Synthesis and NMR study of intramolecular silacyclobutane complexes: 8-aza-5,11-dioxa-4-silaspiro[3,7]undecane and 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane

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Dedicated to Professor E. Ya. Lukevics on the occasion of his 70th birthday

Abstract
The intramolecular silacyclobutane complexes with pentaacoordination at silicon, 8-aza-5,11-dioxa-4-silaspiro[3,7]undecane and 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane, were synthesized by reacting 1,1-dimethoxy- or 1,1-bis(diethylamino)silacyclobutanes with the corresponding diethanolamines. The existence of (Si←N) pentaacoordination at silicon was deduced from the pronounced upfield ^{29}Si and downfield ^{13}C NMR shifts as well as from the low temperature ^{13}C NMR study of their dynamic behavior in solution that proved complexes to appear as two isomers with coalescence barriers of 11.5 kcal/mol and 12.9 kcal/mol for **1** and **2**, respectively.

Keywords: Silacyclobutane, intramolecular complexes, pentacoordination of silicon

Introduction

Known since 1954,[1] silacyclobutanes, the four-membered cycles containing silicon and three carbon atoms, continue to be a subject of great interest due to the peculiar features of their structure and a variety of chemical properties owing to both the dipolar nature of the endocyclic Si-C bond and the four-membered ring strain.[2] Thus, in liquid phase the ring opening

† *Deceased*

polymerization and some other reactions can occur.[3] Silacyclobutanes readily cyclorevert generating transient silenes, the silicon-carbon doubly bonded compounds containing the sp^2-hybridizied silicon.[4] Also, the silicon atom in silacyclobutanes exhibits an increased ability to change its coordination number from four to five and six.[5-8] In particular, the X-ray and NMR data indicate the *peri* interaction between silicon and the dimethylamino group in bis[(8'-(dimethylamino)naphth-1'-yl)-1-silacyclobut-1-yl]ether to be considerably stronger than in bis[(8'-(dimethylamino)naphth-1'-yl)-dimethylsilyl]ether, thus evidencing a greater Lewis acidity of silacyclobutane derivatives.[5] The gas-phase reactions of 1,1-dimethysilacyclobutane with fluorine and allyl anions give rises to 1-silacyclobutane pentacoordinate silicon anions. [6]
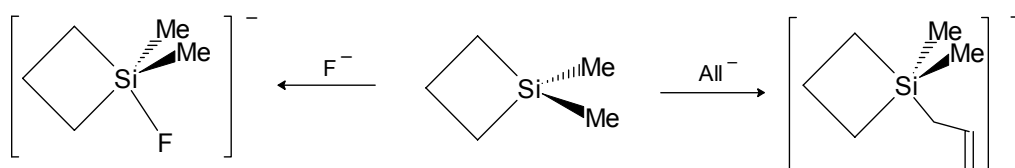
Scheme 1

Treatment of 1,1-dichlorosilacyclobutane with lithium phosphinomethanide leads to a stable intramolecular silacyclobutane complex with hexacoordination at silicon center:[7]
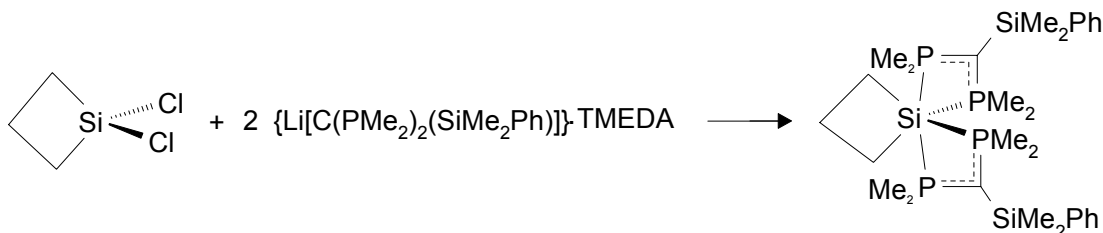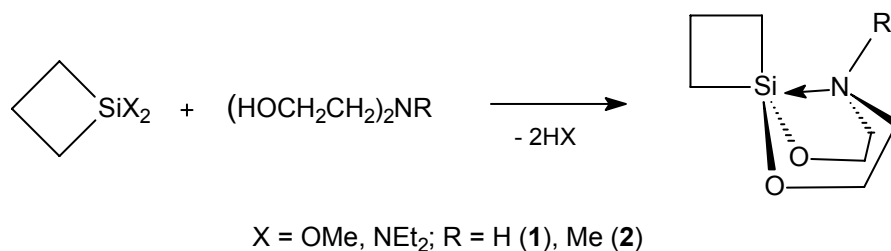

Scheme 2

This is of special interest because hypervalent silacyclobutanes may turn to be precursors for the production of both hypervalent polycarbosilanes and silenes. In fact, a few silenes and silaneimines stabilized with O- and tert-N-donor bases (Si←O and Si←N coordination) are described.[8] Also, the silanediyl, silanethione, and dibenzosilafulvene derivatives of (dimethylaminomethyl)arylsilenes containing intramolecular Si←N coordination bond are known.[9, 10]

Herein, we report the synthesis and NMR study of the effect of intramolecular Si←N bonding on the structure and stereodynamical behavior of the 8-aza-5,11-dioxa-4-silaspiro[3,7]undecane **1** and 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane **2**. These silacyclobutanes contain β,β-aminodiethoxyl ligand that is known to form the transannular Si←N bond in 2,8-dioxa-5-aza-1-silacyclooctanes.[11] Therefore, we expected

silaspiro[3,7]undecanes **1** and **2** to be the hypervalent silacyclobutanes which could, for example, cyclorevert forming hypervalent silenes. Indeed, our recent *ab initio* calculations at the MP2/6-31G(d)//MP2/6-31G(d) level of theory predicted a strong intramolecular Si←N bond (of the length 2.105 Å and energy 19.7 kcal/mol) in 1-methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane, the N-donor stabilization for the Si=C double bond was estimated to be 18.0 kcal/mol.[12]

Results and Discussion

Previously unknown (N-Si)chelate aminodiethoxy derivatives of silacyclobutane, 8-aza-5,11-dioxa-4-silaspiro[3,7]undecane **1** and its homolog 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane **2**, were synthesized by the reactions of 1,1-dimethoxy- or 1,1-bis(diethylamino)silacyclobutanes with diethanolamine and *N*-methyldiethanolamine, respectively:

X = OMe, NEt$_2$; R = H (**1**), Me (**2**)

Scheme 3

The reactions were performed in CHCl$_3$ or CH$_2$Cl$_2$ at very mild conditions (20 ^{o}C, 1 hour) followed by the evaporation of the solvent and a volatile product (ethanol or diethylamine) and drying of a colorless solid residue in vacuum.[‡] The products **1** and **2** melted at 20°C and 45°C, respectively. Notice that the rise of the reaction temperature resulted in the formation of a non-volatile residue. Our attempts to involve 1,1-dichlorosilacyclobutane (X = Cl) and O,O-bis-TMS derivatives of diethanolamines in the above reactions failed. At room temperature reactions would not proceed, whereas at 60° C the cleavage of silacyclobutane Si-C bond in the starting compounds and products suppressed the formation of the target **1** and **2**.

NMR data of **1** and **2** in solution are given in the Table. The upfield ^{29}Si NMR shifts (by 36 and 29 ppm, respectively) relative to that of 1,1-diethoxysilacyclobutane (lit.,[13] δ_{Si} -17.1 ppm), the tetracoordinate organosilicon compound with the same surroundings at silicon atom, was associated to the pentacoordination at silicon. A higher ^{29}Si shielding and smaller temperature coefficient (cf. 0.04 ppm/degree for **1** and 0.06 ppm/degree for **2**) indicate the

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[‡] *However, we failed to obtain a reliable crystal for X-ray study*

Si←N bonding in **1** to be stronger than in **2**. Indeed, the upfield ^{29}Si NMR shifts are common for 2,8-dioxa-6-aza-2-silacyclooctanes $R_2Si(OCH_2CH_2)_2NR'$ in polar solvents[11]. These change similarly on going from R' = H to R' = Me (cf. for R = Ph, R ' = H, $\delta_{si.}$ -44.7 ppm in CDCl$_3$, $\delta_{si.}$ -56.1 ppm in CD$_3$CN and for R = Ph, R ' = Me $\delta_{si.}$ -43.9 ppm in CDCl$_3$, $\delta_{si.}$ - 47.8 ppm in CD$_3$CN) indicating a decrease of coordination interaction Si←N. Presumably, this effect is due to both the steric factors and higher nucleophilicity of nitrogen when the attached hydrogen atom forms intermolecular H-bond with the basic centers of the dissolved substance and solvent.[14]

Table 1. NMR spectroscopic data for **1** and **2** in solution (CDCl$_3$), δ, ppm

Compound	NMR	$(CH_2)_3$	NCH$_2$	OCH$_2$	NR	Si
1	^{1}H	1.31	2.86	3.83	2,40	-
	^{13}C	12.55 (C$_3$); 27.31(C$_2$ and C$_4$)	44.94	58.92	-	-
	^{29}Si	-	-	-	-	-53,4
2	^{1}H	1.44	2.72	3.87	2.35	-
	^{13}C	11.90 (C$_3$) 25.68(C$_2$ and C$_4$)	42.53	58.78	54.56	-
	^{29}Si	-	-	-	-	-45.26

At ambient temperature, a silicon pentacoordination of **1** and **2** manifests itself in greater downfield ^{13}C shift of the carbon atoms attached to silicon (6.5 and 4.9 ppm, respectively) as compared to that of the model tetracoordinate silicon compound, 1,1-diethoxysilacyclobutane (lit.,[13] 20.8 ppm). A single resonance was observed for the Si-CH$_2$ carbons at this temperature. Upon cooling the signals of the Si-CH$_2$ carbons broaden, coalesce (temperature of coalescence at ca -50 ^{o}C for **1** and at ca -20 ^{o}C for **2**) and giving rise to two signals (Figure). The occurrence of C and C* signals most likely indicate the rearrangement resulting in a positional exchange between apical and equatorial carbon atoms (see Scheme 4).
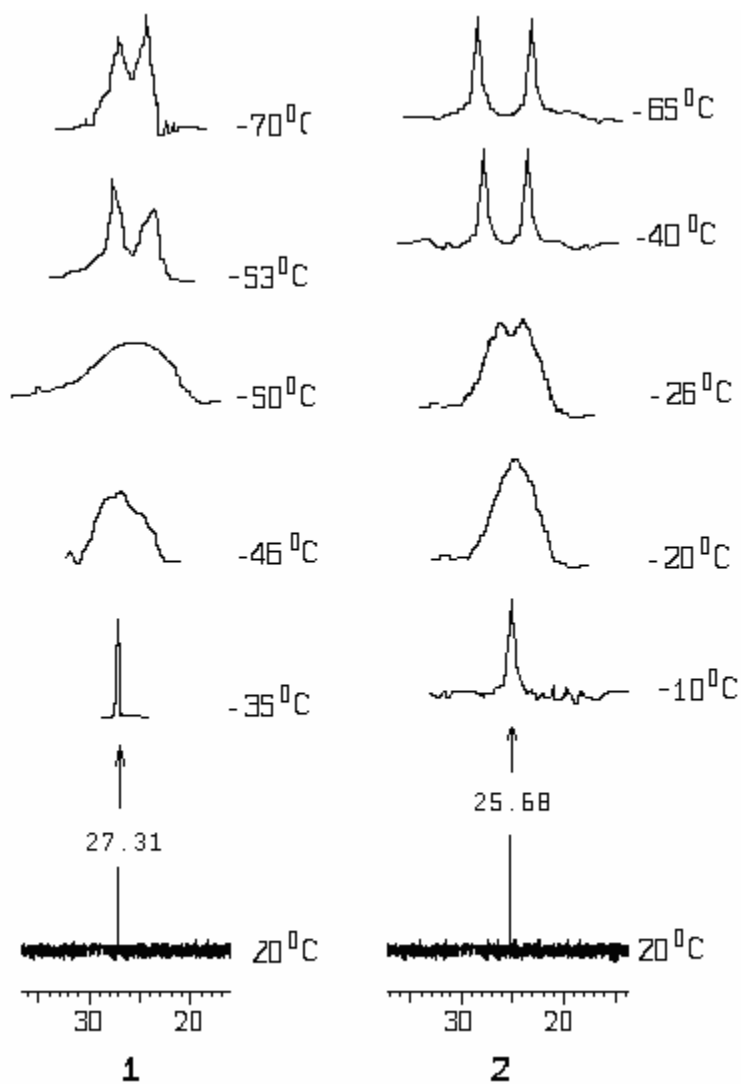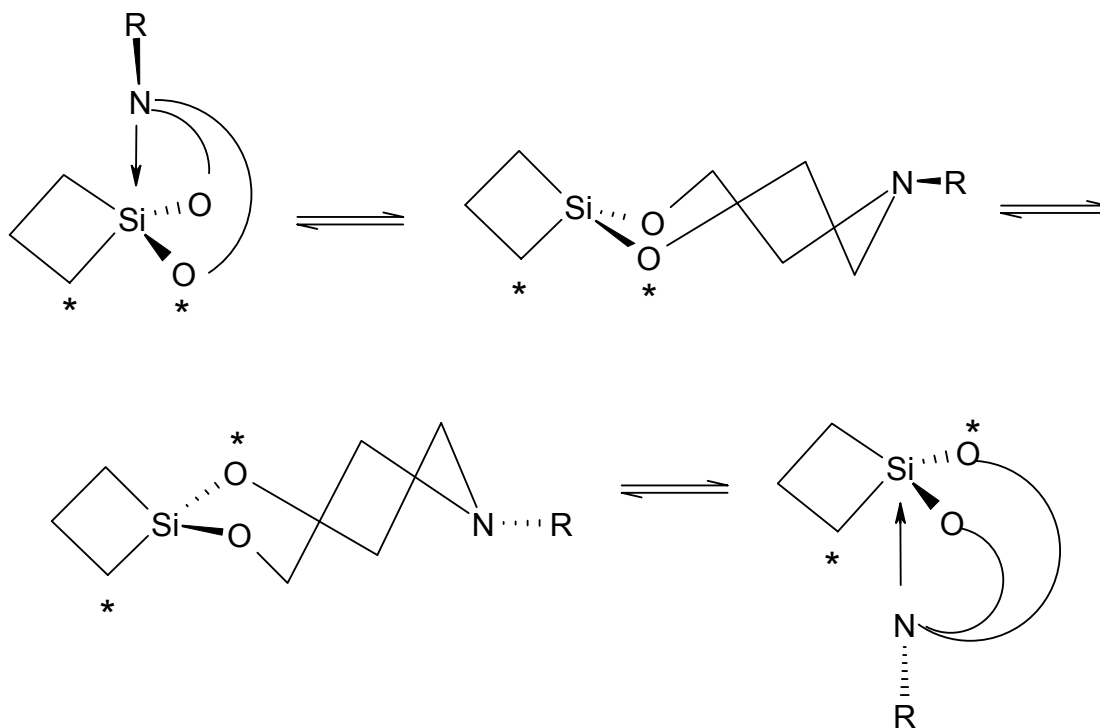
**Figure 1.** Variable-temperature ^{13}C NMR of compounds **1** and **2** (Si-CH$_2$ group)
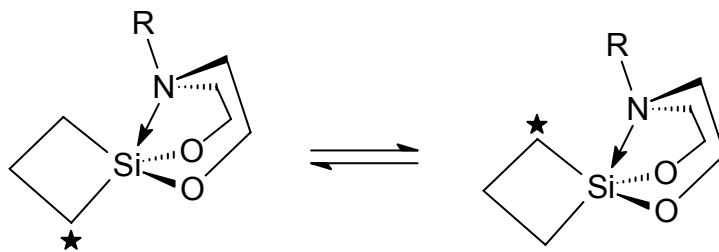
Scheme 4

The rearrangement can be explained in terms of two early suggested mechanisms. The first involves the Si←N bond dissociative-associative process and inversion of the eight-membered heterocycle and the substituent configuration at nitrogen(Scheme 5).

Scheme 5

This mechanism was proposed for an explanation of splitted signals in the NMR spectra of $RR'Si(OCH_2CH_2)_2NR''$.[11] Also, the turnstile mechanism[15] of the ligands exchange at silicon atom may be taken into account (Scheme 6).
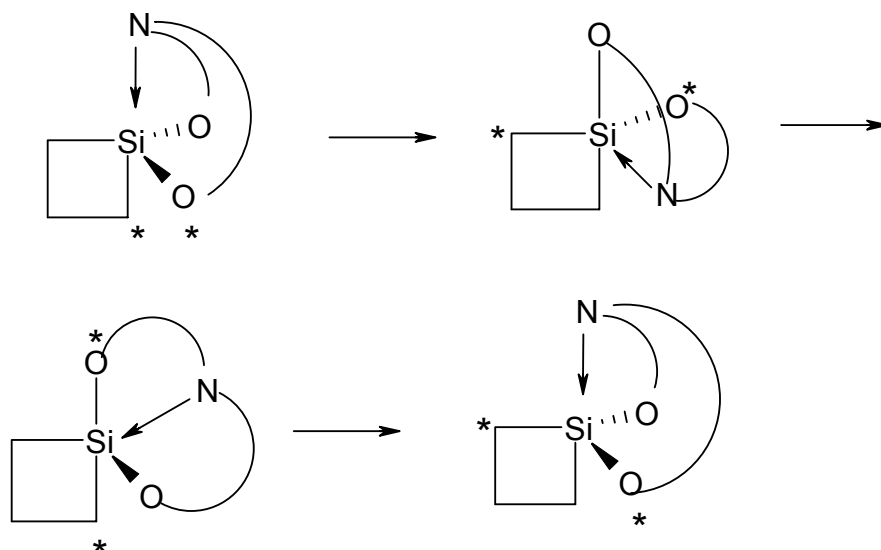
Scheme 6

The rearrangement barrier, ΔG_c^*, of 11.5 kcal/mol was estimated for silacyclobutane **1.**
For silacyclobutane **2** it rised to 12.9 kcal/mol. Taking into consideration that the Si←N bond in
1 is stronger than that in **2**, the opposite ratio between ΔG_c^* values is apparently due to an
essential contribution of the conformational rigidity of the eight-membered ring to the ΔG_c^*
value which increases with N-substitution. The ΔG_c^* value for **2** is higher than those determined
for the related N-methylaminoethoxy derivatives of dimethylsilane (9.3 kcal/mol), 1-
silacyclohexane (10.0 kcal/mol) and 1-silacyclopentane (11.5 kcal/mol) in $(CD_3)_2CO$ solution.[11]
This is in favor of the Si←N coordination bonding in silacyclobutane **2** to be stronger than that
in the related medium-sized silacycles and acyclyc dialkylsilyl analogs. The result is in accord
with the enhanced F⁻ affinity of silacyclobutanes in the gas-phase reactions[6c] and could be
explained by an essential energetic gain upon silicon pentacoordination due to some release of
the four-membered ring strain when carbons adjacent to silicon span one equatorial and one
apical position.

The higher solubility of compound **2** made it possible to measure the values of the one-
bond $^1J(^{29}Si-^{13}C)$ coupling constant for the apical and equatorial carbons. These values were
found to be - 54.2 Hz and - 58.6 Hz, respectively. The coupling constant $(^{29}Si-^{13}C_\alpha)$ in
tetracoordinate 1,1-diethoxysilacyclohexane is the intermediate value (J_{Si-C} = 55 Hz).[13] Such
change of the coupling constant of silicon atom with subsituents well agree with the change of s-
character of the bond with axial and equatorial substituents in TBP.[16]

Experimental Section

^{1}H, ^{13}C, ^{29}Si NMR spectra of 20% solutions (CDCl$_3$) of compounds **1** and **2** were recorded on a JEOL 90Q spectrometer. 1,1-Dimethoxy- and 1,1-bis(diethylamino)silacyclobutanes were synthesized as described in ref. 13. The value of ΔG was calculated using the equation taken from ref. 17.

Preparation of 8-aza-5,11-dioxa-4-silaspiro[3,7]undecane (1)

a. Diethanolamine 0.52 g (5 mmol) in 10 ml of CHCl$_3$ was added dropwise to a solution of 0.66 g (5 mmol) of 1,1-dimethoxysilacyclobutane in 15 ml of dry CHCl$_3$ at 5 ^{0}C. After warming up to room temperature and evaporating the solvent and formed methanol in vacuum, a cream-colored solid residue was filtrated and washed with pentane. After the evaporation of pentane, a colorless solid of **1** (0.45 g; 51%), melting point 45°C (decomp.), remained. Elemental analysis (Found: C, 48.98; H, 9.04; N, 8.35; Si 15.5. Calc. for C$_7$H$_{15}$NO$_2$Si: C, 48.52; H, 8.72; N, 8.08; Si 16.21%).

b. Diethanolamine 0.52 g (5 mmol) in 10 ml of CHCl$_3$ was added dropwise to a solution of 1.07 g (5 mmol) of 1,1-bis(diethylamino)silacyclobutane in 20 ml of dry CHCl$_3$ at 5^{0}C. After slow warming up to room temperature and evaporation of the formed diethylamine and a part (3/4) of the solvent in vacuum, a solid residue was filtrated and washed with pentane. After evaporation of the pentane, a colorless solid of **1** (0.61 g; 71%), melting point 45°C (decomp.), remained. Elemental analysis (Found: C, 48.93; H, 9.01; N, 8.51; Si 15.21. Calc. for C$_7$H$_{15}$NO$_2$Si: C, 48.52; H, 8.72; N, 8.08; Si 16.21%).

Preparation of 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane (2)

a. *N*-Methyldiethanolamine 0.59 g (5 mmol) in 5 ml of CHCl$_3$ was added dropwise to a solution of 0.66 g (5 mmol) of 1,1-dimethoxysilacyclobutane in 5 ml of dry CHCl$_3$ and was stirred for 1 h at room temperature. The solvent and methanol were evaporated and viscous residue was dried in vacuum. The product was purified then by low temperature sublimation in vacuum (20°C, 10^{-3} mm Hg) to yield 0.38 g (40 %) of **2**, melting point 20 ^{o}C. Elemental analysis (Found: C, 49.67; H, 8.75; N, 7.95; Si 15.87. Calc. for C$_8$H$_{17}$NO$_2$Si: C, 51.30; H, 9.15; N, 7.48; Si 14.99%).

b. *N*-Methyldiethanolamine 0.59 g (5 mmol) in 10 ml of CHCl$_3$ was added dropwise to a solution of 1.07 g (5 mmol) of 1,1-bis(diethylamino)silacyclobutane in 20 ml of dry CHCl$_3$ at 5^{0}C. After slow warming up to room temperature and evaporation of diethylamine and a part (4/5) of the solvent in vacuum, an oily product was decanted and washed with pentane. After evaporation of the pentane, a colorless solid of **2** (0.65 g; 68 %), melting point 20°C, remained. Elemental analysis (Found: C, 49.87; H, 8.93; N, 7.37; Si 15.62. Calc. for C$_8$H$_{17}$NO$_2$Si: C, 51.30; H, 9.15; N, 7.48; Si 14.99%).

Acknowledgements

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