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Lewis Basicity of Silatranes and the Molecular Structures of $EtOSi(OCH_2CH_2)_3N$, $Me_2O^+Si(OCH_2CH_2)_3N$, and $CF_3CO_2HEtOSi(OCH_2CH_2)_3N$

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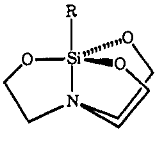
Abstract: The silatranyl group is shown to be sufficiently electron releasing in alkoxysilatranes ($ROSi(OCH_2CH_2)_3N$) to allow isolation of the hydrogen-bonded adduct $CF_3C(O)OHEtOSi(OCH_2CH_2)_3N$ (**7**), the protonated cation $HEtO^+Si(OCH_2CH_2)_3N$ (**13**(BF_4)) and the alkylated cations $R_2O^+Si(OCH_2CH_2)_3N$ (R = Me, **6**(BF_4); R = Et, **12**(BF_4)) of which **7** and **6**(BF_4) and also the alkoxysilatrane $EtOSi(OCH_2CH_2)_3N$ (**5**) have been structured by X-ray means. The SiN_{ax} bond length in **6**(BF_4) (1.965 (5) Å) is the shortest reported for a silatrane, and the O(H)O distance in **7** (2.489 Å) is the shortest recorded for an unsymmetrical hydrogen bond. The SiO_{ax} distance increases by a total of 0.17 Å in the order **5** < **7** < **6** (BF_4). The greatest downfield shifts of a ^1H or ^{13}C resonance in a variety of alkoxysilatranes in hydrogen bonding, protonating, or alkylating environments are observed to occur at the $O_{ax}R$ group. That electrophilic attack can also occur at O_{eq} in solutions of these compounds is suggested by broadening of the OCH_2CH_2N protons of $PhSi(OCH_2CH_2)_3N$ in the presence of Me_3OBF_4. Measurement of phenol $\nu(OH)$ shifts reveals the basicity order $(Me_3Si)_2O < Si(OR)_4 <$ alkoxysilatranes $\leq Me_3SiOMe < Et_2O$, which places the electron-releasing ability of the silatranyl group ahead of $(RO)_3Si$ but below an Et group. Parameters for the X-ray crystallography determined structures are as follows: **5**, monoclinic ($P2_1/n$), $Z = 8$, $a = 10.956$ (4) Å, $b = 11.187$ (2) Å, $c = 17.638$ (8) Å, $\beta = 95.84$ (4)°; **6**(BF_4), monoclinic ($P2_1/c$), $Z = 4$, $a = 8.976$ (2) Å, $b = 11.517$ (1) Å, $c = 12.387$ (2) Å, $\beta = 91.943$ (8)°; **7**, orthorhombic (Pbca), $Z = 8$, $a = 12.655$ (4) Å, $b = 11.446$ (4) Å, $c = 19.489$ (3) Å.

Introduction

The presence of a transannular $N_{ax} \rightarrow Si$ bond in silatranes (**1**) is expected to shift negative charge to the silicon by donation from the axial nitrogen lone pair. Electron density that finds its way onto the equatorial oxygens and the axial R (or OR) group could then influence the nucleophilic reactivity of these sites and also their Lewis basicity in adduct formation.



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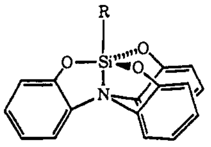

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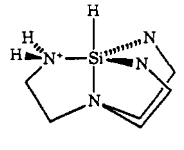

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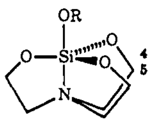
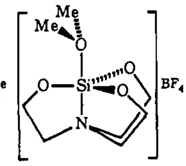
In accord with this notion are hydrolysis rates of alkylsilatranes (**1**, R = alkyl, halide-substituted alkyl, alkoxide) in acidic media which have been observed to be faster than in neutral solutions.[1] The rates of the acid-catalyzed hydrolyses of these compounds also decreases with increasing electronegativity of R. A mechanism involving hydronium ion attack on an equatorial oxygen was invoked to account for the data.[1] A similar intermediate has been proposed for the acid-catalyzed hydrolysis of tribenzo silatranes **2**.[2] Consistent with the hypothesis of an equatorially protonated silatrane species is our recent report of the isolation and the crystal and molecular structure of cation **3**.[3] Silatrane adducts in which the Lewis acid ($TiCl_4$ or $AlCl_3$) is bound to an equatorial oxygen have also been suggested on the basis of IR spectroscopic studies.[4]

A measure of the extent to which axial R substituents accept electron density from the silicon in **1** is an experimentally measured inductive constant σ^* (3.49) which is the largest known for an electron donor substituent.[5] This effect has also been examined in charge-transfer spectral studies of tetracyanoethylene complexes of **1** (R = aryl).[6,7]

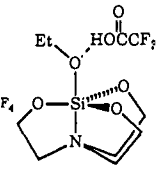
Herein are reported for the first time the isolation and structural characterizations by X-ray means of silatrane adducts in which the exocyclic axial oxygen behaves as the Lewis basic site. Thus silatranes **4** and **5** are fully covalently bonded and hydrogen bonded to their Lewis acid components in the structures of **6**(BF_4) and **7**, respectively. We also report the structure of **5** for comparison. On the basis of the $\nu(OH)$ shift of phenol, we present a comparison of the basicities of **4** and **5** with those of **8–11**, which suggests, among other things, that **4** and **5** are more basic than $Si(OR)_4$ or $(Me_3Si)_2O$, but less basic than Et_3PO or Et_3N.



	R
4	Me
5	Et



6 (BF_4)



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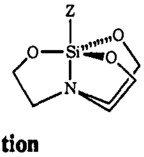

	Z
8	Me
9	$(CH_2)_3OEt$
10	vinyl
11	Ph

Experimental Section

All reactions were carried out with the strict exclusion of moisture. Solvents were dried by standard methods and distilled before use. Tri-

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phenylcarbenium perchlorate[8] and 1-hydridosilatrane[9] were prepared according to published procedures. 1-Ethoxyazasilatrane,[10] prepared by a published method, was kindly provided by Dr. D. Gudat.

Solution NMR spectra were recorded on Nicolet NT 300 (^{1}H, ^{13}C) and Bruker WM 200 (^{29}Si) spectrometers, with deuterated solvents as the internal lock and TMS as an internal standard. The ^{1}H NMR concentration studies were carried out at the ambient temperature of the probe (±0.1 °C). For measurement of solid-state NMR spectra, polycrystalline samples (ca. 50–200 mg) were mixed with $\mathrm{Al_2O_3}$. Spectra were obtained on a Bruker MSL 300 spectrometer (operating at 75.49 MHz (^{13}C) and 59.62 MHz (^{29}Si)) under proton decoupling, with the CP-MAS technique with a polarization transfer delay of 5.00 ms. Spinning rates were in the range of 4–5 kHz. Chemical shifts were referenced to external TMS. Mass spectra were recorded on Kratos MS-50 (70 eV EI, FAB, high-resolution conditions) and Finnigan 4000 (70 eV EI, CI) mass spectrometers. Conductance measurements were recorded for approximately 1 mM solutions on a Marksman Electromark Analyzer Model 4402 standardized with Biopharm Standard BC 4095 (720 μohm^{-1}). Infrared spectra were recorded on an IBM IR-98 FTIR spectrometer operating between 4000 and 600 cm^{-1} with a resolution of four wave numbers. Infrared samples were placed into matched $\mathrm{CaF_2}$ solution cells which had been rinsed and flushed with dry nitrogen gas. Microanalyses were carried out by Schwartzkopf Microanalytical Laboratories, Woodside, NY.

WARNING: Some silatranes are toxic[11] and should be handled with caution.

(Triphenylsiloxy)silatrane (15). A sample provided by Dr. Cecil Frye, Dow Corning, was used without further purification (^{1}H NMR ($\mathrm{CD_2Cl_2}$) 7.7–7.6 (m, 5 H), 7.4–7.3 (m, 10 H), 3.79 (t, $^3J_{\mathrm{HH}}$ = 5.87 Hz, 6 H, $\mathrm{OC}H_2$), 2.83 (t, $^3J_{\mathrm{HH}}$ = 5.88 Hz, 6 H, $\mathrm{NC}H_2$); ^{29}Si NMR ($\mathrm{CDCl_3}$, $\mathrm{Cr(acac)_3}$, inverse gated decoupled) −24.7 ($Si\mathrm{Ph_3}$), −98.1 ($Si\mathrm{(OCH_2CH_2)_3N}$)).

1-Methoxysilatrane (4). This compound was prepared by a previously described procedure[12] in which no NMR data were included (^{1}H NMR ($\mathrm{CD_2Cl_2}$) 0.48 ($\mathrm{NCH_2}$) 0.27 ($\mathrm{OCH_2}$) 0.69 ($\mathrm{CH_3}$); ^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$) 49.47 ($\mathrm{O}C\mathrm{H_3}$), 56.53 ($\mathrm{N}C\mathrm{H_2}$), 50.36 ($\mathrm{O}C\mathrm{H_2}$)).

1-Ethoxysilatrane (5). 1-Ethoxysilatrane was prepared by a previously described method[13] in which no NMR data were included. Colorless single crystals were grown from hexane solution (^{1}H NMR ($\mathrm{CD_3CN}$) 3.68 (t, $^3J_{\mathrm{HH}}$ = 5.87 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.53 (q, $^3J_{\mathrm{HH}}$ = 6.98 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.81 (t, $^3J_{\mathrm{HH}}$ = 5.87 Hz, 6 H, $\mathrm{NC}H_2$), 1.00 (t, $^3J_{\mathrm{HH}}$ = 6.99 Hz, 3 H, $\mathrm{C}H_3$); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$) 3.68 (t, $^3J_{\mathrm{HH}}$ = 5.68 Hz, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.59 (q, $^3J_{\mathrm{HH}}$ = 6.99 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.86 (t, $^3J_{\mathrm{HH}}$ = 5.86 Hz, $\mathrm{NC}H_2$), 1.02 (t, $^3J_{\mathrm{HH}}$ = 6.97 Hz, $\mathrm{C}H_3$); ^{13}C NMR ($\mathrm{CD_3CN}$) 58.2, 58.1 ($\mathrm{O}C\mathrm{H_2CH_3}$, $\mathrm{O}C\mathrm{H_2CH_2}$), 51.7 ($\mathrm{N}C\mathrm{H_2}$), 19.0 ($C\mathrm{H_3}$); ^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$) 56.7 ($\mathrm{O}C\mathrm{H_2CH_3}$, $\mathrm{O}C\mathrm{H_2CH_2}$), 49.3 ($\mathrm{N}C\mathrm{H_2}$), 18.1 ($C\mathrm{H_3}$)).

1-(Dimethyloxonio)silatranium Tetrafluoroborate, 6($\mathbf{BF_4}$). 1-Methoxysilatrane (1.1038 g, 5.3769 mmol) and trimethyloxonium tetrafluoroborate (0.7978 g, 5.394 mmol) were stirred in 15 mL of freshly distilled $\mathrm{CD_2Cl_2}$ at −77 °C for 3 h. A precipitate was filtered from the cold solution. The filtrate was cooled at −25 °C for 26 h, after which time a white powdery precipitate had formed. The resulting mixture was stirred for 3 h at room temperature, and the solution was again cooled at −25 °C. After 5 days, single crystals of **6**($\mathrm{BF_4}$) were vacuum filtered and dried in vacuo for 1 h (^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$) 66.8 ($C\mathrm{H_3}$), 57.7 ($\mathrm{O}C\mathrm{H_2}$), 54.6 ($C\mathrm{H_3}$), 50.1 ($\mathrm{N}C\mathrm{H_2}$); ^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$, dipolar decoupled) 66.8 ($C\mathrm{H_3}$), 54.6 ($C\mathrm{H_3}$); ^{29}Si NMR (CP-MAS, $\mathrm{Al_2O_3}$) −90.2). The ^{1}H NMR spectrum in solution revealed the presence of more than one compound (($\mathrm{CDCl_3}$) 2.86 (t, 3 H), 2.96 (t, 6 H), 3.39 (t, 3 H), 3.49 (s, 1 H), 3.84 (t, 3 H), 3.90 (t, 6 H), 4.02 (m, 7 H).

1-(Diethyloxonio)silatranium Tetrafluoroborate 12($\mathbf{BF_4}$). 1-Ethoxysilatrane (0.2697 g, 1.230 mmol) and triethyloxonium tetrafluoroborate (0.2467 g, 1.299 mmol) were stirred in 15 mL of $\mathrm{CH_2Cl_2}$ for 3 h at −77 °C and then at room temperature for 2 h. The solution was left at −25 °C overnight, and then the solvent was removed by evacuation at room temperature. The resulting solid product (85% yield) melted between 160 and 163 °C. Subsequent attempts to grow X-ray quality single crystals from similar reaction mixtures or from solutions of isolated product failed (Anal. Calcd for $\mathrm{C_{10}H_{22}BF_4NO_4Si}$ (Found): C, 35.84 (33.63); H, 6.62 (6.76); Si, 8.38 (8.51); molar conductance ($\mathrm{Me_2CO}$) 118 cm^2 mol^{-1} ohm^{-1}; ^{1}H NMR ($\mathrm{CD_3CN}$) 4.35 (q, $^3J_{\mathrm{HH}}$ = 6.99 Hz, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.93 (t, ^3J = 6.01 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.16 (t, $^3J_{\mathrm{HH}}$ = 6.05 Hz, 6 H, $\mathrm{NC}H_2$), 1.35 (t, $^3J_{\mathrm{HH}}$ = 7.02 Hz, 6 H, $\mathrm{C}H_3$); ^{1}H NMR ($\mathrm{CDCl_3}$) 4.37 (q, $^3J_{\mathrm{HH}}$ = 7.02 Hz, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.01 (t, $^3J_{\mathrm{HH}}$ = 6.01 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.33 (t, $^3J_{\mathrm{HH}}$ = 6.05 Hz, 6 H, $\mathrm{NC}H_2$), 1.43 (t, $^3J_{\mathrm{HH}}$ = 7.02 Hz, 6 H, $\mathrm{C}H_3$); ^{13}C NMR ($\mathrm{CDCl_3}$) 73.7 ($\mathrm{O}C\mathrm{H_2CH_3}$), 58.7 ($\mathrm{O}C\mathrm{H_2CH_2}$), 51.6 ($\mathrm{N}C\mathrm{H_2}$), 18.4 ($C\mathrm{H_3}$); ^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$) 77.1 ($\mathrm{O}C\mathrm{H_2CH_3}$), 57.9 ($\mathrm{O}C\mathrm{H_2CH_2}$), 49.9 ($\mathrm{N}C\mathrm{H_2}$), 15.1 ($C\mathrm{H_3}$), 11.9 ($C\mathrm{H_3}$); ^{29}Si NMR ($\mathrm{CDCl_3}$) −90.7; ^{29}Si NMR (CP-MAS, $\mathrm{Al_2O_3}$) −89.4).

1-Ethoxysilatrane–Trifluoroacetic Acid Adduct (7). To a suspension of 1-ethoxysilatrane **5** (0.2024 g, 0.9229 mmol) in 20 mL of freshly distilled diethyl ether, trifluoroacetic acid (0.2776 g, 2.435 mmol, 2.6 equiv) was added. The resulting solution was allowed to stir at room temperature for 5 h and placed in the freezer at −25 °C overnight. Crystals of **7** were removed from the reaction mixture for the X-ray structural determination described later. The remainder of the crystalline material (0.2367 g, 0.7106 mmol, 77% yield) was separated from solution by filtration and dried in vacuo at room temperature overnight (Anal. Calcd for $\mathrm{C_{10}H_{18}F_3NO_6Si}$ (Found): C, 36.06 (37.18); H, 5.44 (5.66); F, 17.10 (16.79); ^{1}H NMR ($\mathrm{CDCl_3}$) 11.56 (s, br, 1 H), 3.86 (t, $^3J_{\mathrm{HH}}$ = 5.88 Hz, 6 H, $\mathrm{0C}H_2\mathrm{CH_2}$), 3.82 (q, $^3J_{\mathrm{HH}}$ = 7.03 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.90 (t, $^3J_{\mathrm{HH}}$ = 5.92 Hz, 6 H, $\mathrm{NC}H_2$), 1.20 (t, $^3J_{\mathrm{HH}}$ = 7.18 Hz, 3 H, $\mathrm{C}H_3$); ^{1}H NMR ($\mathrm{CD_3CN}$) 5.5–5.3 (br, 3 H), 3.72 (t, $^3J_{\mathrm{HH}}$ = 5.93 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.64 (q, $^3J_{\mathrm{HH}}$ = 7.03 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.86 (t, $^3J_{\mathrm{HH}}$ = 5.93 Hz, 6 H, $\mathrm{NC}H_2$), 1.06 (t, $^3J_{\mathrm{HH}}$ = 7.02 Hz, 3 H, $\mathrm{C}H_3$); ^{13}C NMR (CP-MAS, $\mathrm{Al_2O_3}$) 56.7, 49.3, 18.1).

Monitoring of mixtures of the starting materials by ^{1}H NMR spectroscopy was employed to gauge the effect of concentration on the nature of the adduct in solution.

(1) **5** (0.0146 g, 0.0666 mmol) and $\mathrm{HCO_2CF_3}$ (0.0076 g, 0.067 mmol) were mixed in 0.7 mL of $\mathrm{CDCl_3}$ (^{1}H NMR ($\mathrm{CDCl_3}$) 3.85 (t, $^3J_{\mathrm{HH}}$ = 5.88 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.79 (q, $^3J_{\mathrm{HH}}$ = 7.00 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.89 (t, $^3J_{\mathrm{HH}}$ = 5.90 Hz, 6 H, $\mathrm{NC}H_2$), 1.20 (t, $^3J_{\mathrm{HH}}$ = 7.02 Hz, 3 H, $\mathrm{C}H_3$)).

(2) **5** (0.0193 g, 0.0880 mmol) and $\mathrm{HCO_2CF_3}$ (0.0127 g, 0.111 mmol, 1.26 equiv) were mixed in 0.7 mL of $\mathrm{CDCl_3}$ (^{1}H NMR ($\mathrm{CDCl_3}$) 3.87 (t, $^3J_{\mathrm{HH}}$ = 5.81 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.82 (q, $^3J_{\mathrm{HH}}$ = 7.08 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.92 (t, $^3J_{\mathrm{HH}}$ = 5.84 Hz, 6 H, $\mathrm{NC}H_2$), 1.21. (t, $^3J_{\mathrm{HH}}$ = 6.96 Hz, 3 H, $\mathrm{C}H_3$); ^{13}C NMR ($\mathrm{CDCl_3}$) 59.0 ($\mathrm{O}C\mathrm{H_2CH_3}$), 57.4 ($\mathrm{O}C\mathrm{H_2CH_2}$), 51.1 ($\mathrm{N}C\mathrm{H_2}$), 17.3 ($\mathrm{C}H_3$)).

(3) **5** (0.0106 g, 0.0483 mmol) and $\mathrm{HCO_2CF_3}$ (0.0145 g, 0.127 mmol, 2.6 equiv) were mixed in 0.7 mL of $\mathrm{CDCl_3}$ (^{1}H NMR ($\mathrm{CDCl_3}$) 3.90 (t, $^3J_{\mathrm{HH}}$ = 5.92 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$) 3.85 (q, $^3J_{\mathrm{HH}}$ = 7.03 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.96 (t, $^3J_{\mathrm{HH}}$ = 5.92 Hz, 6 H, $\mathrm{NC}H_2$), 1.21 (t, $^3J_{\mathrm{HH}}$ = 7.06 Hz, 3 H, $\mathrm{C}H_3$)).

(4) **5** (0.375 g, 1.71 mmol) and $\mathrm{HCO_2CF_3}$ (0.1978 g, 1.735 mmol) were mixed in 3 mL of $\mathrm{CDCl_3}$ (containing 7% v/v TMS (^{29}Si NMR ($\mathrm{CDCl_3}$) −95.2). Additional $\mathrm{HCO_2CF_3}$ (0.1973 g, 1.730 mmol) was then added (^{29}Si NMR ($\mathrm{CDCl_3}$) −96.8).

1-(Ethyloxonio)silatranium Tetrafluoroborate, 13($\mathbf{BF_4}$). (1) Ethoxysilatrane (**5**, 0.2172 g, 0.9904 mmol) and tetrafluoroboric acid–diethyl ether complex (0.4072 g, 2.514 mmol, 2.5 equiv) were stirred in 5 mL of freshly distilled diethyl ether at room temperature. Immediate precipitation occurred, and, after 20 min, the solid title product was filtered from solution and washed in 2 × 3 mL portions of diethyl ether (^{1}H NMR ($\mathrm{CDCl_3}$) 3.86 (t, $^3J_{\mathrm{HH}}$ = 5.85 Hz, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.82 (q, $^3J_{\mathrm{HH}}$ = 7.06 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.94 (t, $^3J_{\mathrm{HH}}$ = 5.85 Hz, $\mathrm{NC}H_2$), 1.23 (t, $^3J_{\mathrm{HH}}$ = 7.05 Hz, $\mathrm{C}H_3$); molar conductance ($\mathrm{CH_3CN}$) 123 cm^2 mol^{-1} ohm^{-1}). Attempts to grow single crystals of X-ray quality from reaction solutions mixed at −77 °C ended in microcrystalline powders.

(2) **5** (0.0171 g, 0.0780 mmol) and $\mathrm{HBF_4{\cdot}Et_2O}$ (0.0126 g, 0.0778 mmol) were mixed in 0.7 mL of $\mathrm{CD_3CN}$, and the ^{1}H and ^{13}C NMR spectra were recorded (^{1}H NMR ($\mathrm{CD_3CN}$) 4.10 (q, $^3J_{\mathrm{HH}}$ = 7.08 Hz, 2 H, $\mathrm{SiOC}H_2\mathrm{CH_3}$), 3.87 (t, $^3J_{\mathrm{HH}}$ = 6.02 Hz, 6 H, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.43 (q, $^3J_{\mathrm{HH}}$ = 7.00 Hz, 4 H, $\mathrm{COC}H_2\mathrm{CH_3}$), 3.12 (t, $^3J_{\mathrm{HH}}$ = 6.02 Hz, 6 H, $\mathrm{NC}H_2$), 1.30 (t, $^3J_{\mathrm{HH}}$ = 7.09 Hz, 3 H, $\mathrm{SiOCH_2C}H_3$), 1.12 (t, $^3J_{\mathrm{HH}}$ = 7.04 Hz, 6 H, $\mathrm{COCH_2C}H_2$); ^{13}C NMR ($\mathrm{CD_3CN}$) 67.0 ($\mathrm{O}C\mathrm{H_2CH_3}$), 59.5 ($\mathrm{O}C\mathrm{H_2CH_2}$), 52.9 ($\mathrm{N}C\mathrm{H_2}$), 16.2 ($C\mathrm{H_3}$)).

(3) **5** (0.0030 g, 0.014 mmol) and $\mathrm{HBF_4{\cdot}Et_2O}$ (0.0280 g, 0.173 mmol, 12 equiv) were mixed in 0.7 mL of $\mathrm{CDCL_3}$, and the ^{1}H NMR spectrum were recorded (^{1}H NMR ($\mathrm{CDCl_2}$) 4.14 (q, $^3J_{\mathrm{HH}}$ = 7.18 Hz, small), 3.95 (q, br, $^3J_{\mathrm{HH}}$ = 6.67 Hz), 1.41. (t, $^3J_{\mathrm{HH}}$ = 7.00 Hz, small), 1.36 (t, $^3J_{\mathrm{HH}}$ = 7.06 Hz)). A solid, isolated by removal of the solvent, proved to be insoluble in DMSO and benzene.

Reaction of 1-Ethoxysilatrane with Trityl Tetrafluoroborate. (1) 1-Ethoxysilatrane (**5**, 0.0482 g, 0.220 mmol) and trityl tetrafluoroborate (0.0735 g, 0.223 mmol) were mixed in 0.7 mL of $\mathrm{(CD_3)_2CO}$, and the ^{1}H NMR peaks assignable to 1-ethyltriphenylmethyloxy)silatranium tetrafluoroborate (0.31 M) were recorded (^{1}H NMR ($\mathrm{(CD_3)_2CO}$) 7.4–7.1 (m, 18 H), 4.21 (q, $^3J_{\mathrm{HH}}$ = 7.10 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.94 (t, $^3J_{\mathrm{HH}}$ = 5.98

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Hz, 6 H, $OC\mathit{H}_2CH_2$), 3.25 (t, $^3J_{HH}$ = 5.98 Hz, 6 H, $NC\mathit{H}_2$), 1.35 (t, $^3J_{HH}$ = 7.09 Hz, 3 H, $C\mathit{H}_3$)). ^1H NMR spectroscopy in $(CD_3)_2CO$ showed that this salt had decomposed after 2 days in solution.

(2) **5** (0.0184 g, 0.0839 mmol) and Ph_3CBF_4 (0.0282 g, 0.0854 mmol) were mixed in 0.7 mL of $(CD_3)_2CO$, and the ^1H NMR spectrum of the resultant 0.12 M of the salt was recorded (^1H NMR ($(CD_3)_2CO$) 7.4–7.1 (m), 4.28 (q, $^3J_{HH}$ = 7.12 Hz, $OC\mathit{H}_2CH_3$), 4.00 (t, $^3J_{HH}$ = 6.01 Hz, $OC\mathit{H}_2CH_2$), 3.33 (t, $^3J_{HH}$ = 6.00 Hz, $NC\mathit{H}_2$), 1.39 (t, $^3J_{HH}$ = 7.10 Hz, $C\mathit{H}_3$)).

(3) **5** (0.0193 g, 0.0880 mmol) and Ph_3CBF_4 (0.0294 g, 0.0890 mmol) were mixed in 0.7 mL of CD_3CN, and the ^1H NMR spectrum of the salt was recorded (^1H NMR (CD_3CN) 7.6–7.2 (m), 4.09 (q, $^3J_{HH}$ = 7.02 Hz, $OC\mathit{H}_2CH_3$), 3.87 (t, $^3J_{HH}$ = 5.93 Hz, $OC\mathit{H}_2CH_2$), 3.11 (t, $^3J_{HH}$ = 5.87 Hz, $NC\mathit{H}_2$), 1.30 (t, $^3J_{HH}$ = 6.98 Hz, $C\mathit{H}_3$)).

(4) **5** (0.0952 g, 0.434 mmol) and Ph_3CBF_4 (0.1442 g, 0.4369 mmol) were stirred for 30 min in 2 mL of $CDCl_3$. The solvent was removed by evacuation, and the resulting solid redissolved in $CDCl_3$. ^1H NMR spectroscopy showed resonances which could not be identified.

Reaction of 1-Ethoxysilatrane and Trityl Perchlorate. (1) 1-Ethoxysilatrane (0.0074 g, 0.034 mmol) and trityl perchlorate (0.0118 g, 0.0344 mmol) were mixed in 0.7 mL of CD_3CN, and the ^1H NMR spectrum of the solution presumably containing 1-(ethyltriphenylmethyloxy)silatranium perchlorate (0.05 M) was recorded (^1H NMR (CD_3CN) 7.4 (m, $C_6\mathit{H}_5$), 4.15 (q, $^3J_{HH}$ = 7.25 Hz, $OC\mathit{H}_2CH_3$), 3.89 (t, $^3J_{HH}$ = 6.06 Hz, $OC\mathit{H}_2CH_2$), 3.14 (t, $^3J_{HH}$ = 6.01 Hz, $NC\mathit{H}_2$), 1.33 (t, $^3J_{HH}$ = 7.13 Hz, $C\mathit{H}_3$) among other small resonances. ^1H NMR spectroscopy showed no evidence of further reaction after 24 h, upon addition of a second equivalent of the trityl salt.

(2) **5** (0.0548 g, 0.250 mmol) and Ph_3CClO_4 (0.0868 g, 0.253 mmol) were dissolved in 0.7 mL of CD_3CN, and the ^1H NMR spectrum of the solution containing a 0.36 M solution of the salt was recorded (^1H NMR (CD_3CN) 7.4 (m), 5.59 (s, $Ph_3C\mathit{H}$), 4.10 (q, $^3J_{HH}$ = 7.05 Hz, $OC\mathit{H}_2CH_3$), 3.87 (t, $^3J_{HH}$ = 6.98 Hz, $OC\mathit{H}_2CH_2$), 3.84 (t, $^3J_{HH}$ = 7.91 Hz), 3.12 (t, $^3J_{HH}$ = 6.50 Hz, $NC\mathit{H}_2$), 3.09 (t, $^3J_{HH}$ = 6.99 Hz), 1.30 (t, $^3J_{HH}$ = 7.10 Hz, $C\mathit{H}_3$)). After 2 days at room temperature, the NMR spectra of the mixture were retaken (^1H NMR (CD_3CN) 7.4 (m), 5.59 (s), 4.17 (q, $^3J_{HH}$ = 7.16 Hz), 3.89 (t, $^3J_{HH}$ = 6.02 Hz), 3.14 (t, $^3J_{HH}$ = 6.03 Hz), 1.33 (t, $^3J_{HH}$ = 7.11 Hz); ^{13}C NMR (CD_3CN) 145.0, 130.8, 130.1, 127.2, 66.7 ($O\mathit{C}H_2CH_3$), 58.9 ($O\mathit{C}H_2CH_2$), 52.3 ($N\mathit{C}H_2$), 15.3 ($\mathit{C}H_3$)). Evacuation of the solvent gave a solid whose ^1H NMR spectrum indicated decomposition.

Reaction of 1-Phenylsilatrane (11) and Trimethyloxonium Tetrafluoroborate. 1-Phenylsilatrane (**11**, 0.0129 g, 0.0514 mmol) and trimethyloxonium tetrafluoroborate (0.0076 g, 0.051 mmol) were mixed in 0.7 mL of CD_2Cl_2. After 30 min, a ^1H NMR spectrum ($CDCl_3$) showed broadened resonances at the chemical shifts observed for **11**. After 26 h at room temperature, ^1H NMR spectroscopy ($CDCl_3$) continued to reveal these broadened peaks and various other unidentified resonances.

Reaction of 1-Ethoxysilatrane (5) with Trifluoromethanesulfonic Acid. 1-Ethoxysilatrane (**5**, 0.0188 g, 0.0857 mmol) and trifluoromethanesulfonic acid (0.0187 g, 0.125 mmol, 1.46 equiv) were mixed in 0.7 mL of $CDCl_3$. Peaks in the ^1H and ^{13}C NMR spectra of the mixture could be assigned to the formation of 1-(ethyloxonio)silatranium trifluoromethanesulfonate (^1H NMR ($CDCl_3$) 4.23 (q, br, $^3J_{HH}$ = 6.60 Hz, $OC\mathit{H}_2CH_3$), 3.96 (t, br, $^3J_{HH}$ = 5.37 Hz, $OC\mathit{H}_2CH_2$), 3.16 (t, br, $^3J_{HH}$ = 5.48 Hz, $NC\mathit{H}_2$), 1.40 (t, br, $^3J_{HH}$ = 6.88 Hz, $C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$) 65.5 ($O\mathit{C}H_3$), 57.6 ($O\mathit{C}H_2CH_2$), 51.5 ($N\mathit{C}H_2$), 14.7 ($\mathit{C}H_3$)).

Reaction of 1-(Triphenylsiloxy)silatrane with Trifluoroacetic Acid. 1-Triphenylsiloxysilatrane (0.856 g, 0.190 mmol), trifluoroacetic acid (0.0228 g, 0.200 mmol), and 10 mg of $Cr(acac)_3$ were mixed in 0.7 mL of $CDCl_3$, and NMR spectra of the solution presumably containing the 1-triphenylsiloxysilatrane–trifluoroacetic acid adduct were recorded (^{29}Si NMR ($CDCl_3$, inverse gated decoupling) −24.1 ($Ph_3\mathit{Si}$), −99.2 ($\mathit{Si}(OCH_2CH_2)_3N$); ^1H NMR ($CDCl_3$) 7.7–7.6 (m, 6 H), 7.4–7.3 (m, 9 H), 3.81 (t, $^3J_{HH}$ = 5.88 Hz, 6 H, $OC\mathit{H}_2$), and various minor resonances).

Reaction of 1-Ethoxy-2-azasilatrane [$EtOSi(HNCH_2CH_2)_3N$, 17] with Trifluoroacetic Acid. 1-Ethoxy-2-azasilatrane (0.0138 g, 0.0638 mmol) and trifluoroacetic acid (0.0100 g, 0.0877 mmol, 1.4 equiv) were mixed in 0.7 mL of $CDCl_3$ and the ^1H NMR spectrum of the solution presumably containing a 1-ethoxy-2-azasilatrane–trifluoroacetic acid adduct was recorded (^1H NMR ($CDCl_3$) 4.6–4.2 (s, br, 4 H), 3.63 (q, $^3J_{HH}$ = 6.97 Hz, $OC\mathit{H}_2$), 3.14 (t, $^3J_{HH}$ = 5.93 Hz, 6 H, $N_{ax}C\mathit{H}_2$), 2.85 (t, $^3J_{HH}$ = 5.92 Hz, 6 H, $N_{eq}C\mathit{H}_2$), 1.25 (s, br, 2 H), 1.10 (t, $^3J_{HH}$ = 6.98 Hz, 3 H, $C\mathit{H}_3$)).

Reactions of Diethyl Ether with Acids. (1) Diethyl ether (0.0391 g, 0.528 mmol) and trifluoroacetic acid (0.0692 g, 0.607 mmol, 15% molar excess) were mixed in 0.7 mL of $CDCl_3$ (^1H NMR ($CDCl_3$) 12.94 (s), 3.67 (q, $^3J_{HH}$ = 7.04 Hz, $C\mathit{H}_2$), 1.26 (t, $^3J_{HH}$ = 7.12 Hz, $C\mathit{H}_3$)).

(2) Diethyl ether (0.0300 g, 0.405 mmol) and trifluoromethanesulfonic acid (0.0749 g, 0.499 mmol, 23% molar excess) were mixed in 0.7 mL of $CDCl_3$ (^1H NMR ($CDCl_3$) 16.5 (s), 4.09 (q, $^3J_{HH}$ = 7.11 Hz, $C\mathit{H}_2$), 1.45 (t, $^3J_{HH}$ = 7.14 Hz, $C\mathit{H}_3$)).

Table I. Phenol OH Infrared Frequency Shifts in CCl_4 Solution

compd	measd ν(O–H–O) (cm^{-1})	$\Delta\nu$(OH)[a] (cm^{-1})	refs
PhOH	3483 w	129[b]	this work
Et_2O	3335 m	279	*c*, *d*
		277	this work
$Si(OEt)_4$	3381 w	231	this work
		219	*c*
$Si(OMe)_4$	3402 m	210	this work
Me_3SiOMe	3339 m	273	this work
$MeSi(OCH_2CH_2)_3N$, **8**	*e*	275	*c*
$EtOSi(OCH_2CH_2)_3N$, **5**	3339 w	273	this work
$EtO(CH_2)_3Si(OCH_2CH_2)_3N$, **9**	*e*	272	*c*
$MeOSi(OCH_2CH_2)_3N$, **4**	3352 m	260	this work
$CH_2CHSi(OCH_2CH_2)_3N$, **10**	3369 m	243	this work
$PhSi(OCH_2CH_2)_3N$, **11**	3377 w	235	this work
$(Me_3Si)_2O$	*e*	169	*c*
CH_3CN	*e*	178	*d*
Et_3PO	*e*	510	*d*
Et_3N	*e*	553	*d*

[a] ν(O–H–O), 3612 cm^{-1}. The OH frequency of unassociated phenols is 3612 cm^{-1}. [b] Self association in the concentration used (see Experimental Section). [c] See: Voronkov, M. G.; Brodskaya, E. I.; Belyaeva, V. V.; Baryshok, V. P.; Sorokin, M. S.; Yarosh, O. G. *Dokl. Phys. Chem.* (*Engl. Transl.*) **1983**, 945. [d] See: Joesten, M. D.; Drago, R. S. *J. Am. Chem. Soc.* **1962**, *84*, 3817. [e] Not reported.

Reactions of Tetraethylorthosilicate with Acids. (1) Tetraethylorthosilicate (0.0458 g, 0.220 mmol) and trifluoroacetic acid (0.0296 g, 0.260 mmol, 18% molar excess) were mixed in 0.7 mL of $CDCl_3$ (^1H NMR ($CDCl_3$) 11.29 (s), 3.92 (q, $^3J_{HH}$ = 7.01 Hz, $C\mathit{H}_2$), 1.27 (t, $^3J_{HH}$ = 7.01 Hz, $C\mathit{H}_3$)).

(2) Tetraethylorthosilicate (0.0460 g, 0.221 mmol) and trifluoromethanesulfonic acid (0.0424 g, 0.282 mmol, 28% molar excess) were mixed in 0.7 mL of $CDCl_3$ (^1H NMR ($CDCl_3$) 13.00 (s, $HOSO_2CF_3$), 4.2 (s, br, small impurity), 3.95 (q, br, $C\mathit{H}_2$), 1.51 (s, br, small impurity), 1.45 (t, br, $^3J_{HH}$ = 6.85 Hz, $C\mathit{H}_3$)).

Reaction of 1-Ethoxysilatrane with Phenol. 1-Ethoxysilatrane (**5**, 0.0215 g, 0.0980 mmol) and phenol (0.0092 g, 0.098 mmol) were mixed in 0.7 mL of $CDCl_3$. After 30 min, ^1H NMR spectroscopy indicated the formation of the adduct **5**·HOPh (^1H NMR ($CDCl_3$) 7.19 (t, $^3J_{HH}$ = 7.88 Hz, $C_6\mathit{H}_4$), 6.90 (d, $^3J_{HH}$ = 7.98 Hz, C_6H_4), 6.85 (t, $^3J_{HH}$ = 7.52 Hz, C_6H_4), 3.82 (t, $^3J_{HH}$ = 5.89 Hz, $OC\mathit{H}_2CH_2$), 3.77 (q, $^3J_{HH}$ = 7.02 Hz, $OC\mathit{H}_2CH_3$), 2.84 (t, $^3J_{HH}$ = 5.88 Hz, $NC\mathit{H}_2$), 1.19 (t, $^3J_{HH}$ = 7.04 Hz, $C\mathit{H}_3$)).

Preparation of Phenol Adducts of Silatranes and Model Compounds for Basicity Studies. Measurements of the ν(OH) shifts for adducts of silatranes and model compounds with phenol in dilute solutions of carbon tetrachloride were made. The following is an example of the method used to prepare such solutions for which the data in Table I were recorded. A solution of phenol (0.0582 g) in CCl_4 (10.00 mL, 0.0618 M) was prepared. 1-Ethoxysilatrane (**5**, 0.0136 g, 0.0620 mol) was placed in a 1-mL volumetric flask, and the phenol stock solution described above was added up to the mark. A sample was placed in the N_2-flushed IR cell with an N_2-flushed syringe, and the infrared spectrum was recorded.

X-ray Crystallographic Solution of 1-Ethoxysilatrane, 5. A colorless crystal of **5** was mounted on a glass fiber and moved to the diffractometer. The cell constants were determined from 15 reflections taken from a rotation photograph and centered by the diffractometer. Details of the data collection and reduction are given in Table II.

Lorentz and polarization corrections were applied. No decay was observed, and a ψ-scan of a reflection with χ near 90° indicated that no absorption correction was necessary.

Systematic absences uniquely defined the space group as $P2_1/n$. The positions of the Si and O atoms of the two independent molecules were found by direct methods.[14] The remaining non-hydrogen atoms were then found from successive structure factor and difference Fourier calculations. The non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized positions and used for the calculation of structure factors only. Calculations were carried out with the programs cited in ref 15.

X-ray Crystallographic Solution of 1-(Dimethyloxonio)silatranium Tetrafluoroborate 6(BF$_4$). A colorless crystal of **6**(BF_4) was mounted

Table II. Crystal Data for **5**, **6**(BF_4), and **7**

compd	**5**	**6**(BF_4)	**7**
formula	$C_8H_{17}NO_4Si$	$C_8H_{18}BF_4NO_4Si$	$C_{10}H_{18}F_3NO_6Si$
formula wt	219.31	307.13	333.34
space group	$P2_1/n$	$P2_1/c$	*Pbca*
a, Å	10.956 (4)	8.976 (2)	12.655 (4)
b, Å	11.187 (2)	11.517 (1)	11.446 (4)
c, Å	17.638 (8)	12.387 (2)	19.489 (3)
β, deg	95.84 (4)	91.943 (8)	
V, $Å^3$	2151 (1)	1279.8 (4)	2823 (3)
Z	8	4	8
d_{calcd}, g/cm^3	1.355	1.596	1.569
crystal size, mm	0.8 × 0.4 × 0.25	0.21 × 0.30 × 0.49	0.35 × 0.20 × 0.25
μ (Mo Kα), cm^{-1}	2.012	2.34	2.193
data collection instrument	Syntex $P2_1$	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.70926 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
orientation reflcns, no., range (2θ)	15, 15° < 2θ < 25°	25, 19.2° < 2θ < 33.9°	25, 17° < 2θ < 32°
temp, °C	25 ± 1	−50 ± 1	−100 ± 2
scan method	ω-scans	θ–2θ	θ–2θ
data col. range, 2θ, deg	3–50	4–50	4–50
no. unique data, total	3784	2533	2469
with $F_o^2 > 3\sigma(F_o^2)$	1054	1463	1247
no. of parameters refined	313	175	144
R[a]	0.068	0.080	0.039
R_w	0.083	0.108[c]	0.048[b]
quality-of-fit indicator[d]	1.98	2.68	1.03
largest shift/esd, final cycle	0.02	<0.01	0.01
largest peak, e/$Å^3$	0.540	0.734	0.296

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|) + 0.001|F_o|^2]$. [d] Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2/N_{obs} - N_{parameters})]^{1/2}$.

on a glass fiber and moved into the cold stream of the low temperature device on the diffractometer. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent crystal and refinement information is given in Table II.

Lorentz and polarization corrections were applied. No decay or absorption corrections were necessary.

The space group $P2_2/c$ was unambiguously assigned based on the systematic absences. The positions of all 19 non-hydrogen atoms were taken from an E-map produced by direct methods.[16] In the final stages of refinement, all non-hydrogen atoms were given anisotropic temperature factors, and hydrogen atoms were used in calculated positions for the calculation of structure factors only. Refinement calculations were carried out with the SHELX-76 programs.[17]

X-ray Crystallographic Solution of the 1-Ethoxysilatrane–Trifluoroacetic Acid Adduct, 7. A colorless crystal of **7** was taken from the mother liquor, mounted on a glass fiber, and immediately placed in the cold stream of the crystal cooling device. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table II.

Lorentz and polarization corrections were applied, and an absorption correction was made based on a series of ψ-scans.

All 21 non-hydrogen atoms were located by direct methods.[16] Following several cycles of full-matrix least-squares refinement, a difference Fourier map indicated the positions of all of the expected hydrogen atoms. The hydrogen atoms bound to carbon were then placed in idealized positions 1.0 Å from the carbon atoms and used for the calculation of structure factors only. The acidic hydrogen atom (bound to O(5) of the trifluoroacetic acid) was then included in the final cycles of refinement, in which only the Si, F, O, and N atoms were given anisotropic temperature factors. Refinement calculations were carried out with the CAD4-SDP programs.[18] Neutral atom scattering factors and anomalous scattering corrections were taken from ref 21 for each of the structure determinations of **5**, **6**(BF_4) and **7**.

Discussion

Structures of 5–7. Positional parameters and ORTEP drawings for **5**, **6**(BF_4), and **7** appear in Tables III, IV, and V and in Figures 1, 2, and 3, respectively.

The Si–N_{ax} distances in silatranes of type **1** (where R also can be a very electronegative substituent such as a fluorine or chlorine) lie between 1.87 Å[20] (the sum of the covalent radii of silicon and nitrogen) and the sum of the van der Waals radii (3.65 Å)[21] of these atoms.[1] This distance for **5** (2.152 Å), **6**(BF_4) (1.965 Å), and **7** (2.050 Å) decreases substantially (ca. 0.1–0.2 Å) from **5** to **6**(BF_4) and **7**. The SiN_{ax} distance in **6** (is the shortest ever recorded for a silatrane, the next shortest being that in $ClSi(OCH_2CH_2)_3N$ (2.02 Å).[1] The exceptionally short Si–N_{ax} distance in cation **6** can be attributed to the high effective electronegativity of the Me_2O^+ group. The effective electronegativity of the hydrogen-bonded $CF_3C(O)OH$–OEt moiety in **7** must also be quite large to give rise to its very short Si–N_{ax} distance. This conjecture is in accord with the unusually short distance (2.489 Å) between the oxygens containing the hydrogen which is engaged in hydrogen bonding. This distance is comparable to those in hydrogen-bonded acid salts of carboxylic acids[22] and in the recently reported tetramesityl-1,3-difluorohydrogen bisulfonate (2.43 Å)[23] and in 1,2,3-benzotriazolium dihydrogen phosphate (2.48 Å).[24] These

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Table III. Positional Parameters[a] (×10^4) for EtOSi(OCH$_2$CH$_2$)$_3$N, **5**[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Si(1)	0.1956 (4)	0.0708 (4)	0.3570 (3)	4.3 (2)
Si(2)	0.1519 (4)	−0.5916 (4)	0.6663 (3)	4.2 (2)
O(1)	0.3079 (9)	0.1666 (8)	0.3752 (6)	5.8 (4)
O(2)	0.0997 (10)	0.0501 (8)	0.4222 (6)	5.6 (4)
O(3)	0.1519 (10)	0.0342 (8)	0.2687 (5)	5.1 (4)
O(4)	0.2783 (10)	−0.0531 (8)	0.3734 (5)	5.3 (3)
O(5)	0.2339 (10)	−0.6952 (8)	0.6273 (6)	6.3 (4)
O(6)	0.1870 (10)	−0.5547 (9)	0.7564 (5)	5.8 (4)
O(7)	0.0118 (9)	−0.5645 (8)	0.6255 (5)	4.8 (3)
O(8)	0.2220 (9)	−0.4748 (7)	0.6334 (5)	4.6 (3)
N(1)	0.0896 (12)	0.2281 (10)	0.3288 (7)	5.5 (5)
N(2)	0.0608 (12)	−0.7408 (9)	0.7148 (6)	4.8 (5)
C(1)	0.2889 (15)	0.2897 (15)	0.3782 (11)	8.1 (7)
C(2)	0.1786 (18)	0.3240 (13)	0.3322 (15)	11.5 (10)
C(3)	−0.0019 (18)	0.1246 (15)	0.4290 (10)	7.2 (7)
C(4)	0.0122 (21)	0.2350 (16)	0.3841 (13)	11.0 (9)
C(5)	0.0856 (16)	0.1095 (14)	0.2167 (8)	6.0 (6)
C(6)	0.0341 (24)	0.2063 (19)	0.2542 (11)	13.0 (11)
C(7)	0.3419 (20)	−0.0785 (17)	0.4460 (10)	9.8 (8)
C(8)	0.4281 (20)	−0.1624 (16)	0.4503 (11)	9.8 (9)
C(9)	0.2266 (17)	−0.8180 (13)	0.6445 (12)	8.6 (8)
C(10)	0.1036 (17)	−0.8451 (13)	0.6746 (12)	7.7 (7)
C(11)	0.1304 (19)	−0.6115 (17)	0.8171 (9)	8.2 (7)
C(12)	0.1026 (16)	−0.7388 (16)	0.7944 (9)	7.1 (7)
C(13)	−0.0858 (14)	−0.6490 (13)	0.6264 (9)	5.6 (6)
C(14)	−0.0720 (14)	−0.7183 (14)	0.6979 (9)	5.8 (6)
C(15)	0.2328 (15)	−0.4566 (13)	0.5568 (9)	5.5 (6)
C(16)	0.3580 (17)	−0.4742 (16)	0.5361 (9)	7.7 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)*[a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

Table IV. Positional Parameters for [Me$_2$OSi(OCH$_2$CH$_2$)$_3$N]BF$_4$, **6**(BF$_4$)[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Si	0.5351 (2)	0.00049 (9)	0.2659 (1)	0.85 (3)
O(1)	0.7291 (5)	−0.0412 (3)	0.2465 (3)	1.09 (8)
O(2)	0.5132 (5)	0.0305 (3)	0.1371 (3)	1.68 (9)
O(3)	0.5891 (4)	0.0996 (3)	0.3538 (3)	1.19 (8)
O(4)	0.4965 (5)	−0.1312 (3)	0.3085 (3)	1.68 (9)
N	0.3271 (6)	0.0455 (4)	0.2873 (3)	1.2 (1)
C(1)	0.8132 (8)	−0.0901 (4)	0.3396 (5)	1.9 (1)
C(2)	0.8257 (8)	0.0339 (4)	0.1830 (5)	1.8 (1)
C(3)	0.3736 (7)	0.0856 (5)	0.1030 (4)	1.5 (1)
C(4)	0.2561 (7)	0.0475 (5)	0.1758 (4)	1.5 (1)
C(5)	0.4738 (8)	0.1636 (4)	0.4084 (4)	2.0 (1)
C(6)	0.3333 (8)	0.1619 (4)	0.3390 (4)	1.8 (1)
C(7)	0.3442 (7)	−0.1581 (4)	0.3248 (5)	1.7 (1)
C(8)	0.2629 (8)	−0.0466 (5)	0.3578 (5)	1.9 (1)
B	0.956 (1)	0.2407 (5)	−0.0552 (5)	2.0 (2)
F(1)	0.9688 (6)	0.2229 (4)	−0.1651 (3)	3.4 (1)
F(2)	1.0677 (7)	0.1807 (4)	−0.0018 (4)	5.1 (2)
F(3)	0.9721 (6)	0.3566 (3)	−0.0325 (4)	4.0 (1)
F(4)	0.8159 (7)	0.2017 (4)	−0.0280 (4)	4.6 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)*[a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

examples are known to be symmetrically bonded around the hydrogen, whereas **7** is unsymmetrically bonded. As a representative of the latter type of hydrogen bonding, **7** contains the shortest reported *O*(H)*O* distance.

The polarizing effect of the Me$^+$ in cation **6** and of the proton in the hydrogen bond of CF$_3$C(O)OH in adduct **7** can be seen from the increase in Si–O$_{ax}$ distance in the order **5** (1.658 Å) < **7** (1.710 Å) < **6**(BF$_4$) (1.830 Å). The same trend is seen in the shrinkage of the distance of the silicon from the plane of the equatorial oxygens from **5** (0.179 Å) to **7** (0.102 Å) to **6**(BF$_4$) (0.017 Å) as the geometry around silicon becomes an almost idealized TBP for cation **6**. This movement toward an idealized TBP is also reflected in the widening of the O$_{eq}$–Si–O$_{eq}$ from **5** (118.9°) to **7** (119.6°) to cation **6** (120.0°), with a concomitant narrowing of the O$_{eq}$–Si–O$_{ax}$ angle (96.4 to 93.6 to 90.6°, respectively). Also in accord with the increased interaction of the Lewis acid from **7** to **6** is the narrowing of the Si–O$_{ax}$–C angle from **5** (122.7°) to **7** (121.1) to **6** (118.7°).

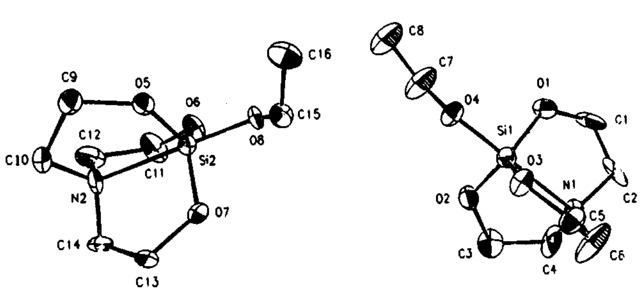

Figure 1. ORTEP drawing of **5** with ellipsoids at the 50% probability level.

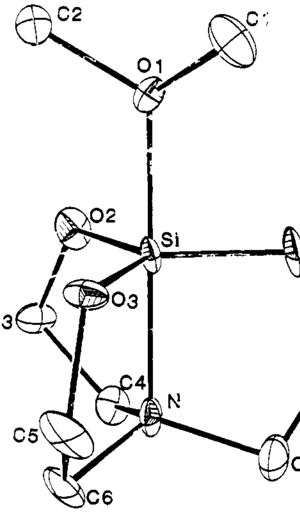

Figure 2. ORTEP drawing of the cation in **6**(BF$_4$) with ellipsoids at the 50% probability level.

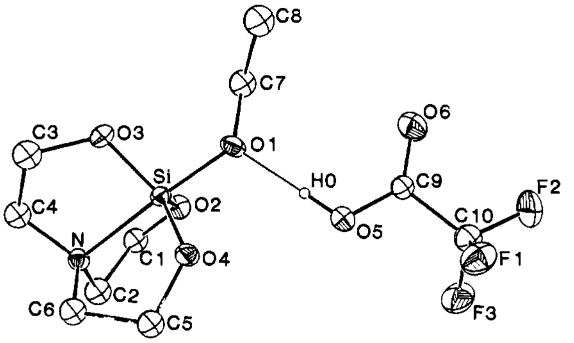

Figure 3. ORTEP drawing of **7** with ellipsoids at the 50% probability level. The size of the hydrogen atom shown is arbitrary.

From a linear plot of the Si–N$_{ax}$ distance versus the distance of the silicon to the plane of the equatorial oxygens in a set of silatranes, it was concluded from the position of the intercept that the Si–N$_{ax}$ distance would be 1.83 Å if the silicon were coplanar with the equatorial oxygens.[1] The structural metrics discussed above suggest that such a plot is not trustworthy at short Si–N$_{ax}$ distances, because the virtually ideal TBP geometry displayed by cation **6** features an Si–N$_{ax}$ bond which is at least 0.1 Å longer than 1.83 Å. The Si–O$_{eq}$ bond lengths are considerably shorter in silatranes than their covalent bond distance (1.83 Å)[19] and are quite constant in magnitude[1,25] (**5**, 1.648; **6**(BF$_4$) (1.642); **7**, 1.652 Å). Even in *trans*-(Me$_2$PhP)$_2$PtCl[Si(OCH$_2$CH$_2$)$_3$N][26] wherein

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(25) Hencsei, P.; Parkanyi, L. *Rev. Silicon Germanium Tin Lead Compd.* **1985**, *8*, 191.

(26) Eaborn, C.; Odell, K. J.; Pidcock, A.; Scollary, G. J. *J. Chem. Soc., Chem. Commun.* **1976**, 317.

Table V. Positional Parameters for $CF_3CO_2H\cdot EtOSi(OCH_2CH_2)_3N$, **7**[a]

atom	x	y	z	B^b (Å^2)
Si	0.53942 (8)	0.23509 (9)	0.72373 (5)	1.25 (2)
F(1)	0.7823 (2)	0.6029 (2)	0.5547 (1)	2.80 (5)
F(2)	0.8161 (2)	0.5084 (3)	0.4625 (1)	3.27 (6)
F(3)	0.8837 (2)	0.4524 (2)	0.5580 (1)	3.19 (6)
O(1)	0.5285 (2)	0.2895 (2)	0.6423 (1)	1.70 (5)
O(2)	0.6058 (2)	0.1176 (2)	0.7005 (1)	1.72 (5)
O(3)	0.4111 (2)	0.2231 (2)	0.7376 (1)	1.84 (6)
O(4)	0.6015 (2)	0.3554 (2)	0.7479 (1)	1.66 (5)
O(5)	0.6898 (2)	0.3978 (3)	0.6064 (1)	2.37 (6)
O(6)	0.6420 (3)	0.3926 (3)	0.4956 (1)	3.09 (7)
N	0.5600 (2)	0.1782 (3)	0.8226 (2)	1.41 (6)
C(1)	0.6337 (3)	0.0316 (4)	0.7500 (2)	2.04 (7)*
C(2)	0.6468 (4)	0.0916 (4)	0.8192 (2)	2.27 (8)*
C(3)	0.3738 (4)	0.2006 (4)	0.8062 (2)	2.33 (8)*
C(4)	0.4574 (4)	0.1275 (4)	0.8429 (2)	2.09 (7)*
C(5)	0.6503 (3)	0.3624 (4)	0.8144 (2)	1.93 (8)*
C(6)	0.5883 (3)	0.2840 (4)	0.8630 (2)	1.94 (7)*
C(7)	0.4745 (3)	0.2245 (4)	0.5890 (2)	2.14 (7)*
C(8)	0.3928 (4)	0.3013 (4)	0.5560 (2)	2.60 (9)*
C(9)	0.6990 (3)	0.4204 (4)	0.5425 (2)	1.55 (7)*
C(10)	0.7963 (3)	0.4967 (4)	0.5289 (2)	2.03 (7)*
H(0)	0.637 (4)	0.350 (5)	0.617 (3)	4 (2)*

[a] Starred atoms were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)^*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos \gamma)^*B(1,2) + ac(\cos \beta)^*B(1,3) + bc(\cos \alpha)^*B(2,3)]$.

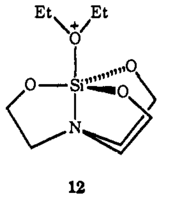
Table VI. ^1H NMR Downfield Shifts (ppm) Relative to **5** for **5** in the Presence of Various Lewis Acids

			cage protons		ethoxy protons	
acid[a]	concn[b]	medium	NCH_2	OCH_2	CH_2	CH_3
Et_3OBF_4[c]		$CDCl_3$	0.47	0.17	0.64	0.23
HO_2CCF_3[d]		CD_3CN	0.04	0.02	0.08	0.00
HO_2CCF_3[d]		$CDCl_3$	0.05	0.04	0.11	0.06
HO_2CCF_3		$CDCl_3$	0.03	0.01	0.05	0.00
HO_2CCF_3 (1.26 equiv)		$CDCl_3$	0.06	0.03	0.09	0.01
HCO_2CF_3 (2.5 equiv)		$CDCl_3$	0.10	0.06	0.11	0.01
PhOH		$CDCl_3$	0.04	0.02	0.05	0.00
HSO_3CF_3 (1.45 equiv)		$CDCl_3$	0.30	0.12	0.50	0.20
$HBF_4\cdot Et_2O$		CD_3CN	0.31	0.21	0.58	0.30
Ph_3CClO_4	0.05 M	CD_3CN	0.33	0.23	0.62	0.33
Ph_3CClO_4	0.36 M	CD_3CN	0.31	0.21	0.57	0.30
Ph_3CClO_4[e]	0.36 M	CD_3CN	0.33	0.23	0.64	0.33
Ph_3CBF_4		CD_3CN	0.30	0.19	0.56	0.30
Ph_3CBF_4	0.12 M	$(CD_3)_2CO$	0.57	0.32	0.69	0.37
Ph_3CBF_4	0.31 M	$(CD_3)_2CO$	0.39	0.26	0.63	0.33

[a] One equivalent of Lewis acid present, unless otherwise noted. [b] Routine NMR concentration, unless otherwise specified. [c] Isolated sample of **14**(BF_4). [d] Isolated sample of **7**. [e] After 2 days.

the N_{ax}–Si distance is exceptionally long (2.89 (1) Å) and the OSiO angles are near tetrahedral (av 110.1 (5)°), the SiO distances average to 1.649 (9) Å, a value very close to the analogous distances in **5**, **6**(BF_4), and **7**. These observations accord with the notion that bond length sensitivity to stereoelectronic changes decreases with increasing bond order.[20]

Syntheses of New Silatranes. In this section are discussed the syntheses of the isolable silatranes **6**(BF_4), **7**, **12**(BF_4), and **13**(BF_4).



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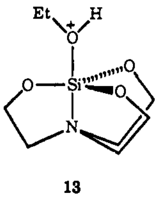

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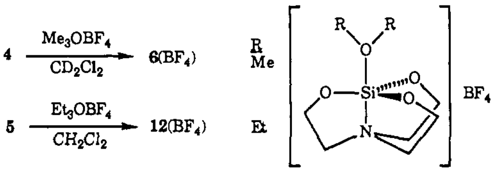
Table VII. ^{13}C NMR Shifts[a] (ppm) Relative to **5** for **5** in the Presence of Various Lewis Acids

		cage carbons		ethoxy carbons	
acid[c]	medium	NCH_2	OCH_2	CH_2	CH_3
Et_3OBF_4[c]	$CDCl_3$	0.5	1.1	15.5	−5.1
HO_2CCF_3 (1.26 equiv)	$CDCl_3$	0.1	−0.2	0.8	−1.1
HO_3SCF_3 (1.45 equiv)	$CDCl_3$	0.4	0.0	7.8	−3.7
$HBF_4\cdot Et_2O$	CD_3CN	1.5	1.3	8.8	−2.7
Ph_3CClO_4	$CDCl_3$	0.9	0.8	8.5	−3.6

[a] Positive and negative values denote downfield and upfield shifts, respectively. [b] Approximately 1 equiv unless otherwise noted. [c] Dissolved sample of isolated **12**(BF_4).

The syntheses of **6**(BF_4) and **12**(BF_4) are summarized in reactions 1 and 2. Although **6**(BF_4) forms crystals of X-ray quality, its ^1H NMR spectrum in solution appears to represent a mixture.

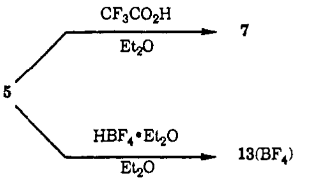


(1)

(2)

However, the downfield shifts in its tentatively assigned protons relative to the corresponding protons in **4** (see Experimental Section) are consistent with those observed for **12**(BF_4) in Table VI. ^{13}C NMR spectra consistent with the structure of cation **6** were obtained in the solid state. By contrast, **12**(BF_4) resisted single-crystal growth but gave a ^1H, ^{13}C, and ^{29}Si NMR solution spectra (vide infra) and a molar conductance indicative of pure product.

As shown in reactions 3 and 4, two different types of products are formed when **5** is reacted with acids. As shown in the previous section, **7** is a hydrogen-bonded adduct whereas **13**(BF_4) is a protonated salt. The latter tentative conclusion is based on the greater downfield ^1H NMR chemical shifts of **13**(BF_4) than **7** compared with **5**, these downfield shifts being similar to those observed in the isolated alkylated salts **6**(BF_4) and **12**(BF_4) and also in solutions of **5** and CF_3SO_3H (see Experimental Section). That reaction 3 is an equilibrium was shown by the increasing downfield ^1H NMR shifts upon increasing the ratio of CF_3CO_2H to **5** (see Experimental Section).



(3)

(4)

In general, the greatest downfield ^1H and ^{13}C NMR shifts upon hydrogen-bonded adduct formation, protonation, or alkylation occur at the axial methylene (**5**) or methyl group (**4**), suggesting predominant ligation of the electrophilic group at the axial oxygen in solution, although some fluxional ligation at the equatorial oxygens cannot be ruled out.

NMR Spectroscopic Characterization. In this section we discuss the NMR spectroscopic parameters for the isolable new silatranes and for species formed in solution in the presence of protonic acids and carbenium ions.

Although ^1H NMR spectra of **6**(BF_4) showed evidence of decomposition, its analogue **12**(BF_4) did not. From Table VI it is seen from the first row of entries that relative to its parent compound **5**, **12**(BF_4) displays downfield ^1H NMR shifts which for the OCH_2CH_3 protons is the most pronounced. This is consistent with alkylation of the axial oxygen. From the second row of entries in Table VI, the same can be said for the adduct **7** although the shifts are quite small. In the fourth through the sixth rows of this table, however, the increasing CF_3CO_2H concentration

Table VIII. Solution and Solid-State ^{29}Si NMR Chemical Shifts of Silatranes

	solution		solid
compound	shift (ppm)	medium	shift (ppm)
$MeOSi(OCH_2CH_2)_3N$, **4**	−95.4[a]	*b*	−95.4
$EtOSi(OCH_2CH_2)_3N$, **5**	−95.2 −94.7[a]	$CDCl_3$ *b*	−96.1[c] *d*
$Ph_3SiOSi(OCH_2CH_2)_3N$, **15**	−98.1[e]	$CDCl_3$	*d*
$CF_3CO_2HEtOSi(OCH_2CH_2)_3N$, **7**	−96.8	$CDCl_3$	*d*
$CF_3CO_2HPh_3SiOSi(OCH_2CH_2)_3N$, **16**	−99.2	$CDCl_3$[f]	*d*
$[Me_2OSi(OCH_2CH_2)_3N]BF_4$, **6**($BF_4$)	*d*		−90.2
$[Et_2OSi(OCH_2CH_2)_3N]BF_4$, **12**($BF_4$)	−90.7	$CDCl_3$	−89.4

[a] See ref 15. [b] Solvent not reported. [c] Average of the two values observed (−95.6 and −96.6 ppm). [d] Not measured. [e] δ^{29}Si −24.7 ($SiPh_3$). [f] Adduct dissociates on evaporation of solution. δ^{29}Si −24.7 ($SiPh_3$).

Table IX. ^{1}H NMR Downfield Shifts for Reaction Products of Miscellaneous Compounds with Lewis Acids

			cage protons		ethoxy protons	
compound	acid[a]	medium	NCH_2	OCH_2	CH_2	CH_3
$Ph_3SiOSi(CH_2CH_2)_3N$, **15**	HO_2CCF_3	CD_2Cl_2	0.03	0.02		
$EtOSi(NHCH_2CH_2)_3N$, **17**	HO_2CCF_3	$CDCl_3$	0.08	0.15[b]	0.03	0.02
Et_2O	HO_2CCF_3	$CDCl_3$			0.21	0.06
Et_2O	HO_3SCF_3	$CDCl_3$			0.61	0.24
$Si(OEt)_4$	HO_2CCF_3	$CDCl_3$			0.06	0.02
$Si(OEt)_4$	HO_3SCF_3	$CDCl_3$			0.10	0.04

[a] Approximately 1 equiv. [b] $N_{eq}CH_2$ protons.

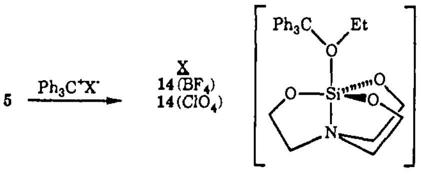
in $CDCl_3$ is shown to augment the downfield movement of all but the CH_3 protons. These results suggest the presence of an equilibrium of the type shown below.

$$\mathbf{5} \underset{-CF_3CO_2H}{\overset{CF_3CO_2H}{\rightleftharpoons}} \mathbf{7} \qquad (5)$$

Equilibria involving further hydrogen bonding at the equatorial or axial oxygens cannot be ruled out. That the axial oxygen of 1-alkoxysilatranes such as **4** and **5** is alkylated both in the solid and solution states is also seen by comparing the downfield ^{13}C NMR shifts for **6**(BF_4) compared with **4** in the solid state (see Experimental Section) and for **12**(BF_4) compared with **5** in the solution state (see first row of entries in Table VII). Included in Table VII are ^{13}C NMR data for **7** (second row of entries) which are in accord with hydrogen bonding at the axial oxygen. The ^{29}Si NMR shifts collected in Table VIII reveal that the alkylation of **4** or **5** producing **6**(BF_4) or **12**(BF_4), respectively, causes this nucleus to resonate at lower applied fields, whereas allowing **5** to hydrogen bond in **7** does not appreciably influence the position of this resonance.

Features of several of the solid-state NMR spectra are worthy of note. Compound **5** displays two ^{29}Si NMR resonances (Table VIII), and as was shown herein (vide supra) the unit cell of **5** contains two independent molecules in the unit cell. Related observations are the two $^{13}CH_3$ resonances observed for **6**(BF_4) and **12**(BF_4). In **6**(BF_4) these chemical shifts are separated by 12 ppm, while in **12**(BF_4) this separation is 3 ppm (see Experimental Section). The existence of a chemical shift difference for **6**(BF_4) is consistent with the two different intramolecular CH_3 environments found from the crystal structure determination of this salt described earlier herein, although the large magnitude of the chemical shift difference (12 ppm) is somewhat puzzling. Even more puzzling is the $^{13}CH_3$ chemical shift difference in the ethyl analogue **12**(BF_4), which is seen in the absence of any detectable difference for the adjacent CH_2 carbons which are presumably closer to the molecular source of the unsymmetrical environment. In view of the results with **6**(BF_4), a chemical shift difference in the neighborhood of 12 ppm might have been expected for the CH_2CH_3 carbons of **12**(BF_4). Admittedly we have no knowledge of the crystal structure **12**(BF_4) because of failure in our attempts to grow adequate single crystals.

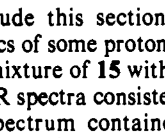
Alkylated silatrane species stable only in solution are now briefly discussed. The downfield shifts (Table VI) in the ^{1}H NMR spectra of solutions of equimolar mixtures of the reactants shown in reaction 6 support the formation of cation **14**. These compounds decompose rather easily in solution, however, and **14**(BF_4) did not survive isolation. That equatorial alkylation (and presumably protonation) may occur in these silatranes is suggested by the broadened ^{1}H resonances observed for **11** in the presence of Me_3OBF_4. This broadening may be attributed to fluxionality of the methyl carbocation ion among the three equatorial oxygens. Upon standing, additional resonances suggestive of decomposition began to appear. Because the solution NMR spectra we have seen under alkylation/protonation conditions are generally sharp with the strongest downfield shifts associated with the axial protons and carbons, it is concluded that the predominant site of electrophilic attack is also the axial oxygen in these compounds.



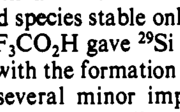
(6)

14

We conclude this section with a discussion of the NMR characteristics of some protonated species stable only in solution. A reaction mixture of **15** with CF_3CO_2H gave ^{29}Si (Table VIII) and ^{1}H NMR spectra consistent with the formation of **16** though the latter spectrum contained several minor impurity peaks. Interestingly, the ^{1}H NMR spectrum of azasilatrane **17** in the presence of CF_3CO_2H gives the greatest downfield shift for the N_{eq} CH_2 rather than the O_{ax} CH_2 protons (Table IX). From this we may infer that the dominant species is **18** wherein preferential protonation is fluxionally occurring on the presumably more basic equatorial nitrogens. The X-ray crystal structure of an analogous



15 Z = nothing
16 Z = CF_3CO_2H



17 Z = nothing
18 Z = H$^+$

cation (where OEt is replaced by H in **18**) was recently carried out in our laboratories.[27] The ^{1}H downfield shifts experienced by **5** in the presence of PhOH (Experimental Section) are nearly the same as those induced by CF_3CO_2H (Table IX).

For comparison with **5** (Table VI), Et_2O and $Si(OEt)_4$ were also reacted with acids (Table IX). The downfield ^{1}H shifts relative to the unprotonated compounds are in the order $Si(OEt)_4$ < **5** < Et_2O, which accords with the basicity order of these compounds (see next section).

Phenol OH Infrared Shifts. A measure of the basicity of a series of similar bases can be obtained from the shift of the OH stretching frequency of phenol.[28] In Table I are collected the relevant IR data for a series of silatranes and several other compounds for comparison. The data in this table imply the approximate basicity order $(Me_3Si)_2O$ < MeCN < $Si(OMe)_4$ < $Si(OEt)_4$ < **11** < **12** ≅ **10** < **4** < **9** ≅ **5**, **8**, Me_3SiOMe < Et_2O. Restricting our attention to the ethers in this ordering ($(Me_3Si)_2O$ < $(RO)_3SiOR$ < **12** < **4** < **5** < Me_3SiOMe < Et_2O) we see that silatranyl moieties are more basic than an $(RO)_3Si$ group, undoubtedly owing to the coordinate nature of the $N_{ax} \rightarrow Si$ bond. Whether π interaction involving silicon 3d orbitals in the ether linkages play a role here is still controversial.[29] Silatrane **8** must be hydrogen bonding at O_{eq} while **4**, **5**, and **9** could be doing so at either or both oxygen sites. In the cases of **4** and **5**, the axial oxygen may be preferentially involved in hydrogen bonding on the bases of the ^{1}H NMR spectroscopic argument made in the previous section for **5** in the presence of PhOH and on our structural determination of **7**. The decreasing basicity order **8** > **10** > **11** can be attributed to the corresponding increasing electron-withdrawing ability of the axial hydrocarbon substituent.

Conclusions. Polarization of the axial oxygen in alkoxysilatranes such as **4** and **5** by strong hydrogen bonding (**7**) or alkylation (**6**(BF_4)) leads to significant shortening (~0.1–0.2 Å) of the transannular SiN_{ax} bond and lengthening (up to 0.17 Å) of the SiO_{ax} link. The conclusion reached by others[1] that silatranes in which the Si atom is coplanar with the equatorial oxygens will exhibit an SiN_{ax} bond length of 1.83 Å is apparently not valid for **6**(BF_4) in which coplanarity is realized within experimental error and in which the SiN_{ax} bond length (1.965 Å) though the shortest thus far reported for a silatrane is >0.1 Å longer than the predicted[1] 1.83 Å. Consistent with the crystal structures of our new silatranes **6**(BF_4) and **7**, solution ^{1}H and solution and solid-state ^{13}C NMR chemical shifts for several hydrogen bonded, protonated, and alkylated alkoxysilatranes indicate electrophilic attack at the O_{ax} site. Where the axial group is a phenyl (**11**) or where the equatorial atoms are nitrogens (**17**), the solution NMR data suggest equatorial atom protonation. For compounds featuring O_{ax} and O_{eq} atoms (e.g., **5**) ^{1}H NMR studies as a function of acid concentration suggest equilibria involving protonation of both sites. The observed basicity order $(Me_3Si)_2O$ < $Si(OMe)_4$ < **4** < **5** ≅ Me_3SiOMe < Et_2O derived from phenol ν(OH) shift data is consistent with the order $(H_3Si)_2O$ < H_3SiOCH_3 < H_3COCH_3,[26] with the added feature that a silatranyl group bound to an OR group is more basic than a similarly bound $(RO)_3Si$ moiety, whereas it is less basic than a Me_3Si or Et group linked to an OR group.

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Supplementary Material Available: Tables of thermal parameters, bond lengths, bond angles, and general displacement expressions (24 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Stereospecific Preparation of Polyfunctional Olefins by the Carbometalation of Alkynes with Polyfunctional Zinc–Copper Organometallics. Stereospecific Preparation of Five-Membered Carbocycles by Intramolecular Carbocupration

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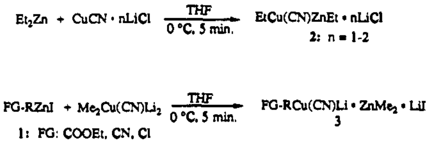
Abstract: The addition of copper reagents prepared by transmetalation from polyfunctional organozinc iodides to reactive alkynes such as 1-(methylthio)-1-hexyne, phenylacetylene and acetylene, leads to stereochemically well-defined (syn addition), highly functionalized alkenylcopper reagents that after protonation, allylation, iodolysis, or stannylation afford stereochemically pure di-, tri-, and tetrasubstituted olefins. A similar intramolecular carbocupration has allowed the preparation of highly substituted five-membered carbocycles. Compared to lithium– or magnesium–copper reagents, the highly functionalized copper reagents can contain an ester, nitrile, or chloride function. However, they display a lower reactivity than the lithium– or magnesium–copper reagents and do not react with unactivated terminal alkynes.

The carbocupration of alkynes by lithium– and magnesium–copper reagents is one of the most efficient ways for preparing stereoisomerically pure di-, tri-, or tetrasubstituted double bonds.[1] The reaction proceeds generally in good yields and is highly regio- and stereoselective. However, the method has some synthetic limitations: internal alkynes are usually unreactive[2] toward carbocupration; and aryl- alkenyl-,[3] allyl-, and alkynylcopper

Scheme I



$$\mathrm{Et_2Zn + CuCN\cdot nLiCl \xrightarrow[0\ ^\circ C,\ 5\ min.]{THF} EtCu(CN)ZnEt\cdot nLiCl}$$

2: n = 1-2

$$\mathrm{FG\text{-}RZnI + Me_2Cu(CN)Li_2 \xrightarrow[0\ ^\circ C,\ 5\ min.]{THF} FG\text{-}RCu(CN)Li\cdot ZnMe_2\cdot LiI}$$

1: FG: COOEt, CN, Cl

3

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