

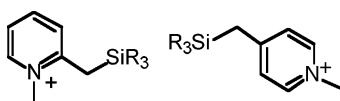
Comparison of Carbon–Silicon Hyperconjugation at the 2- and 4-Positions of the *N*-Methylpyridinium Cation

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N-Methyl-2-trialkylsilylmethylpyridinium cations **6a–c** and 4-trialkylsilylmethylpyridinium cations **5a–c** were prepared and investigated using ^{29}Si and ^{13}C NMR and single-crystal X-ray crystallography. Systematic differences in the ^{29}Si chemical shifts and ^{29}Si – ^{13}C one-bond coupling constants for these cations suggested that the Si–CH₂ bond interacts more strongly at the 2-position of the electron-deficient pyridinium ring than at the 4-position. This result is supported by the X-ray structures of the pyridinium cations **5b** and **6b**.

Introduction

The stabilization of positive charge by β -silicon (the silicon β -effect) has been the subject of much mechanistic interest over the past decade.^{1,2} This stabilization results from strong hyperconjugation between the polarizable C–Si bond and the vacant carbenium p-orbital (Figure 1).

Important insights into the silicon β -effect have been provided by a variety of methods, including solvolyses studies of β -trimethylsilyl-substituted esters,³ by ab initio calculations,^{4,5} which have been performed on primary, secondary, and tertiary β -silyl-carbocations, and X-ray structural studies on the stabilized β -triethylsilyl-substituted tropylium cation.⁶ The calculated structures of these, with some relevant structural parameters for the open cations, are summarized in Figure 2. The structural effects of $\sigma_{\text{C–Si}}-\text{p}$ conjugation in these cations are reflected in the C _{α} –SiH₃ bond distances, which are longer than normal C–Si single bonds, and the C _{α} –C _{β} bond distances, which are shorter than normal C–C single bonds. Comparison of these structural parameters between the primary, secondary, and tertiary cations



FIGURE 1. Carbon–silicon hyperconjugation.

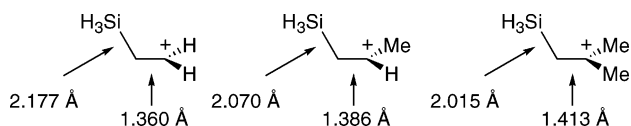


FIGURE 2. Calculated structures of primary, secondary, and tertiary β -silyl-carbenium ions.

shows that the contributions of the double-bond–no-bond resonance form (Figure 1) to the structures of these β -silyl cations varies with the electron demand of the cation, as does the degree of stabilization that β -silicon imparts on a cation. Thus β -silicon stabilizes primary, secondary, and tertiary cations by 38, 28, and 18 kcal/mol, respectively, compared to corresponding silicon-free cations.

The C–Si bond also interacts with neighboring π -systems of an aromatic ring by strong hyperconjugation, which can be represented by the valence structures **1–4**.² This interaction has profound effects on the properties of the aromatic ring, as demonstrated by a number of techniques including ^{19}F and ^{13}C NMR spectroscopy^{7,8} and electron spectroscopic measurements on the charge-

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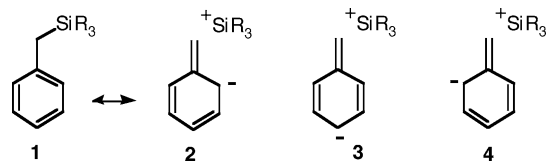
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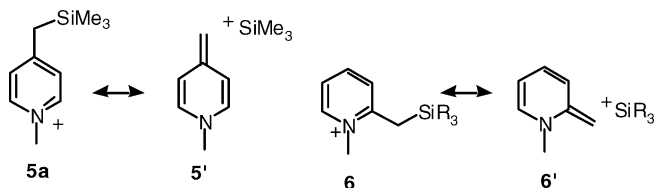
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transfer complexes of various benzyl-substituted group 4 derivatives with π -deficient systems.⁹



Lambert provided further evidence for the effects of silicon (and its larger congeners germanium and tin) hyperconjugation by measuring the one-bond coupling constants $^{13}\text{C}-\text{M}$ ($\text{M} = ^{29}\text{Si}$, ^{119}Sn) and $^{13}\text{C}-^{13}\text{C}$ in a series of 4-substituted benzyl-silanes, -germanes, and -stannanes.¹⁰ We recently investigated the structural effects arising from $\sigma-\pi$ conjugation between a C-Si bond and the π -deficient pyridinium ring in the triflate salt of **5a**.¹¹ The Si-CH₂ distance was significantly lengthened and the CH₂-C(aryl) bond distance was shortened compared to standard values for these types of bonds;¹² in addition to these structural effects, smaller but systematic effects on the C-C bond distance within the pyridinium ring were also observed. These structural effects reflect significant contributions of the resonance form **5'** to the ground-state structure; further support for this was provided in solution by systematic effects on the $^{29}\text{Si}-^{13}\text{C}$ one-bond coupling constant and by smaller effects on the $^{13}\text{C}-^{13}\text{C}$ one-bond coupling constant.



We were interested to compare the effects of hyperconjugation of C-Si bonds at the 4-position of the electron-deficient pyridinium cation with hyperconjugation at the 2-position, as represented by the resonance forms **6** and **6'**.

Results and Discussion

To this end, the *N*-methyl-4-trialkylsilylmethylpyridinium ions **5b** and **5c** and the *N*-methyl-2-trialkylsilylmethylpyridinium ions **6a-c** were prepared according to Scheme 1.

The ^{29}Si NMR data and $^{29}\text{Si}-^{13}\text{C}$ one-bond coupling constants for **6a-c**, **5a-c**, and the substituted pyridine precursors **7a-c** and **8a-c** are presented in Table 1.

Methylation of the substituted pyridine derivatives **7a-c** and **8a-c** to give the corresponding pyridinium ions **6a-c** and **5a-c** was achieved using methyl iodide, methyl triflate, or methyl tosylate. The resulting cations

SCHEME 1

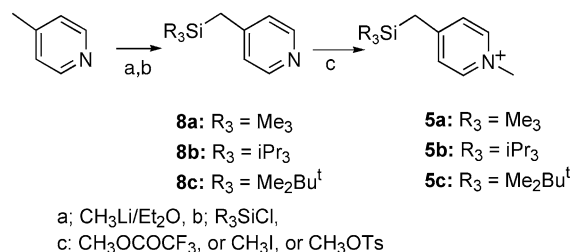
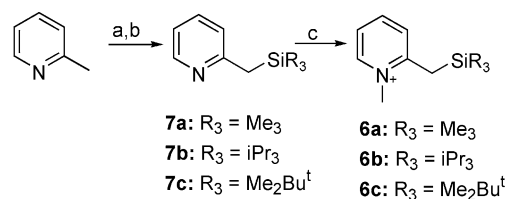


TABLE 1. Selected One-Bond Couplings (Hz) for Compounds 5a-c, 6a-c, 7a-c, and 8a-c

cmpd	CH ₂ -Si	Si-C(R)	δ ^{29}Si	cmpd	CH ₂ -Si	Si-C(R)	δ ^{29}Si	ΔJ^a (Hz)
5a^b	35.9	52.7		8a	41.8	51.9	6.9	-5.9
5b	35.0	52.6	15.5	8b	40.4	52.6	6.3	-6.4
5c	33.6 ^c	51.9	16.8	8c	41.9	51.2	8.8	-8.3 ^c
6a	35.8	52.6	12.8	7a	43.5	52.1	7.2	-7.7
6b	32.8	53.4	17.0	7b	41.2	51.9	6.6	-8.4
6c	33.0	51.9	18.5	7c	42.7	51.1	9.1	-9.7

^a This is the change in the Si-CH₂ coupling constant upon methylation. ^b The ^{29}Si δ value for **5a** could not be reliably determined due to slow desilylation during data acquisition. ^c The $^{13}\text{C}-^{29}\text{Si}$ coupling constant for **6c** could not be reliably determined due to the overlap of ^{13}C peaks.

were characterized by ^{29}Si and ^{13}C NMR. Notable changes in the spectra for the pyridine precursors **7a-c** and **8a-c** (for which relatively weak neutral hyperconjugation¹⁰ exists between the C-Si bond and the aromatic π -system) upon conversion to the ions **6a-c** and **5a-c** included a downfield shift of the ^{29}Si chemical shift and a marked decrease in the Si-CH₂ one-bond coupling constant. This is consistent with stronger C-Si hyperconjugation in these highly π -electron-deficient systems, as represented by the increasing contributions of resonance forms analogous to **6'** for the 2-substituted derivatives and **5'** for the 4-substituted derivatives. It is noteworthy that the changes in both the ^{29}Si chemical shift and the Si-CH₂ coupling constant are more pronounced for the 2-substituted derivatives, suggesting that C-Si hyperconjugation with the pyridinium cation is significantly stronger at the 2-position (ions **6a-c**) than at the 4-position (ions **5a-c**) of the pyridinium ion. We were intrigued to establish whether the apparent differences in hyperconjugation at the 2- and 4-positions would manifest as noticeable differences in the crystal structures of these ions. Therefore, we attempted to determine the crystal structure of the *N*-methyl-2-trimethylsilylmethylpyridinium triflate **6a**, so that the structural parameters could be compared with the previously determined structure of the 4-substituted derivative **5a**. However, we found that, upon crystallization from a variety of solvents, **6a** desilylated to afford the corresponding 2-methylpyridinium ion **9** (Scheme 2). The desilylation of **6a** could

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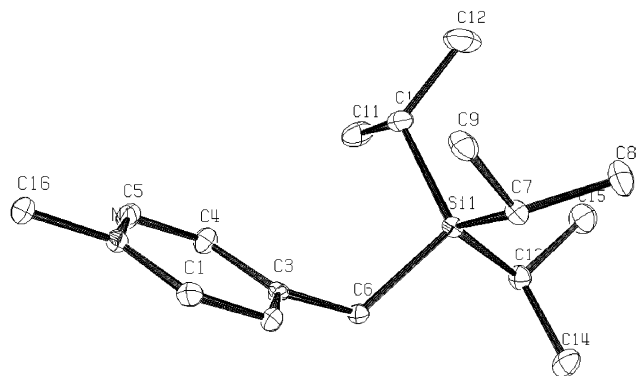
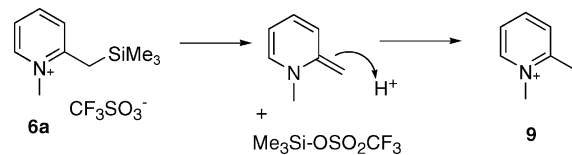


FIGURE 3. Thermal ellipsoid plot of **5b**·tosylate. Ellipsoids are at the 20% probability level.

SCHEME 2



not be avoided and occurred readily with triflate, tosylate, and iodide counterions.

Desilylation of silyl-substituted cations is an associative process involving nucleophilic attack at the silicon.¹³ In the case of **6a** this is probably initiated by attack of the counterion at the silicon (Scheme 2). This process is expected to be facile when C–Si hyperconjugation is strong, as contributions of resonance form **6'** render the silicon more Lewis acidic. Thus, facile desilylation of **6a** when compared to **5a** suggests qualitatively that C–Si hyperconjugation is stronger at the 2-position than at the 4-position on the pyridinium ring. Nucleophilic attack at silicon is very sensitive to the steric bulk of the substituents at the silicon;¹⁴ thus, not surprisingly, the sterically congested triisopropylsilylmethyl derivatives **5b** and **6b** were found to be stable for several weeks in solution, and suitable crystals for X-ray structure determination of **5b**·tosylate and **6b**·triflate were obtained by ether diffusion from methanol over several days.

Crystal data for **5b** and **6b** were measured at low temperature to minimize the unwanted effects of thermal motion. Crystal data and structure refinement details for **5b** and **6b** are summarized in Table 2; selected bond distances, angles, and dihedral angles are in Table 3; and perspective diagrams are presented in Figures 3 and 4. The crystal structure of **5b** contained a molecule of triisopropylsilanol (carried through as an impurity from the first step in Scheme 1) and a molecule of water of crystallization.

In both structures the Si–C–C(ipsa)–C(ortho) dihedral angle is close to orthogonal, a conformation which is favored on steric grounds and on electronic grounds, as it allows for effective overlap between the CH₂–Si and the pyridinium π -system. The Si–CH₂ bond distance is significantly longer in the 2-triisopropylsilylmethyl-substituted derivative **6b** (1.930(2) Å) than in the corre-

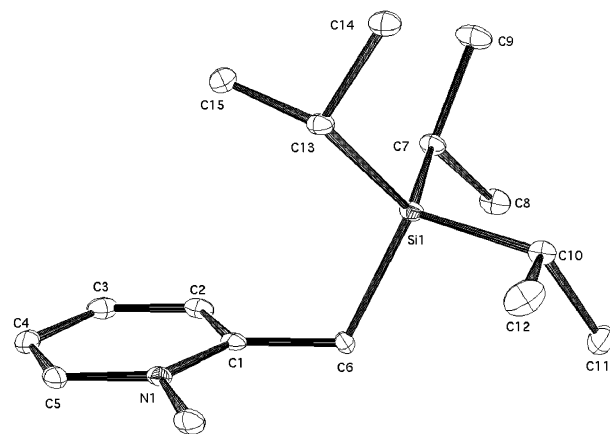


FIGURE 4. Thermal ellipsoid plot of **6b**·triflate. Ellipsoids are at the 20% probability level.

TABLE 2. Crystal Data and Structure Refinement for **5b**·Tosylate·*i*-Pr₃SiOH and **6b**·Triflate

	5b	6b
empirical formula	C ₁₆ H ₃₀ NSi·C ₇ H ₇ SO ₃ ·C ₉ H ₂₂ SiO	C ₁₆ H ₃₀ NSi·CF ₃ SO ₃
formula weight	619.05	413.57
temperature (K)	130.0(2)	130.0(2)
wavelength (Å)	0.71073	0.71073
crystal system	monoclinic	triclinic
space group	C2/c	P1
unit cell dimensions		
A (Å)	30.727(4)	8.249(1)
B (Å)	8.2906(10)	10.741(2)
C (Å)	29.838(4)	12.618(2)
α (°)		83.686(2)
β (°)	104.767(2)	75.608(2)
γ (°)		70.555(2)
V (Å ³)	7350.0(15)	1020.8(3)
μ (Mo K α)	0.188	0.260
D _{calc} (Mg m ⁻³)	1.119	1.346
Z	8	2
F(000)	2712	440
crystal size (mm ³)	0.50 × 0.50 × 0.08	0.5 × 0.4 × 0.3
θ range for data collection	1.37 – 25.00	1.67 – 28.64
limiting indices	–36 ≤ h ≤ 36 –9 ≤ k ≤ 9 –35 ≤ l ≤ 24	–10 ≤ h ≤ 10 –14 ≤ k ≤ 14 –16 ≤ l ≤ 16
reflns collected/unique	18671/6437 R(int) = 0.0874	8605/4565 R(int) = 0.0303
absorption correction		multiscan
max min trans		1.0 and 0.52
goodness-of-fit on F ²	0.854	1.040
final R indices [I > 2 σ (I)]	R1 = 0.0491 wR2 = 0.0908	R1 = 0.0400 wR2 = 0.1065
R indices (all data)	R1 = 0.0854 wR2 = 0.0987	R1 = 0.0454 wR2 = 0.1104
largest diff peak and hole (e/Å ³)	0.377 and –0.230	0.474 and –0.338

TABLE 3. Selected Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) for Compounds **5b** and **6b**

	5b	6b	5b	6b
N1–C1	1.346(3)	1.364(2)	C6–Si	1.907(2)
C1–C2	1.364(3)	1.397(2)	Si–CH _{av}	1.883
C2–C3	1.389(3)	1.373(2)	Si–C6–C1	117.2(2)
C3–C4	1.392(3)	1.387(3)	Si–C6–C1–N1	–98.6(15)
C4–C5	1.359(3)	1.365(3)	Si–C6–C1–C2	81.8(2)
C5–N1	1.335(3)	1.358(2)	Si–C6–C3–C2	na
C1–C6	1.488(3)	1.474(2)	Si–C6–C3–C4	na
				87.2(3)

sponding 4-substituted derivative **5b** (1.907(2) Å), suggesting stronger $\sigma_{C-Si}-\pi$ hyperconjugation in **6b**; also consistent with this is the significantly shorter CH₂–

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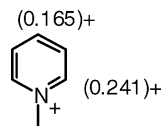


FIGURE 5. Huckel charges in the pyridinium cation.

C(ipso) bond distance in **6b** (1.472(2) Å) than in **5b** (1.488(2) Å). These structural effects indicate greater contributions of the resonance form **6'** to the ground-state structure of **6b** than **5'** makes to the ground-state structure of **5b**. The charge distributions on the simple pyridinium cation from Huckel calculations shown in Figure 5¹⁵ show that there is a greater degree of charge at the 2-position than at the 4-position.

Conclusion

Both solution phase ²⁹Si and ¹³C NMR data and X-ray crystallographic data provide evidence that C–Si hyperconjugation with the pyridinium cation is stronger at the 2-position than at the 4-position. This result suggests that the electron demand of the pyridinium cation is expected to be greater at the 2-position than at the 4-position.

Experimental Section

1. X-ray Crystallography. Crystals were grown of **5b** from methanol/ether and of **6b** from acetonitrile/ether. The temperature was maintained at 130.0(1) using an Oxford Cryostream cooling device. Intensity data were collected with a Bruker SMART Apex CCD detector using Mo K α radiation (graphite crystal monochromator $\lambda = 0.71073$). Data were reduced using the program SAINT.¹⁶

The structure was solved by direct methods and difference Fourier synthesis.

2. Synthesis. (a) General Procedure for the Preparation of 2-Trimethylsilylmethylpyridine (7a), 2-Triisopropylsilylmethylpyridine (7b), and 2-tert-Butyldimethylsilylmethylpyridine (7c). To a solution of 2-picoline (2.0 g, 21 mmol) in ether (20 mL) was added methyl lithium (1.4 M in ether, 15 mL, 21 mmol), and the solution was refluxed for 30 min. The reaction was cooled to -78 °C (dry ice/acetone) prior to the dropwise addition of the respective trialkylsilyl chloride (1.4 equiv). The mixture was slowly warmed to room temperature and stirred for a further 3 h. The product was extracted with 1 M HCl (2 \times 50 mL) and washed with ether (50 mL). The aqueous layer was basified (pH = 12) with concentrated NaOH solution, and the product was extracted with ether (3 \times 50 mL). The combined ether layers were dried (MgSO₄), and the solvent was removed under reduced pressure.

(i) 2-Trimethylsilylmethylpyridine (7a). A clear oil (1.8962 g, 42.7%) was isolated by K \ddot{u} gelrohr distillation (60 °C, 1 mmHg). ¹H NMR: δ (CDCl₃) 8.42 (1H, d, $J = 4.6$ Hz, H6), 7.52 (1H, ddd, $J = 7.7, 7.7, 1.5$ Hz, H4), 6.97 (2H, m, H3/5), 2.37 (2H, s, CH₂), 0.01 (9H, s, SiMe₃). ¹³C NMR: δ (CDCl₃) 161.1, 148.7, 135.7, 122.0, 119.0, 30.1, -1.8 . ²⁹Si NMR: δ (CDCl₃) 7.17. ESI MS (m/z): 166 (M + 1).

(ii) 2-Triisopropylsilylmethylpyridine (7b). Yellow oil (69% yield). ¹H NMR: δ (CDCl₃) 8.39 (1H, d, $J = 4.5$ Hz, H6), 7.48 (1H, dd, $J = 7.7, 7.7$ Hz, H4), 7.04 (1H, d, $J = 7.9$ Hz, H3), 6.97 (1H, m, H5), 2.45 (2H, s, CH₂), 1.04 (21H, m, Si-CH(CH₃)₂). ¹³C NMR: δ (CDCl₃) 161.8, 148.7, 135.5, 122.5,

119.0, 22.6, 18.4, 10.9. ²⁹Si NMR: δ (CDCl₃) 6.66. ESI MS (m/z): 250.1985 (M + 1), 206.1360 (M - CH(CH₃)₂).

(iii) 2-tert-Butyldimethylsilylmethylpyridine (7c). Yellow oil (49% yield). ¹H NMR: δ (CDCl₃) 8.34 (1H, dd, $J = 4.9, 1.6$ Hz, H6), 7.42 (1H, ddd, $J = 7.7, 7.7, 1.7$ Hz, H4), 6.89 (2H, m, H3/5), 2.28 (2H, s, CH₂), 0.84 (9H, s, Si-C(CH₃)₃), -0.18 (6H, s, Si-CH₃). ¹³C NMR: δ (CDCl₃) 161.4, 148.6, 135.7, 122.3, 119.0, 26.3, 25.8, 16.6, -6.50 . ²⁹Si NMR: δ (CDCl₃) 9.09. ESI MS (m/z): 208.1 (M + 1).

(b) General Procedure for the Preparation of 4-Triisopropylsilylmethylpyridine (8b) and 4-tert-Butyldimethylsilylmethylpyridine (8c). To a solution of 4-picoline (2.0 g, 21 mmol) in ether (20 mL) was added methyl lithium (1.4 M in ether, 15 mL, 21 mmol), and the solution was refluxed for 30 min. The reaction was cooled to -78 °C (dry ice/acetone) prior to the dropwise addition of the trialkylsilyl chloride (25 mmol). The mixture was slowly warmed to room temperature and stirred for a further 3 h. The product was extracted with 1 M HCl (2 \times 50 mL) and washed with ether (50 mL). The aqueous layer was basified (pH = 12) with concentrated NaOH solution, and the product was extracted with ether (3 \times 50 mL). The combined ether layers were dried (MgSO₄), and the solvent was removed under reduced pressure to afford the product as an oil.

(i) 4-Triisopropylsilylmethylpyridine (8b). (4.653 g, 89%). ¹H NMR: δ (CDCl₃) 8.27 (2H, d, $J = 4.65$ Hz, H2/6), 6.96 (2H, d, $J = 4.5$ Hz, H3/5), 2.13 (2H, s, CH₂), 0.97 (21H, m, Si-CH(CH₃)₂). ¹³C NMR: δ (CDCl₃) 151.4, 148.7, 124.0, 19.4, 18.4, 10.8. ²⁹Si NMR: δ (CDCl₃) 6.30. ESI MS (m/z): 250.1985 (M + 1).

(ii) 4-tert-Butyldimethylsilylmethylpyridine (8c). Yellow oil (63% yield). ¹H NMR: δ (CDCl₃) 8.37 (2H, d, $J = 5.8$ Hz, H2/6), 6.92 (2H, d, $J = 5.9$ Hz, H3/5), 2.09 (2H, s, CH₂), 0.90 (9H, s, C(CH₃)₃), -0.11 (6H, s, CH₃). ¹³C NMR: δ (CDCl₃) 150.4, 149.1, 123.6, 26.3, 22.8, 16.6, -6.8 . ²⁹Si NMR: δ (CDCl₃) 8.77. ESI MS (m/z): 208.1 (M + 1).

(c) Preparation of N-Methyl-2-trimethylsilylmethylpyridinium Iodide (6a-iodide). A solution of **7a** (100 mg) in deuteriochloroform (0.5 mL) was treated with methyl iodide (1.1 equiv); after 24 h the ¹H and ¹³C NMR signals characteristic of **7a** had disappeared and were replaced with those of **6a**. ¹H NMR: δ (CD₃CN) 9.04 (1H, d, $J = 6.4$ Hz, H6), 8.14 (1H, dd, $J = 7.9$ Hz, H4), 7.60 (1H, d, $J = 8.3$ Hz, H3), 7.55 (1H, dd, $J = 6.4$ Hz, H5), 4.19 (3H, s, N-CH₃), 2.76 (2H, s, CH₂), 1.89 (9H, SiMe₃). ¹³C NMR: δ (CD₃CN) 159.3, 145.1, 143.5, 127.6, 122.8, 46.5, 26.6, -1.53 .

(d) Preparation of N-Methyl-2-triisopropylsilylmethylpyridinium Triflate (6b-triflate). A solution of **7b** (100 mg) in deuterio acetonitrile (0.5 mL) was treated with neat methyl triflate (1.05 equiv). After the NMR had been recorded, ether was allowed to diffuse into the solution overnight to afford colorless plates suitable for X-ray analysis, mp 117–121°. ¹H NMR: δ (CD₃CN) 8.59 (1H, d, $J = 6.4$ Hz, H6), 8.26 (1H, dd, $J = 7.7, 7.7$ Hz, H4), 7.76 (1H, d, $J = 8.2$ Hz, H3), 7.66 (1H, dd, $J = 7.0, 6.5$ Hz, H5), 4.22 (3H, s, N-CH₃), 2.79 (2H, s, CH₂), 1.23 (3H, sept, $J = 7.25$ Hz, Si-CH(CH₃)₂), 0.96 (18H, d, $J = 7.3$ Hz, Si-CH(CH₃)₂). ¹³C NMR: δ (CD₃CN) 162.1, 146.8, 145.2, 130.2, 125.5, 47.32, 20.3, 18.8, 12.5. ²⁹Si NMR: δ (CD₃CN) 17.03.

(e) Preparation of N-Methyl-2-tert-butyldimethylsilylmethylpyridinium Triflate (6c-triflate). A solution of **6c** (100 mg) in deuterio acetonitrile (0.5 mL) was treated with neat methyl triflate (1.05 equiv). ¹H NMR: δ (CD₃CN) 8.51 (1H, d, $J = 6.4$ Hz, H6), 8.24 (1H, m, H4), 7.65 (1H, m, H3/5), 4.11 (3H, s, N-CH₃), 2.77 (2H, s, CH₂), 1.03 (9H, s, C(CH₃)₃), 0.04 (6H, s, CH₃). ¹³C NMR: δ (CD₃CN) 161.7, 146.8, 145.2, 129.5, 124.3, 47.0, 26.5, 23.1, 17.9, -5.62 . ²⁹Si NMR: δ (CD₃CN) 18.49.

(f) Preparation of N-Methyl-4-triisopropylsilylmethylpyridinium Triflate (5b-triflate). A solution of **8b** (100 mg) in deuterio acetonitrile (0.5 mL) was treated with neat methyl triflate (1.05 equiv). After the NMR had been recorded,

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ether was allowed to diffuse into the solution overnight to afford crystals which were unfortunately unsuitable for X-ray analysis. ^1H NMR: δ (CD_3CN) 8.33 (2H, d, $J = 6.8$ Hz, H2/6), 7.66 (2H, d, $J = 6.5$ Hz, H3/5), 4.26 (3H, s, N–CH₃), 2.65 (2H, s, CH₂), 1.10 (3H, m, Si–CH(CH₃)₂), 1.04 (18H, d, $J = 6.6$ Hz, Si–CH(CH₃)₂). ^{13}C NMR: δ (CD_3CN) 165.7, 144.8, 128.1, 48.0, 23.6, 18.9, 12.0. ^{29}Si NMR: δ (CD_3CN) 15.50.

(g) Preparation of *N*-Methyl-4-triisopropylsilylpyridinium Tosylate (5b·tosylate). A solution of **8b** (100 mg) in acetonitrile (0.5 mL) was treated with neat methyl tosylate (1.05 equiv); after stirring overnight ether was allowed to diffuse into the reaction mixture, giving **8b**·tosylate as thick slabs.

(h) Preparation of *N*-Methyl-4-*tert*-butyldimethylsilylmethylpyridinium Triflate (5c·triflate). A solution of **8c** (100 mg) in deuterio acetonitrile (0.5 mL) was treated with neat methyl triflate (1.05 equiv). ^1H NMR: δ (CD_3CN) 8.43 (2H, d, $J = 5.9$ Hz, H2/6), 7.61 (2H, d, $J = 6.1$ Hz, H3/5), 4.20

(3H, s, N–CH₃), 2.57 (2H, s, CH₂), 0.94 (9H, s, C(CH₃)₃), –0.07 (6H, s, CH₃). ^{13}C NMR: δ (CD_3CN) 164.8, 144.7, 127.6, 47.8, 26.8, 26.6, 17.8, –6.5. ^{29}Si NMR: δ (CD_3CN) 16.85.

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Supporting Information Available: Crystallographic data supplied in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. These data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 254307 and 254308. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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