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Neutral pentacoordinate silicon complexes with SiO_2FC skeleton: Synthesis, structural characterization and stereodynamical behavior

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ABSTRACT

A series of new pentacoordinate intramolecular organosilicon complexes $F(Ar)Si(OCH_2CH_2)_2NMe$ (Ar = 4-MeC_6H_4 (**1**), 4-$MeOC_6H_4$ (**2**), 4-ClC_6H_4 (**3**), 2-BrC_6H_4 (**4**), 3-$NO_2C_6H_4$ (**5**)) has been synthesized by transsilylation of aryltrifluorosilanes $ArSiF_3$ by *N*-methyl-*bis*(2-trimethylsiloxyethyl)amine. Compounds **1**–**5** have been fully characterized by ^1H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopy and X-ray diffraction analysis (for compound **3**). Variable-temperature ^{19}F NMR studies of **5** indicate stereodynamic process of the ligand exchange with activation barrier $\Delta G_c^{\neq}$ of 13.1 kcal mol^{-1}.

Introduction

One of the main areas of research in silicon chemistry is highly coordinate organosilicon compounds whose specific dative bonding and high reactivity have attracted considerable attention over a long time [1a–f]. Organosilicon derivatives of triethanolamines $XSi(OCH_2CH_2)_3N$ (silatranes) [2a–d] and diethanolamines $R'R''Si(OCH_2CH_2)_2NR$ (quasisilatranes) [3a–d] with intramolecular dative N → Si bond are the subject of our continuing interest.

Molecular and stereoelectronic structure as well as chemical and biological properties of silatranes are reported in several reviews [2a–d,4]. A large body of data shows that the extent of the N → Si intramolecular bonding in silatranes depends on the electronegativity and the leaving group ability of the substituent at the silicon atom. The substituent effects on the N → Si bond strength in quasisilatranes are less studied. According to ^{29}Si NMR data for phenyl substituted complexes $PhRSi(OCH_2CH_2)_2NMe$, the silicon pentacoordination is decreased on going from R = Ph to R = Me whereas electronegative substituents favor pentacoordination [5a–c,6]. However, there is a lack of information about the structure of these compounds determined by X-ray diffraction. Recently we have reported determination the structure of a series of quasisilatranes $F(R')Si(OCH_2CH_2)_2NR$ (R = H, R′ = F; R = H, R′ = Me; R = Me, R′ = Ph) by X-ray diffraction analysis [6]. The combined X-ray and ^{29}Si NMR analysis showed that the presence of electronegative fluorine atom at silicon results in strengthening of the N → Si coordination. Thus, the N → Si bond in F(R) $Si(OCH_2CH_2)_2NH$ becomes shorter on going from R = Me (2.059 Å) to R = F (1.981 Å) [6]. In continuation of these studies, we report here the synthesis and characterization of new aryl substituted complexes $F(Ar)Si(OCH_2CH_2)_2NMe$ **1**–**5**, X-ray diffraction analysis for compound **3**, and NMR spectroscopic study of dynamic behavior of compound **5** in solution. Note that there are only a few data about the effect of variation in aryl substituents on the N → Si bonding in quasisilatranes [7a,b].

Results and discussion

Synthesis

Fluoro derivatives of quasisilatranes can be prepared by the cleavage of the Ph–Si bond in phenyltrifluorosilane by diethanolamines [6]. A more easy and convenient route is the transsilylation

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reaction of $PhSiF_3$ by bissilylated diethanolamines allowing to avoid the HF evolution and to increase the product yield [6]. Using this protocol, compounds **1**–**5** have been obtained as colorless crystals in good yield (75–93%) by treating aryltrifluorosilanes $ArSiF_3$ with equimolar amount of *N*-methyl-*bis*(2-trimethylsiloxyethyl)amine at 30–40 °C (Scheme 1).

Compounds **1**–**5** are air-sensitive in solution and in the solid state, and can be stored for several weeks under an inert atmosphere at room temperatures. They are readily soluble in common organic solvents such as benzene, chloroform and DMSO. Their structure was established by elemental analysis, ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopy, mass-spectrometry. Toxicity study of a novel quasisilatrane **3** on white mice showed that the compound is moderately toxic (LD_{50} 535 mg/kg) and much less toxic than 1-(4-chlorophenyl)silatrane 4-$ClC_6H_4Si(OCH_2CH_2)_3N$ (LD_{50} 0.22 mg/kg) [8].

*X-ray structure of crystal **3***

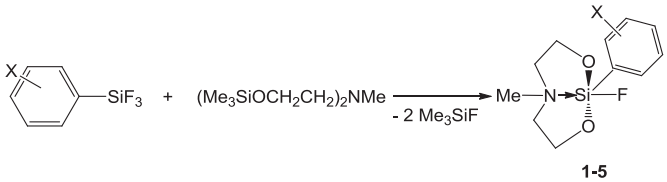
X-ray quality crystals of compound **3** were obtained by recrystallization from chloroform/hexane (2:1 v/v). Crystallographic data and structural refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structure of compound **3** is shown in Fig. 1.

Single-crystal X-ray analysis reveals that **3** crystallizes in the orthorhombic $Pca2_1$ space group. The coordination spheres of the hypercoordinate Si atom can be described as distorted trigonal bipyramid with a chelated OSiO ligand and the fluorine and nitrogen atoms in axial positions. The equatorial plane is formed by C5, O1 and O2 atoms. Deviation from a regular TBP polyhedron is seen in the apical F–Si–N angle of 172.3° and in the sum of the angles in the equatorial plane of 356.9°. Deviation from the ideal angle 90° is observed for F–Si–O1 and F–Si–C5 angles (4.3 and 8.7°, respectively). Generally, the structure of compounds **3** and **6** is very similar (Table 2). The N → Si dative bond in **3** is somewhat longer than that in **6** whereas the axial Si–F bond distance in **3** is slightly shorter than in **6**.

*NMR spectroscopic studies of quasisilatranes **1**–**5***

Both ^{29}Si chemical shifts and $^{1}J_{SiF}$ coupling constants of compounds **1**–**5** (Table 3) are very similar to those of 1-fluoro-1-phenyl-5-methylquasisilatrane **6** ([6]) and suggest pentacoordination at silicon in solution.

The room temperature ^{1}H NMR spectra of **1**–**4** exhibit a broad singlet of the MeN group. In complex **5** with the most electronegative substituent (3-$NO_2C_6H_4$) the MeN signal is strongly broaden due to dynamic ligand exchange (Scheme 2). The ^{29}Si resonance signals of **1**–**4** are also broadened, which is a clear indication of a fast exchange equilibrium between stereoisomers **A** and **E** in solution (Scheme 2). In compound **5**, the ^{29}Si resonance at room temperature is so broaden that it does not allow to detect the signal.



X = 4-Me (**1**), 4-MeO (**2**), 4-Cl (**3**), 2-Br (**4**), 3-NO_2 (**5**)

Scheme 1.

Table 1
Crystallographic parameters for compound **3**.

Empirical formula	$C_{11}H_{15}NO_2ClFSi$
Fw	275.78
Space group	$Pca2_1$
a [Å]	12.146(1)
b [Å]	13.966(2)
c [Å]	7.5543(9)
α, *β*, *γ* [°]	90, 90, 90
V [Å^3]	1281.5(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.429
Crystal size (mm)	0.35 × 0.21 × 0.18
T [K]	296(2)
μ (mm^{-1})	0.398
R_1 [$F_o > 4\sigma(F_o)$]/all	0.0486/0.1080
wR_2	0.0928
GOF	1.011

Table 2
Selected bond lengths (Å) and angles (°) in the crystal structures of **3** and **6**.

	3	**6**[a] [6]
N → Si	2.251(4)	2.175(1)
Si–F	1.626(3)	1.645(1)
Si–O1	1.638(3)	1.656(1)
Si–O2	1.642(3)	1.657(1)
Si–C5	1.851(4)	1.868(1)
O1–C1	1.411(5)	1.430(1)
O2–C3	1.410(6)	1.421(1)
N–C11	1.451(6)	1.477(1)
ΔSi	0.17(1)	0.13(1)
ΔN	0.45(1)	0.45(1)
N–Si–F	172.3(2)	172.0(3)
F–Si–O1	94.3(2)	93.5(3)
F–Si–O2	94.4(2)	93.0(3)
N–Si–O1	81.9(1)	83.1(3)
N–Si–O2	82.1(2)	83.0(3)
O1–Si–O2	121.9(2)	124.0(1)
O1–Si–C5	117.1(2)	115.8(1)
O2–Si–C5	117.9(2)	118.3(1)
F–Si–C5	98.7(2)	97.4(1)
C1–O1–Si	126.1(3)	123.8(1)
C3–O2–Si	123.8(3)	123.2(1)
O1–C1–C2	109.8(4)	108.9(1)
O2–C3–C4	108.3(4)	106.5(1)
C2–N–C4	111.8(4)	113.2(1)
C2–N–C11	107.9(4)	110.5(1)
C4–N–C11	113.5(4)	110.0(1)

[a] $PhFSi(OCH_2CH_2)_2NMe$.

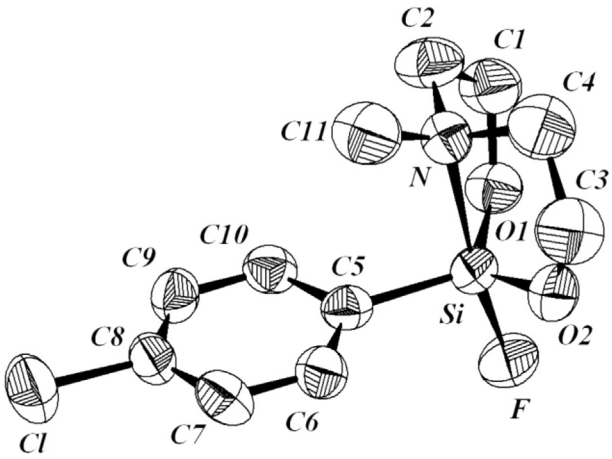
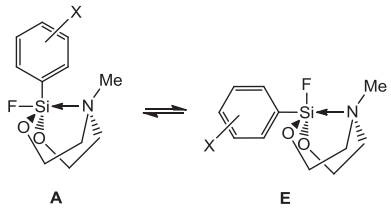


Fig. 1. Molecular structure of **3**.

Table 3
^{19}F and ^{29}Si Chemical shifts (ppm) and coupling constants (Hz) in $CDCl_3$ for quasi-silatrane **1**–**5** and **6**.

	1	2	3	4	5	6 [6]
$\delta(^{29}Si)$	−79.2	−79.1	−82.5 (br. d)	−84.8	– −86.1 (253 K) −95.5 (253 K)	−80.6
$\delta(^{19}F)$	−120.6 −128.8	−120.1	−119.2	−120.0	−119.6; −131.7 (298 K) −115.3 (253 K) −131.9 (253 K)	−121.5
$^1J_{SiF}$	217.0	215.8	–	210.0	– 201.6[a] 283.0[a]	214.3

[a] $^1J_{SiF}$ at 253 K.



Scheme 2.

The room temperature ^{19}F NMR spectra of compounds **2**–**4** show one broad signal, whereas in the case of compounds **1** and **5** two separate signals are observed: two broaden peaks for the former and two relatively narrow peaks for the latter (Table 3). This suggests a slower ligand exchange in compounds **1** and **5** as compared to compounds **2**–**4**.

For compound **5**, lowering the temperature to 253 K results in appearance of two sharp ^{19}F signals at δ −115.3 and −131.9 ppm in a 2:1 ratio with $^1J_{SiF}$ of 201.6 and 283.0 Hz, respectively. At this temperature the ^{29}Si NMR spectrum of **5** exhibits two doublets at −86.1 and −95.5 ppm. Bearing in mind a large difference of the $^1J_{SiF}$ constants for the axial and equatorial fluorine atoms, we performed theoretical calculations of the chemical shifts and coupling constants in compound **5** for a reliable assignment of the signals to the axial (**A**) and equatorial (**E**) isomers as depicted in Scheme 2. The calculations were performed by the GIAO method on the B3LYP/6-311 + G** optimized geometry using the Gaussian09 suite of programs [9]. The calculated $^1J_{SiF_{eq}}$ coupling constant for isomer **E** is by 64 Hz larger than the $^1J_{SiF_{ax}}$ coupling constant for isomer **A**. Such a large difference in the calculated coupling constants comparable with the experimental one can be considered as a reliable criterion, which allows to assign the major isomer of **5** (65% from the ^{19}F NMR) to the axial isomer **A**. The calculated ^{29}Si chemical shift in isomer **E** is shifted to a higher field relative to isomer **A** by 5.6 ppm. This is consistent with the experiment in which the lower-field signal having a smaller coupling constant $^1J_{SiF}$ is more intense and refers to the predominant axial isomer **A**. Unfortunately, the difference in the calculated ^{19}F chemical shifts (less than 3 ppm) is too small to make any reliable conclusions.

The assignment of the lower-field signals in the ^{19}F and ^{29}Si NMR spectra of compound **5** at 253 K to the predominant isomer **A** with the axial fluorine atom is consistent with the X-ray structure of compound **3** also having an electronegative substituent in the aryl group (Fig. 1). For compound **5**, with respect to compound **3**, the equilibrium **A** ⇆ **E** is shifted to the isomer with the axial aryl group **5-E** so that its content reaches 35% due to a stronger acceptor character of the *m*-NO_2 relative to *p*-Cl substituent.

Heating of the $CDCl_3$ solution of **5** up to 318 K causes changes typical of dynamic exchange processes, *viz.* broadening and coalescence of the signals. From the coalescence temperature of the ^{19}F signals and using the Eyring equation the activation barrier $\Delta G_C^{\neq}$ for the ligand exchange of 13.1 kcal mol^{-1} was calculated. This value is by ~3 kcal mol^{-1} lower than that found for the related pentacoordinate complexes $Ph(R)Si(OCH_2CH_2)_2NMe$ (R = Me, Ph) [5c].

The room temperature ^1H NMR spectra also provide indications for the presence of comparable amounts of the **A** and **E** isomers of **5**. Two very broad signals of the MeN protons appear at 2.58 and 1.90 ppm. While the former value is typical for MeN groups in similar compounds [5c,10], the latter one is much lower, as are chemical shifts for the MeN protons for all other compounds **1**–**4**, **6** (Table 3), which are shielded by the equatorial aryl group [5c,10].

Thus, the position of the equilibrium depends on the substituent in the aryl group. As follows from Table 3, compounds **1** and **5** show two signals in the room-temperature ^{19}F NMR spectrum, corresponding to the axial (~−120 ppm) and equatorial (~−130 ppm) fluorine atoms. The ratio F_{ax}/F_{eq} is 5:1 for **1** and 1.8:1 for **5**, in compliance with different electronegativity of the aryl groups.

Conclusion

A series of new pentacoordinate intramolecular organosilicon complexes was prepared from aryltrifluorosilanes and *N*-methyl-*bis*(2-trimethylsiloxyethyl)amine, and their solid (**3**) as well as solution state structures were studied. Single crystal X-ray diffraction study of complex **3** showed a distorted trigonal bipyramidal coordination geometry around the silicon atom. In solution all complexes undergo fast intramolecular ligand site exchange. The exchange equilibrium position is affected by the nature of the aryl ligand, and for the most electronegative substituent (*m*-NO_2) the amount of the isomer with the axial aryl group reaches 35% at 253 K.

Experimental

General comments

All reactions were carried out under argon atmosphere. Standard precautions to avoid moisture were taken. Benzene and hexane were purified by distillation from sodium. DMSO-d_6 was kept over 4 A molecular sieves.

Compounds of $XC_6H_4SiCl_3$ (X = 4-Me, 4-MeO, 4-Cl, 2-Br, 3-NO_2) were prepared following the described procedures [11]. The corresponding trifluorosilanes $XC_6H_4SiF_3$ were prepared by the reaction of $XC_6H_4SiCl_3$ with antimony trifluoride [12].

X-ray diffraction studies

X-ray diffraction intensities were collected with a Bruker AXS Smart APEX II diffractometer with CCD detector using Mo Kα radiation (graphite-monochromated, λ[Mo Kα] = 0.71073 Å) at room temperature. Multi-scan absorption corrections were applied by the SADABS program [13]. Structure was solved by direct methods and refined by the full-matrix least-squares procedure. All non-hydrogen atoms were refined anisotropically. As long as the structure is noncentrosymmetric the absolute structure was defined on the base of the Flack parameter [14]. All calculations were performed with the Bruker SHELXL program package [15]. Details of crystallographic data and experimental conditions are presented in Table 1.

Spectroscopic studies

The ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on a Brucker DPX-400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{15}N,

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