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Molecular Scissors for Tailor-Made Modification of Siloxane Scaffolds

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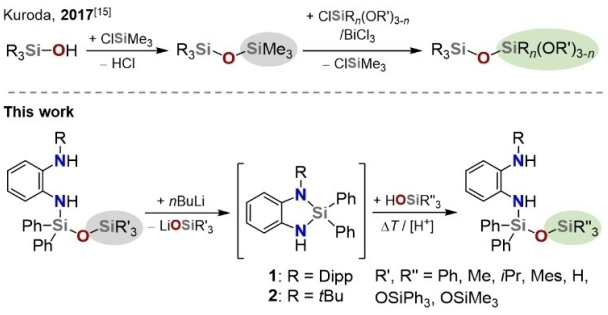
Abstract: The controlled design of functional oligosiloxanes is an important topic in current research. A consecutive Si–O–Si bond cleavage/formation using siloxanes that are substituted with 1,2-diaminobenzene derivatives acting as molecular scissors is presented. The method allows to cut at certain positions of a siloxane scaffold forming a cyclic diaminosilane or -siloxane intermediate and then to introduce new functional siloxy units. The procedure could be extended to a direct one-step cleavage of chlorooligosiloxanes. Both siloxane formation and cleavage proceed with good to excellent yields, high regioselectivity, and great variability of the siloxy units. Control of the selectivity is achieved by the choice of the amino substituent. Insight into the mechanism was provided by low temperature NMR studies and the isolation of a lithiated intermediate.

The Si–O–Si bond is omnipresent in our nature[1] and forms an integral part in many technical products that are used in our everyday life.[2] In the past few years, there have been impressive developments in the stepwise and tailor-made construction of functional oligo- and polysiloxanes.[3,4] New methodologies for the formation of silicon–oxygen bonds are constantly stimulating progress in this research area.[5] Bulky, well-defined oligosiloxanols are important precursors for building molecular siloxide models to study structure and reactivity in aluminosilicates.[6] The extraordinary properties of the Si–O–Si bond[7] (high thermodynamic stability, low basicity, resistance towards heat, radiation, and chemicals) renders the targeted cleavage of the siloxane bond a particularly demanding undertaking.[8] The selective cleavage of an Si–O–Si linkage must therefore meet special requirements, such as the presence of amino side arms within the siloxane framework.[9] Acid-catalyzed[10] and alkyllithium-mediated[11] cleavage of siloxanes have been known for a long time. Examples of siloxane cleavage with lithium amides are limited to reactions with cyclic dimethylsilicones.[12] The search for sustainable and environmentally friendly processes for recycling end-of-life silicone materials has become a major concern in modern times.[13] Si–O–Si cleavage reactions have therefore mainly been investigated in the context of the depolymerization of polysiloxanes into valuable low-molecular-weight compounds as feedstocks for new polymers.[13,14] However, all these cleavage reactions on siloxane oligo- and polymers are rather unselective and often lead to a large number of different cleavage products, thus being unsuitable for targeted and regioselective bond breaking for the precise equipment of siloxane frameworks with special functions.

Kuroda et al. described the use of trimethylsilyl (TMS) units as protecting and leaving groups for the construction of alkoxysiloxane oligomers (Scheme 1).[15] This is, to the best of our knowledge, so far the only example of an utilization of a controlled siloxane bond formation/cleavage for the step-by-step synthesis of functional siloxanes. However, a method in which Si–O–Si linkages can be selectively cleaved at certain positions and individual siloxy groups replaced by other units appears to be a novelty in the field of preparative siloxane chemistry.

Herein, a convenient method that allows for a tailor-made modification of siloxane scaffolds is reported (Scheme 1). Unsymmetrically substituted 1,2-diaminobenzene derivatives act as molecular scissors, which can be installed at specific positions and split off again at the end. The cyclic diaminosilane intermediates readily react with functionalized silanols and siloxanols under ring opening. By incorporating molecular



Scheme 1. Consecutive Si–O–Si bond cleavage/formation to easily exchange individual siloxy groups in oligosiloxanes (Dipp = 2,6-di-*iso*-propylphenyl).

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scissors into the siloxane backbone, followed by controlled cutting at a certain position by cleaving the Si–O–Si bond and replacing siloxy units through the formation of a new siloxane bond, new perspectives open up for the design of functional polymers and molecular siloxide models.

The premise of the work was the development of a flexible molecular system that would easily allow the cleavage and introduction of a variety of siloxy groups for tailoring and equipping oligosiloxanes with functional units. In order to provide a compound library that adequately reflects the diversity of the siloxane units, the diaminocyclosilanes **1** (R = Dipp) and **2** (R = *t*Bu) as suitable model systems were first prepared and reacted with a number of silanols (Table 1). Sterically demanding NH(R) units were chosen in order to achieve high selectivity for the ring-opening attack of the silanols at the heterocyclic silicon atom. The reactions with the silanols resulted in a regioselective opening of the Si–N(R) bond. Di- and trisiloxanes **3**–**11** were synthesized in excellent to moderate yields. In general, the reaction shows a high tolerance towards the steric hindrance of the silanol used. The best results were obtained when the more electrophilic compound **1** was reacted with Me_3SiOH (reaction at RT, entry 4) and iPr_3SiOH (entry 6), with both disiloxanes **5** and **7** being isolated in 98% yield.

Some reactions with less nucleophilic arylsilanols[16] (entries 3 and 9–11) required catalytic amounts of *p*TsOH, which facilitated ring opening by protonation of the amine function. The described method even enables the introduction of synthetically highly valuable hydrosiloxy units[17] (entries 8–10), which are of particular interest for the cross-linking of oligosiloxanes[18] and the construction of complex siloxane architectures[19] by Piers-Rubinsztajn coupling of hydrosilanes with alkoxysilanes.[20] Entry 11 shows that also longer and sterically demanding siloxanols can easily be introduced with good isolated yields of 75%.

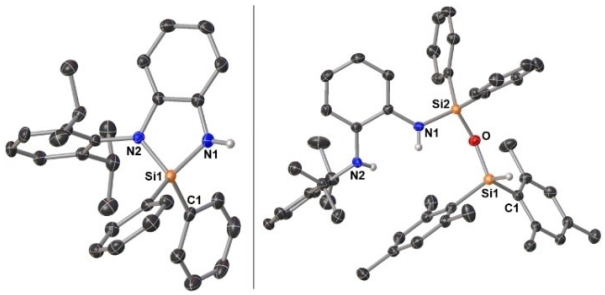
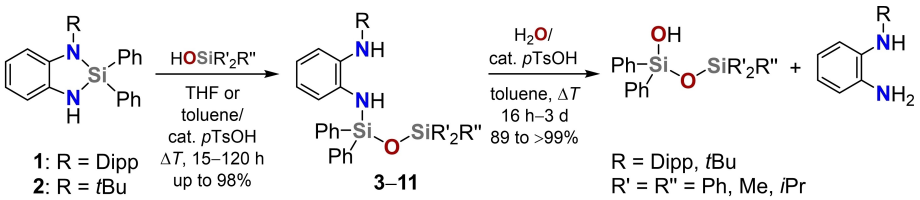


Figure 1. Molecular structures of **1** (left) and **9** (right) in the crystal (displacement ellipsoids are set at the 50% probability level). Hydrogen atoms, except for the N–H and Si–H groups, are omitted for clarity. Only one molecule of the asymmetric unit of **1** is shown. Selected bond lengths [Å] and angles [°]: Compound **1**: Si1–N1 1.7257(11), Si1–N2 1.7460(10), N1–Si1–N2 91.50(5). Compound **9**: Si1–O 1.6406(10), Si2–O 1.6302(10), Si2–N1 1.7215(13), Si1–O–Si2 137.31(7).

Diaminocyclosilanes **1** and **2** as well as aminodisiloxanes **3**, **4**, and **9** were characterized by single-crystal X-ray diffraction analysis (for details, see the Supporting Information). The molecular structures of cyclosilane **1** and hydrodisiloxane **9** are shown in Figure 1. The two Si–N bond lengths in **1** differ significantly with 1.7257(11) Å for Si–N(H) and 1.7460(10) Å for Si–N(Dipp), indicating the latter bond to be the weaker of the two. This structural finding nicely explains the regioselective ring opening in the reactions with silanols, which is also confirmed through X-ray crystallography of in total three ring-opened amino-substituted disiloxanes (see Figure 1, right, and the Supporting Information).

Table 1. Introduction of different siloxy groups starting from diaminosilanes **1** and **2**,[a] and removal of the 1,2-diaminobenzene derivative with formation of a siloxanol.



Entry	R	R′	R″	Product	Solvent	Additive	Reaction time [h]	Yield [%][b]
1	Dipp	Ph	Ph	**3**	THF	–	120	42 (68)
2	*t*Bu	Ph	Ph	**4**	THF	–	15	n.r.
3	*t*Bu	Ph	Ph	**4**	toluene	*p*TsOH	15	76
4[c]	Dipp	Me	Me	**5**	THF	–	15	98
5	*t*Bu	Me	Me	**6**	THF	–	120	27[d] (70)
6	Dipp	*i*Pr	*i*Pr	**7**	THF	–	15	98
7	*t*Bu	*i*Pr	*i*Pr	**8**	THF	–	120	30
8	Dipp	Mes	H	**9**	THF	–	120	(18)
9	Dipp	Mes	H	**9**	toluene	*p*TsOH	120	36[e] (78)
10	*t*Bu	Mes	H	**10**	toluene	*p*TsOH	15	70
11	*t*Bu	Ph	$OSiPh_3$	**11**	toluene	*p*TsOH	100	75

[a] Reaction conditions: Silane **1** or **2** (1.0 equiv.) and the respective silanol (1.0 equiv.) were dissolved in THF or toluene and, if indicated, catalytic amounts of *p*TsOH (1 mol%) were added. Unless otherwise stated, the solution was heated at reflux for the indicated time. [b] Yields of isolated products. Yields of products determined by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard are given in parentheses. [c] The reaction was carried out at room temperature. [d] The product was isolated by distillation. [e] Isolated single-crystalline product after recrystallization from pentane.

Although 1,2-diaminobenzene derivatives have been used in the stabilization of silylenes,[21] their synthetic potential to serve as molecular scissors is yet completely undiscovered. In the further course of the work, it was found that the open form of the diamino fragment in siloxanes **3**–**11** act as precise molecular scissors when adding *n*-butyllithium (Table 2). This leads to cleavage of the Si–O–Si bond with ring closure and formation of a lithium siloxide. Surprisingly, the Si–O–Si cleavage occurs intramolecularly by an in situ-formed lithium amide function and not by the alkyllithium reagent, which enables a high degree of control over the specific position of the cleavage in the siloxane structure. The NH(R) function rather than the Si–N(H) moiety is deprotonated, although the latter was actually expected to be more acidic. Probably the main factor behind the high thermodynamic driving force of these unusual reactions is the formation of stable aggregates of the cut-off lithium siloxide.[22]

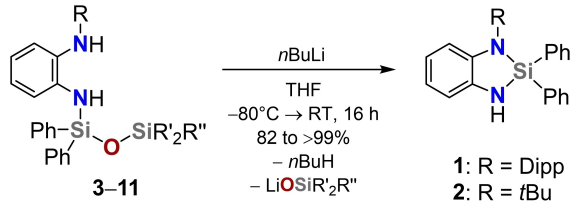
The incorporated diamine scissors show excellent reactivity and selectivity towards cleavage of a wide range of siloxy units leading to yields from 82% (entry 6) up to >99% (entries 1, 2, and 8 in Table 2).[23] Due to the presence of two different silicon–nitrogen bonds in the heterocyclic intermediates **1** and **2**, new siloxy groups can now successively be inserted or the 1,2-diaminobenzene scissors completely split off through simple hydrolysis (see Table 1; for details, see the Supporting Information). The formed siloxanols are precious building blocks not only for further Si–O–Si couplings[24] but also for the design of molecular models to mimic complex siloxide frameworks.[6]

The next step was to find out whether the method can be extended to a one-step cleavage of chlorooligosiloxanes (Schemes 2, 3 and 4). For this purpose, it was first investigated whether the diaminobenzenes **12** and **13** can be introduced selectively into the siloxane framework, with the location of the chlorine substituent determining the location of the cleavage. In line with previous studies by the authors,[25] the presence of a siloxy group required the use of the more nucleophilic lithium amides to substitute a Si–Cl bond. Therefore, chloropentaphenyldisiloxane (**14**)[26] was chosen as a simplified model compound and treated with both deprotonated **12** (Path A) and **13** (Path B), which were each obtained from the reaction of the respective diamine with one equivalent of *n*BuLi (Scheme 2).

Interestingly, only in the case of diamine **13** (R = *t*Bu) was the monosubstituted disiloxane **4** the major product, which was formed in 63% yield together with 29% of the cyclic silane **2** (Scheme 2, Path B). When carrying out the reaction with the Dipp-substituted diamine **12**, the open form (compound **3**) was not obtained. Instead, cyclosilane **1** was formed as the only product in 50% yield (Path A). Apparently, there are fundamental differences in the stability of the lithiated intermediates depending on whether the amino function is equipped with an electron-withdrawing (Dipp) or an electron-donating group (*t*Bu). It appears that diamine **12** preferably forms a dilithiated rather than a monolithiated species. In the case of diamine **13**, the situation seems to be the opposite when one equivalent of *n*BuLi is used, with the monolithiated diamine being the predominant species (Scheme 2, bottom). The highly selective formation of compound **1** (with the maximum possible amount of 50%) can now be explained by the attack of the dilithium diamide **12-Li$_2$** at chlorodisiloxane **14** via the short-living intermediate **3-Li** (Scheme 2).

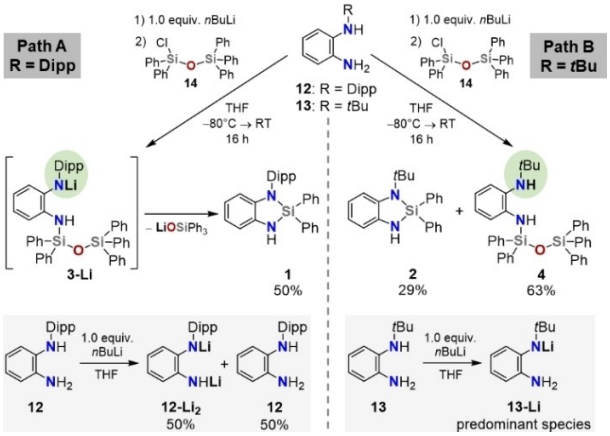
Remarkably, a mixture of diamine **12** and one equivalent of *n*BuLi in THF gave only single-crystals of the double lithiated diamine, which were suitable for X-ray diffraction analysis. This substantiated the assumption that the dilithiated rather than the monolithiated structure was preferentially formed (Figure 2). **12-Li$_2$** crystallized in a previously unknown structure type for dilithiated 1,2-diaminobenzenes.[27] It forms the dimer **[12-Li$_2$·(THF)$_2$]$_2$**, which exhibits two sets of lithium atoms with different coordination spheres. Low temperature NMR spectroscopy of single-crystals of **[12-Li$_2$·(THF)$_2$]$_2$** in THF at –80 °C

Table 2. Si–O–Si bond cleavage in 1,2-diaminobenzyl-functionalized siloxanes **3**–**11**, initiated by treatment with *n*BuLi.[a]



Entry	Substrate	R	R′	R″	Product	Yield [%][b]
1	**3**	Dipp	Ph	Ph	**1**	>99
2	**4**	*t*Bu	Ph	Ph	**2**	>99
3	**5**	Dipp	Me	Me	**1**	83
4	**6**	*t*Bu	Me	Me	**2**	83
5	**7**	Dipp	*i*Pr	*i*Pr	**1**	87
6	**8**	*t*Bu	*i*Pr	*i*Pr	**2**	82
7	**9**	Dipp	Mes	H	**1**	90
8	**10**	*t*Bu	Mes	H	**2**	>99
9	**11**	*t*Bu	Ph	$OSiPh_3$	**2**	90

[a] Reaction conditions: Siloxanes **3**–**11** (1.0 mmol) were each dissolved in 10 mL of THF and cooled to –80 °C. *n*BuLi (1.1 equiv.) was added dropwise, the solution slowly warmed to room temperature, and stirred for 16 h. [b] Yields of products were determined by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard.



Scheme 2. Proposed mechanism for the direct Si–O–Si cleavage of chlorodisiloxanes using lithiated 1,2-diaminobenzene derivatives. Yields determined by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard.

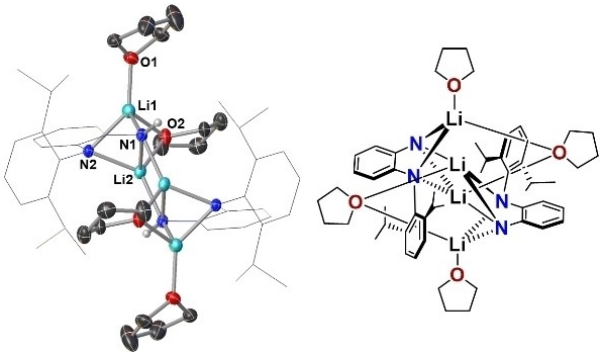
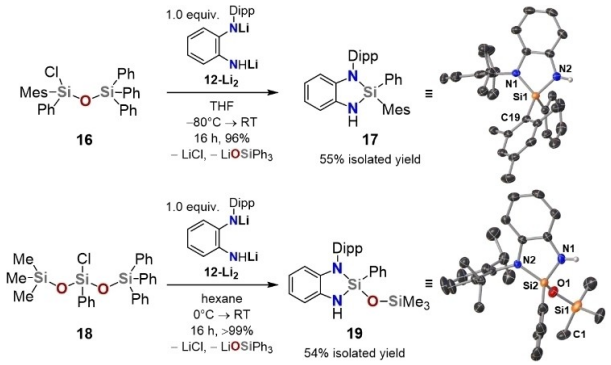


Figure 2. Molecular structure of double lithiated Dipp-substituted 1,2-diaminobenzene [**12-Li$_2$**·**(THF)$_2$**]$_2$ in the crystal (displacement ellipsoids are set at the 50% probability level). Hydrogen atoms, except for the N–H groups, are omitted for clarity.



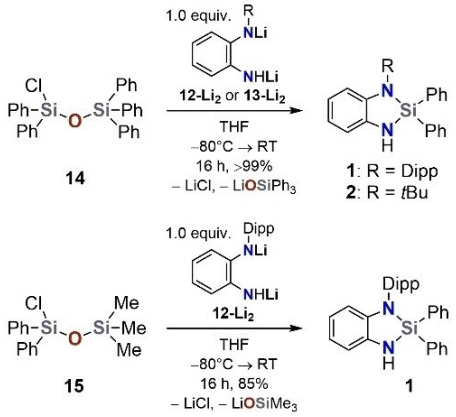
Scheme 4. Variation of the substituents on the attacked silicon atom (top). Regioselectivity of the Si–O–Si cleavage in an unsymmetrically substituted chlorotrisiloxane (bottom). Molecular structures of compounds **17** and **19** in the crystal (Mes = mesityl).

showed only one set of signals in the ^{1}H NMR spectrum, but two signals in the ^{7}Li NMR spectrum at $\delta = 1.55$ and 1.47 ppm, which corresponds to two inequivalent lithium centers. This indicates that the structure of **12-Li$_2$** in solution correlates well with the molecular structure in the solid-state.[28]

When one equivalent of *n*BuLi is added to diamine **12** in THF at –80 °C, two sets of signals now appear in the ^{1}H NMR spectrum and only one signal in the ^{7}Li NMR spectrum ($\delta =$ 1.56 ppm). This suggests a simultaneous presence of the dilithiated species **12-Li$_2$** and diamine **12** in solution, presumably in the form of a coordination compound with equivalent coordination spheres around the lithium centers. The structural and spectroscopic findings explain the outcome of the reactions in Scheme 2 very well.

A quantitative, direct one-step cleavage of the Si–O–Si linkage of disiloxane **14** took place in all cases when using two equivalents of *n*BuLi, with compounds **1** and **2** being obtained in NMR yields of >99%. Not only Ph_3SiO but also Me_3SiO groups in chlorodisiloxanes can be cut off by the dilithiated diamines, as exemplified for disiloxane **15** (Scheme 3).

The method could easily be extended to other substitution patterns on the attacked silicon atom, as shown for the mesitylphenyl-substituted compound **16**[25a] (Scheme 4, top). Excellent regioselectivity of the Si–O–Si cleavage was observed when using an unsymmetric trisiloxane (**18**) (Scheme 4, bottom). Exclusively the bond to the triphenylsiloxy group is split off, most likely because of the better charge stabilization in the Ph_3SiOLi leaving group. It therefore appears that the steric hindrance of the NH(R) function has no discriminatory influence on the cleavage of the siloxy unit, but rather that the stability of the split-off lithium siloxide controls the regioselectivity.



Scheme 3. Direct Si–O–Si cleavage of chlorodisiloxanes.

In conclusion, a powerful concept for the application-oriented design of siloxanes was provided. The method can have a direct impact on the development of new functional oligosiloxane scaffolds and the targeted construction of molecular siloxide models. The authors are currently working on testing this concept on silsequioxanes as the next step on the way to more complex Si–O–Si-based materials and elaborating an asymmetric version of this method for the desymmetrization of silanols.

Experimental Section

Experimental procedures for the synthesis of all compounds, characterization data, and X-ray crystallographic details are provided in the Supporting Information.

Deposition Numbers 2110741 (for **1**), 2110739 (for **2**), 2110743 (for **3**), 2110742 (for **4**), 2110745 (for **9**), 2116391 (for **17**), 2110744 (for **19**), and 2110740 (for [**12-Li$_2$**·**(THF)$_2$**]$_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: molecular scissors · Si–O–Si cleavage · silicon · siloxanes · synthetic methods

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