of the silanol or disiloxane byproduct was identified by comparison of its ^{1}H and ^{29}Si NMR chemical shifts with the shifts of an authentic sample. The NMR signals assigned to silylnitrilium TFPB are listed in Tables I and II, and those for Ph_3CH and TFPB are as follows: ^{1}H NMR (400 MHz, CDCN) δ 5.63 (s, 1 H, $Ph_3C\mathit{H}$), 7.15–7.30 (m, 15 H, Ph_3CH), 7.68 (s, 4 H, borate H_p), 7.73 (s, 8 H, borate H_o); ^{13}C NMR (100.5 MHz, CD_3CN) δ 57.60, 127.3, 129.4, 130.3, 145.2 (Ph_3CH), 118.7 (m, borate C_p), 125.0 (q, J_{CF} = 273 Hz, CF_3), 130.1 (m, borate C_m), 135.7 (borate C_o), 162.7 (q, J_{BC} = 50 Hz, borate C_{ipso}); ^{11}B NMR (128.3 MHz, CD_3CN) δ -6.04; ^{19}F NMR (376.1 MHz, CD_3CN) δ -62.66.

Treatment of Silylnitrilium TFPB with Water. A nitrile solution of silylnitrilium TFPB (0.045–0.090 mmol, 0.08–0.18 M) was hydrolyzed by exposure to air for a few minutes or addition of excess water. The formation of silanol *t*-Bu_2(*s*-Bu)SiOH or disiloxanes $(Et_3Si)_2O$, $(Ph_2MeSi)_2O$, (*t*-$BuMe_2Si)_2O$, or (*t*-$Bu_2HSi)_2O$ in >90% yield (determined by GC) with respect to the starting silylnitrilium ion was confirmed by comparison of the ^{1}H and ^{29}Si NMR chemical shifts and GC–MS data with those of an authenic sample. Authenic samples of disiloxanes were prepared by hydrolysis of the chlorosilane, and *t*-Bu_2(*s*-Bu)SiOH was prepared by a previously reported method.[28] **$(Et_3Si)_2O$:** MS (EI) 246 (M^+, 0.8), 217 (M^+ - Et, 100), 189 (M^+ - Et - C_2H_4, 92). **(*t*-$BuMe_2Si)_2O$:** ^{29}Si NMR (butyronitrile) δ 10.17; MS (EI) 246 (M^+, 0.6), 189 ($M^+ - C_4H_9$, 15), 147 (100). **$(Ph_2MeSi)_2O$:** ^{29}Si NMR (CH_3CN) δ -9.39; MS (EI) 410 (M^+, 10), 395 (M^+ - Me, 100), 317 (M^+ - Me - C_6H_6, 57). **(*t*-$Bu_2HSi)_2O$:** ^{29}Si NMR (CD_3CN) δ 6.72; MS (EI) 302 (M^+, 1.6), 245 ($M^+ - C_4H_9$, 11), 133 (100). ***t*-Bu_2(*s*-Bu)SiOH:** ^{29}Si NMR ($CDCl_3$) δ 10.52; MS (EI) 159 ($M^+ - C_4H_9$, 19), 117 (22), 75 (100).

Reaction of [*t*-Bu_2(*s*-Bu)Si(NCPr)]$^+$TFPB$^-$ with MeOH, BuOH, Pyridine, and CsF. A butyronitrile solution of [*t*-Bu_2(*s*-Bu)Si(NCPr)]$^+$TFPB$^-$ (0.090 mmol, 0.18 M) was treated with 1 equiv of MeOH or BuOH to give >90% conversion of the silylnitrilium ion to

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t-Bu_2(*s*-Bu)SiOMe and *t*-Bu_2(*s*-Bu)SiOBu as determined by GC. Formation of these alkoxysilanes was verified by comparing GC–MS data with published data.[21,29] Addition of 5 equiv of dry pyridine resulted in a disappearance of the ^{29}Si NMR signal at δ 30.3 for the silylnitrilium ion and the appearance of a new peak at δ 33.26 corresponding to silylpyridinium TFPB. Addition of excess water gave quantitative conversion (determined by ^{29}Si NMR) to *t*-Bu_2(*s*-Bu)SiOH. Addition of 1 equiv of CsF to a CD_3CN solution described above produced >90% yield (determined by GC) of *t*-Bu_2(*s*-Bu)SiF determined by comparison of its ^{29}Si NMR chemical shift and GC–MS data with those of an authentic sample (data given below).

Treatment of Hydridosilanes and Trityl TFPB in CH_2Cl_2. Trityl TFPB (100 mg, 0.090 mmol) and 0.5 mL of CH_2Cl_2 were mixed in a 5-mm NMR tube. Hydridosilane (1 equiv) (Et_3SiH, Ph_2MeSiH, Ph_3SiH, *t*-Bu_2(*s*-Bu)SiH) was added by syringe and the contents were shaken. The mixture turned dark brown or green (in minutes or several hours depending on the silane used), and GC–MS analysis showed that Ph_3CH and the only identifiable silicon-containing product, the fluorosilane, were the major products. Formation of fluorosilane (Et_3SiF, Ph_2MeSiF, Ph_3SiF) was determined by comparison of its GC–MS data and/or ^{29}Si NMR chemical shift with an authenic sample obtained from fluorination of the chlorosilane with Na_2SiF_6.[30] *t*-Bu_2(*s*-Bu)SiF was synthesized as described below.

***sec*-Butyldi-*tert*-butylfluorosilane.** Equal molar amounts of trityl perchlorate and *t*-Bu_2(*s*-Bu)SiH were mixed together in acetonitrile for 12 h followed by the addition of 1 equiv of CsF. The solvent was removed by vacuum, and pure samples of *t*-Bu_2(*s*-Bu)SiF were obtained by preparatory GC: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93, 1.30, 1.82 (m, 1 H each, CH and CH_2), 0.98 (t, $J = 7.3$ Hz, 3 H, CH_3), 1.08 (s, 18 H, *t*-Bu), 1.13 (d, $J = 7.3$ Hz, 3 H, CH_3); ^{13}C NMR (67.94 MHz, $CDCl_3$) δ 13.90, 14.56, 24.92 (*s*-Bu), 20.86 (d, $J_{CF} = 12.6$ Hz, *C*H), 21.29, 21.39 (d, $J_{CF} = 7.2$ Hz, diastereotopic $\mathit{C}(CH_3)_3$), 27.98, 28.06 (diastereotopic $C(\mathit{C}H_3)_3$); ^{29}Si NMR (53.67 MHz, $CDCl_3$) δ 21.6 (d, $J_{SiF} = 305$ Hz); ^{19}F NMR ($CDCl_3$) δ −184.4; MS (EI) 218 (M^+, 3.5), 161 ($M^+ - C_4H_9$, 20), 77 (100). Anal. Calcd for $C_{12}H_{27}FSi$: C, 65.98; H, 12.46. Found: C, 66.21; H, 12.75.

Acknowledgment. Financial support from the Air Force Office of Scientific Research through Grant No. 91-0197 and from Dow Corning Corporation is gratefully acknowledged. We also thank Dr. Stephen Castellino for helpful discussions concerning the interpretation of NMR spectra and Ioana Stoenescu and Lisa Hasvold for technical assistance.

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