The synthesis and structure of bis(pyridine-2-carboxy)difluoro(λ^6)- and bis(pyridine-2-carboxy)fluorophenyl(λ^5)siliconium

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Dedicated to Professor Usein M. Dzhemilev on the occasion of his 65th birthday

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Abstract
Reactions of silicon fluorides with picolinic acid (PicH) and its *O*-trimethylsilyl derivative afforded neutral hexa- or pentacoordinate complexes F_2SiPic_2 (**5**) and $PhFSiPic_2$ (**6**). According to NMR data, complex **5** with $SiO_2N_2F_2$ fragment exists as a mixture of two isomers with equivalent **5a** and non-equivalent **5b** fluorine atoms in a 1.5:1 ratio. Quantum chemical calculations at the B3LYP/6-311G** level confirm the stability of the lowest-energy *trans*-structure of **5a**.

Keywords: Hypervalent silicon compounds, phenyltrifluorosilane, picolinic acid, DFT calculations

Introduction

Hypercoordinate organosilicon compounds have attracted much attention due to their unusual bonding properties and enhanced reactivities. They are considered as models of intermediate or transition state of S_N2 reactions and as synthons in preparing new silicon compounds. A large variety of neutral and ionic penta- or hexacoordinate complexes have been prepared where silicon is bonded to *O*,*O*-, *O*,*N*- or *N*,*N*-bidentate ligands.[1]

Previously it had been shown that a Ph-Si bond cleavage reaction provides a convenient approach that was used to obtain hypervalent fluoro complexes with N→Si or O→Si coordination bond.[2] For example, the reaction of phenyltrifluorosilane with ethanolamine and its

N-methyl or *N*,*N*'-dimethyl derivatives and with diethanolamine and its *N*-methyl derivative afforded pentacoordinate silicon complexes **A** and **B**, respectively (Chart 1).

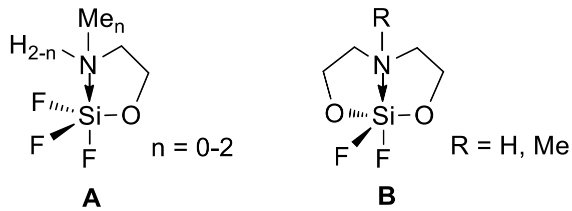


Chart 1

We also described the preparation of spirocyclic complex **C**, bis(2-methyl-4-pyrone-3-oxy)difluoro(λ^6)siliconium, by treatment of 3-hydroxy-2-methyl-pyran-4-one (maltol) with $PhSiF_3$. According to X-ray diffraction data, multinuclear NMR and IR spectral data, and quantum-chemical calculations, the silicon atom has an octahedral environment with two *cis*-arranged C=O$\rightarrow$Si bonds (Chart 2).[3]

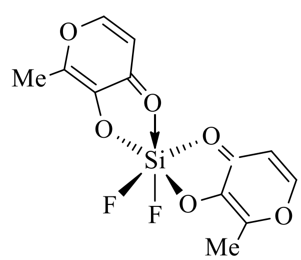


Chart 2

In this study our interest was focused on using a new ligand derived from pyridine-2-carboxylic (picolinic) acid for coordination expansion at silicon. It is known that picolinic acid can act as a bidentate ligand for a wide range of elements (Ag, Cu, Zn, Cd, Co, Ni, Sn) to form metallacycles upon coordination to a metal atom.[4] Thus, in the solid state X-ray analysis reveals that the tin atom in complex $Me_2ClSnPic$ is located in the center of a distorted octahedron (Chart 3).[5]

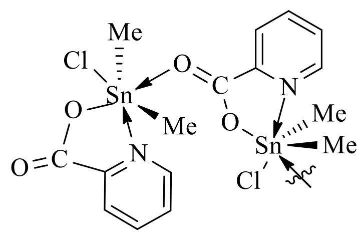
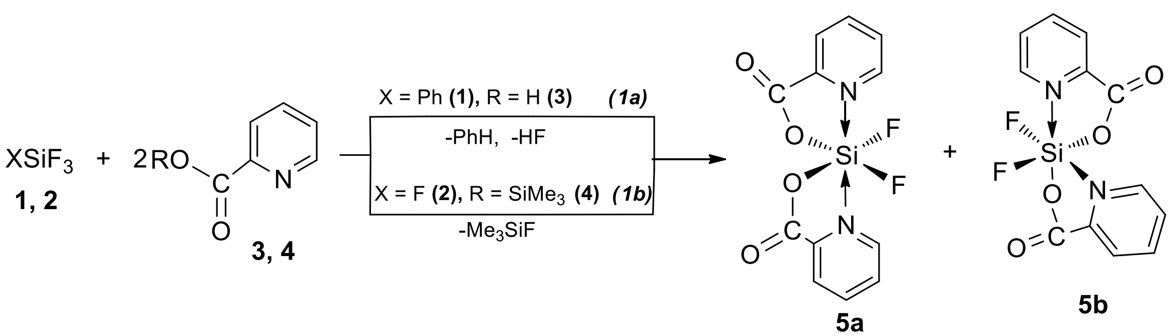


Chart 3

However, there is no data on the silicon halides complexes with this ligand. We report herein the synthesis and characterization of the first hexa- and pentacoordinate silicon fluoride complexes, bis(pyridine-2-carboxy)difluoro(λ^6)- (F_2SiPic_2) and bis(pyridine-2-carboxy)-fluorophenyl(λ^5)siliconium ($PhFSiPic_2$).

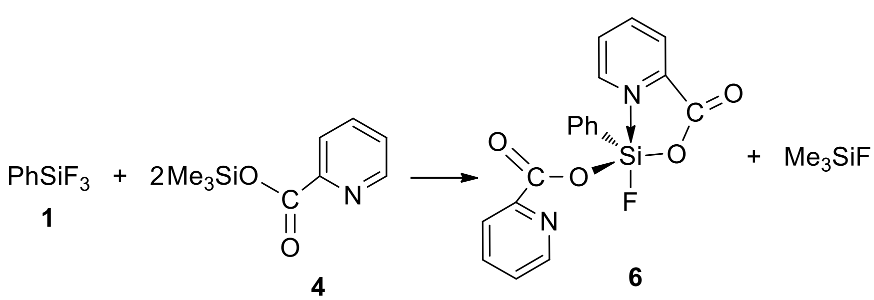
Discussion

We found that reaction of phenyltrifluorosilane **1** with pyridine-2-carboxylic acid **3** proceeds *via* cleavage the Si-C and Si-F bonds to give a mixture of two isomeric bicyclic compounds bis(pyridine-2-carboxy)difluoro(λ^6)siliconium **5a** and **5b** in a ratio of 1.5:1 (58% overall yield) (Scheme 1a). Alternatively, the same complexes with a $SiO_2N_2F_2$ skeleton were obtained by passing an excess of SiF_4 gas **2** through the hexane solution of *O*-trimethylsilyl derivative of picolinic acid **4** in 45% yield (Scheme 1b).



Scheme 1. Synthesis of bis(pyridine-2-carboxy)difluoro(λ^6)siliconium **5**.

In contrast to Scheme 1, treatment of **4** with $PhSiF_3$ **1** afforded the pentacoordinate silicon complex **6**, bis(pyridine-2-carboxy)-1-fluoro-1-phenyl(λ^5)siliconium, in 60% yield (Scheme 2).



Scheme 2. Formation of bis(pyridine-2-carboxy)-1-fluoro-1-phenyl(λ^5)siliconium **6**.

Complexes **5** and **6** are stable under an inert atmosphere. They are soluble in common organic solvents and can be crystallized as colorless powders from chloroform solutions.

The structures of the complexes **5** and **6** were confirmed by multinuclear ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si NMR and IR spectroscopies, and quantum-chemical calculations.

The ^{1}H and ^{13}C NMR spectra of F_2SiPic_2 **5** display two different sets of resonance signals of the pyridine ring indicating the existence of two isomers with the N→Si coordination bond. In the ^{1}H NMR spectrum of complex **5** the signals from the proton of the pyridine ring are shifted to lower field relatively to those for PicH **3**, especially in positions 4 and 5 (more than 0.5 ppm). Besides, the shielding the *α*-carbon atoms (by 3-7 ppm) and deshielding the *β*- and *γ*-carbons (by 2-6 ppm) of pyridine ring in the ^{13}C NMR spectrum of **5** as compared with those for **3** is observed. These data are indicative of increasing positive charge on nitrogen because of involving heteroatom in the coordination N-Si bonding. Similar behavior has been observed for protonated pyridine derivatives.[7]

The fluorine atoms of major hexacoordinate complex **5a** appear as a sharp singlet in the ^{19}F NMR spectrum at δ -119.77 ppm with silicon satellite ($J_{Si\text{-}F}$ = 148 Hz) showing fluxional behavior due to a rapid exchange process on the NMR time scale. Minor **5b** exhibits a ^{19}F NMR resonance as two doublets at δ -139.19 ppm ($J_{F\text{-}F}$ = 24.4 Hz, $J_{Si\text{-}F}$ = 135.8 Hz) and δ -141.04 ppm ($J_{Si\text{-}F}$ = 122.1 Hz) corresponding to two non-equivalent atoms of fluorine.

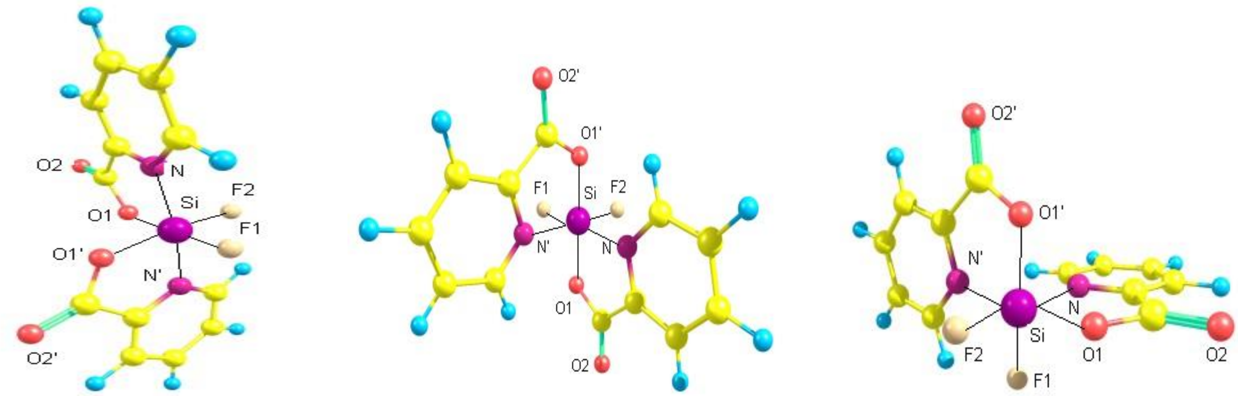
The ^{29}Si NMR spectrum of complex **5** in DMSO-d_6 at room temperature shows unresolved multiplet resonances of two isomers (from δ -175 ppm to δ -182 ppm) in the range typical for hexacoordinate silicon compounds.[1]

Two ^{15}N resonances **5a** at δ -105.8 ppm (major) and **5b** δ -117.1 ppm (minor) are observed in the ^{15}N NMR of **5** which are greatly shielded (by 40‒60 ppm) a higher field compared to that for pyridine.

Complex **6** exhibits the ^{19}F and ^{29}Si NMR resonances at δ -130.56 and δ -75.1 ppm, respectively that are consistent with five-coordinate silicon complexes.[1] Decrease in the coupling constant ^{29}Si-^{19}F (244.0 Hz) in comparison with model phenylfluorodi(benzoyloxy)silane $PhFSi[OC(O)Ph]_2$ (δ_{Si} = -60.3 ppm, δ_F = -140.8 ppm, $J_{Si\text{-}F}$ = 270 Hz)[8] also suggests pentacoordination of the silicon atom.

The geometry of complex **5** in gas phase was optimized by using density functional theory (DFT) method. DFT calculations were carried out with B3LYP at the 6-311G** level of theory.

The optimized structures of isomers **5a**, **5a'** and **5b** correspond to minima on the potential energy surface (Figure 1).

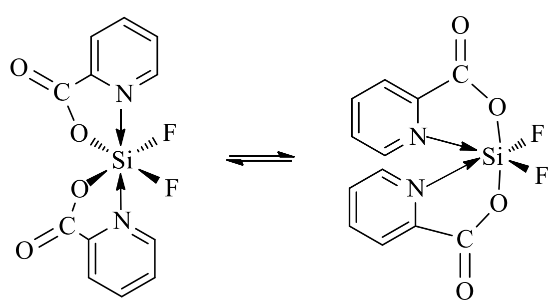


5a $\Delta E = 0$ kcal mol^{-1} **5a'** ($\Delta E = 4.6$ kcal mol^{-1}) **5b** ($\Delta E = 6.7$ kcal mol^{-1})

Figure 1. The molecular structure of complexes **5a**, **5a'**, **5b** and relative energy (ΔE), (B3LYP/6-311G**).

In all isomers the silicon centre is in a slightly distorted octahedral environment due to two intramolecular coordination bonds N→Si. The structure **5a** with *trans*-orientated nitrogen atoms and *cis*-orientated fluorine and oxygen atoms is the most stable structure. Isomer **5a'** having the oxygens ligands in *trans* arrangement relative to each other is less favorable ($\Delta E = 4.63$ kcal mol^{-1}). It has higher dipole moment (10.21 D) in comparison with **5a** (3.48 D) so that it can be stabilized in such polar media as $CDCl_3$. The least stable structure **5b** ($\Delta E = 6.74$ kcal mol^{-1}) with non-equivalent fluorine atoms in fragments O−Si−F and N→Si−F has the largest value μ (12.68 D).

It can be assumed that complex **5a** is a mixture of two hexacoordinate isomers with N–*trans*- and N–*cis*-orientation rapid fluxional exchange (on the NMR time scale) (Chart 4).



5a **5a'**

Chart 4

Similar type of conformational exchange was reported previously for hexacoordinate complexes with $SiO_2N_2X_2$ fragment.[6]

Selected angles for **5a**, **5a'** and **5b** are listed in Table 1.

Table 1. Selected Angles (deg) for **5a**, **5a'** and **5b**

	5a	**5a'**	**5b**
NSiN’	171.0	88.1	90.9
O1SiO1’	88.5	163.0	92.2
O1SiF1	175.8	93.8	97.4
O1'SiF1	90.0	97.2	164.0
O1SiF2	90.0	97.2	96.5
O1'SiF2	175.8	93.7	95.0
O1SiN'	89.4	86.4	171.8
F1SiF2	91.8	99.2	96.6
F1SiN	91.8	173.0	84.6
F1SiN'	94.4	86.5	87.1
F2SiN	94.4	86.5	178.7
F2SiN'	91.8	173.0	89.7

These values are consistent well with those found for hexacoordinate silicon compounds.[9] The Si-N distance for **5a** (1.937 Å) is shorter by 0.1 Å than distance between atoms of nitrogen and silicon in complex **5a'** (2.062 Å). The Si-N and Si-N' distances for **5b** are 2.085 and 2.009 Å respectively. The Si-F distances of fragments O-Si-F in the structure **5a** (1.662 Å) and **5b** (1.659 Å) and N→Si-F in the structure **5a'** (1.631 Å) and **5b** (1.632 Å) are similar. The existence of two stable isomeric structures **5a** and **5b** which is evident from the above calculations is consistent with the NMR data.

In IR spectra of pyridine metal complexes, a shift of the stretching vibrational bands of C=C and C=N bonds to higher frequency is commonly used as a criteria for metal coordination[10]. A comparison of the intense bands ν(C=C) and ν(C=N) in the IR spectra of complex **5** (1615 cm^{-1}) with those of compounds PicH **3** (1598 cm^{-1}) and Me_3SiPic **4** (1590, 1570 cm^{-1}) showed a major shift to higher frequencies. These data indicate coordination of the nitrogen atom to silicon. Similarly, a shift to a higher frequency is observed on going from compound **4** to its hydrochloride (1624 cm^{-1}) due an increase in electron density on the nitrogen atom upon protonation.

In IR spectra of hexacoordinated silicon compounds with N→Si bond absorption bands in the region 900-500 cm^{-1} are attributed to vibrations ν(Si–F) that are largely mixed with deformational vibrations δ(C–H) bonds of aliphatic and aromatic fragments of molecules.[11] The experimental frequencies ν(Si–F) were assigned by their comparison with those obtained from the calculated spectra. The vibrations ν_{as}(Si–F) and ν_s(Si–F) for **5a'** (865, 822 cm^{-1}) and **5b** (847, 795 cm^{-1}) has been calculated to be intense. In contrary, calculated for **5a** vibrations ν(Si–F) (891, 799, 724 and 519 cm^{-1}) are low intense and mixed with vibrations δ(C–H) of the pyridine ring. These values agree closely with the ν(Si–F) observed in the IR spectrum of complex **5** which shows a weak band at 547 cm^{-1} and a doublet band of a small intensity (904, 886 cm^{-1}), an intense band out plane deformational vibrations of CH bond at 759 cm^{-1} having two shoulders at 806 and 743 cm^{-1}. The minor component **5b** has weak bands in the region of 900-800 cm^{-1}. In the IR spectrum of complex **6**, an intense band of vibrations νSi-F is observed at 892 cm^{-1} which is close to calculated value of 857 cm^{-1}.

Conclusion

In summary, hexacoordinate complex **5** with $SiO_2N_2F_2$ fragment exists as a mixture of two isomers **5a** and **5b** with equivalent and non-equivalent fluorine atoms. In five-membered complex **6** the silicon atom is pentacoordinate.

Experimental Section

General. Picolinic acid was purchased from commercial sources (Acros) and was used as received. IR spectra of compounds were recorded on a FT-IR Spectrometer Bruker Vertex 70 (thin films or KBr pellets). ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (^{1}H, 400.13 MHz, ^{13}C, 100.61 MHz, ^{15}N, 40.56 MHz, ^{19}F, 376.50 MHz, ^{29}Si 79.49 MHz) at room temperature. Compounds **1**, **3–6** were recorded as solutions in $CDCl_3$ and DMCO-d_6 (Me_4Si as internal standard) at room temperature. ^{29}Si NMR spectra were obtained by using the INEPT pulse sequence. The precision of measurements of the ^{1}H- and ^{13}C-chemical shifts was 0.01 and 0.02 ppm, respectively and 0.1 ppm ^{29}Si. Analysis and assignment of the ^{1}H NMR data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HSQC experiments. Assignment of the ^{13}C NMR data was supported by ^{13}C, ^{1}H HSQC experiments. Assignment of the ^{15}N NMR data was supported by HMBC(^{15}N–^{1}H) experiments.

The calculations were performed by the DFT method using the B3LYP exchange correlation potential and the 6-311G** basis set as implemented in the Gaussian03 program package.[12] All calculated structures correspond to minima on the potential energy surface (PES) as proved by positive eigenvalues of the corresponding Hessian matrices. All energies were calculated with the ZPE correction.

Microelemental analysis was carried out in Analytical Group of the Physical Chemistry Laboratory of our Institute.

Bis(pyridine-2-carboxy)difluoro(λ^{6})siliconium (5) (route a). Phenyltrifluorosilane **1** (1.81 g, 11 mmol) was added dropwise to a solution of PicH **3** (0.6 g, 5 mmol) in C_6H_6 (10 ml). After stirring for 5 h the precipitate was filtered and washed with benzene to yield **5** (0.88 g, 58 %), m.p. 105-107°C. Anal. Calc. for $C_{12}H_8N_2O_4F_2Si$: C, 46.45; H, 2.60; N, 9.03; F, 12.25; Si, 9.05. Found: C, 46.12; H, 2.78; N, 8.87; F, 11.86; Si, 9.14.

5a. ^{1}H NMR (DMSO-d_6): δ 8.13 (dt, 3H, $J_{3\text{-}4}$ = 7.7 Hz), δ 8.33 (dd, 4H, $J_{4\text{-}5}$ = 6.7 Hz), δ 7.90 (dd, 5H, $J_{5\text{-}6}$ = 5.3 Hz), δ 8.72 (dt, 6H). ^{13}C NMR (DMSO-d_6): δ 143.59 (C-2); δ 122.93 (C-3); δ 142.46 (C-4); δ 128.51 (C-5); δ 142.86 (C-6); δ 162.14 (CO). ^{15}N NMR (DMSO-d_6): -117.1.
5b. ^{1}H NMR (DMSO-d_6): δ 8.22 (dt, 3H, $J_{3\text{-}4}$ = 7.7 Hz), δ 8.28 (dd, 4H, $J_{4\text{-}5}$ = 6.7 Hz), δ 7.87 (dd, 5H, $J_{5\text{-}6}$ = 4.9 Hz), δ 8.79 (dt, 6H). ^{13}C NMR (DMSO-d_6): δ 145.63 (C-2), δ 125.86 (C-3), δ 141.51 (C-4), δ 128.51 (C-5), δ 147.29 (C-6), δ 164.27 (CO). ^{15}N NMR (DMSO-d_6): -105.8.
(route b). Gaseous SiF_4 **2** (prepared from 37.82 g, 20 mmol Na_2SiF_6 and 19.6 g, 20 mmol conc. H_2SO_4) was passed through a solution of $PicSiMe_3$ **4** (1.95 g, 10 mmol) in hexane (10 ml) for 1 h. Filtration of a solid product followed by dried in vacuum gave **5** (1.39 g, 45%), m.p. 105-107°C.

Bis(pyridine-2-carboxy)fluorophenyl(λ^5)siliconium (6). The compound **6** (1.98 g, 60 %), was obtained from phenyltrifluorosilane **1** (1.53 g, 9 mmol) and $PicSiMe_3$ **4** (1.85 g, 9 mmol) in benzene (10 ml) using the above procedures for **5** (route a), m.p. 89-91°C. Anal. Calc. for $C_{18}H_{13}N_2O_4FSi$: C, 58.69; H, 3.56; N, 7.60; F, 5.16; Si 7.62. Found: C, 58.51; H, 3.78; N, 7.22; F, 5.03; Si, 7.69.

(Pyridine-2-carboxy)trimethylsilane $PicSiMe_3$ (4). Hexamethyldisilazane (7.74 g, 48 mmol) was added dropwise to PicH (3.60 g, 29 mmol). After stirring for 20 h at 80-90°C the reaction mixture was distilled to give **4** (3.21 g, 57 %), m.p. 115°C / 7 мм Hg. Anal. Calc. for $C_9H_{13}O_2NSi$: C, 55.35; H, 6.71; N, 7.17; Si, 14.38. Found: C, 55.01; H, 6.93; N, 6.92; Si, 14.67. ^{1}H NMR (DMSO-d_6): δ 8.01 (dt, 3H, $J_{3\text{-}4}$ = 7.8 Hz), δ 7.72 (dd, 4H, $J_{4\text{-}5}$ = 7.7 Hz), δ 7.35 (dd, 5H), δ 8.65 (dt, 6H, $J_{6\text{-}5}$ = 4.1 Hz). ^{13}C NMR (DMSO-d_6): δ 148.81 (C-2), δ 125.31 (C-3), δ 136.78 (C-4), δ 126.58 (C-5), δ 149.76 (C-6), δ 165.11 (CO).

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