

Formation of Hypervalent Complexes of PhCCSiF₃ with Pyridine through Intermolecular Silicon···Nitrogen Interaction

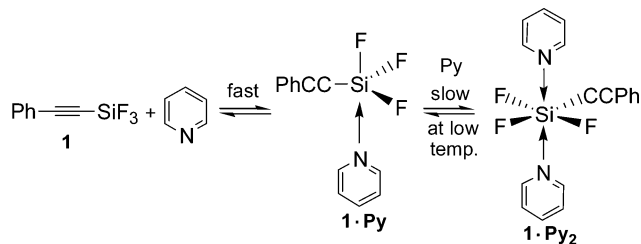
Moshe Nakash* and Michael Goldvaser

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences,
Tel Aviv University, Tel Aviv 69978, Israel

Received December 18, 2003; E-mail: nakashm@post.tau.ac.il

Increasing the number and chemical diversity of intermolecular interactions that can be used in supramolecular chemistry,¹ beyond those commonly used, will lead to the construction of ever more complex supramolecular arrays, with greater application potential. Recent synthetic and mechanistic studies in the field of silicon chemistry have led to new types of organo-silicon compounds and revealed some of the possible reaction pathways and intermediate species involved in the rich chemistry displayed by silicon.² However, until now, studies in silicon chemistry revolved mainly around covalent bonds to silicon. Herein, we report the synthesis of trifluoro-phenylethynyl-silane (**1**)³ that forms with pyridine (Py), through intermolecular Si···N interaction, the pentacoordinate **1**·Py complex and at low temperatures also the hexacoordinate **1**·Py₂ complex (see Scheme 1). As derivatives of **1** can serve as basic building blocks in host molecules that incorporate several units such as **1**, the hypervalent complexes of **1** with Py described here imply a possible application of such Si···N intermolecular interactions in supramolecular chemistry.

Scheme 1



Relative to carbon, silicon has a much smaller tendency to form compounds with coordination number less than four but a pronounced capacity for the enlargement of the coordination sphere. Indeed, isolable hypervalent silicon compounds are known, and numerous X-ray crystallographic penta- and hexacoordinate silicon structures have been reported in recent years.⁴ 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 SiF₄ were also reported. In this case, the majority are 1:2 adducts such as SiF₄·Py₂⁵ or 1:1 complexes with bidentate ligands, such as 2,2'-bipyridine (bipy) as in SiF₄·bipy.⁶

Gradual addition of pyridine to a solution of silane **1** in CDCl₃ leads to complexation-induced shifts (CIS) of the quartet for **1** in the ²⁹Si NMR as a function of the pyridine concentrations (Figure 1, left). This suggests a fast equilibrium in the NMR time scale for making and breaking of the **1**·Py complex (Scheme 1). Furthermore, evidence for a pentacoordinate structure for the **1**·Py complex, in which an intermolecular Si···N bond is formed, is provided by the

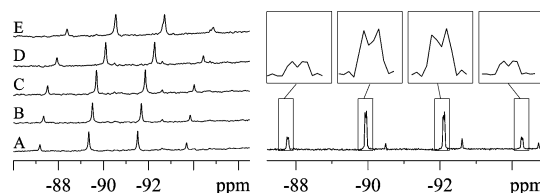


Figure 1. ²⁹Si NMR spectra (99.33 MHz, 298 K) in CDCl₃. Left side: complexation induced shifts⁸ of the quartet for the SiF₃ group in **1** (0.1 M) induced by pyridine. (A) Free **1** (before adding Py), (B) **1** with 0.5 equiv of Py, (C) **1** with 1 equiv of Py, (D) **1** with 2 equiv of Py, (E) **1** with 3 equiv of Py.⁹ Right side: a 1:2 mixture of **1** (0.1 M) and ¹⁵N-pyridine, respectively, exhibiting a doublet of quartet. For clarity the individual peaks of the quartet are enlarged and shown in the dashed boxes. The small triplet at -92.6 ppm is for the siloxane, (PhCCSiF₂)₂O, formed due to a trace amount of H₂O in solution.¹⁰

doublet of quartets observed in the ²⁹Si NMR spectrum for a 1:2 mixture of PhCCSiF₃ and isotopically labeled ¹⁵N-pyridine (Figure 1, right). The quartet is due to coupling of the silicon to the three fluorine atoms in the SiF₃ group (¹J_{Si-F} = 215 Hz), and the doublet is due to coupling between the ²⁹Si and ¹⁵N atoms in the Si···N intermolecular bond in the **1**·Py complex (¹J_{Si-N} = 4 Hz). This is, to the best of our knowledge, the first intermolecular ²⁹Si···¹⁵N one-bond coupling reported for a pentavalent complex of silicon.⁷

A temperature dependence of the chemical shifts in the ¹H, ¹⁹F, ²⁹Si, and ¹⁵N NMR spectra was observed for a mixture of **1** and pyridine in CDCl₃,¹⁰ indicating a fast equilibrium in forming the pentacoordinate **1**·Py complex (Scheme 1). For example, an upfield shift upon cooling and a downfield shift upon heating were observed for the quartet of **1** in the ²⁹Si NMR spectra for a mixture of **1** and pyridine as expected for Si···N bond making and -breaking, respectively.^{10,11} These shifts remained in the region typical for a pentacoordinate silicon structure.⁴

In addition, upon cooling (below 288 K), new signals develop in the ¹H, ¹⁹F, ²⁹Si, and ¹⁵N NMR spectra,¹⁰ suggesting the formation of the **1**·Py₂ complex (Scheme 1). For example, in the ²⁹Si NMR spectra for a mixture of **1** and pyridine at low temperatures a doublet of triplets develops at -181.8 ppm at 233 K (Figure 2, left), a typical region for a hexacoordinate silicon structure⁴ and about 90 ppm upfield with respect to the quartet of **1** (Figure 1, left). The doublet (¹J_{Si-F} = 155 Hz) of triplets (¹J_{Si-F} = 191 Hz) is due to coupling of the silicon to the one and the two nonequivalent fluorine atoms, respectively, in the **1**·Py₂ complex (Scheme 1). 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 (in the NMR time scale) equilibrium in making and breaking of the **1**·Py₂ complex. Further evidence for a hexacoordinate structure of the **1**·Py₂ complex, in which two intermolecular Si···N bonds are formed, is provided by the doublet of triple triplets observed in the ²⁹Si NMR spectrum for a 1:2 mixture of **1** and

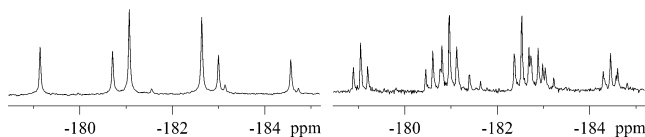


Figure 2. ^{29}Si NMR spectra (99.33 MHz, 233 K) in CDCl_3 . Left side: a 1:2 mixture of **1** (0.1 M) and pyridine, respectively, exhibiting a doublet of triplet due to the two different geometries of the fluorines in the **1**· Py_2 complex (Scheme 1). Right side: a 1:2 mixture of **1** (0.1 M) and ^{15}N -pyridine, respectively, exhibiting a doublet of triple triplet. The additional triplet demonstrates the $^{15}\text{N}\cdots^{29}\text{Si}$ coupling due to the two symmetrically equivalent pyridine ligands in the **1**· Py_2 complex (Scheme 1). The small quintet and triple quintet at -183.1 ppm, partly seen in the left and right spectra, respectively, are due to a trace amount of $\text{SiF}_4\cdot\text{Py}_2$ formed due to the presence of a trace amount of H_2O in solution.¹⁰

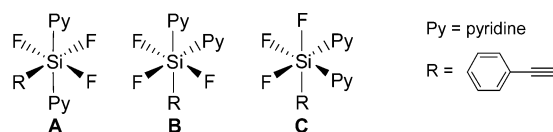


Figure 3. Possible isomers, **A**, **B**, and **C** for the **1**· Py_2 complex.

isotopically labeled ^{15}N -Py (see Figure 2, right). The additional (with respect to Figure 2, left) triplet ($^1J_{\text{Si-N}} = 15.6$ Hz) is due to coupling between the ^{29}Si atom and the two symmetrically equivalent ^{15}N atoms that are intermolecularly bonded in the **1**· Py_2 complex (Scheme 1). This is, to the best of our knowledge, the first intermolecular $^{29}\text{Si}\cdots^{15}\text{N}$ one-bond coupling reported for a hexacoordinate complex of silicon.⁷ In addition, ^{19}F and ^{15}N NMR spectra measured at low temperatures allowed us to obtain also the $^{19}\text{F}\text{---}\text{Si}\cdots^{15}\text{N}$ two bonds spin-spin interaction in the **1**· Py_2 complex.^{10,12}

Three isomeric structures are possible for the **1**· Py_2 complex (Figure 3). The detailed multinuclear NMR data that we obtained for the **1**· Py_2 complex allowed the determination of its isomeric preference. In addition to the ^{29}Si NMR spectra shown in Figure 2, we measured in the ^1H NMR spectra only one signal for the α -hydrogens of the two Py ligands in the **1**· Py_2 complex,¹⁰ and in the ^{19}F NMR spectra a doublet and a triplet (F-F coupling) in a ratio of 2:1, respectively, and a triple doublet and triple triplet when ^{15}N -pyridine was used (triple due to F-N coupling, and in both 200 and 500 MHz spectrometers) in a ratio of 2:1, respectively.¹⁰ In addition, only one doublet of triplets (N-F coupling) is observed in the ^{15}N NMR spectra of the **1**· Py_2 complex.¹⁰ All these data together indicate that the two Py ligands in the **1**· Py_2 complex 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 3).

Quantum mechanical ab initio calculations that we have carried out (at the MP2/6-31G* level) show a distorted trigonal bipyramid structure for the **1**·Py complex and a nearly ideal octahedral structure for the **1**· Py_2 complex, having $\text{Si}\cdots\text{N}$ bond lengths of 2.257 and 1.994 Å respectively.¹⁰ The shorter $\text{Si}\cdots\text{N}$ bond length calculated for the **1**· Py_2 complex is in agreement with the larger $\text{Si}\cdots\text{N}$ spin-spin coupling measured for the **1**· Py_2 complex (vs the **1**·Py complex, see above). The trans isomer **A** (Figure 3) is calculated to be more stable than isomers **B** and **C** by 1.0 and 2.0 kcal/mol, respectively. A trans structure was found also in the crystal structure of $\text{SiF}_4\cdot\text{Py}_2$.^{5,13}

In summary, we have described the synthesis of silane **1** and its binding modes with Py. Studies aiming to utilize this and other $\text{Si}\cdots\text{N}$ interactions in supramolecular complexes are under investigation in this laboratory.

Acknowledgment. This work was supported by the Israel Science Foundation, founded by the Israel Academy of Sciences and Humanities, and by a Tel Aviv University Start-Up grant.

Supporting Information Available: Synthetic procedure and spectroscopic data for **1**, ^1H , ^{19}F , ^{29}Si , and ^{15}N NMR spectra for a mixture of **1** and Py at various temperatures as well as calculated structures, Cartesian coordinates and energies for the **1**·Py complex and isomer **A** of the **1**· Py_2 complex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., Macnicol, D. D., Vögtle, F., Eds.; Elsevier: Oxford, 1996.
- (2) (a) *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley, Chichester, 1989.
- (3) Silane **1** was characterized by HRMS, ^1H , ^{13}C , ^{29}Si , and ^{19}F NMR, and its synthetic details are presented in the Supporting Information.
- (4) For recent reviews on hypervalent silicon compounds, see: (a) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 1339–1445. (b) Pestunovich, V.; Kirpichenko S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 1447–1537. (c) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (d) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (e) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley, Chichester, 1989; pp 1241–1288. (f) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99.
- (5) Bain, V. A.; Killean, R. C. G.; Webster, M. *Acta Crystallogr.* **1969**, *B25*, 156.
- (6) Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszczuk, M. *Inorg. Chem.* **1972**, *11*, 1402.
- (7) The only other reports for dative $^{29}\text{Si}\cdots^{15}\text{N}$ one-bond coupling are for pentacoordinated silicon compounds having an intramolecular $\text{Si}\cdots\text{N}$ bond, see: (a) Kalikhman, I.; Krivonos, S.; Kost, D.; Kottke, T.; Stalke, D. In *Organosilicon Chemistry IV: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, 2000; pp 494–499. (b) Kupce, E.; Liepins, E.; Lapsina, A.; Urtane, I.; Zalcans, G.; Lukevics, E. *J. Organomet. Chem.* **1985**, *279*, 343.
- (8) The ^{29}Si chemical shifts for pentacoordinate Si usually exhibit an upfield shift relative to tetra-coordinate Si.
- (9) Titration of silane **1** with Py or titration of Py with **1** displayed a CIS for **1** (in the ^{19}F and ^{29}Si NMR) or for Py (in the ^{15}N NMR), respectively. However, a standard nonlinear least-squares data treatment for these titrations using a 1:1 binding model¹⁴ gave poor curve fits. This was due to the presence of a small amount of the $\text{SiF}_4\cdot\text{Py}_2$ complex formed throughout the titration (due to a trace amount of H_2O in solution).¹⁰ Therefore, in the case of silane **1** and Py, we were not able to obtain a reasonably accurate binding constant for the formation of the **1**·Py complex.
- (10) See Supporting Information for details.
- (11) (a) Upfield shift for the quartet of **1** was observed also when Py was added to a **1** solution in CDCl_3 (see Figure 1, left side). (b) Upfield shift upon cooling and downfield shift upon increasing the temperature were found for pentacoordinate silicon structures having an intramolecular $\text{Si}\cdots\text{N}$ bond and were used as a measure for the existence of coordination between the silicon and the coordinating nitrogen, see: Helmer, B. J.; West, R.; Corriu, R. J. P.; Poirier, M.; Royo, G.; De Saxce, A. *J. Organomet. Chem.* **1983**, *251*, 295.
- (12) The only reported coupling across the $\text{Si}\cdots\text{N}$ coordinative bond is related to hexacoordinate silicon compounds having intramolecular $\text{Si}\cdots\text{N}$ bonds, see: Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D. *Organometallics* **1997**, *16*, 3255.
- (13) Unfortunately, many attempts to obtain crystals suitable for X-ray crystallography for the complexes of **1** with Py from different solvents combinations and temperatures were unsuccessful.
- (14) Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375 and references therein.

JA031801F