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Formation of Hypervalent Complexes of Trifluorosilanes with Pyridine and with 4-Methoxypyridine, through Intermolecular Silicon···Nitrogen Interactions

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Herein we report that trifluorohexylsilane (**2**), trifluorophenylsilane (**3**) and trifluoro(pentafluorophenyl)silane (**4**) form new hypervalent complexes with pyridine (py) and with 4-methoxypyridine (MeO-py), through intermolecular Si···N interactions. In general, stronger and more efficient binding is observed for the more electron poor (Si atom in) silane **4** and for the more electron rich (N atom in) 4-methoxypyridine. Binding constants of 15 ± 2, 25 ± 5, and 550 ± 100 M^{-1} at 25 °C in benzene were measured for the formation of the pentacoordinate **2**·py, **3**·py, and **3**·MeO-py complexes, respectively. In addition, silane **3** also forms the hexacoordinate **3**·2py and **3**·2MeO-py complexes at low temperatures and silane **4** forms the **4**·2py complex below room temperature and the **4**·2MeO-py complex already at room temperature and in a high concentration. The various types of hypervalent complexes and different binding strengths described here for silanes **2**–**4** and previously for trifluoro(phenylethynyl)silane (**1**) and the possibility to modulate the binding modes (penta- vs hexacoordination) of these complexes (by the type of amine used, concentration, and the temperature applied) suggest that such new intermolecular Si···N interactions could be used as efficient and versatile binding motifs in supramolecular chemistry.

Introduction

Recent synthetic and mechanistic studies in the field of silicon chemistry have led to new types of organosilicon compounds and have revealed some of the possible reaction pathways and intermediate species involved in the rich chemistry displayed by silicon.[1] However, until now, these studies have revolved mainly around covalent bonds to silicon. Characterization and quantification of pairwise interactions and ultimate control over them through manipulation of the microenvironment is a major goal in supramolecular chemistry.[2] Intermolecular interactions such as hydrogen bonding, metal−ligand bonding, and hydrophobic and $\pi-\pi$ interactions constitute the basis for information transfer between molecules in living systems as well as in synthetic supramolecular structures. Aiming to increase the number and chemical diversity of intermolecular interactions that can be used in supramolecular chemistry, beyond those commonly used, we are studying the possible application of intermolecular Si···N interactions. Recently, we have reported the synthesis of trifluoro(phenylethynyl)silane (**1**) that forms with pyridine (py), through intermolecular Si···N interaction, the pentacoordinate **1**·py complex and at low temperatures also the hexacoordinate **1**·2py complex (Scheme 1).[3] We have also reported that silane **1** forms, through bidentate intermolecular Si···N interactions, with 2,2′-bipyridine (bipy) the hexacoordinate **1**·bipy-A and **1**·bipy-B complexes and with 1,10-phenanthroline (phen) the hexacoordinate **1**·phen-A and **1**·phen-B complexes (Scheme 2).[4] Compared to the somewhat loose pentacoordinate complex of **1** with py,[3] more useful tight complexes of **1** are formed with the bidentate bipy and phen ligands. The 1:1 stoichiometric binding constants of ∼440 and ∼2800 M^{-1} were measured at 25 °C in $CDCl_3$ for the formation of the **1**·bipy and **1**·phen complexes, respectively.[4]

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(1) (a) *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989.

(2) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., Macnicol, D. D., Vögtle, F., Eds.; Elsevier: Oxford, U.K., 1996.

(3) Nakash, M.; Goldvaser, M. *J. Am. Chem. Soc.* **2004**, *126*, 3436.

(4) Nakash, M.; Goldvaser, M.; Goldberg, I. *Inorg. Chem.* **2004**, *43*, 5792.

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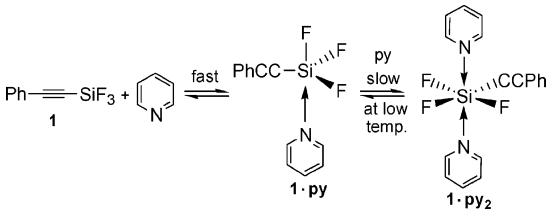
Scheme 1



Scheme 2

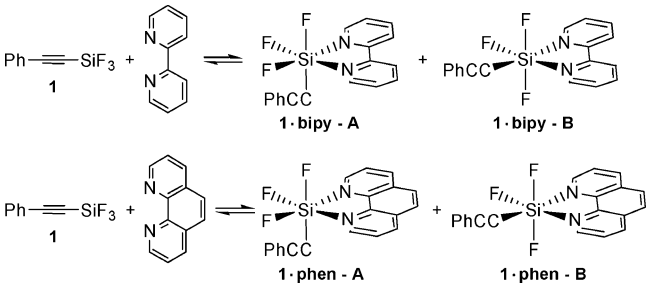
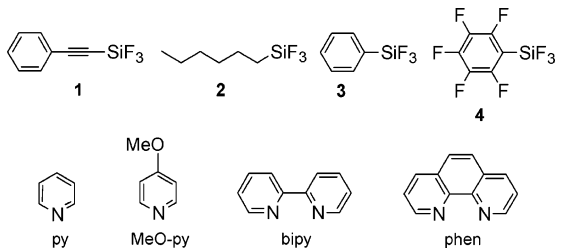


Chart 1



To further establish the utility of hypervalent silicon complexes as possible new motifs in supramolecular chemistry, we now report that trifluorohexylsilane (**2**), trifluorophenylsilane (**3**) and trifluoro(pentafluorophenyl)silane (**4**) form new hypervalent complexes with py and with MeO-py (Chart 1) with varying binding strengths. The silanes and amines studied here vary in their electronic and coordination properties. Stronger binding is observed with the more electron poor (Si atom in) silane **4** and with the more electron rich (N atom in) 4-methoxypyridine. In contrast to silane **1**, only very weak complexation (if at all) between bipy or phen and silanes **2**−**4** is suggested by NMR. In general, the interacting silane−amine systems that we have studied (Chart 1) display versatile binding modes that can be modulated by the type of amine used, concentration, and the temperature applied. In addition, useful strong complexation is observed for some of these silane−amine systems, suggesting a possible application of new intermolecular Si···N interactions in supramolecular chemistry.

In contrast to carbon, silicon has a marked tendency to increase its coordination number.[5] Indeed, isolable hypervalent silicon compounds are known and numerous X-ray crystallographic penta- and hexacoordinate silicon structures have been reported in recent years.[5] For neutral hypervalent structures of silicon these are mostly compounds having intramolecular coordination, forming mainly five-membered rings that include the dative bond to silicon. A few neutral complexes having intermolecular bonds to silicon, mainly for the sterically accessible and highly electron poor silicon atom in SiF_4, have also been reported. In this case, the majority are 1:2 adducts such as SiF_4·2py[6] or 1:1 complexes with bidentate ligands, such as 2,2′-bipyridine as in SiF_4·bipy.[7]

Experimental Section

Materials. Trifluoro(pentafluorophenyl)silane was synthesized according to a literature procedure.[8] All other reagents and solvents were obtained from commercial sources. Benzene-d_6 and toluene-d_8 were dried and distilled over a Na/K alloy prior to use. Pyridine and 4-methoxypyridine were dried and distilled over KOH. Isotopically labeled ^{15}N-pyridine (98%) was obtained from a commercial source and used without further purification. All reactions were carried out under an atmosphere of dry argon. Air-sensitive products and reagents were handled by standard Schlenk techniques.

Instrumentation. ^{1}H and ^{19}F NMR were recorded on a Bruker AC 200 MHz spectrometer (operating at 200 and 188.15 MHz for ^{1}H and ^{19}F, respectively) and on a Bruker ARX 500 MHz spectrometer (operating at 500 and 470.39 MHz, respectively). ^{13}C NMR was recorded on a Bruker ARX 500 MHz spectrometer (operating at 125.76 MHz). ^{29}Si and ^{15}N NMR spectra were recorded on a Bruker ARX 500 MHz spectrometer (operating at 99.33 and 50.67 MHz for ^{29}Si and ^{15}N, respectively). ^{19}F and ^{15}N chemical shifts (δ) were referenced to the external standards $CFCl_3$ and nitromethane, respectively, at $\delta = 0$ ppm. ^{1}H, ^{13}C, and ^{29}Si chemical shifts were referenced to Me_4Si using the solvent resonance as a standard lock. (s = singlet, d = doublet, t = triplet, q = quartet).

Binding Studies. The binding constants (K) for the formation of the pentacoordinate **2**·py, **3**·py, and **3**·MeO-py complexes were determined by ^{1}H NMR, ^{15}N NMR, and ^{19}F NMR spectroscopy, respectively, employing standard NMR titration method. In the titrations of silane **2** with py, of ^{15}N-py with silane **3**, and of silane **3** with MeO-py, we probed the chemical induced shifts (CIS) of the α-hydrogens adjacent to the Si atom in silane **2**, the N atom in ^{15}N-py, and the F atoms in silane **3**, respectively. A typical titration procedure is described here for the titration of ^{15}N-py with silane **3**. Similar procedures were used in the titrations of silanes **2** and **3** with py and with MeO-py, respectively (in these cases the silane was titrated with the amine). A 2.5 mL benzene solution of ^{15}N-pyridine, $[py]_0 = 0.01$ M, was transferred to a 10 mm dried NMR tube under inert conditions, and the NMR spectrum was taken to determine the initial chemical shift of free py (δ_{py}). Aliquots of silane **3** were added under inert conditions to the pyridine solution. The spectrum, depicting the rapidly equilibrating pyridine with the pentacoordinate **3**·py complex, was recorded after each addition,

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(6) Bain, V. A.; Killean, R. C. G.; Webster, M. *Acta Crystallogr.* **1969**, *B25*, 156.

(7) For the X-ray structure of SiF_4·bipy, see: Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402.

(8) Frohn, H. J.; Giesen, M.; Klose, A.; Lewin, A.; Bardin, V. V. *J. Organomet. Chem.* **1996**, *506*, 155.

and 10 points were obtained overall. No hexacoordinate **3**·2py complex was observed throughout the titration. The binding constant (*K*) for the formation of the **3**·py complex was determined by using nonlinear least-squares data treatment [with KaleidaGraph version 3.5 (Synergy Software)] to fit the chemical shift changes of the pyridine nitrogen in the ^{15}N NMR spectra to the molar equivalent of silane **3**. The titration curve was well fitted to the expression of a 1:1 binding equation under fast exchange conditions that can be written as follows:[9]

$$\delta = \delta_{py} - \left(\frac{\delta_{py} - \delta_C}{2}\right)\left(B - \sqrt{B^2 - 4\frac{[\mathbf{3}]_0}{[py]_0}}\right) \quad (1)$$

Here δ is the observed chemical shift, δ_{py} is the chemical shift for free pyridine, δ_C is the chemical shift for the **3**·py complex, $[\mathbf{3}]_0$ is the initial concentration of silane **3**, $[py]_0$ is the initial concentration of pyridine, and

$$B = 1 + \frac{[\mathbf{3}]_0}{[py]_0} + \frac{1}{K[py]_0} \quad (2)$$

Titration of silane **4** with py or with MeO-py displayed CIS for **4** in the ^{19}F NMR spectra, in addition to the signals for the corresponding hexacoordinate complexes (**4**·2py and **4**·2MeO-py, respectively) that formed at room temperature and in increasing amounts throughout the titration. Therefore, as expected, a standard nonlinear least-squares data treatment for these titrations using a 1:1 binding model[9] gave only poor curve fits for the silane **4**−py system and was not possible for the silane **4**−MeO-py system. We were therefore unable to obtain a reasonably accurate binding constant for the formation of the pentacoordinate **4**·py and **4**·MeO-py complexes.

Pentacoordination at 298 K. NMR data (δ) measured at 298 K for a 1:1 mixture of the silane and amine that are rapidly equilibrating with the pentacoordinate silane·amine complex are reported below:

2 and py. ^{1}H NMR (200 MHz, 0.9 M in C_6D_6): 8.50 (d, 2H, J = 4.1 Hz, H^2 py), 6.98 (tt, 1H, J = 7.6, 1.8 Hz, H^4 py), 6.65 (ddd, 2H, J = 7.8, 4.2, 1.5 Hz, H^3 py), 1.1 (m, 8H, $CH_2$$^{2-5}$ **2**), 0.83 (t, 3H, J = 7.0 Hz, CH_3^{6} **2**), 0.40 (bs, 2H, CH_2^{1} **2**). ^{19}F NMR (188.15 MHz, 0.9 M in C_6D_6): −137.6 (s, 3F). ^{29}Si NMR (99.33 MHz, 0.9 M in C_6D_6): −57.6 (s, 1Si). ^{13}C NMR (125.76 MHz, 0.9 M in C_6D_6): 149.8 (s, 2C, *C*H^2 py), 135.0 (s, 1C, *C*H^4 py), 123.2 (s, 2C, *C*H^3 py), 31.8 (s, 1C, *C*H$_2$^{3} **2**), 31.0 (s, 1C, *C*H$_2$^{4} **2**), 22.3 (s, 1C, *C*H$_2$^{5} **2**), 20.9 (s, 1C, *C*H$_2$^{2} **2**), 13.8 (s, 1C, *C*H$_3$^{6} **2**).

3 and py. ^{1}H NMR (200 MHz, 0.02 M in C_6D_6): 8.50 (d, 2H, J = 4.1 Hz, H^2 py), 7.32 (d, 2H, J = 6.5 Hz, H^2 **3**), 7.00 (m, 5H, H^4 py, H^3 and H^4 **3**), 6.64 (dd, 2H, J = 7.5, 4.1 Hz, H^3 py). ^{19}F NMR (188.15 MHz, 0.02 M in C_6D_6): −140.6 (s, 3F). ^{29}Si NMR (99.33 MHz, 0.05 M in C_6D_6): −72.4 (bs, 1Si). ^{15}N NMR (50.67 MHz, 0.02 M in C_6D_6): −65.2 (s, 1N).

3 and MeO-py. ^{1}H NMR (200 MHz, 0.02 M in C_6D_6): 8.35 (d, 2H, J = 6.3 Hz, H^2 MeO-py), 7.45 (d, 2H, J = 6.5 Hz, H^2 **3**), 7.07 (t, 1H, H^4 **3**), 6.93 (t, 2H, H^3 **3**), 6.32 (d, 2H, J = 6.4 Hz, H^3 MeO-py), 3.02 (s, 3H, CH_3 MeO-py). ^{19}F NMR (188.15 MHz, 0.02 M in C_6D_6): −137.9 (s, 3F). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8): −72.3 (bs, 1Si).

4 and py. ^{1}H NMR (200 MHz, 0.03 M in C_6D_6): 8.51 (d, 2H, J = 3.7 Hz, H^2 py), 6.96 (t, 1H, J = 7.6 Hz, H^4 py), 6.65 (dd, 2H, J = 7.5, 5.5 Hz, H^3 py). ^{19}F NMR (188.15 MHz, 0.03 M in C_6D_6): −126.1 (m, 2F), −133.2 (t, 3F, $^4J_{F-F}$ = 10.3 Hz, Si*F*), −144.0 (m, 1F), −159.1 (m, 2F). ^{29}Si NMR (99.33 MHz, 0.01 M in C_6D_6): −78.3 (q, 1Si, J_{Si-F} = 248 Hz). ^{15}N NMR (50.67 MHz, 0.03 M in C_6D_6): −63.7 (s, 1N).

4 and MeO-py. ^{1}H NMR (200 MHz, 0.03 M in C_7D_8): 8.32 (bs, 2H, H^2 MeO-py), 6.19 (bs, 2H, H^3 MeO-py), 3.00 (s, 3H, CH_3 MeO-py). ^{19}F NMR (188.15 MHz, 0.03 M in C_7D_8): −126.7 (m, 2F), −130.1 (bs, 3F, Si*F*), −146.3 (m, 1F), −159.7 (m, 2F). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8): −89.8 (q, 1Si, J_{Si-F} = 242 Hz).

Hexacoordination at Low Temperatures. NMR data for the hexacoordinate silane·2amine complexes (hexa) and for the corresponding silane and amine that are rapidly equilibrating with the pentacoordinate silane·amine complex (penta), measured for a 1:1 mixture of the silane and amine at low temperatures, are reported below:

3 and py. ^{1}H NMR (200 MHz, 0.02 M in C_7D_8, 193 K): 9.02 (d, 4H, J = 5.5 Hz, H^2 hexa py), 8.52 (d, 2H, J = 5.5 Hz, H^2 penta py), 8.27 (d, 2H, J = 8.0 Hz H^2 hexa **3**), 7.15 (m, 6H), 6.79 (t, 3H, J = 7.8 Hz, H^3 penta **3**, H^4 penta py), 6.50 (t, 2H, J = 6.7 Hz, H^3 penta py), 6.25 (t, 2H, J = 8.0 Hz, H^3 hexa **3**), 5.98 (t, 4H, J = 6.5 Hz, H^3 hexa py). ^{19}F NMR (188.15 MHz, 0.02 M in C_7D_8, 193 K): −112.0 (t, 1F, J = 13.8 Hz, hexa **3**), −126.2 (d, 2F, J = 13.8 Hz, hexa **3**), −139.0 (s, 3F, penta **3**). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8, 188 K): −73.3 (q, 1Si, J_{Si-F} = 268 Hz, penta **3**), −171.6 (dt, 1Si, J_{Si-F} = 226 (t), 144 (d) Hz, hexa **3**). Conversion of **3** to the hexacoordinated complex at 188 K = ∼15%.

3 and MeO-py. ^{1}H NMR (200 MHz, 0.03 M in C_7D_8, 218 K): 8.83 (d, 4H, J = 6.5 Hz, H^2 hexa MeO-py), 8.35 (d, 2H, J = 5.3 Hz, H^2 penta MeO-py), 8.32 (d, 2H, J = 7.8 Hz, H^2 hexa **3**), 7.15 (m, 8H), 6.12 (d, 2H, J = 5.3 Hz, H^3 penta MeO-py), 5.60 (d, 4H, J = 6.5 Hz, H^3 hexa MeO-py), 2.84 (s, 3H, CH_3, penta MeO-py), 2.52 (s, 6H, CH_3, hexa MeO-py). ^{19}F NMR (188.15 MHz, 0.03 M in C_7D_8, 218 K): −112.3 (t, 1F, J = 14.5 Hz, hexa **3**), −126.4 (d, 2F, J = 14.5 Hz, hexa **3**), −138.9 (s, 3F, penta **3**). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8, 223 K): −74.3 (q, 1Si, J_{Si-F} = 260 Hz, penta **3**), −173.2 (dt, 1Si, J_{Si-F} = 226 (t), 146 (d) Hz, hexa **3**). Conversion of **3** to the hexacoordinated complex at 218 K = ∼30%.

4 and py. ^{1}H NMR (200 MHz, 0.03 M in C_7D_8, 273 K): 8.90 (d, 4H, J = 5.3 Hz, H^2 hexa py), 8.47 (d, 2H, J = 4.3 Hz, H^2 penta py), 6.91 (t, 1H, J = 7.6 Hz, H^4 penta py), 6.69 (t, 2H, J = 7.8 Hz, H^4 hexa py), 6.59 (t, 2H, J = 6.3 Hz, H^3 penta py), 6.39 (t, 4H, J = 6.7 Hz, H^3 hexa py). ^{19}F NMR (188.15 MHz, 0.03 M in C_7D_8, 273 K): −115.1 (s, 1F, Si*F*, hexa **4**), −116.0 (t, 2F, $^4J_{F-F}$ = 18.8 Hz, Si*F*, hexa **4**), −126.6 (m, 2F, penta **4**), −129.2 (m, 2F, hexa **4**), −132.0 (t, 3F, $^4J_{F-F}$ = 9.2 Hz, penta **4**), −144.8 (t, 1F, J = 21.1 Hz, penta **4**), −159.3 (m, 3:1 F:F hexa **4**, 2F penta **4**), −164.7 (m, 2F, hexa **4**). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8, 213 K): −177.7 (dt, 1Si, J_{Si-F} = 215 (t), 157 (d) Hz, hexa **4**). ^{15}N NMR (50.67 MHz, 0.03 M in C_7D_8, 223 K): −122.6 (dt, 2N, J_{N-F} = 17.6 (d), 8.5 (t) Hz, hexa **4**). Conversion of **4** to the hexacoordinated complex at 273 K = ∼25%.

4 and MeO-py (Hexacoordination). ^{1}H NMR (200 MHz, 0.03 M in C_7D_8, 298 K): 8.77 (bs, 4H, H^2 MeO-py), 6.06 (bs, 4H, H^3 MeO-py), 2.85 (s, 6H, CH_3 MeO-py). ^{19}F NMR (188.15 MHz, 0.03 M in C_7D_8, 298 K): −115.2 (s, 1F, Si*F*), −115.6 (t, 2F, $^4J_{F-F}$ = 18.8 Hz, Si*F*), −128.6, (m, 2F), −159.7 (m, 1F), −164.8 (m, 2F). ^{29}Si NMR (99.33 MHz, 0.03 M in C_7D_8, 238 K): −179.0 (dt, 1Si, J_{Si-F} = 214 (t), 156 (d) Hz, hexa **4**). Conversion of **4** to the hexacoordinated complex at 298 K = ∼35%. For **4** and MeO-py that are rapidly equilibrating with the **4**·MeO-py complex, see pentacoordination at 298 K above.

(9) Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375 and references therein.

Scheme 3

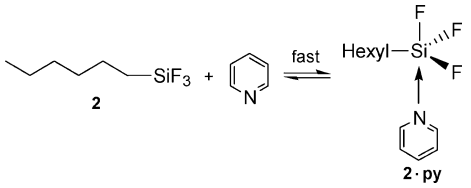


Table 1. Binding Constants for the Formation of Various Silane·Amine Complexes Measured at 25 °C

silane·amine complex	binding constants (M^{-1})
1·bipy	~440[a]
1·phen	~2800[a]
2·py	15 ± 2[b]
3·py	25 ± 5[b]
3·MeO-py	550 ± 100[b]

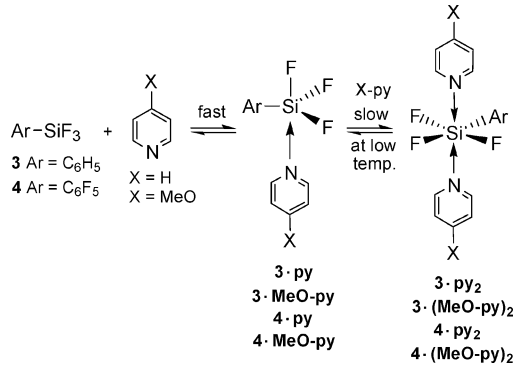
[a] In $CDCl_3$.[4] [b] In C_6D_6.

Results and Discussion

Titration of Silane 2 with py. Gradual addition of py to a solution of silane **2** in benzene leads to complexation-induced shifts (CIS) of the signal at 0.32 ppm in the ^{1}H NMR spectrum of free **2,** which corresponds to the hydrogens in the α position to the silicon atom, as a function of the py concentrations.[10] In contrast, the triplet at 0.83 ppm that corresponds to the terminal CH_3 group in **2** shows no significant CIS throughout the titration. This suggests a fast equilibrium in the NMR time scale for making and breaking of the **2**·py complex (Scheme 3). Nonlinear least-squares data treatment to fit the observed CIS of the signal that corresponds to the α-hydrogens in **2** in the ^{1}H NMR spectra to the added molar equivalents of py was well fitted to the expression of a 1:1 binding equation under fast-exchange conditions[10,11] and led to a binding constant of 15 ± 2 M^{-1} at 25 °C in benzene for the formation of the **2**·py complex (Table 1). Similar binding constants were measured by probing the CIS of the singlet of **2** in the ^{19}F NMR spectra and of the two signals in the ^{13}C NMR spectra that correspond to the two carbon atoms adjacent to the silicon in **2**. Due to the low natural abundance and sensitivity of the ^{29}Si nucleus (and therefore long measurement durations), ^{29}Si NMR titration experiments were impractical.

Further evidence for the formation of the **2**·py complex is provided by the spin−spin couplings to the fluorine atoms in **2**. In the ^{1}H NMR spectrum of free silane **2** a $^3J_{H-F}$ coupling is observed for the signal at 0.32 ppm of the α-hydrogens in **2**, in the ^{13}C NMR spectrum a $^2J_{C-F}$ coupling of 18.4 Hz is observed for the quartet at 6.0 ppm of the carbon atom attached to the silicon in **2**, and in the ^{29}Si NMR spectrum a $^1J_{Si-F}$ coupling of 283 Hz is observed for the quartet at −57.5 ppm (and also as satellites of the singlet at −137.3 ppm in the ^{19}F NMR) of **2**. However, these spin−spin couplings to the fluorine atoms observed for free **2** are lost upon mixing of **2** with py in benzene (even when a large excess of silane **2** is present). This indicates a fast intermolecular fluorine exchange (in the NMR time scale) for **2** in the presence of py. This could result from the formation of the **2**·py complex through an intermolecular Si···N interaction that weakens the Si−F bonds in the complex and that could lead to a low concentration of F^- in solution. Indeed, the spin−spin couplings to the fluorine atoms in free silane **2** observed in the ^{29}Si, ^{19}F, ^{13}C, and ^{1}H NMR spectra are lost upon addition of 1% of $Bu_4N^+F^-$ to a solution of silane **2** in benzene. In this case, and in others previously reported,[12] fluorine-bridged structures could also explain a fast intermolecular fluorine exchange. These spin−spin couplings to the fluorine atoms reappear upon cooling to −90 °C of a 1:1 mixture (0.9 M) of **2** and py in toluene, indicating that the intermolecular fluorine exchange can be stopped in the NMR time scale at low temperatures.

Scheme 4



Titrations of Silane 3 with py and with MeO-py. Addition of py or MeO-py to a solution of silane **3** in benzene leads to CIS of the signals for the silicon atom in **3**, for the nitrogen atom in ^{15}N-pyridine, and for the atoms adjacent to the forming Si···N bond, the fluorine atoms in **3**, and the α-hydrogen atoms in py, as can be probed by ^{29}Si ^{15}N, ^{19}F, and ^{1}H NMR, respectively. For example, gradual addition of silane **3** to a 0.01 M solution of ^{15}N-py in benzene leads to CIS of the signal at −61.7 ppm in the ^{15}N NMR spectra that corresponds to the nitrogen atom in free ^{15}N-py, as a function of the silane **3** concentrations.[10] In addition, gradual addition of MeO-py to a 0.01 M solution of silane **3** in benzene leads to CIS of the singlet at −140.9 ppm in the ^{19}F NMR spectra that corresponds to the fluorine atoms in free **3**, as a function of the MeO-py concentrations.[10] The CIS observed in these ^{15}N and ^{19}F NMR spectra suggests a fast equilibrium in the NMR time scale for making and breaking of the **3**·py and of the **3**·MeO-py complexes, respectively (Scheme 4).

Nonlinear least-squares data treatment was employed to fit the observed CIS of the signal at −61.7 ppm that corresponds to the nitrogen atom in ^{15}N-py in the ^{15}N NMR spectra to the molar equivalent of silane **3** and to fit the observed CIS of the singlet at −140.9 ppm that corresponds to the fluorine atoms in **3** in the ^{19}F NMR spectra to the molar equivalent of MeO-py. The results were well fitted to

(10) See Supporting Information.
(11) See Experimental Section for details.
(12) For mixtures of $MeSiF_3$ and $Pr_4N^+MeSiF_4^-$ or of $PhSiF_3$ and $Pr_4N^+PhSiF_4^-$ in CH_2Cl_2 solution, no spin−spin couplings to the fluorine atoms were observed, suggesting fast intermolecular fluorine exchange for these cases also; see: Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 3845.

a 1:1 binding equation under fast-exchange conditions.[11] This led to binding constants of 25 ± 5 and 550 ± 100 M^{-1} at 25 °C in benzene for the formation of the pentacoordinate **3**·py and **3**·MeO-py complexes, respectively (Table 1). Similar binding constants were measured when we probed the CIS of the singlet of **3** in the ^{19}F NMR spectra for a titration of **3** with py or when we probed the CIS of the signal for the α-hydrogens of **3** in the ^{1}H NMR spectra for a titration of **3** with MeO-py. In all of the above titration experiments, no hexacoordinate silane·2amine complexes were observed in the NMR spectra throughout the titrations. A weak coordination between py and silanes **2** and **3** but a much stronger and efficient binding between the electron rich (N atom in) MeO-py and silane **3** is evident from the binding constants measured for the pentacoordinate **2**·py, **3**·py, and **3**·MeO-py complexes (Table 1).

Further evidence for the formation of the **3**·py and **3**·MeO-py complexes is provided by the spin−spin coupling to the fluorine atoms in **3**. A $^{1}J_{Si-F}$ coupling of 268 Hz is observed for the quartet at −72.3 ppm in the ^{29}Si NMR (and also as satellites of the singlet at −140.9 ppm in the ^{19}F NMR) of free **3**. However, as in the case of silane **2**, this $^{1}J_{Si-F}$ coupling for free silane **3** is lost upon mixing of **3** with py or with MeO-py in benzene (even when a large excess of silane **3** is present). This indicates a fast intermolecular fluorine exchange (in the NMR time scale) for **3** in the presence of py or MeO-py. Indeed, the spin−spin coupling to the fluorine atoms in free silane **3** observed in the ^{29}Si and ^{19}F NMR spectra is lost upon addition of 1% of $Bu_4N^+F^-$ to a solution of silane **3** in benzene.[12] The spin−spin coupling to the fluorine atoms reappears upon cooling to −65 °C of a 1:1 mixture (0.03 M) of **3** and py in toluene, indicating that the intermolecular fluorine exchange can be stopped in the NMR time scale at low temperatures. In contrast to silanes **2** and **3**, the spin−spin couplings to the fluorine atoms in free silanes **1** and **4**, observed in the ^{29}Si and ^{19}F NMR spectra, are retained even when py or MeO-py is added to a solution of silanes **1** or **4** in benzene. This indicates that in these cases either no or slow (in the NMR time scale) Si−F bond breaking occurs and, therefore, suggests stronger Si−F bonds in the pentacoordinate complexes of **1** and **4** (vs silanes **2** and **3**) with py and with MeO-py.

Formation of the Hexacoordinate 3·2py, 3·2MeO-py, 4·2py, and 4·2MeO-py Complexes. Upon cooling of toluene solutions of **3** and py, **3** and MeO-py, **4** and py, and **4** and MeO-py, new signals develop in the ^{29}Si, ^{1}H, and ^{19}F NMR spectra, suggesting the formation of the hexacoordinate **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes (Scheme 4). For silane:amine mixtures in a 1:1 ratio (0.03 M in toluene) these signals are observed at temperatures below −65 °C for a solution of **3** and py, below −35 °C for a solution of **3** and MeO-py, below 25 °C for a solution of silane **4** and py, and below 45 °C for a solution of **4** and MeO-py. In the same experimental conditions the previously observed hexacoordinate **1**·2py complex[3] is NMR detectable at −10 °C. For silanes **1**, **3**, and **4**, increasing the concentration leads to a higher conversion of the silane to the hexacoordinate complex at a given temperature. However, for a 1:1 mixture of silane **2** and py, no hexacoordinate complex was observed by NMR even at −90 °C and in a high concentration of 0.9 M. This, and the weak binding constant measured for the pentacoordinate **2**·py complex (15 ± 2 M^{-1} at 25 °C in benzene), indicate that, out of silanes **1**−**4**, silane **2** forms the weakest intermolecular Si···N interaction with py. Due to the formation of the hexacoordinate **4**·2py and **4**·2MeO-py complexes at room temperature, we were unable to measure the 1:1 binding constants for the formation of the pentacoordinate **4**·py and **4**·MeO-py complexes.[11]

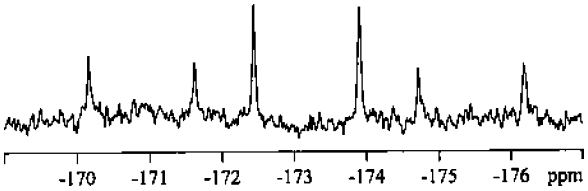


Figure 1. ^{29}Si NMR spectra (99.33 MHz, 233 K) for a 1:1 mixture of **3** (0.03 M) and MeO-py in toluene, exhibiting a doublet ($^{1}J_{Si-F}$ = 146 Hz) of triplets ($^{1}J_{Si-F}$ = 226 Hz) at −173.2 ppm for **3**·2MeO-py due to the two different geometries of the fluorines in the **3**·2MeO-py complex (Scheme 4).

In the ^{29}Si NMR spectra for a 1:1 mixture (0.03 M in toluene) of **3** and py, **3** and MeO-py, **4** and py, and **4** and MeO-py, a doublet of triplets develops at −171.6 ppm at 188 K, −173.2 ppm at 233 K (see for example Figure 1), −177.7 ppm at 213 K, and at −179.0 ppm at 238 K, respectively, a typical region for a hexacoordinate silicon structure[5] and about ∼100 ppm upfield with respect to the quartets ($^{1}J_{Si-F}$) at −72.3 and −77.2 ppm of free silanes **3** and **4**, respectively. The doublet of triplets[11] is due to coupling of the silicon to the one and the two nonequivalent fluorine atoms, respectively, in the **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes (Scheme 4). These new signals disappear and reappear when the temperature is raised or lowered, respectively, and their chemical shifts remain in the region typical for a hexacoordinate silicon structure, indicating a reversible and slow equilibrium (in the NMR time scale) in making and breaking of the **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes.

In addition, for the above 1:1 mixtures (0.03 M in toluene) of the silane and amine, the signals for the hexacoordinate **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes observed in the ^{1}H and ^{19}F NMR spectra exhibit the same dynamic behavior as observed in the corresponding ^{29}Si NMR spectra and resonate at distinct chemical shift regions. We observed in the ^{1}H NMR spectra one signal for the α-hydrogens of py or of MeO-py which are rapidly equilibrating with the pentacoordinate **3**·py or **4**·py or with the **3**·MeO-py or **4**·MeO-py complexes, respectively, and only one additional new signal for the α-hydrogens of the two py or of the two MeO-py ligands in the **3**·2py and **4**·2py or in the **3**·2MeO-py and **4**·2MeO-py complexes, respectively (see for example in Figure 2).[11] For the **3**·2py and **3**·2MeO-py complexes we also observed in the ^{19}F NMR spectra a doublet and a triplet (F−F coupling due to the one and the two nonequivalent fluorine atoms in these complexes, Scheme 4) in a ratio of 2:1, respectively, at −126.2 (d) and

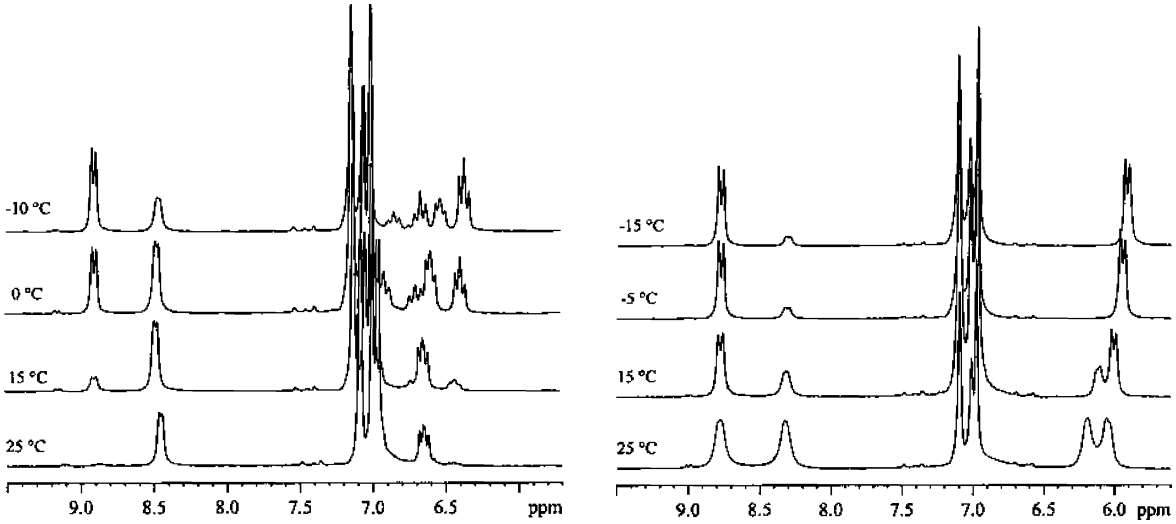


Figure 2. ^{1}H NMR spectra (200 MHz) in toluene at various temperatures. Left side: 1:1 mixture of **4** (0.03 M) and py. The signal at 8.5 ppm at 25 °C corresponds to the α-hydrogens of the rapidly equilibrating free pyridine with the **4**·py complex. The signal at 8.9 ppm at 15 °C corresponds to the α-hydrogens of the two pyridine ligands in the **4**·2py complex. Right side: 1:1 mixture of **4** (0.03 M) and MeO-py. The signal at 8.3 ppm at 25 °C corresponds to the α-hydrogens of the rapidly equilibrating free MeO-pyridine with the **4**·MeO-py complex. The signal at 8.8 ppm at 25 °C corresponds to the α-hydrogens of the two MeO-pyridine ligands in the **4**·2MeO-py complex.

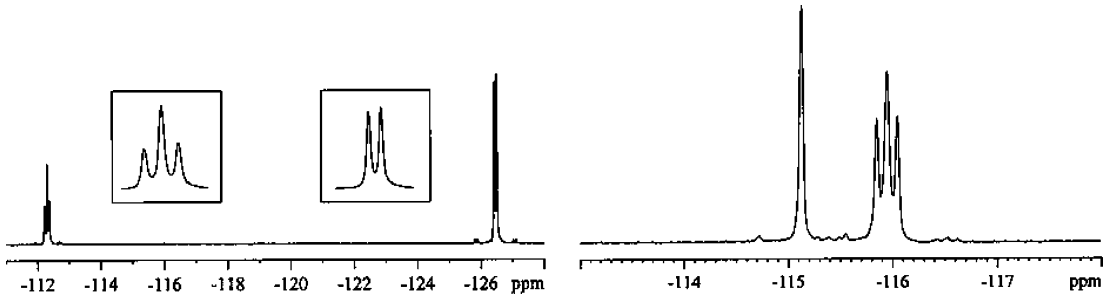


Figure 3. ^{19}F NMR spectra (188.15 MHz) in toluene. Left side: 1:1 mixture of **3** (0.03 M) and MeO-py at 218 K, exhibiting a triplet (−112.3 ppm, $^{2}J_{F-F}$ = 14.5 Hz) and a doublet (−126.4 ppm, $^{2}J_{F-F}$ = 14.5 Hz), due to the two different geometries of the fluorines in the **3**·2MeO-py complex and in a ratio of 1:2, respectively. For clarity, the triplet and doublet are enlarged in the boxes. A singlet at −138.9 ppm (not shown) that corresponds to the three fluorine atoms in **3**, which is rapidly equilibrating with the **3**·MeO-py complex, was also observed. Right side: 1:1 mixture of **4** (0.03 M) and MeO-py at 258 K, exhibiting a singlet at −115.1 ppm and a triplet ($^{4}J_{F-F}$ = 18.5 Hz) at −115.9 ppm in a 1:2 ratio, respectively, due to the two different geometries of the fluorines in the **4**·2MeO-py complex. A broad singlet at −129.0 ppm (not shown) that corresponds to the three fluorine atoms in **4**, which is rapidly equilibrating with the **4**·MeO-py complex, was also observed.

−112.0 (t) ppm at 193 K for the **3**·2py complex and at −126.4 (d) and −112.3 (t) ppm at 218 K for the **3**·2MeO-py complex (see for example in Figure 3, left).[11]

For silane **4** the $^{2}J_{F-F}$ spin−spin coupling between the two types of fluorine atoms that are connected to the silicon atom in the hexacoordinate **4**·2py or **4**·2MeO-py complexes (Scheme 4) was not observed, suggesting a small $^{2}J_{F-F}$ coupling compared to the signals width in these cases. Nevertheless, two signals for the two types of fluorine atoms in the hexacoordinate **4**·2py and **4**·2MeO-py complexes are observed in the ^{19}F NMR spectra, a singlet at −115.1 ppm and a triplet ($^{4}J_{F-F}$ = 18.8 Hz) at −116.0 ppm in a 1:2 ratio, respectively, at 273 K for the hexacoordinate **4**·2py complex and a singlet at −115.1 ppm and a triplet ($^{4}J_{F-F}$ = 18.5 Hz) at −115.9 ppm in a 1:2 ratio, respectively, at 258 K for the **4**·2MeO-py complex (Figure 3, right). The $^{1}J_{Si-F}$ coupling observed as satellites to these signals in the ^{19}F NMR spectra are the same as those observed in the corresponding ^{29}Si NMR spectra for the hexacoordinate **4**·2py and **4**·2MeO-py complexes, confirming the assignment for these signals. Other examples of hypervalent compounds of silicon, in which the fluorine atoms connected to the silicon exhibit distinct signals with no (measurable) $^{2}J_{F-F}$ coupling, are known.[13]

Further evidence for hexacoordinate structures of the **3**·2py and the **4**·2py complexes, in which two intermolecular Si···N bonds are formed, is provided by ^{19}F and ^{15}N NMR spectra that we measured at low temperatures when ^{15}N-pyridine was used, allowing us to obtain the ^{19}F−Si···^{15}N two-bond spin−spin coupling interaction in the **3**·2py and **4**·2py complexes. For the **3**·2py complex a triple ($^{2}J_{F-N}$ = 9 Hz) doublet ($^{2}J_{F-F}$ = 14 Hz) at −126.2 ppm and a triple ($^{2}J_{F-N}$ = 14 Hz) triplet ($^{2}J_{F-F}$ = 14 Hz) at −112.0 ppm in

(13) (a) At low temperatures *o*-$(Me_2NCH_2)C_6H_4SiF_3$ displays in the ^{19}F NMR spectrum a triplet and a doublet of relative intensities 1 and 2, respectively, while under the same conditions *o*-$(Me_2NCH_2)C_6H_4SiMeF_2$ displays in the ^{19}F NMR spectrum two singlets of relative intensities 1 and 1. For both compounds the ^{19}F NMR spectrum is consistent with a trigonal bipyramidal geometry about the silicon atom, having an intramolecular Si···N interaction; see: Breliere, C.; Carre, F.; Corriu, R. J. P.; De Saxce, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1. (b) Other analogous examples for anionic hexacoordinate fluorosilicates are also known; see: Breliere, C.; Carre, F.; Corriu, R. J. P.; Douglas, W. E.; Poirier, M.; Royo, G.; Wong Chi Man, M. *Organometallics* **1992**, *11*, 1586 and references therein.

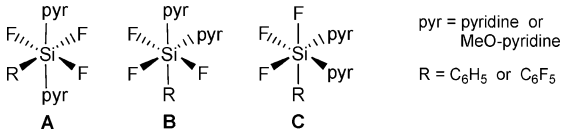


Figure 4. Possible isomers **A**−**C** for the **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes.

a ratio of 2:1, respectively, are observed in the ^{19}F NMR spectra at 188 K when ^{15}N-pyridine was used. The additional coupling to the nitrogen ($^2J_{F-N}$) is due to coupling between the ^{19}F atoms and the two symmetrically equivalent ^{15}N atoms that are intermolecularly bonded in the **3**·2py complex (Scheme 4).[14] In the ^{15}N NMR spectra measured at 223 K for the **4**·2py complex, only one doublet ($^2J_{F-N}$ = 17.6 Hz) of triplets ($^2J_{F-N}$ = 8.5 Hz) is observed at −122.6 ppm when ^{15}N-pyridine was used.[14] This coupling pattern is due to the spin−spin interaction between the two symmetrically equivalent ^{15}N atoms and the one and the two nonequivalent fluorine atoms in the **4**·2py complex (Scheme 4).

Possible Isomeric Structures for the 3·2py, 3·2MeO-py, 4·2py, and 4·2MeO-py Complexes. Three isomeric structures are possible for the **3**·2py, **3**·2MeO-py, **4**·2py, and **4**·2MeO-py complexes (Figure 4). The detailed multinuclear NMR data that we obtained for the **3**·2py and **4**·2py complexes allowed the determination of their isomeric preference. All the data together obtained for the hexacoordinate **3**·2py and **4**·2py complexes (a doublet of triplets in the ^{29}Si NMR spectra, a doublet and a triplet in a ratio of 2:1, respectively, in the ^{19}F NMR spectra, only one signal observed in the ^{1}H NMR spectra for the α-hydrogens of the two py ligands in the **3**·2py and **4**·2py complexes, and the pattern of the ^{19}F−Si···^{15}N two-bond spin−spin coupling observed in the ^{15}N and ^{19}F NMR spectra) indicate that the two py ligands in the **3**·2py and **4**·2py complexes are both chemically and magnetically equivalent in all nuclei probes used, excluding isomers **B** and **C** and, therefore, suggesting that only isomer **A** is present in solution (Figure 4). Similar chemical shifts and spin−spin coupling patterns are also observed in the ^{1}H, ^{19}F, and ^{29}Si NMR spectra for the hexacoordinate **1**·2py complex, for which the same isomeric preference (**A** type isomer, Figure 4) was suggested by NMR data.[3] A trans structure was determined also in the crystal structure of the SiF_4·2py adduct.[6,15]

Similar NMR data was also obtained for the **3**·2MeO-py and **4**·2MeO-py complexes. However, as isotopically labeled ^{15}N-methoxypyridine was not available to us, we could not measure the ^{19}F−Si···^{15}N two-bond spin−spin coupling for the **3**·2MeO-py and **4**·2MeO-py complexes. Therefore, the other NMR data available for the **3**·2MeO-py and **4**·2MeO-py complexes allowed us to exclude only isomer **B** (Figure 4) as a possibility for these complexes in solution. Although we cannot unequivocally exclude isomer **C** for the **3**·2MeO-py and **4**·2MeO-py complexes, the similar chemical shifts observed in the ^{1}H and ^{29}Si NMR spectra that we measured for the **3**·2py and **3**·2MeO-py complexes versus the **4**·2py and **4**·2MeO-py complexes, respectively, imply a preferred **A** type isomeric structure also for the **3**·2MeO-py and **4**·2MeO-py complexes.

Relative Stabilization in Forming the Complexes of Silanes 1−4 with py. As described above, for a 1:1 mixture (0.03 M in toluene) of silanes **1**−**4** with py, the hexacoordinate **1**·2py, **3**·2py, and **4**·2py complexes are NMR detectable at temperatures below −10, −65, and 25 °C, respectively, and no hexacoordinate **2**·2py complex was observed in NMR even at −90 °C and in a high concentration of 0.9 M. These results suggest a greater stabilization in forming complexes of py with the more electron poor (Si atom in) silane **4** than with silanes **1**−**3**. The stronger intermolecular Si···N binding suggested by this NMR data for the case of the more electron poor silane **4** is in agreement with previous results obtained for silanes having intramolecular Si···N coordination, which confirmed that the greater total electronegative substitution on the silicon leads to stronger coordination of the nitrogen and, therefore, results in higher barriers for cleavage of the Si···N coordination bond.[16] Even stronger binding is observed when the electron poor (Si atom in) silane **4** is mixed in toluene at 25 °C with 1 equiv (0.03 M) of the electron rich (N atom in) MeO-py, forming the hexacoordinate **4**·2MeO-py complex in a high concentration, ∼35% conversion of silane **4** to the hexacoordinate **4**·2MeO-py complex (Figure 2, right). The remarkable stability observed for the interacting silane **4** and MeO-py suggests that this new intermolecular Si···N interaction is expected to be efficient in forming supramolecular complexes. For example, it should be possible to construct host molecules that consist of several trifluoro(perfluoroaryl)silane units, having several silicon binding sites, which should prove useful in forming large supramolecular arrays with 4-alkoxypyridine derivatives.

Possible Formation of Hexacoordinate Complexes of Silanes 2−4 with bipy or with phen. We have also studied the possible formation of hexacoordinate complexes of silanes **2**−**4** with the bidentate bipy or phen ligands. As in the case for binding py to silanes **2** and **3**, the $^1J_{Si-F}$ coupling observed in the ^{29}Si and ^{19}F NMR spectra for free silanes **2** and **3** is lost upon mixing of **2** or **3** with bipy or with phen

(14) (a) A similar pattern for the ^{19}F−Si···^{15}N two-bond spin−spin coupling was observed for the **1**·2py complex in which the two py ligands are in trans position with respect to each other.[3] (b) The only other reported coupling across the Si···N coordinative bond is related to hexacoordinate silicon compounds having intramolecular Si···N bonds; see: Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D. *Organometallics* **1997**, *16*, 3255.

(15) Unfortunately, many attempts to obtain crystals suitable for X-ray crystallography for the various complexes studied here from different solvent combinations and temperatures were unsuccessful. For the case of the larger bipy and phen ligands, forming the **1**·bipy and **1**·phen complexes, X-ray structures were previously reported.[4] Other examples for X-ray structures of neutral compounds having intramolecular Si···N interaction are known.[5] For examples, see: (a) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **2001**, *20*, 2331. (b) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 1066. (c) Mercado, R.-M. L.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 1686. (d) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1998**, *17*, 5114.

(16) (a) Carre, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C.; Belin, C. *J. Organomet. Chem.* **1994**, *470*, 43. (b) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; de Saxce. A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1. (c) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Corey, J. Y. *J. Organomet. Chem.* **1984**, *277*, C25.

(even when a large excess of silanes **2** or **3** is present). This indicates a fast intermolecular fluorine exchange (in the NMR time scale) for **2** or **3** in the presence of bipy or phen and could imply the formation of intermolecular Si···N interactions between these silanes and amines. However, no significant chemical shifts or new signals are observed in the ^{29}Si, ^{19}F, and ^{1}H NMR spectra for mixtures in various ratios of silanes **2**−**4** with bipy or with phen in benzene at room temperature. Therefore, these NMR experiments suggest only very weak binding (if at all) for silanes **2**−**4** with bipy or with phen. This is in contrast to the results obtained for silane **1**, which forms tighter complexes with the bidentate bipy and phen ligands (vs py).[3,4] In the case of silane **1**, upon complexation no significant steric hindrance occurs between bipy or phen and the phenyl ring of silane **1** (which is separated by a C−C triple bond from the Si center).[3] However, in the case of silanes **2**−**4**, the flexible hexyl or the large aryl substituents in silanes **2** or **3** and **4**, respectively, are directly connected to the silicon atom and might therefore lead to significant steric interactions that develop upon binding of bipy or phen to silanes **2**−**4**, resulting in very weak binding.

Conclusions

In this study we have described the binding modes of silane **2** with py and of silanes **3** and **4** with py and MeO-py. In general, stronger binding was observed for the more electron rich (N atom in) MeO-py and for the more electron poor (Si atom in) silane **4**. The various types of complexes and different binding strengths described here for silanes **2**−**4** and previously for silane **1**,[3,4] and the possibility to modulate the binding modes (penta vs hexa coordination) of these complexes (by the type of amine used, concentration, and the temperature applied), suggest that such new intermolecular Si···N interactions are expected to be efficient and versatile binding motifs in supramolecular chemistry. Complexes of the related SiF_4 with amines are limited in size and cannot be further extended, as four fluorine atoms are connected to the silicon atom. However, it should be possible to construct host molecules that have several silicon binding sites. It is anticipated that such host molecules, making use of the more efficient intermolecular Si···N interactions that we have studied, should prove useful in forming large supramolecular arrays with various amine derivatives. Studies aiming to utilize these intermolecular Si···N interactions in supramolecular complexes are under investigation in this laboratory.

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Supporting Information Available: ^{1}H NMR titration of silane **2** with py in benzene, a titration curve of silane **2** with py in benzene, ^{15}N NMR titration of ^{15}N-py with silane **3** in benzene, ^{19}F NMR titration of silane **3** with MeO-py in benzene, and ^{1}H NMR spectra for a 1:1 mixture of **3** (0.03 M) and py and of **3** (0.03 M) and MeO-py in toluene at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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