Silicon/Lithium-Centered Chirality

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From an α-Functionalized Silicon-Stereogenic N,O-Silane to a Monomeric and Tetracoordinate *t*BuLi Adduct with Lithium-Centered Chirality**

*Jonathan O. Bauer and Carsten Strohmann**

Dedicated to Professor Michael Veith on the occasion of his 70th birthday

Abstract: *Donor-functionalized silanes with stereogenic silicon centers are extremely rare. A convenient stereocontrolled route to a nitrogen-oxygen-functionalized silicon-chiral compound with an additional aminomethyl function is presented. This silane was directly achieved in stereochemically pure form by a simple nucleophilic substitution reaction. Owing to the unique asymmetry of this silane and the presence of three donor functions, the first monomeric butyllithium compound with lithium-centered chirality could be isolated; the configuration was assigned by X-ray crystallography. This [silane·tBuLi] complex undergoes an unexpected deprotonation/stereospecific substitution sequence in toluene, leading to the development of a convenient one-pot synthesis of a functionalized silicon-chiral benzylsilane, which proceeds with inversion of configuration and complete preservation of the stereochemical integrity at silicon.*

In recent times, the development of stereoselective methods for providing molecules with asymmetrically substituted silicon atoms has grown to an intensely studied field in silicon chemistry,[1,2] not least because silicon-stereogenic compounds are multifarious reagents with many applications.[1,3,4] They are successfully used as chiral auxiliaries in asymmetric organic synthesis[3] and provide valuable assistance as stereochemical probes for elucidating reaction mechanisms.[4]

Si–C–N subunits provide the basis for an industrially relevant class of reactive silanes, as it is known that donor functions in a geminal position to a silicon atom can strongly influence the reactivity in hydrolysis processes (so-called α-effect).[5] Geminal systems (**A**) with stereogenic silicon atoms and further reactive functionalities are thus very interesting with respect to use as mechanistic probes (Figure 1). However, owing to the lack of asymmetric routes that are compatible with additional functionalities in the substrate backbone, there are only a few examples among the hitherto reported silicon-stereogenic compounds with an ancillary donor functionality within their substitution pattern, and all of these molecules have been prepared by resolution.[6] We recently established a stereoselective method giving rise to a new class of nitrogen-oxygen-functionalized silanes with stereogenicity at silicon, which allow further transformations.[2j] We assume that this synthetic concept can provide a basis for the straightforward design of silicon-stereogenic compounds with novel structural motifs for wide and new applications, which cannot be achieved on the basis of carbon chemistry so easily.[7]

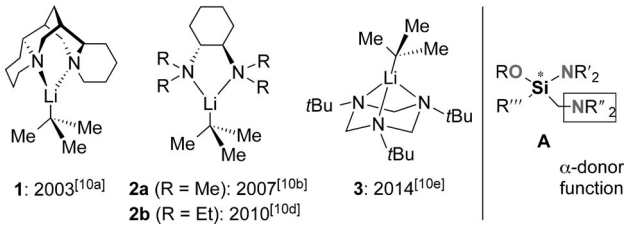

Figure 1. Previously known chiral monomeric *t*BuLi adducts (**1** and **2a**,**b**) and first achiral fourfold coordinate *t*BuLi monomer (**3**). α-Functionalized target structure (**A**) in the present work.

Herein, we begin to combine our achievements in the chemistry of functionalized silicon-chiral silanes with our knowledge on structural elucidation of organolithium compounds. For that purpose, we considered that centering chirality onto silicon would lead to a precise predefinition of the functional groups that are either directly attached to or around the stereogenic third row element. As a result, the design of chelating silicon-based ligands with novel coordination modes should be achievable (Figure 1). These compounds might be of interest for stabilizing reactive intermediates and applied as chiral silanes with docking sites in metal-mediated[1a,3c–e] reactions.

Alkyllithiums are prominent reagents in preparative chemistry, ranging from a use as strong bases to nucleophilic reagents.[8] One of the major challenges in this area of research still remains the development of catalytic and asymmetric methods for the deprotonation of C–H bonds.[9] Among the five hitherto-known monomeric *tert*-butyllithium adducts,[10] only three chiral *t*BuLi monomers have been reported to date, each with a threefold coordinate lithium atom, that is [(−)-sparteine·*t*BuLi] (**1**)[10a] and the (1*R*,2*R*)-

[*] Dipl.-Chem. J. O. Bauer, Prof. Dr. C. Strohmann
Anorganische Chemie, Technische Universität Dortmund
Otto-Hahn-Strasse 6, 44227 Dortmund (Germany)
E-mail: mail@carsten-strohmann.de

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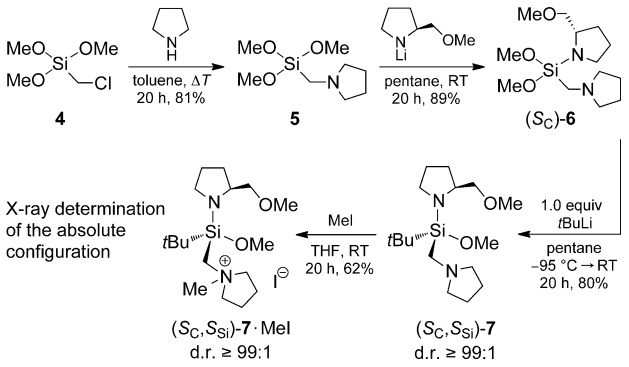
N,*N*,*N*′,*N*′-tetraalkylcyclohexane-1,2-diamine adducts [(*R*,*R*)-TMCDA·*t*BuLi] (**2a**)[10b] and [(*R*,*R*)-TECDA·*t*BuLi] (**2b**)[10d] (Figure 1). Quite recently, Mitzel and co-workers reported a fourfold coordinate achiral *t*BuLi monomer (**3**) with three lithium-nitrogen contacts (Figure 1).[10e] Monomeric complexes comprising an alkyllithium reagent and Lewis bases are often considered as incipient intermediates in deprotonation reactions.[8] Therefore, structural insight into such kinds of species is of utmost importance for a better mechanistic understanding.

Herein, we initially report on the first stereocontrolled synthesis of a silicon-stereogenic silane [(S_C,S_{Si})-**7**] bearing an ancillary aminomethyl function and that was achieved in stereochemically pure form in only three steps by employing our recently established strategy[2j] on the chiral precursor (S_C)-**6** (Scheme 1). As will be then shown, (S_C,S_{Si})-**7** acts as



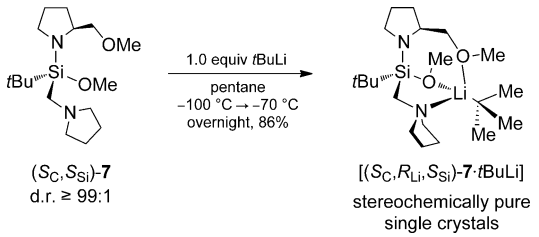
Scheme 1. Three-step synthesis of the stereochemically pure, aminomethyl-functionalized silicon-stereogenic compound (S_C,S_{Si})-**7**.

a donor ligand with a previously unknown binding mode in a monomeric coordination complex with *t*BuLi, which features remarkable reactivity in a toluene solution. The latter finding will guide us to a new kind of stereospecific transformation at silicon and hence to a silicon-stereogenic silane with four substituents of different sterical and functional quality.

Starting with (chloromethyl)trimethoxysilane (**4**), we first introduced an additional donor-functionalized side arm by amination of the chloromethyl unit[11] followed by an exchange of a methoxy group for an amine function (Scheme 1).[12] This Si–N bond formation was easily achieved by conversion of the lithium salt of (2*S*)-2-(methoxymethyl)-pyrrolidine (SMP) with **5**. In the third step, (S_C)-**6** was reacted with *t*BuLi, resulting in a diastereoselective substitution with an exceptionally high stereochemical control of the nucleophilic attack. Thus, we directly obtained the N,O-functionalized silane (S_C,S_{Si})-**7** in high yield (80%) and with excellent stereochemical purity (d.r. ≥ 99:1) without the need for any additional step of optical enrichment (Scheme 1).

The stereochemical integrity of the asymmetrically substituted silicon atom in (S_C,S_{Si})-**7** was verified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (for details, see the Supporting Information). The absolute configuration at the silicon center was determined by single-crystal X-ray diffractional analysis of the ammonium iodide (S_C,S_{Si})-**7**·MeI, which crystallized from tetrahydrofuran/2-propanol in the orthorhombic crystal system in the space group $P2_12_12_1$ (Scheme 1 and Figure 3).

Astonishingly, treatment of (S_C,S_{Si})-**7** with one equivalent of *t*BuLi at −100 °C in pentane and warming the solution to −70 °C resulted in the formation of yellow single crystals of [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] overnight in high yield (86%), which were suitable for X-ray crystallographic analysis (Scheme 2 and Figure 2). The substitution pattern of (S_C,S_{Si})-**7**, consisting



Scheme 2. Deaggregation of *t*BuLi leading to the monomeric and lithium-stereogenic adduct [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi].

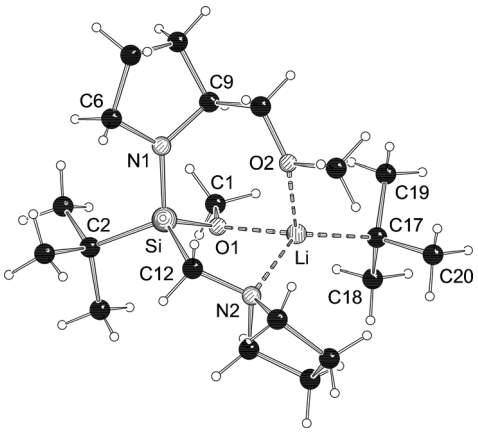


Figure 2. Molecular structure of the monomeric C,Li,Si-chiral adduct [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] in the crystal.[15] Selected bond lengths [Å] and angles [°]: C1–O1 1.428(3), C2–Si 1.886(3), C12–N2 1.474(3), C12–Si 1.888(3), C17–Li 2.090(5), Li–O1 2.026(5), Li–O2 2.021(5), Li–N2 2.158(5), Li–Si 2.978(5), N1–Si 1.7047(19), O1–Si 1.645(2); O2-Li-O1 98.8(2), O2-Li-N2 94.9(2), O1-Li-N2 86.6(2), C6-N1-C9 110.29(19), C6-N1-Si 123.9(2), C9-N1-Si 125.7(2), C1-O1-Si 125.27(17), C1-O1-Li 120.8(2).

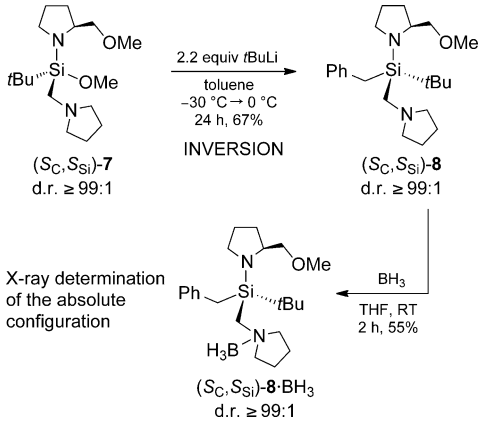
of different nitrogen and oxygen donor functions, is obviously predestined for breaking the tetrameric *tert*-butyllithium aggregate, as it appears in hydrocarbon solvents,[8d,13] into a monomeric species. The *tert*-butyl group plays an important role in sterical shielding and completely prevents the molecule from a second nucleophilic attack of a *t*BuLi molecule.

[(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] crystallized from pentane in the orthorhombic crystal system in the space group $P2_12_12_1$ (Figure 2). As shown at the molecular structure, we succeeded in isolating a chiral monomeric *tert*-butyllithium compound. This is the first example of a tetracoordinate monomeric adduct in which oxygen donor functions are involved.[10e]

Different from all other monomeric alkyllithium species, the lithium atom of *t*BuLi in [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] is bound to two oxygen atoms and one nitrogen atom. But certainly the most striking structural feature of this chiral monomer is its asymmetrically coordinate lithium atom. This originates from the asymmetry of the S_C,S_{Si}-configured tridentate ligand **7**, which is able to force a single and precise configuration at the metal center of the butyllithium reagent for the first time. Owing to the predetermined chirality of (S_C,S_{Si})-**7**, only one defined stereoisomer of the *t*BuLi adduct featuring the R_{Li} configuration at the lithium atom can thus be formed. This explains the homogeneity of the crystalline sample as well. The lithium atom of *t*BuLi in [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] is part of a five- and a seven-membered ring with a distorted tetrahedral coordination sphere around the metal center and shows a short carbon–lithium bond (C17–Li 2.090(5) Å), which is comparable with the C–Li length in **3** (2.083(2) Å)[10e] and between the lengths in the known chiral diamine adducts **1** (C–Li 2.114(4) Å)[10a] and **2a** (C–Li 2.064(15) Å)[10b] (Figure 1). The silicon-bound methoxy group exhibits pronounced donor ability within the lithium complex. The Li–O1 (2.026(5) Å) and Li–O2 contacts (2.021(5) Å) are in the same range, indicating a rather strong interaction even between the metal center and the oxygen atom of the Si–OMe group, which can thus be ascribed to a strong Lewis basic character of the silicon-bound oxygen atom O1 (Figure 2). To the best of our knowledge, with this isolated [silane·*t*BuLi] complex, we could moreover provide first experimental evidence that Si–OR structural motifs can indeed be involved in complex formation of presubstitution intermediates comprising organometallic reagents and alkoxysilanes, which have only been postulated in plausible theoretical mechanistic considerations[2c,14] as yet.

In accordance with the commonly observed low basicity of amine groups that are attached to silicon by an N–Si bond, the nitrogen atom N1 is not involved in coordination to the lithium atom. This is also reflected by the short N1–Si bond (1.7047(19) Å) and the planar geometry (sum of angles: 359.9(6)°) around N1, assuming that electron density at nitrogen is particularly polarized by the adjacent silicon atom (Figure 2).[16] The latter finding might be one reason for the high efficiency of our stereocontrolled substitution method (Scheme 1) arising from a reduced electrophilicity of nitrogen-substituted silicon atoms and from the resultant increase in diastereotopic differentiating selectivity in the course of the nucleophilic attack.

In a further attempt, we explored the reactivity of silane (S_C,S_{Si})-**7** towards *t*BuLi. We mixed (S_C,S_{Si})-**7** and one equivalent of *t*BuLi in toluene at −30 °C. What we found in the GC/EI-MS and NMR analysis of a sample of this reaction mixture after one day stirring at room temperature was that (S_C,S_{Si})-**7** had been transformed into the benzyl-substituted silane (S_C,S_{Si})-**8** with 50 % conversion.[17] However, this turnover could only negligibly be increased by prolonging the reaction time for further three days. Apparently, *t*BuLi deprotonates toluene in the presence of the chiral N,O-silane (S_C,S_{Si})-**7**,[18] which is subsequently attacked by benzyllithium itself, resulting in a substitution of the methoxy group. When we repeated this experiment by using two equivalents of *t*BuLi in toluene, the formation of the silicon-chiral benzyl-*tert*-butylsilane (S_C,S_{Si})-**8** occurred with high conversions up to 95 % and yields of 67 % after a reaction time of 24 h at 0 °C (Scheme 3).[19] A deuterium labeling experiment unambiguously showed that the initially formed benzylsilane (S_C,S_{Si})-**8** is deprotonated at the benzylic position, explaining the need of two equivalents of *t*BuLi for completeness of the reaction (for details, see the Supporting Information). Access to (S_C,S_{Si})-**8** could also easily be provided in a one-pot three-step synthesis starting from **5** with three equivalents of *t*BuLi in an overall yield of 44 %.



Scheme 3. Stereospecific methoxy/benzyl exchange after an in situ generation of benzyllithium from toluene and elucidation of the stereochemical course at the stereogenic silicon center.

The substitution reaction smoothly led to one defined stereoisomer (d.r. ≥ 99:1) in a stereospecific manner. After derivatization of (S_C,S_{Si})-**8** to the borane adduct (S_C,S_{Si})-**8**·BH_3 and crystallization from tetrahydrofuran/diethyl ether, single-crystal X-ray structural analysis showed an S_{Si}-configured stereogenic silicon atom. It follows from this result that the substitution of the methoxy group by benzyllithium proceeds with inversion of configuration at the stereogenic silicon center (Scheme 3 and Figure 3). As far as we know, there exist no prior reports on the stereochemical course of an alkoxy/alkyl exchange reaction mediated by a nucleophilic attack of an organometallic reagent at a stereogenic silicon atom that is integrated in RO–Si–NR_2 structural units.

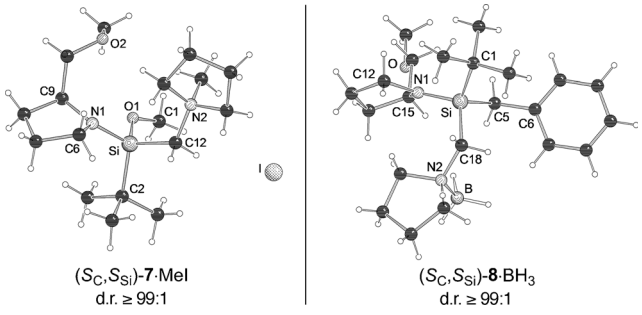


Figure 3. Molecular structures of (S_C,S_{Si})-**7**·MeI and (S_C,S_{Si})-**8**·BH_3 in the crystal for the determination of the absolute configuration at the stereogenic silicon atom.[15]

The high stereocontrol in all herein reported substitution reactions is quite atypical for transformations at stereogenic silicon atoms in general. In the light of stereospecific reactions proceeding with a similar high selectivity that were studied by Oestreich,[1a,3c–e] Tomooka,[2d,g,4g] and also by Shintani and Hayashi[2i] using chiral *tert*-butylsilanes, it seems to be a general observation that the presence of a *tert*-butyl group renders substitutions at silicon exceedingly stereoselective. In consequence of a substantial investigation concerning the stereochemistry of substitution reactions at asymmetrically substituted silicon atoms, Sommer and Korte came to the conclusion that displacement of methoxy leaving groups by benzyltype organolithium and Grignard reagents predominantly proceeds with inversion of configuration.[14a] In their mechanistic picture, two lithium reagents participate in the substitution process in which one of them plays the role of a Lewis acid activating the leaving methoxy group. Against this background, our complex [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] illustrates a plausible presubstitution model, as a backside attack of a second alkyllithium reagent is now strongly preferred owing to the effectively shielded front side (Figure 2). This would result in a substitution with inversion of configuration as actually observed (Scheme 3).

In conclusion, we developed a stereochemically pure functionalized silane, (S_C,S_{Si})-**7**, having an asymmetrically substituted silicon atom with the ability for breaking alkyllithium compounds into lower-molecular species. This was shown for the monomeric *t*BuLi adduct [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi] containing a stereogenic lithium atom in a simple alkyllithium for the first time, which provides a new perspective in the study of substitution processes at silicon. We gained insight into an unexpected sequence involving an in situ formation of benzyllithium and a subsequent stereospecific substitution of a silicon-bound methoxy group with inversion of configuration. This led to a facile one-pot synthesis of the silicon-chiral benzyl-*tert*-butylsilane (S_C,S_{Si})-**8**, a promising functionalized precursor for further synthetic applications and transformations. In view of the recent achievements in using silicon-stereogenic hydrosilanes as effective chiral reagents in hydrosilylation[2g,4f,h,i] and Si–O coupling reactions,[3b–e] we are currently investigating the utilization of our herein described method to first provide silicon-stereogenic hydrosilanes with an additional amine function because it seems to us that this can open up new possibilities in the field of silicon stereochemistry.

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[15] CCDC 995888 [(S_C,R_{Li},S_{Si})-**7**·*t*BuLi], CCDC 995889 [(S_C,S_{Si})-**7**·MeI], and CCDC 995890 [(S_C,S_{Si})-**8**·BH_3] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] After stirring a solution of (S_C,S_{Si})-**7** and one equivalent of *t*BuLi in pentane at room temperature for 24 h and subsequent trapping with [D_4]-methanol, the ligand was completely reisolated. Thus, no decomposition of (S_C,S_{Si})-**7** occurs in the presence of *t*BuLi in pentane.

[18] For recent examples of the benzylic deprotonation of toluene, see: a) T. Tatic, S. Hermann, M. John, A. Loquet, A. Lange, D. Stalke, *Angew. Chem.* **2011**, *123*, 6796 – 6799; *Angew. Chem. Int. Ed.* **2011**, *50*, 6666 – 6669; b) C. Unkelbach, D. F. O'Shea, C. Strohmann, *Angew. Chem.* **2014**, *126*, 563 – 567; *Angew. Chem. Int. Ed.* **2014**, *53*, 553 – 556; see also Ref. [8d].

[19] On the synthesis of enantiomerically enriched silicon-stereogenic benzylsilanes using silyllithium reagents and benzylhalides was already reported (see Ref. [6c]).

