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Communication

Formation of Hexacoordinate Complexes of PhCCSiF₃ with 2,2′-Bipyridine and with 1,10-Phenanthroline through Intermolecular Silicon···Nitrogen Interactions

**Moshe Nakash,* Michael Goldvaser, and Israel Goldberg**

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

Bidentate intermolecular Si···N interactions were utilized to form new hypervalent complexes of trifluoro-phenylethynyl-silane with 2,2′-bipyridine and with 1,10-phenanthroline. X-ray structures obtained for these complexes display a somewhat distorted octahedral geometry about the silicon atom. Binding constants ranging from 170 to 1600 M^{-1} at 25 °C in CDCl₃ were measured for the formation of these complexes, suggesting that such hypervalent complexes of silicon could be used as new motifs in supramolecular chemistry.

Silicon chemistry has grown tremendously over the last two decades, due to the inherent interest in this higher congener of carbon and due to its many practical applications.[1] However, until now, studies in silicon chemistry revolved mainly around covalent bonds to silicon. Aiming to increase the number and chemical diversity of intermolecular interactions that can be used in supramolecular chemistry,[2] beyond those commonly used, we have recently 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**·py₂ complex.[3] Herein, we report that silane **1** forms, through bidentate intermolecular Si···N interactions, the hexacoordinate **1**·bipy-A and **1**·bipy-B complexes with 2,2′-bipyridine (bipy) and the hexacoordinate **1**·phen-A and **1**·phen-B complexes with 1,10-phenanthroline (phen) (see Scheme 1). 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 used here. Binding constants ranging from 170 to 1600 M^{-1} at 25 °C in CDCl₃ were

Scheme 1
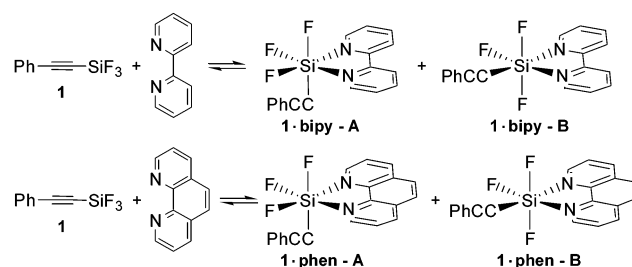
measured for the formation of the complexes shown in Scheme 1. As derivatives of **1** can serve as basic building blocks in host molecules that incorporate several units such as **1**, the hypervalent complexes of **1** with bipy and with phen described here suggest a possible application of such new Si···N intermolecular interactions in supramolecular chemistry.

In contrast to carbon, silicon has a marked tendency to increase its coordination number.[4] Neutral hypervalent structures of silicon 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, have also been reported. In this case, the majority are 1:2 adducts such as SiF₄·py₂[5] or 1:1 complexes with bidentate ligands, such as bipy and phen as in SiF₄·bipy[6] and SiF₄·phen.[6b]

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* To whom correspondence should be addressed. E-mail: nakashm@post.tau.ac.il.

(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, 1996.
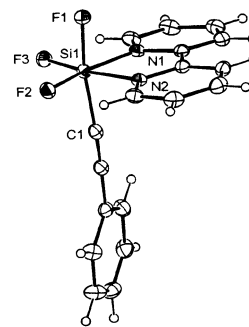(3) Nakash, M.; Goldvaser, M. *J. Am. Chem. Soc.* **2004**, *126*, 3436.

(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, U.K., 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, U.K., 1998; pp 1447–1537. (c) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; pp 495–511. (d) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (e) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (f) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 1241–1288. (g) 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.
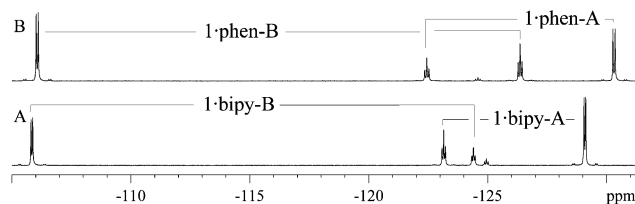
Figure 1. ^{19}F NMR spectra (188.15 MHz, 273 K) in CDCl$_3$ for a 1:1 mixture of (A) **1** and bipy (0.015 M), (B) **1** and phen (0.015 M). A singlet at −137.6 ppm (not shown) for free **1** is also observed. At higher temperatures, the relative height (and integration) of the singlet for free **1** increases as the binding become weaker. The two small triplets at −124.9 ppm (spectrum A) and at −124.7 ppm (spectrum B), correspond to the complexes of bipy and phen, respectively, with a trace amount of SiF$_4$ formed due to a trace amount of H$_2$O in solution.[6b,8] Similar spectra (with poorer fine structure) and peak ratios for the spectrum range shown here are also observed at 298 K.

The two possible isomeric complexes of **1** and bipy and of **1** and phen (Scheme 1) are formed in solution. In comparison with the ^{19}F NMR spectrum of free **1** in CDCl$_3$, where only one singlet at −137.6 ppm is observed, the ^{19}F NMR spectra for a 1:1 mixture of bipy and of phen with **1** in CDCl$_3$ display additional new peaks in distinct chemical shifts (Figure 1),[7] as well as the singlet for free **1**. This suggests a slow equilibrium, on the NMR time scale, in forming the complexes shown in Scheme 1. In Figure 1, parts a and b, two sets of peaks are observed. Each set consists of a doublet and a triplet in a ratio of 2:1, respectively, and corresponds to one of the complexes shown in Scheme 1. This coupling pattern observed in Figure 1 results from a coupling ($^2J_{F-F}$) between the one and the two nonequivalent fluorine atoms in each of the complexes shown in Scheme 1.

With both bipy and phen, a weak preference (of ∼3:2) for the formation of one of the two possible isomeric complexes (Scheme 1) is evident in the ^{19}F NMR spectra (Figure 1) and also in the corresponding ^{1}H NMR spectra.[8] Owing to the different symmetry of complexes type A and B (Scheme 1), the ^{1}H NMR spectra[8] provide evidence as to which of these complexes are preferred in solution and allow us to assign the peaks shown in Figure 1.[9] Therefore, for a 1:1 mixture of bipy or of phen and silane **1**, integrating the singlet for free **1** and the signals for the complexes of **1** in the ^{19}F NMR spectra allowed us to

(6) (a) For X-ray structure of SiF$_4$·bipy see: Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402. (b) For ^{19}F NMR spectra of SiF$_4$·bipy and SiF$_4$·phen see: Nguyen, T. Q.; Qu, F.; Huang, X.; Janzen, A. F. *Can. J. Chem.* **1992**, *70*, 2089.

(7) The corresponding ^{29}Si NMR spectra exhibit a doublet ($^1J_{Si-F}$) of triplets ($^1J_{Si-F}$) for each of the complexes shown in Scheme 1 at about 76−88 ppm upfield with respect to the quartet ($^1J_{Si-F}$) at −91.0 ppm of free **1**,[8] and at a typical region for a hexacoordinate silicon structure.[4]

(8) See Supporting Information for details.

(9) For complexes of both types A and B (Scheme 1), one doublet and one triplet are observed in the ^{19}F NMR spectra in Figure 1. However, due to the different symmetry of complexes **1**·bipy-A and **1**·phen-A versus complexes **1**·bipy-B and **1**·phen-B, respectively, only one signal for the α-hydrogens of the **1**·bipy-A and the **1**·phen-A complexes is observed but two signals for the α-hydrogens of the **1**·bipy-B and the **1**·phen-B complexes are observed in the corresponding ^{1}H NMR spectra.[8] Therefore, integrating the α-hydrogens (of the complexes shown in Scheme 1) in the corresponding ^{1}H NMR spectra,[8] and hence determining the preferred isomeric complex in solution, allowed us to assign the peaks shown in Figure 1, which exhibit the same isomeric complex ratio as in the corresponding ^{1}H NMR spectra.

Figure 2. Thermal ellipsoid plot (50% probability) of the **1**·bipy-A complex. Selected bond lengths (Å) and angles (deg): Si(1)−N(1) 1.9752-(14), Si(1)−N(2) 1.9798(14), Si(1)−F(1) 1.6650(10), Si(1)−F(2) 1.6430-(10), Si(1)−F(3) 1.6459(10), N(1)−Si(1)−N(2) 79.77(6), N(2)−Si(1)−F(2) 90.52(5), F(2)−Si(1)−F(3) 97.67(5), F(3)−Si(1)−N(1) 92.06(5), F(1)−Si-(1)−C(1) 171.54(6).

determine the (microscopic) binding constants for the formation of each of the complexes shown in Scheme 1. These binding constants at 25 °C in CDCl$_3$ for the formation of the **1**·bipy-A, **1**·bipy-B, **1**·phen-A, and **1**·phen-B complexes were determined to be 270 ± 70, 170 ± 40, 1200 ± 300, and 1600 ± 400 M^{-1}, respectively. The stoichiometric binding constant to form the **1**·bipy or **1**·phen complexes is the sum of the two respective (isomeric) microscopic 1:1 binding constants,[10] being ∼440 and ∼2800 M^{-1} at 25 °C in CDCl$_3$, respectively. The stronger binding with phen (vs bipy) could result from a better preorganization for binding to **1** of the phen ligand.

We also were able to obtain single crystals suitable for X-ray crystallography for the **1**·bipy and **1**·phen complexes which were grown in dichloromethane from a 1:1 mixture of silane **1** and bipy or phen, respectively. While the crystals obtained from the mixture of **1** and bipy consist of only one isomer, **1**·bipy-A (Figure 2),[11] the single crystal grown from **1** and phen contains the two possible isomeric complexes, **1**·phen-A and **1**·phen-B (Figure 3).[12] The observation that the two stereoisomers, **1**·phen-A and **1**·phen-B, cocrystallized in a single crystal is rather unusual as it is anticipated that equilibrating isomers formed in solution fully convert, upon crystallization, to the one that crystallizes out first, and ultimately form a pure single crystal of a single isomer. The Si···N bond lengths in the complexes shown in Figures 2 and 3 are in the range 1.9752(14)−2.019(3) Å, and are longer

(10) Connors, K. A. In *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley: New York, 1987; pp 21−24.

(11) Crystal data for the **1**·bipy-A complex: C$_{18}$H$_{13}$F$_3$N$_2$Si, $M = 342.39$, monoclinic, space group $P2_1/c$, $a = 10.3750(3)$ Å, $b = 14.4760(4)$ Å, $c = 10.4990(2)$ Å, $\beta = 102.416(2)°$, $V = 1539.95(7)$ Å^3, $Z = 4$, $T = 110$ K, $D_{calc} = 1.477$ g·cm^{-3}, μ(Mo Kα) = 0.19 mm^{-1}, 12693 measured and 3692 unique reflections ($R_{int} = 0.032$). Final R1 = 0.040 for 2952 observations with $F_o > 4\sigma(F_o)$, R1 = 0.055 (wR2 = 0.104) for all unique data.

(12) Crystal data for **1**·phen complexes (A and B): C$_{20}$H$_{13}$F$_3$N$_2$Si· CH$_2$Cl$_2$, $M = 451.34$, triclinic, space group $P\bar{1}$, $a = 8.8300(3)$ Å, $b = 11.3530(4)$ Å, $c = 19.7990(8)$ Å, $\alpha = 97.390(2)°$, $\beta = 90.396(1)°$, $\gamma = 91.589(2)°$, $V = 1967.44(12)$ Å^3, $Z = 4$, $T = 110$ K, $D_{calc} = 1.524$ g·cm^{-3}, μ(Mo Kα) = 0.43 mm^{-1}, 16403 measured and 8605 unique reflections ($R_{int} = 0.051$). Final R1 = 0.063 for 6047 observations with $F_o > 4\sigma(F_o)$, R1 = 0.099 (wR2 = 0.142) for all unique data.

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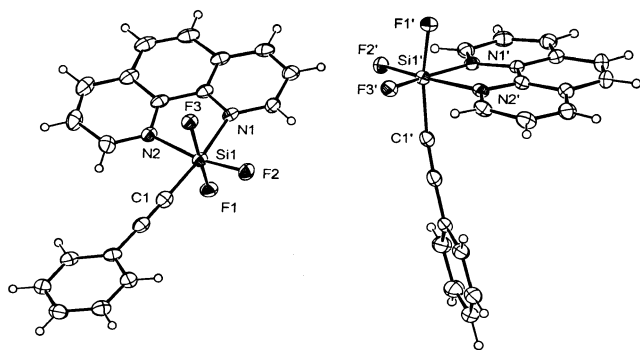
Figure 3. Thermal ellipsoid plot (50% probability) of the **1**·phen-A (right side) and the **1**·phen-B (left side) complexes. Both complexes were found in the same single crystal. The relative orientation of the complexes shown in this figure does not reflect their relative packing pattern in the crystal. Two solvent molecules (dichloromethane) found in the unit cell have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for the **1**·phen-A complex: Si′(1)−N′(1) 2.005(3), Si′(1)−N′(2) 2.011(3), Si′(1)−F′(1) 1.6540(19), Si′(1)−F′(2) 1.646(2), Si′(1)−F′(3) 1.646(2), N′(1)−Si′(1)−N′(2) 80.21(11), N′(2)−Si′(1)−F′(3) 90.79(10), F′(3)−Si′(1)−F′(2) 98.20(10), F′(2)−Si′(1)−N′(1) 90.81(11), F′(1)−Si′(1)−C′(1) 170.13-(13). For the **1**·phen-B complex: Si(1)−N(1) 2.005(3), Si(1)−N(2) 2.019-(3), Si(1)−F(1) 1.664(2), Si(1)−F(2) 1.645(2), Si(1)−F(3) 1.6731(19), N(1)−Si(1)−N(2) 79.71(11), N(2)−Si(1)−C(1) 92.79(13), C(1)−Si(1)−F(2) 98.27(13), F(2)−Si(1)−N(1) 89.23(11), F(1)−Si(1)−F(3) 168.76(11).

than normal covalent Si−N bonds (1.74 Å)[13] but much shorter than the sum of the van der Waals radii of the silicon and nitrogen (3.5 Å).[14] This suggests a rather tight complexation between bipy or phen with silane **1**.[15]

All three complexes shown in Figures 2 and 3 display a similar and somewhat distorted octahedral geometry about the silicon atom. These deviations from a regular octahedral symmetry could result from an inherent geometrical constraint in the bidentate ligands that keeps the two nitrogen atoms in bipy and in phen at a more or less fixed distance from each other, and thus imposes an N−Si−N angle of only 79.77(6)°, 80.21(11)°, and 79.71(11)° in the **1**·bipy-A,

1·phen-A, and **1**·phen-B complexes, respectively (Figures 2 and 3). Indeed, the geometrically unrestricted SiF$_4$·py$_2$ adduct, in which two distinct pyridine ligands are bound to the silicon, shows a nearly ideal octahedral structure.[5] The angular distortions of the octahedral structure and the bond lengths to the silicon atom in the **1**·bipy-A complex (Figure 2) are nearly identical to those found for the adduct of the sterically accessible SiF$_4$ with bipy.[6a] This implies that upon complexation no significant steric hindrance occurs between the two large groups in the **1**·bipy-A complex, the bipy ligand and the phenyl ring in **1**, which are kept apart by the triple bond connecting the phenyl ring to the silicon atom in **1**.[16]

Complexes of 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 consist of several trifluoro-arylethynyl-silane units such as **1**, having several silicon binding sites. As in the case of silane **1**, the SiF$_3$ groups in such host molecules are expected to be sterically accessible and to efficiently bind bidentate ligands such as bipy and phen. This implies that such host molecules should prove useful in forming large supramolecular arrays with bipy or phen derivatives.

In summary, we have described the binding modes of silane **1** with 2,2′-bipyridine and with 1,10-phenanthroline in solution and in the solid state. Studies aiming to utilize these and other intermolecular Si···N interactions in supramolecular complexes are under investigation in this laboratory.

Supporting Information Available: Experimental details and ^{1}H NMR spectra for a 1:1 mixture of bipy and of phen with **1** (PDF). X-ray crystallographic data for complexes **1**·bipy and **1**·phen (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; p 181−265.
(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(15) Longer Si···N intermolecular bond length, of 2.257 Å, was calculated for the pentacoordinate complex of silane **1** with pyridine.[3]
(16) This is also evident in the CPK representation of the complexes shown in Figures 2 and 3.