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

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

DOI: http://dx.doi.org/10.3998/ark.5550190.0012.812

Abstract
Reactions of silicon fluorides with picolinic acid (PicH) and its O-trimethylsilyl derivative afforded neutral hexa- or pentacoordinate complexes F\(_2\)SiPic\(_2\) (5) and PhFSiPic\(_2\) (6). According to NMR data, complex 5 with SiO\(_2\)N\(_2\)F\(_2\) 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\(_N\)2 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\(\rightarrow\)Si or O\(\rightarrow\)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(\(\lambda^6\))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→Si bonds (Chart 2).

![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\(_2\)ClSnPic is located in the center of a distorted octahedron (Chart 3).

![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(λ⁶)- (F₂SiPic₂) and bis(pyridine-2-carboxy)-fluorophenyl(λ⁵)siliconium (PhFSiPic₂).

**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(λ⁶)siliconium 5a and 5b in a ratio of 1.5:1 (58% overall yield) (Scheme 1a). Alternatively, the same complexes with a SiO₂N₂F₂ skeleton were obtained by passing an excess of SiF₄ 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(λ⁶)siliconium 5.](image)

In contrast to Scheme 1, treatment of 4 with PhSiF₃ 1 afforded the pentacoordinate silicon complex 6, bis(pyridine-2-carboxy)-1-fluoro-1-phenyl(λ⁵)siliconium, in 60% yield (Scheme 2).

![Scheme 2. Formation of bis(pyridine-2-carboxy)-1-fluoro-1-phenyl(λ⁵)siliconium 6.](image)
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 $^1\text{H}$, $^{13}\text{C}$, $^{15}\text{N}$, $^{19}\text{F}$, $^{29}\text{Si}$ NMR and IR spectroscopies, and quantum-chemical calculations.

The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of F$_2$SiPic$_2$ 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 $^1\text{H}$ 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 $\alpha$-carbon atoms (by 3-7 ppm) and deshielding the $\beta$- and $\gamma$-carbons (by 2-6 ppm) of pyridine ring in the $^{13}\text{C}$ 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 $^{19}\text{F}$ NMR spectrum at $\delta$ -119.77 ppm with silicon satellite ($J_{\text{Si-F}} = 148$ Hz) showing fluxional behavior due to a rapid exchange process on the NMR time scale. Minor 5b exhibits a $^{19}\text{F}$ NMR resonance as two doublets at $\delta$ -139.19 ppm ($J_{\text{F-F}} = 24.4$ Hz, $J_{\text{Si-F}} = 135.8$ Hz) and $\delta$ -141.04 ppm ($J_{\text{Si-F}} = 122.1$ Hz) corresponding to two non-equivalent atoms of fluorine.

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

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

Complex 6 exhibits the $^{19}\text{F}$ and $^{29}\text{Si}$ NMR resonances at $\delta$ -130.56 and $\delta$ -75.1 ppm, respectively that are consistent with five-coordinate silicon complexes.\(^1\) Decrease in the coupling constant $^{29}\text{Si-}^{19}\text{F}$ (244.0 Hz) in comparison with model phenylfluorodi(benzoyloxy)silane PhFSi[OC(O)Ph]$_2$ ($\delta_{\text{Si}}$ = -60.3 ppm, $\delta_{\text{F}}$ = -140.8 ppm, $J_{\text{Si-F}} = 270$ 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).
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 (ΔE = 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 CDCl₃. The least stable structure 5b (ΔE = 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).

Similar type of conformational exchange was reported previously for hexacoordinate complexes with SiO₂N₂X₂ fragment.⁶

Selected angles for 5a, 5a' and 5b are listed in Table 1.
Table 1. Selected Angles (deg) for 5a, 5a' and 5b

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<tr>
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<th>5a</th>
<th>5a'</th>
<th>5b</th>
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<td>97.2</td>
<td>164.0</td>
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<td>F2SiN'</td>
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<td>173.0</td>
<td>89.7</td>
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</table>

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 \(\nu(C=C)\) and \(\nu(C=N)\) in the IR spectra of complex 5 (1615 cm\(^{-1}\)) with those of compounds PicH 3 (1598 cm\(^{-1}\)) and Me\(_3\)SiPic 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 \(\nu(Si–F)\) that are largely mixed with deformational vibrations \(\delta(C–H)\) bonds of aliphatic and aromatic fragments of molecules.\(^11\) The experimental frequencies \(\nu(Si–F)\) were assigned by their comparison with those obtained from the calculated spectra. The vibrations \(\nu_a(Si–F)\) and \(\nu(Si–F)\) for 5a' (865, 822 cm\(^{-1}\)) and 5b (847, 795 cm\(^{-1}\)) has been calculated to be intense. In contrary, calculated for 5a vibrations \(\nu(Si–F)\) (891, 799, 724 and 519 cm\(^{-1}\)) are low intense and mixed with vibrations \(\delta(C–H)\) of the pyridine ring. These values agree closely with the \(\nu(Si–F)\) 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 vSi-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\(_2\)N\(_2\)F\(_2\) 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\(_4\)Si 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(\(\lambda^6\))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\(_6\)H\(_6\) (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\(_8\)N\(_2\)O\(_4\)F\(_2\)Si: 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-$d_6$): $\delta$ 8.13 (dt, 3H, $J_{3-4} = 7.7$ Hz), $\delta$ 8.33 (dd, 4H, $J_{4-5} = 6.7$ Hz), $\delta$ 7.90 (dd, 5H, $J_{5-6} = 5.3$ Hz), $\delta$ 8.72 (dt, 6H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 143.59 (C-2); $\delta$ 122.93 (C-3); $\delta$ 142.46 (C-4); $\delta$ 128.51 (C-5); $\delta$ 142.86 (C-6); $\delta$ 162.14 (CO). $^{15}$N NMR (DMSO-$d_6$): -117.1.

5b. $^1$H NMR (DMSO-$d_6$): $\delta$ 8.22 (dt, 3H, $J_{3-4} = 7.7$ Hz), $\delta$ 8.28 (dd, 4H, $J_{4-5} = 6.7$ Hz), $\delta$ 7.87 (dd, 5H, $J_{5-6} = 4.9$ Hz), $\delta$ 7.89 (dt, 6H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 145.63 (C-2), $\delta$ 125.86 (C-3), $\delta$ 141.51 (C-4), $\delta$ 128.51 (C-5), $\delta$ 147.29 (C-6), $\delta$ 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$_2$SiF$_3$ and 19.6 g, 20 mmol conc. H$_2$SO$_4$) 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($\lambda^3$)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$_2$O$_4$FSi: 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 mm Hg. Anal. Calc. for C$_9$H$_{13}$O$_2$NSi: 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-$d_6$): $\delta$ 8.01 (dt, 3H, $J_{3-4} = 7.8$ Hz), $\delta$ 7.72 (dd, 4H, $J_{4-5} = 7.7$ Hz), $\delta$ 7.35 (dd, 5H), $\delta$ 8.65 (dt, 6H, $J_{6-5} = 4.1$ Hz). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 148.81 (C-2), $\delta$ 125.31 (C-3), $\delta$ 136.78 (C-4), $\delta$ 126.58 (C-5), $\delta$ 149.76 (C-6), $\delta$ 165.11 (CO).

References


