

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 pentacoordination 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) pentacoordination at silicon was deduced from the pronounced upfield ²⁹Si and downfield ¹³C NMR shifts as well as from the low temperature ¹³C 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.

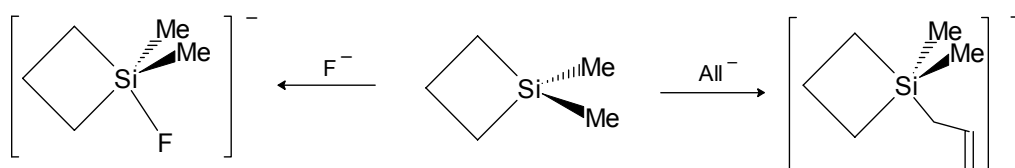
Keywords: Silacyclobutane, intramolecular complexes, pentacoordination of silicon

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

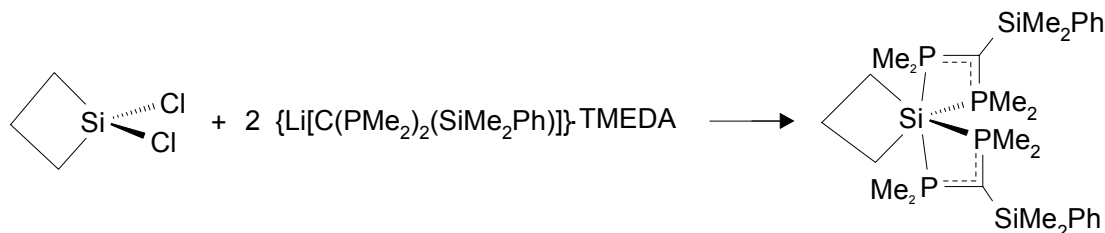
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polymerization and some other reactions can occur.³ Silacyclobutanes readily cyclorevert generating transient silenes, the silicon-carbon doubly bonded compounds containing the sp^2 -hybridized silicon.⁴ Also, the silicon atom in silacyclobutanes exhibits 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-dimethylsilacyclobutane 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

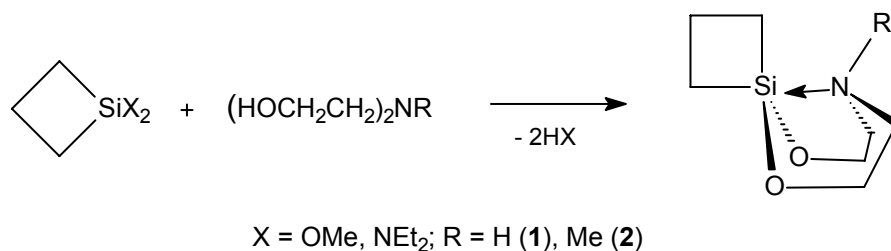
This is of special interest because hypervalent silacyclobutanes may turn to be precursors for the production of both hypervalent polycarbosilanes and silenes. In fact, a few silenes and silaneimines stabilized with O- and tert-N-donor bases ($Si \leftarrow O$ and $Si \leftarrow N$ coordination) are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

Herein, we report the synthesis and NMR study of the effect of intramolecular $Si \leftarrow N$ 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 $Si \leftarrow N$ 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:



Scheme 3

The reactions were performed in CHCl₃ or CH₂Cl₂ at very mild conditions (20 °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 ²⁹Si 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 ²⁹Si shielding and smaller temperature coefficient (cf. 0.04 ppm/degree for **1** and 0.06 ppm/degree for **2**) indicate the

[‡] 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 $\text{R}_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}'$ in polar solvents¹¹. These change similarly on going from $\text{R}' = \text{H}$ to $\text{R}' = \text{Me}$ (cf. for $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$, δ_{Si} -44.7 ppm in CDCl_3 , δ_{Si} -56.1 ppm in CD_3CN and for $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ δ_{Si} -43.9 ppm in CDCl_3 , δ_{Si} - 47.8 ppm in CD_3CN) 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	$(\text{CH}_2)_3$	NCH_2	OCH_2	NR	Si
1	^1H	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	^1H	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 °C for **1** and at ca -20 °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).

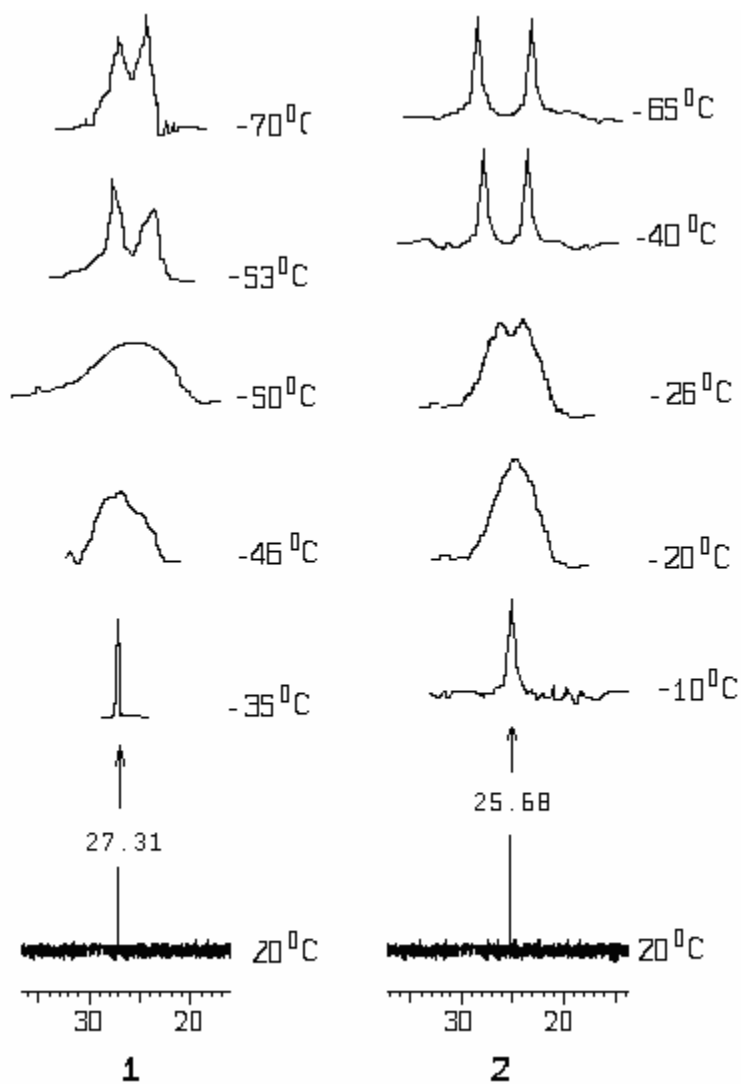
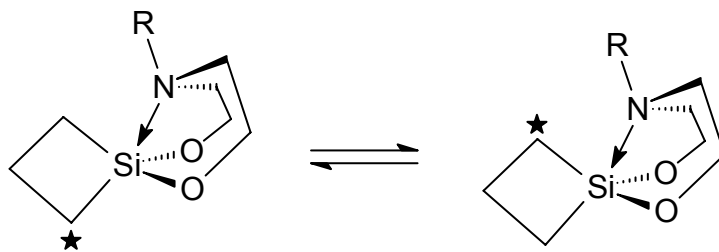
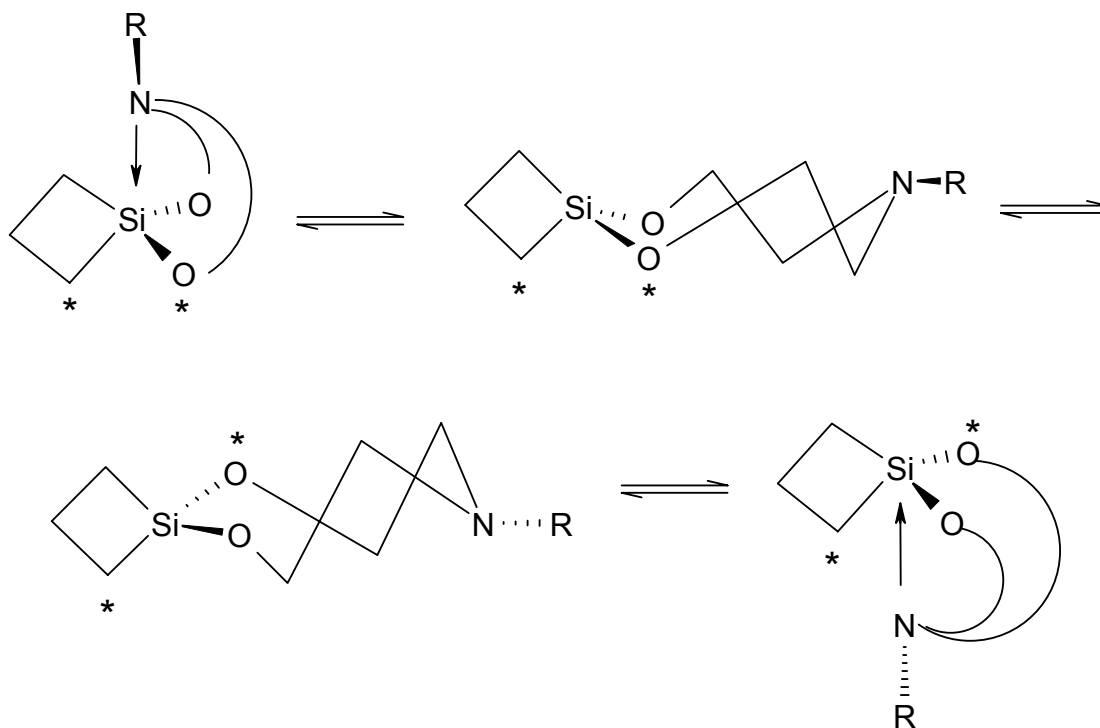


Figure 1. Variable-temperature ^{13}C NMR of compounds **1** and **2** (Si-CH₂ group)



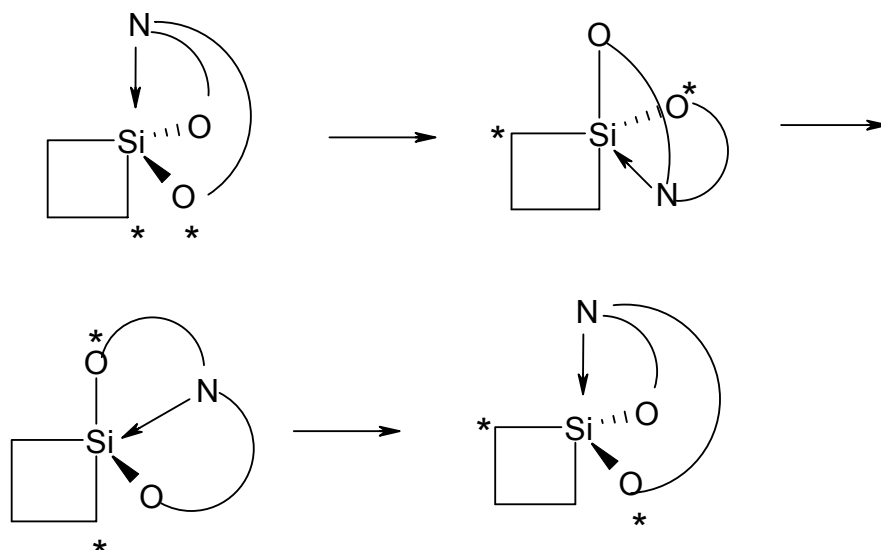
Scheme 4

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 mechanism¹⁵ 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 acyclic 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

^1H , ^{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°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 $\text{C}_7\text{H}_{15}\text{NO}_2\text{Si}$: 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°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 $\text{C}_7\text{H}_{15}\text{NO}_2\text{Si}$: 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°C . Elemental analysis (Found: C, 49.67; H, 8.75; N, 7.95; Si 15.87. Calc. for $\text{C}_8\text{H}_{17}\text{NO}_2\text{Si}$: 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°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 $\text{C}_8\text{H}_{17}\text{NO}_2\text{Si}$: C, 51.30; H, 9.15; N, 7.48; Si 14.99%).

Acknowledgements

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