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Intramolecular rearrangement of organosilyl groups between oxygen and nitrogen in aminosiloxanes – a joint experimental–theoretical study, part II

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Abstract

Lithium amino-di-*tert*-butylsilanolate reacts with halosilanes to give 1-silylamino-1,3-siloxanes (**1**–**7**). The tetrakis(1-silylamino)siloxane thermally condenses yielding a spirocyclic six-membered ring (**8**). One six-membered ring of **8** forms a boat and the other has a twist conformation. Lithium salts of amino-disiloxanes form silylamino-silanolates or amido-disiloxanes. The first includes a 1,3-silyl group migration from the oxygen to the nitrogen atom. The energies of the isomeric lithium salts of model compounds are calculated and show that the lithium-trimethylsilylamino-dimethylsilanolate **III** is 0.7 kcal/mol more stable than the isomeric lithium-1,3-disiloxaneamide **V**. Experiments show that the lithium salts of amino-1,3-disiloxanes, $(Me_3C)_2SiNH_2–O–R$ ($R = SiMe_3$, $SiMe_2Ph$, SiF_2CMe_3) reacts with $ClSiMe_3$, $FSiMe_2Ph$ or F_3SiCMe_3 under a 1,3-O-N-silyl group migration to give the 1-silylamino-1,3-disiloxanes **9**–**11**. If the trimethylsilyl group is substituted by $SiMeF_2$, the difference between the isomers **III**′ and **V**′ is even smaller, 0.12 kcal/mol, and the barrier to reaction via the dyotropic transition state is calculated to be 10.1 kcal/mol. Interestingly, the fluorine atoms allow for two other isomers **VI** and **VIII** which are even lower in energy. The low difference in the energies of **III** and **V** respectively **VI** and **VIII** explains that in absence of steric and/or electronic restraints the lithium salts of amino-1,3-disiloxanes react halosilanes to give both isomeric silylamino-1,3-disiloxanes, e. g. the lithiated $(Me_3C)_2SiNH_2–O–SiF_2CMe_3$ reacts with F_2SiMe_2 or F_3SiPh to give the structural isomers **12**, **13**, and **14**, **15**.

The silyl group migration can be prevented kinetically, e. g. the lithium salts of $(Me_3C)_2SiNH_2–O–R$ ($R = SiF(N(CHMe_2)_2)_2$, $SiH(CMe_3)_2$) react with F_2SiMe_2 or $F_2Si(CMe_3)_2$ to **16** and **17**. A thermodynamically prevented rearrangement is observed in the reaction of lithiated $(Me_3C)_2SiNH_2–O–SiMe_3$ with F_3SiR ($R = CMe_3$ (**18**), Ph (**19**), $N(SiMe_3)_2$ (**20**), C_6H_2 $(CMe_3)_3$ (**21**). **18**–**21** ($(Me_3C)_2SiNHSiF_2R)–O–SiMe_3$) are formed.

LiF-elimination from $(Me_3C)_2SiNHLiO-SiF_2Me$ leads to the formation of the eight-membered (SiOSiN)-ring **22**. The most stable lithium salts of 1-silylamino-1,3-disiloxanes form amides. This explains that in further reactions with halosilanes, the new ligand is bonded with the nitrogen atom (**28**–**30**). In results of crystal structure determinations new lithium-1-fluorosilylamino-1,3-disiloxanes of **20**, (**21**, **23**–**25**) are presented. **23** crystallizes as tricyclic, **24** as an unknown pentacyclic, and **25**, as monomeric compound. In **25** the shortest Si-N bond length (157.9 pm) with four coordinate silicon is found. Lithium salts of 1-fluorosilylamido-1,3-disiloxanes lose thermally LiF with formation of siloxane substituted cyclodisilazanes, **26** and **27**. Crystal structures of **4**, **8**, **17**, **20**, **21**, **22**, **23**, **24**, **25**, **26**, **28** are presented.

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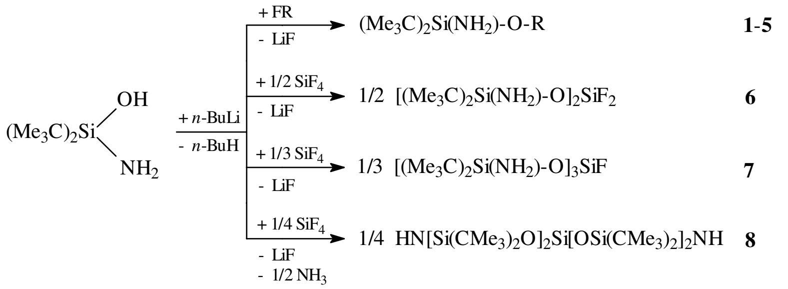
1. Introduction

Aminosilanes, silanols and aminosilanols can be stabilized kinetically by bulky groups, e.g. $(Me_3C)_2Si(OH)NH_2$ [1–12]. The lithium salt of this species was characterized as a tetramer, forming a Li–O cubane [1], while the sodium and potassium salts crystallize as hexagonal prisms [4]. The aminosilanolate reacts with halosilanes to give amino-1,3-siloxanes. In reactions of lithiated aminosiloxanes with halosilanes often a 1,3-silyl group migration from oxygen to the nitrogen is observed. 1-Silyl-amino-1,3-disiloxanes are formed. However, 1,3-silyl group migration does not occur in reactions of lithiated 1-silylamino-1,3-disiloxanes [1].

In this work, we present our experimental results – especially X-ray crystal structure determinations of unusual lithium salts of 1-fluorosilyl-1,3-disiloxanes – and rationalize them by means of quantum-chemical calculations. All theoretical results given in this work are obtained from density functional calculations employing the variant B3LYP and the large 6-311+G(2d,p) basis set (see Section 3.9 for further details).



(1)

	1	2	3	4	5
R	$SiH(CMe_3)_2$	SiFMePh	SiF_2Ph	$SiF_2C(SiMe_3)_3$	2,2,6,6-Tetramethyl-piperidine

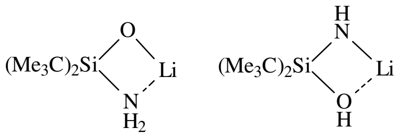
The unstable tetrakis-(1-amino-siloxane) condenses thermally yielding a spirocyclic six-membered ring (**8**) and NH_3.

2. Results and discussion

2.1. 1-Aminosiloxanes

The aminosilanolate anion **I** is 15.9 kcal/mol more stable than the isoelectronic amidosilanol anion **II** (see Fig. 1).

Both isomers form four-membered ring systems where the lithium is bonded both to the nitrogen and oxygen atoms. In the $Me_2Si(NH_2)OLi$ species **I**, the lithium is closely bound to the oxygen atom (r(O–Li) = 173.8 pm), while the contact to the nitrogen is as large as 206.0 pm. The Si–O bond is relatively short (159.5 pm), whereas the Si–N bond distance amounts to 184.1 pm. The Si–O–Li angle is obtained to be 94.1° and the Si–N–Li angle measures 77.3°.



I (0 kcal/mol) **II** (15.9 kcal/mol)

Fig. 1. Relative energies of isomeric lithium salts **I** and **II**.

The less stable isomer $Me_2Si(OH)NHLi$ (**II**) has two almost similar O–Li (189.5 pm) and N–Li (181.3 pm) distances. As expected, the Si–N bond (167.2 pm) is shortened and the Si–O distance (175.0 pm) has become longer. The Si–N–Li angle (92.1°) has considerably increased while the Si–O–Li angle (87.0°) is only slightly smaller than in **I**.

The stability of the alkaline amino-silanolate explains the position of substituents. E.g. in reactions with halosilanes, numerous mono-, bis-, tris- and tetrakis-1-amino-siloxanes are formed [1–4].

The unstable tetrakis-(1-amino-siloxane) condenses thermally yielding a spirocyclic six-membered ring (**8**) and NH_3.

Crystal structure of $(Me_3C)_2Si(NH_2)$*–O–*$SiF_2C(SiMe_3)_3$*(4)*. Compound **4** (Fig. 2, Table 1) crystallizes from n-hexane in the space group $P(2)1/n$. Due to the electron withdrawing effect of the fluorine atoms, the Si(1)–O(1) bond length is 7.2 pm shorter than the Si(2)–O(1) bond.

Crystal structure of $HN[Si(CMe_3)_2O]_2Si[OSi(CMe_3)_2]_2NH$*(8)*. Crystals of **8** were obtained from n-hexane, space group $P(2)1/c$. This spirocyclic compound has some interesting structural features. One six-membered

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