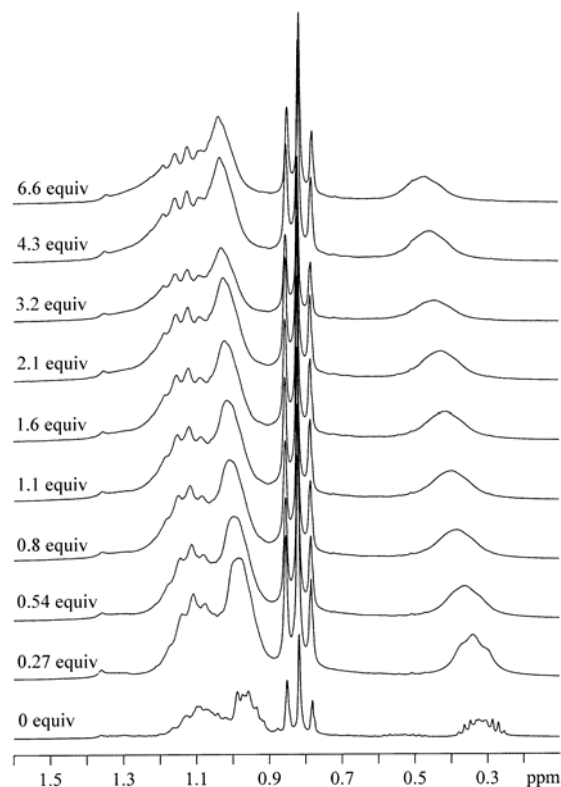


**Formation of Hypervalent Complexes of Various Trifluoro-silanes with Pyridine  
and with 4-Methoxy-pyridine, through Intermolecular Silicon···Nitrogen  
Interactions**

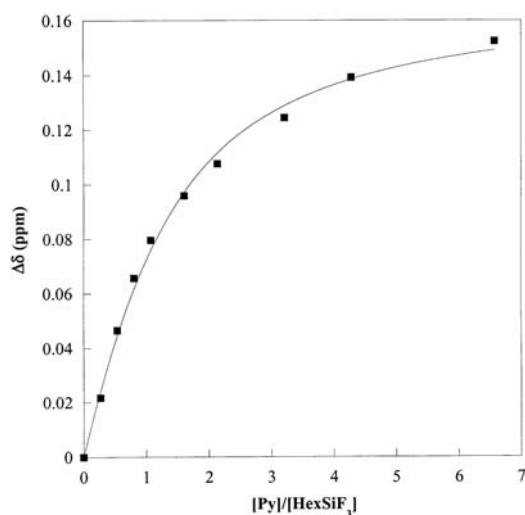
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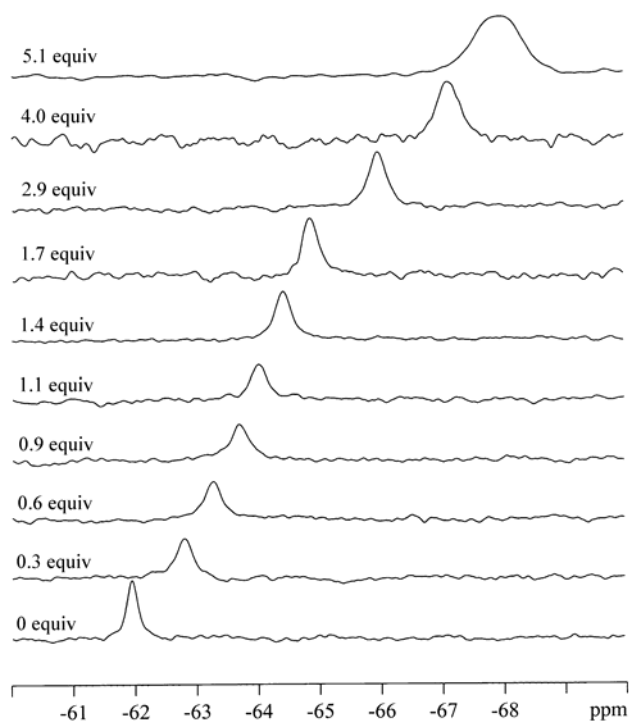
**Supporting Information**



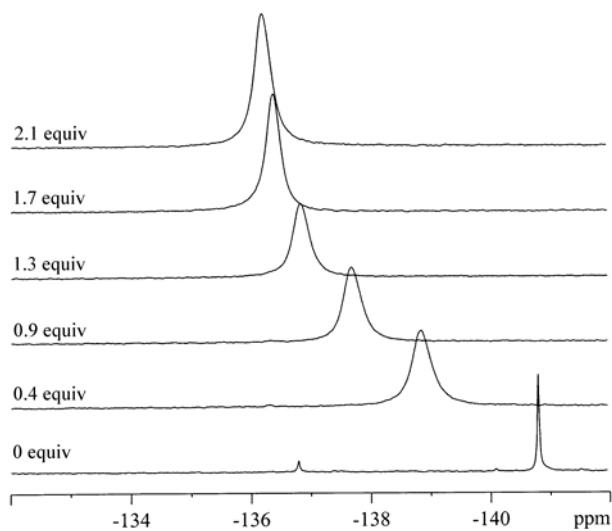
**Figure S1.**  $^1\text{H}$  NMR titration of silane **2** (0.9 M) with py in benzene at 298 K. The number of equivalents (equiv) of py added is indicated on the left. Only the aliphatic region of the spectra is shown. The signals at 0.32 and 0.83 ppm in the spectrum of free **2** correspond to the  $\alpha$ -hydrogens ( $\text{CH}_2^1$ ) and terminal methyl ( $\text{CH}_3^6$ ), respectively, in **2**. All the signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of free silane **2** in benzene were assigned using 2D COSY and HMQC NMR spectroscopy.



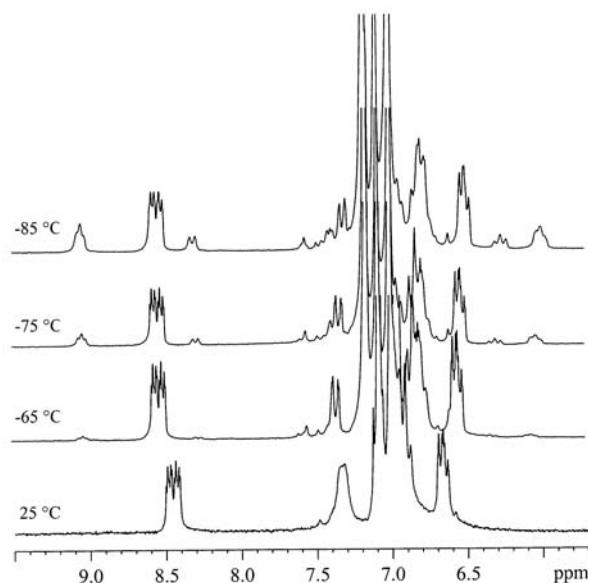
**Figure S2.** Titration curve of silane **2** with py in benzene, exhibiting the chemical induced shifts of the  $\alpha$ -hydrogens in silane **2** ( $\Delta\delta$ ) vs. the added molar equivalents of py (as shown in Figure S1). Filled squares represent experimental data points; the line represents the best curve fit obtained by utilizing nonlinear least-squares data analysis.



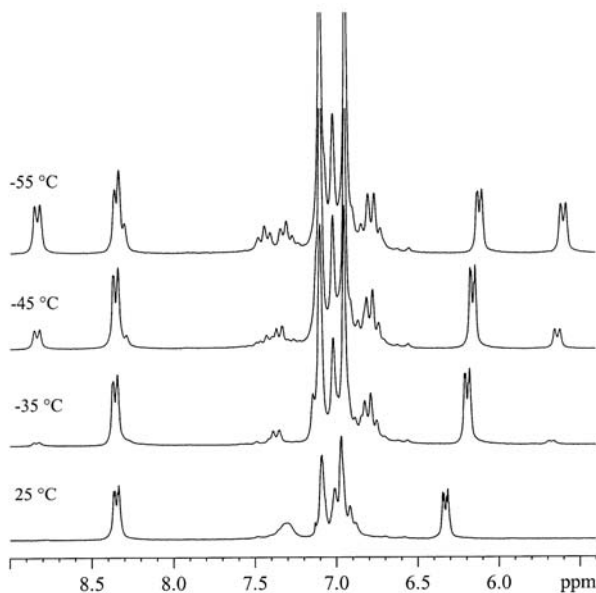
**Figure S3.**  $^{15}\text{N}$  NMR titration of  $^{15}\text{N}$ -py (0.01 M) with silane **3** in benzene at 298 K. The number of equivalents (equiv) of silane **3** added is indicated on the left.



**Figure S4.**  $^{19}\text{F}$  NMR titration of silane **3** (0.01 M) with MeO-py in benzene at 298 K. The number of equivalents (equiv) of MeO-py added is indicated on the left.



**Figure S5.**  $^1\text{H}$  NMR spectra (200 MHz) for a 1:1 mixture of **3** (0.03 M) and  $^{15}\text{N}$ -py in toluene at various temperatures. The signal at 8.6 ppm at  $-85\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of the rapidly equilibrating free  $^{15}\text{N}$ -pyridine with the **3**-py complex. The signal at 9.1 ppm at  $-85\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of the two pyridine ligands in the **3**-py<sub>2</sub> complex. Additional couplings to the  $^{15}\text{N}$  atoms in these complexes are observed. The same dynamic behavior and chemical shifts were observed also with the non isotopically ( $^{15}\text{N}$ ) enriched pyridine. The signal at 8.3 ppm at  $-85\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of **3** in the **3**-py<sub>2</sub> complex.



**Figure S6.**  $^1\text{H}$  NMR spectra (200 MHz) for a 1:1 mixture of **3** (0.03 M) and MeO-py in toluene at various temperatures. The signal at 8.4 ppm at  $-55\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of the rapidly equilibrating free MeO-pyridine with the **3**-MeO-py complex. The signal at 8.8 ppm at  $-55\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of the two MeO-pyridine ligands in the **3**-(MeO-py)<sub>2</sub> complex. The signal at 8.3 ppm at  $-55\text{ }^\circ\text{C}$  corresponds to the  $\alpha$ -hydrogens of **3** in the **3**-(MeO-py)<sub>2</sub> complex.