DOI: 10.1002/ejic.201000834

Mechanistic Insights into the Reaction of Enantiomerically Pure Lithiosilanes and Electrophiles: Understanding the Differences between Aryl and Alkyl Halides

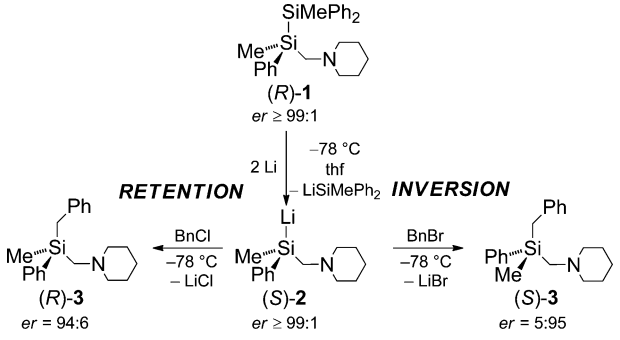
Christian Däschlein,[a] Simeon O. Bauer,[a] and Carsten Strohmann*[a]

Keywords: Silicon / Lithium / Silanes / Lithiosilanes / Substituent effects / Reaction mechanisms / Chirality

The reactivity of enantiomerically pure lithiosilanes against aliphatic and aromatic halo electrophiles has been investigated with the focus on product composition and enantiomeric ratios as a basis for a better understanding of ongoing mechanisms. Both parameters are strongly influenced by both the organic group and the corresponding halide of the used electrophile. Thus, high stereoselectivities and yields are only obtained if one distinct reaction mechanism dominates. In the case of aliphatic electrophiles, experimental and quantum chemical studies support the preference of an S_N2 mechanism for chlorides resulting in retention of configuration on silicon, whereas bromides tend to react under inversion through a halide–lithium exchange (ate complex). For aromatic electrophiles these relationships change: chlorides and bromides both favor the formation of an ate complex over nucleophilic aromatic substitution, leading to inversion of configuration on silicon.

Introduction

The reaction of organolithium reagents with electrophiles is amongst the most important reactions for the synthesis of a multitude of functionalized systems in almost all fields of chemistry.[1] Although a variety of reactions have been intensively investigated to date,[2] this method can generally not be used for the synthesis of enantio- or diastereomerically enriched and pure systems due to the relative high configurative lability of lithiated carbon centers.[3,4–6] In contrast, due to hybridization defects from the third period on,[7,8] stereogenic lithiated silicon centers (lithiosilanes)[9,10] have been shown to be suitable for the introduction of stereoinformation and the synthesis of stereochemically enriched and pure products.[11] During the last decade, the reaction of highly enantiomerically enriched lithiosilanes[12,13] with chlorosilanes and chlorogermanes has proven to be an elegant method for stereoselective transformations.[12d,12e,14] Nevertheless, reactions of lithiosilanes with functionalized halo electrophiles have been of little interest and not well investigated due to low yields and often undesired side-products (e.g., those obtained through Si–Si or C–C coupling reactions due to halide–lithium exchange).[15] Furthermore, for the reaction of lithiosilanes and organic electrophiles (or the formed halosilane/lithiumorganyl after halide–lithium exchange), pathways by nucleophilic substitution but also by e.g. radical intermediats or other substitution mechanisms are possible so that these reactions do not necessarily proceed under preservation of the stereoinformation. Depending on the subsiding mechanisms, stereochemically pure, enriched, or racemic products may be obtained. For instance, our group was able to show that the reaction of enantiomerically pure lithiosilane (*S*)-**2** with benzyl chloride or benzyl bromide results in the formation of the (*R*)- and (*S*)-configuration, respectively, as the main stereoisomer in the formed product, only depending on the halide used [Scheme 1; enantiomeric ratios are given as (*R*)/(*S*)].[10a]



Scheme 1. Reaction of the enantiomerically pure lithiosilane (*S*)-**2** with benzyl chloride and benzyl bromide: different mechanisms lead to different main stereoisomers.[19,20] The *er* values refer to (*R*)/(*S*), expect for (*S*)-**2**.

Thereby, the stereochemical probe at silicon could be used to gain crucial insights into the reaction mechanisms. Whereas the reaction with the chloride preferably proceeds through an S_N2 mechanism under retention of the absolute configuration on silicon, based on the reactant (*R*)-**1**,[16] the

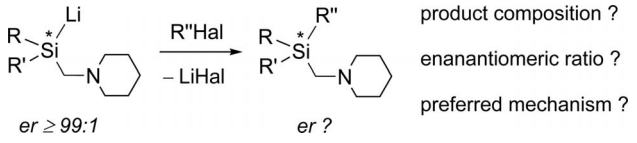
[a] Anorganische Chemie, Technische Universität Dortmund, Otto-Hahn-Straße 6, 44227 Dortmund, Germany
Fax: +49-231-755-7063
E-mail: mail@carsten-strohmann.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000834.

reaction with the bromide preferably proceeds through a halide–lithium exchange (ate complex)[17,18] with inversion of configuration, based on the reactant (*R*)-**1**. Quantum chemical calculations have been used to confirm both proposed mechanisms.[19]

Information concerning the obtained product composition as well as the enantiomeric ratio of the product and therefore the dominating reaction mechanisms are of crucial necessity for a wider application of enantiomerically pure lithiosilanes and the synthesis of chiral silicon compounds. The synthesis of chiral silicon compounds is recently gaining importance, as silanes with a stereogenic silicon center can be used as auxiliaries for stereoselective syntheses, such as Mannich reactions,[21] cycloaddition reactions,[22] or Friedel–Crafts alkylations.[23,24]

As part of our studies on functionalized lithiosilanes, we present our latest results concerning the reactions of enantiomerically pure lithiosilanes and halo electrophiles. The systematic variation of the halide, as well as the organic group, in combination with quantum chemical studies was used to answer the three most important questions (Scheme 2): (i) What products are formed and in what ratio (product composition)?; (ii) is the stereoinformation retained, inverted, or lost during the reaction process (enantiomeric ratio)?; and (iii) what is the preferred reaction mechanism?

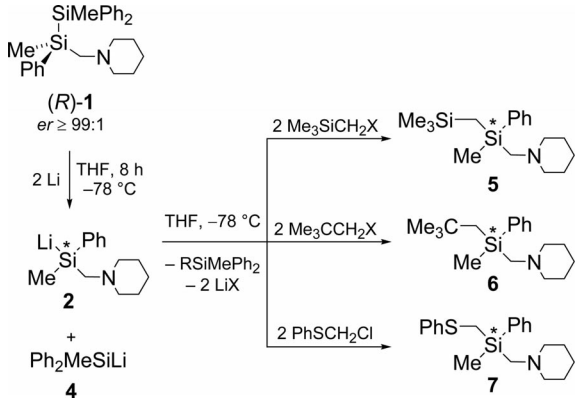


Scheme 2. Reaction of enantiomerically pure lithiosilanes with halo electrophiles and the main questions concerning these transformations.

Results and Discussion

Reaction of Lithiosilane 2 with Aliphatic Halo Electrophiles

For a systematic study of the reactivity of enantiomerically pure lithiosilanes and halo electrophiles, we first investigated the reaction of the enantiomerically pure lithiosilane **2** with aliphatic electrophiles. Based on the trapping reaction of **2** with benzyl chloride and benzyl bromide and its differing main stereoisomers,[10a] we have chosen the generally related (halomethyl)trimethylsilanes, neopentyl halides, and (chloromethyl)phenyl sulfide as trapping reagents (see below for more details on the choice of trapping reagents). First, disilane (*R*)-**1** was reacted at –78 °C in thf with elemental lithium to form enantiomerically pure (*S*)-**2** after a reaction time of 8 h.[12d,25] To monitor the completeness of the Si–Si bond cleavage, a small part of the solution of lithiosilane **2** was trapped with Me_3SiCl and investigated by NMR spectroscopy.[26] On complete formation of **2**, the solution of the lithiosilane was divided into three parts and each added to a twofold excess of the corresponding trapping reagent (Scheme 3). After removal of all volatiles under reduced pressure, the oily residue was dissolved in a minimum amount of *n*-pentane and separated from all salts. The obtained product mixtures were then investigated by using NMR spectroscopy and GC/MS analysis without further purification.[27]



Scheme 3. Synthesis of the functionalized silanes **5**, **6**, and **7**; X = Cl, Br, I; R = Me_3SiCH_2, Me_3CCH_2, $PhSCH_2$.

These reactions were also carried out with *rac*-**1** and the corresponding chloro-organyl as electrophile to synthesize the racemic compounds (reaction time: 6 h[28]). The crude products were purified yielding silanes *rac*-**5**, *rac*-**6**, and *rac*-**7**. The racemic silanes were used to perform NMR spectroscopic studies in the presence of (*R*)-mandelic acid (for **5** and **7**) and (2*R*,3*R*)-di-*O*-benzoyltartaric acid (for **6**). Thus, a method for the separation of the different stereoisomers and therefore a possible method to analyze the enantiomeric ratios was developed, which was then utilized in the reactions of the enantiomerically pure system.[29] In the following, we will first describe the results for each electrophile (R–CH_2–X; X = halide, R = functional group = $SiMe_3$, CMe_3, SPh) before comparing the different trapping reagents.

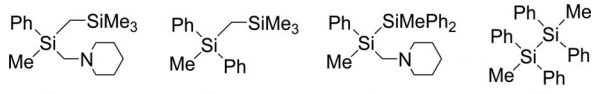
A) Reaction of 2 with Me_3SiCH_2X

The reaction of *rac*-**2** and (chloromethyl)trimethylsilane yielded *rac*-**5** in good yield (86%) after distillation. Silane **8** was the only by-product obtained from the reaction and is due to the reaction of **4** with Me_3SiCH_2Cl. In contrast, reaction of the lithiosilane with the corresponding bromo- and iodo-compounds yielded not only compounds **5** and **8**, but also silanes **1** and **9** obtained by a Si–Si bond-coupling reaction. Table 1 summarizes the product distribution (the compounds were identified by GC/MS; their ratio was determined by NMR spectroscopy).

Consequently, the trapping of **2** with (chloromethyl)trimethylsilane is the only reaction to proceed without the formation of multiple by-products. Noticeably, the disilane **10**, a possible by-product formed through Si–Si coupling (Figure 1) was not identified in any case.

The highly selective reaction of **2** and the chloride is also confirmed by the stereochemical course of the reaction determined by NMR spectroscopy of **5** in the presence of

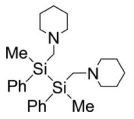
Table 1. Identified products and proportions [%] of the reaction of *rac*-**2** with (halomethyl)trimethylsilanes.[a,b]



5 **8** **1** **9**

Trapping reagent	Identified products [%] **5**	**8**	**1**	**9**
(Chloromethyl)trimethylsilane	50	50	n.i.	n.i.
(Bromomethyl)trimethylsilane	36	18	34	12
(Iodomethyl)trimethylsilane	43	28	23	6

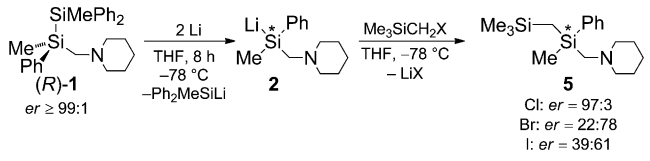
[a] n.i.: not identified. [b] The given values are obtained from NMR spectroscopic integration.[30]



10

Figure 1. Compound **10** – not identified from the reactions of *rac*-**2** with trimethylsilanes.

three equivalents of (*R*)-mandelic acid in $CDCl_3$. Under these conditions, the resonance signals of the methyl groups of the $SiMe_3$ group could be integrated separately in the ^1H NMR spectrum. Thereby, the reaction of enantiomerically pure **2** with Me_3SiCH_2Cl yielded an enantiomeric ratio *er* – (*R*)/(*S*) – of 97:3, whereas the reaction with Me_3SiCH_2Br yielded a ratio of 22:78. The reaction of enantiomerically pure **2** with Me_3SiCH_2I yielded a ratio of only 39:61. Thus, the reaction with the chloride resulted in the formation of the opposing stereochemical configuration to that of the bromide and the iodide. This is a crucial observation and hints at the viability of different reaction mechanisms for the three halides. Scheme 4 summarizes the described results; all relevant ^1H NMR spectra can be found in the Supporting Information.

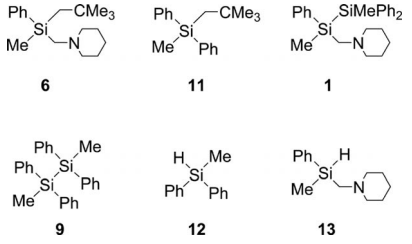


Scheme 4. Summary of the *er* in the reaction of enantiomerically pure **2** with Me_3SiCH_2X (X = Cl, Br, I). The *er* values refer to (*R*)/(*S*).

B) Reaction of 2 with Me_3CCH_2X

Reaction of *rac*-**2** and neopentyl chloride yielded *rac*-**6** (39%) and several by-products. In addition to silane **11**, which is formed due to the reaction of **4** with Me_3CCH_2Cl, disilanes **1** and **9** as well as silanes **12** and **13** were identified in the reaction mixture. Almost all of these by-products were identified in the reaction of **2** with both Me_3CCH_2Br and Me_3CCH_2I; the amount of the **1** increases from the chloride to the iodide. Again, the Si–Si coupling product **10** (Figure 1) was not formed in any trapping reaction. Table 2 summarizes the product distribution.

Table 2. Identified products and proportions [%] of the reaction of *rac*-**2** with neopentyl halides.[a,b]

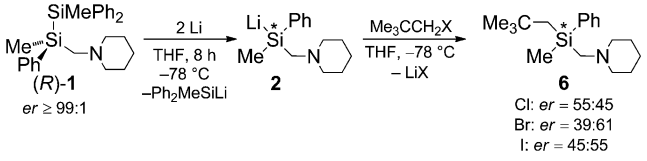


6 **11** **1** **9** **12** **13**

Trapping reagent	Identified products [%] **6**	**11**	**1**	**9**	**12**	**13**
Neopentyl chloride	36	25	21	15	1.3	1.7
Neopentyl bromide	32	9	37	22	n.i.	n.i.
Neopentyl iodide	29	traces	49	17	2.6	2.3

[a] n.i.: not identified. [b] The given values are obtained from NMR spectroscopic integration.[30]

Significantly lower stereoselectivities for the reactions of **2** with the neopentyl halides – in comparison with the (halomethyl)trimethylsilanes – could be determined by ^1H NMR spectroscopic studies in the presence of 1.5 equiv. of (2*R*,3*R*)-di-*O*-benzoyltartaric acid in $CDCl_3$. Under these conditions, the resonance signals of the methyl groups at the stereogenic silicon centers could be integrated separately. Thus, the reaction of enantiomerically pure **2** with Me_3CCH_2Cl yielded a ratio [(*R*)/(*S*)] of 55:45, Me_3CCH_2Br yielded a ratio of 39:61, and Me_3CCH_2I of 45:55. Although the formation of the opposite stereoisomer is again favored for the chloride, all three trapping reagents strongly tend to racemization of the stereogenic silicon center. As a consequence, none of the reactions of **2** with neopentyl halides proceed by the preference of one distinct mechanism. Scheme 5 summarizes the described results; all relevant ^1H NMR spectra can be found in the Supporting Information.



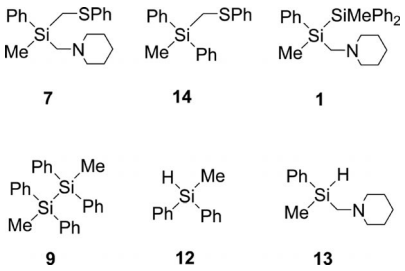
Scheme 5. Summary of the *er* in the reaction of enantiomerically pure **2** with Me_3CCH_2X (X = Cl, Br, I). The *er* values refer to (*R*)/(*S*).

C) Reaction of 2 with $PhSCH_2Cl$

Finally, we were specifically interested in the influence of a sulfur atom in the α-position to the halide due to the high relevance of sulfur-containing compounds in various reactions.[31] The reaction of *rac*-**2** with (chloromethyl)-phenyl sulfide yielded *rac*-**7** (28%) and the same by-products as detected for the reaction of **2** with neopentyl halides (silane **14** is formed instead of **11**). Table 3 summarizes the obtained product compositions. A high amount of compound **1** was formed in the reaction with the sulfide; the reason for this is currently under investigation. Although the yield is lower than in the case of the neopentyl chloride,

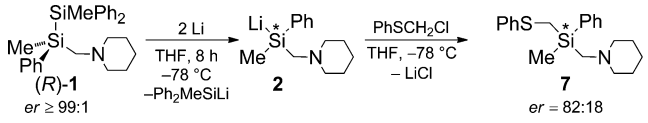
the reaction of enantiomerically pure **2** with $PhSCH_2Cl$ resulted in a considerably better *er* value [(*R*)/(*S*)] of 82:18 for compound **7**, determined by the treatment of the crude product with three equivalents of (*R*)-mandelic acid and separate integration of the signals of the methyl group at the stereogenic silicon center. Scheme 6 summarizes the described results; all relevant ^1H NMR spectra can be found in the Supporting Information.

Table 3. Identified products and proportions [%] of the reaction of of *rac*-**2** with (chloromethyl)phenyl sulfide.[a]



	Identified products [%]					
Trapping reagent	**7**	**14**	**1**	**9**	**12**	**13**
(Chloromethyl)phenyl sulfide	25	13	40	19	1.4	1.6

[a] The given values are obtained from NMR spectroscopic integration.[30]



Scheme 6. Summary of the *er* in the reaction of enantiomerically pure **2** with $PhSCH_2Cl$. The *er* values refer to (*R*)/(*S*).

D) Comparison of the Different Trapping Reagents: New Mechanistic Insights

The (halomethyl)trimethylsilanes, neopentyl halides, and (chloromethyl)phenyl sulfide have been chosen due to their similarity to the benzyl halides that have been previously investigated;[10a] all reagents are able to stabilize a negative charge in the α-position to the corresponding substituent R (R–CH_2–X; X = halide, R = Me_3Si, Me_3C, PhS, Ph). As this property is differently pronounced in the investigated systems, we focused on the influence of this difference on the obtained product composition and stereoselectivity. Related to this is the question of the relevant mechanisms for a better understanding of the resulting enantiomeric ratios, and for further more controlled synthetic applications. Table 4 summarizes all experimentally determined *er* values of the reaction of enantiomerically pure **2** with aliphatic halo electrophiles; the reaction of enantiomerically pure **2** with benzyl halides is included for completeness, see ref.[10a]

Based on these results, the following conclusions can be drawn:

i) In all cases, the reaction of enantiomerically pure **2** with the corresponding chloride results in the preferential formation of the opposite stereoisomer to the bromide and iodide, indicating different mechanisms.

Table 4. Enantiomeric ratios obtained from the reactions of **2** with R–CH_2–X; X = halide, R = functional group = Me_3Si, Me_3C, PhS, Ph[a] [*er* values based on (*R*)-**1**; (*R*)/(*S*)].

Trapping reagent	*er* (chloride)	*er* (bromide)	*er* (iodide)
$PhCH_2X$	94:6[a]	5:95[a]	n.d.[b]
Me_3SiCH_2X	97:3	22:78	39:61
$PhSCH_2X$	82:18	n.d.	n.d.
Me_3CCH_2X	55:45	39:61	45:55

[a] See ref.[10a] [b] n.d.: not determined.

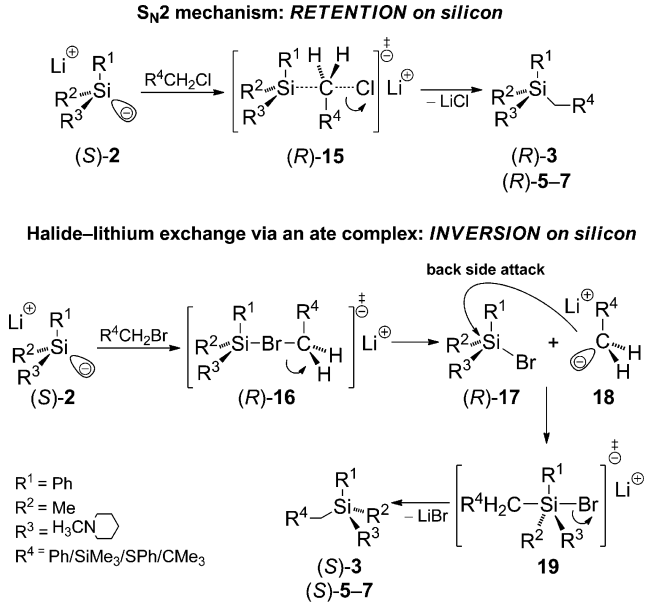
ii) Starting with the benzyl halides, there is a decrease of stereoselectivity over the trimethylsilyl halides and (chloromethyl)phenyl sulfide to the neopentyl halides.[32]

iii) High stereoselectivities – benzyl chloride, benzyl bromide, (chloromethyl)trimethylsilane – hint to the strong domination of one distinct reaction mechanism, further confirmed by the lack of by-products in the GC/MS analysis. In all other cases, additional, competing mechanisms have to exist.

R–CH_2–Cl and R–CH_2–Br (R = Me_3Si, Me_3C, PhS, Ph)

In general, the preferred reaction mechanism should be identical for chemically related trapping reagents. In 2004, our group showed that for the reaction of enantiomerically pure **2** and benzyl chloride, an S_N2 mechanism on carbon, resulting in retention of configuration on silicon based on (*R*)-**1**, is preferred. In contrast, for the reaction of enantiomerically pure **2** and benzyl bromide, a halide–lithium exchange via an ate complex leading to inversion of configuration on silicon is preferred.[10a] Scheme 7 displays these two main reaction mechanisms with the three newly investigated trapping reagents already included (see Scheme 1 for the formation of **2**).[20] It is important for the mechanism through the ate complexes, that both experimental[9,10a] and quantum chemical calculations[33] support the selective reaction of lithiumorganyls with chloro- and bromosilanes from the back side under inversion at silicon. This assumption is the basis for the following discussion.[34] It also has to be emphasized that, due to the change of substituents on silicon, the priorities of the CIP nomenclature change and thus the absolute configurations are inverted in some cases, although no actual change of the stereoinformation takes place.[20]

To investigate the mechanisms for the newly studied trapping reagents, we carried out quantum chemical calculations on model systems for the reaction of **2** with (chloromethyl)trimethylsilane and (bromomethyl)trimethylsilane, (both for the ate complex and the S_N2 mechanism). Therefore, the geometries of the stationary points of H_3Si^-/Me_3SiCH_2Cl and H_3Si^-/Me_3SiCH_2Br were optimized using density functional theory with the hybrid B3LYP functional and the 6-31+G(d) basis set. Since S_N2 reactions are strongly influenced by solvent effects, calculations including solvent models were performed. The stationary points were energy optimized in thf solution (ε = 7.58 for thf) by means of the self-consistent reaction field (SCRF) method. The energies for the structures obtained were calculated with the polarizable conductor calculation model (CPCM).[16,35]



Scheme 7. Preferred mechanisms for the reactions of lithiosilane (*S*)-**2** with chloro (top) and bromo electrophiles (bottom).[20]

Harmonic vibrational frequency analyses – to establish the nature of the stationary points – were performed on the same level, showing one imaginary frequency each. Figure 2 displays these calculated stationary points and their relative energies.

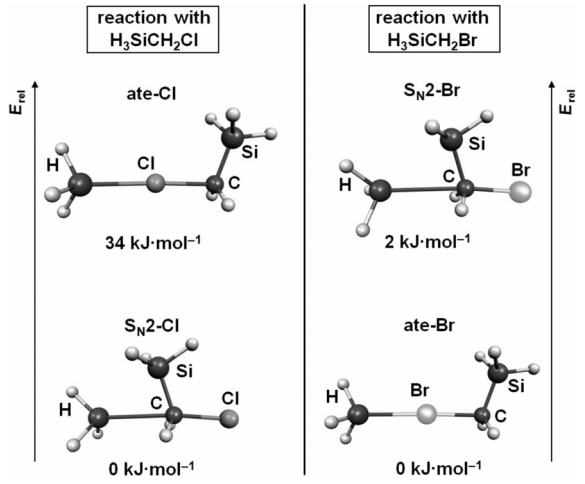


Figure 2. Calculated stationary points for the studied model systems H_3Si^-/Me_3SiCH_2Cl (left) and H_3Si^-/Me_3SiCH_2Br (right) [B3LYP/6-31+G(d), CPCM]; in both cases, an ate complex (ate-X, X = Cl, Br) and the S_N2 mechanism (S_N2-X, X = Cl, Br) were optimized; *Molekel* plots.[36]

From these calculations, the following trends for the model systems studied were obtained: in case of (chloromethyl)trimethylsilane, the transition state **ate-Cl** for a chloride–lithium exchange lies 34 kJ mol^{-1} higher than the alternative path through direct substitution of the halide (**S_N2-Cl**). The preference of the S_N2 reaction is in agreement with our previous calculations for the reaction of (*S*)-**2** and benzyl chloride.[10a] The energetic difference between the two possible transition states is even higher for Me_3SiCH_2Cl (ΔE = 34 kJ mol^{-1}) than for $PhCH_2Cl$ (ΔE = 13 kJ mol^{-1}), explaining the experimentally obtained, slightly higher *er* for the silicon-containing trapping reagent. For (bromomethyl)trimethylsilane these energy relationships are reversed and the bromide–lithium exchange (**ate-Br**) is favored by 2 kJ mol^{-1} over the substitution (**S_N2-Br**). Although this energetic difference is only very small, this is in accordance with the experimentally obtained lower *er* [(*R*)/(*S*) = 22:78]. Furthermore, this value is also significantly smaller than the *er* obtained for the reaction of **2** and $PhCH_2Br$ [(*R*)/(*S*) = 5:95][10a] in which the ate complex lies 10 kJ mol^{-1} below the substitution (for energy values, see Table 5).

Table 5. Relative energies E_{rel} of the calculated stationary points for the model systems $H_3Si^-/PhCH_2Cl$, $H_3Si^-/PhCH_2Br$, H_3Si^-/Me_3SiCH_2Cl, and H_3Si^-/Me_3SiCH_2Br.[a,b]

Model system	Nucleophilic substitution (S_N2) [kJ mol^{-1}]	Halide–lithium exchange (ate complex) [kJ mol^{-1}]
$H_3Si^-/PhCH_2Cl$	0[c]	13[c]
$H_3Si^-/PhCH_2Br$	10[c]	0[c]
H_3Si^-/Me_3SiCH_2Cl	0	34
H_3Si^-/Me_3SiCH_2Br	2	0

[a] Values not relative to each other. [b] B3LYP/6-31+G(d), CPCM. [c] See ref.[10a]

Thus, the DFT calculations of the model systems confirm all trends observed in the experiment. A S_N2 mechanism with retention of configuration on silicon is preferred for the reaction of enantiomerically pure lithiosilanes with chlorohalides, whereas a halide–lithium exchange under inversion of configuration on silicon is preferred for the reaction with bromides. Furthermore, an important conclusion can be drawn based on the decreasing stereochemical purity (simplified: *er* $PhCH_2X \geq Me_3SiCH_2X > PhSCH_2X >> Me_3CCH_2X$, X = Cl, Br) for all investigated chlorides and bromides; the higher the ability of the used organyl to stabilize the negative charge of the respective transition state (pentacoordinate for the S_N2 mechanism, ate complex for the halide–lithium exchange), the higher the obtained *er* value of the main product. In the case of $PhCH_2Ph$, this negative charge is highly stabilized by the phenyl group, whereas it is the silicon α-effect for Me_3SiCH_2X. This stabilization is still pronounced (although smaller) for $PhSCH_2X$ (negative hyperconjugation of sulfur), but almost no stabilization is present in the case of Me_3CCH_2X. The smaller this stabilizing effect, the less pronounced the preferred mechanism and competing reaction mechanisms become important.

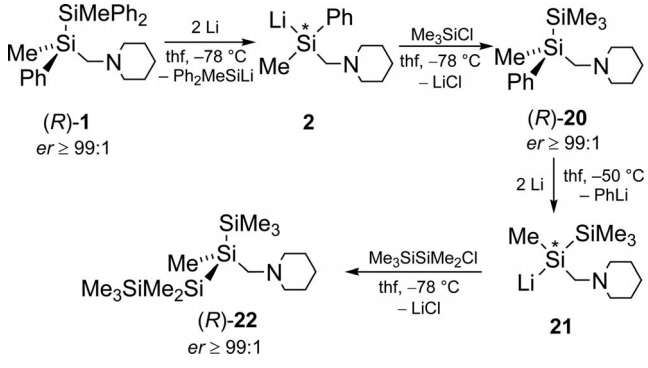
Iodides

The reaction of enenatiomerically pure **2** and aliphatic iodides as trapping reagents provided worse results considering both the chemoselectivity and the enantiomeric ratios (predominantly racemization in the investigated systems). Thus, there is not one dominating reaction mechanism for R–CH_2–I (R = Me_3Si, Me_3C). This loss of stereo-

information was also observed in our group in previous investigations and was attributed to the formation of silyl radicals:[37] To elucidate a competing radical mechanism in these reactions, enenatiomerically pure **2** was treated with cyclopropylmethyl halides, which are commonly used in the literature as radical scavengers.[38] These studies yielded – in addition to products formed through polar mechanisms – a high amount of products formed through radical mechanisms. Thus, the amount of the products formed by the polar mechanism is strongly decreasing from the chloride to the iodide, thus indicating the preference of radical mechanisms for the reaction of iodo electrophiles (preference of a mechanism through the silyl radicals: R–I > R–Br > R–Cl). This is also in agreement with comparable studies performed by Krusic et al.[39] Under consideration of these results, the low stereochemical purities in the reaction of (*S*)-**2** and R–CH_2–I can be understood, although, in principle, a mechanisms via an ate complex, like that for the bromides, should also be dominant for the iodides the formation of a silyl radical in the first step seems to get almost equal importance. Whereas the reaction through an ate complex results in the formation of the product under inversion of configuration on silicon, the reaction through a silyl radical proceeds under retention.[40] Thus, no significant stereochemical enrichment, but almost complete racemization, is obtained in the corresponding products (slight preference of the ate complex).

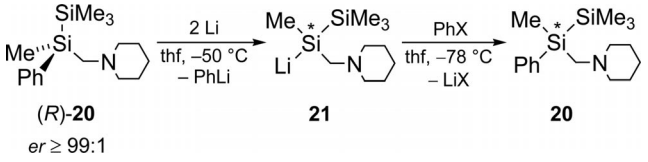
Reaction of Lithiosilane 21 with Halobenzenes

In 2007, we reported the synthesis of the enantiomerically pure disilane (*R*)-**20** through the reaction of enenatiomerically pure **2** with chlorotrimethylsilane (Scheme 8). The subsequent reaction of (*R*)-**20** with elemental lithium afforded the selective cleavage of the Si–C bond to the phenyl group forming the enantiomerically pure lithiosilane **21**, which could then be reacted with chlorosilanes. This led to the first enantiomerically pure tetrasilane (*R*)-**22** synthesized under full preservation of the stereoinformation on silicon.[12e]



Scheme 8. Synthesis of the enantiomerically pure lithiosilanes **2** and **21** through selective Si–Si and selective Si–C cleavage in the respective reactant and their trapping reactions with chlorosilanes. The *er* values refer to (*R*)/(*S*).

In addition to the above reactions of **2** with electrophiles, we also wanted to investigate the reactivity of the enantiomerically pure lithiosilane **21** with halobenzenes to enable us to expand our studies to aromatic electrophiles. The questions about the preferred mechanism, the resulting products and their absolute configurations in the reaction of lithiosilanes and aromatic electrophiles are even less explored than the described reactions of **2** with aliphatic trapping reagents. To get a deeper insight into these reactions, disilane (*R*)-**20** was reacted at –50 °C in thf with elemental lithium to form enenatiomerically pure **21** after a reaction time of 6.5 h.[41] To determine complete cleavage of the S–C bond, a portion of the solution of lithiosilane **21** was trapped with $Me_3SiSiMe_2Cl$ and subjected to NMR spectroscopy.[42] On complete formation of **21**, the solution of the lithiosilane was divided into three parts and each added to a twofold excess of PhX (X = Cl, Br, I) (Scheme 9). After removal of all volatiles under reduced pressure, the oily residue was dissolved in a minimum amount of *n*-pentane and separated from all salts.

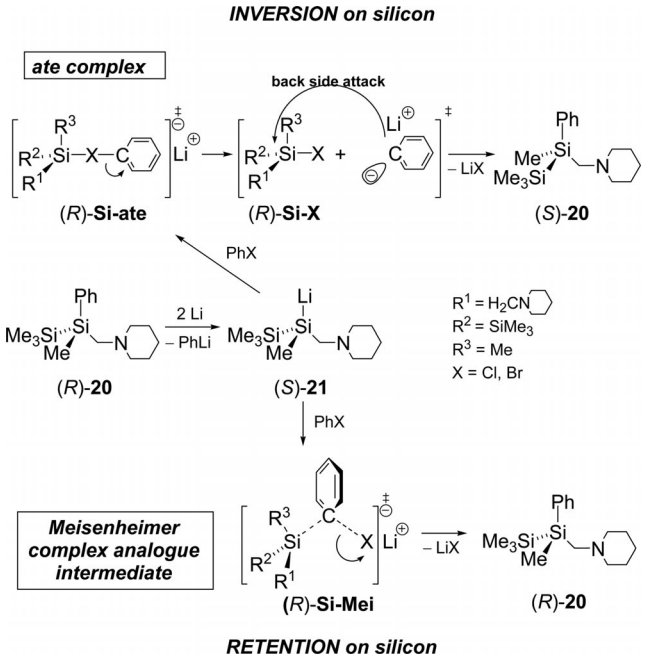


Scheme 9. Reaction of (*S*)-**21** with halobenzenes; X = Cl, Br, I. The *er* values refer to (*R*)/(*S*).

The product mixtures were subject to investigation by NMR spectroscopy and GC/MS analysis without further purification.[27] Disilane **20** and biphenyl (by-product due to the reaction of PhLi and PhX) could be identified in all three reactions almost exclusively (only small amounts of one additional compound with a molecular ion peak of *m*/*z* = 367 could be identified). Thus, the first crucial observation is that the reaction of enantiomerically pure **21** with PhCl, PhBr, and PhI is highly selective with regard to the yield of the major product in each case. The determination of the *er* was accomplished by using three equivalents of (*R*)-mandelic acid (all relevant ^{1}H NMR spectra can be found in the Supporting Information).[12e,43] The trapping reaction of (*S*)-**21** with PhCl [(*R*)/(*S*) = 22:78] as well as with PhBr (30:70) both resulted in the preference of the (*S*)-enantiomer,[44] formed under inversion of configuration on silicon; an almost full racemization was obtained for PhI (56:44). Thus, contrary to the reactions of enantiomerically pure **2** with aliphatic chloro and bromo electrophiles, the trapping reaction of (*S*)-**21** with the aromatic halides (PhCl and PhBr) obviously proceeds through the same preferred reaction mechanism leading to the same main enantiomer.

How can these selectivities be understood? Contrary to the reaction of lithiosilanes and aliphatic organyls, an S_N2 mechanism is of no relevance for aromatic systems. Furthermore, as the lithiosilane itself is reacting as a nucleophile, these reactions cannot be discussed by electrophilic aromatic substitution. The two most likely mecha-

nisms are the reaction through an ate complex (proceeding under inversion of configuration based on (*R*)-**20**; see also Scheme 7) or through a Meisenheimer complex analogue intermediate (proceeding under retention of configuration; Scheme 10).



Scheme 10. Possible mechanisms of the reaction of lithiosilane **21** with aromatic electrophiles: via an ate complex under inversion of configuration on silicon (top) and via an intermediate analogous to a Meisenheimer complex under retention of configuration on silicon (bottom).

For a better understanding of these reactions, we performed quantum chemical calculations [B3LYP/6-31+G(d)] on model systems for the reaction of **21** with PhCl and PhBr (both the ate complex and Meisenheimer complex analogue). The geometries of the stationary points of H_3Si^-/PhCl and H_3Si^-/PhBr were optimized by using the same procedure [SCRF, CPCM] as described above for H_3Si^-/Me_3SiCH_2Cl and H_3Si^-/Me_3SiCH_2Br.[35] Figure 3 displays the calculated stationary points and their relative energies.

In both cases, the ate complexes (**PhCl-ate**, **PhBr-ate**) possess significantly lower energies than the alternative Meisenheimer complex analogue intermediates (**PhCl-Mei**, **PhBr-Mei**): $\Delta E_{chloride}$ = 27 kJ mol^{-1}, $\Delta E_{bromide}$ = 66 kJ mol^{-1}. Thus, although the energetic difference between both possible mechanisms is even higher for the bromide (this should result in a higher *er* value for PhBr compared to PhCl in the experiment), these calculations confirm the preferred formation of the (*S*)-enantiomer via an ate complex under inversion of configuration. Nevertheless, the smaller experimental *er* of BrPh might be explained by a competing mechanism through a silyl radical, which would result in the formation of the opposite stereoisomer (described above, formation of radicals preferred R–I > R–Br > R–Cl). The formation of a silyl radical could also explain the incomplete preservation of the stereoinformation in the

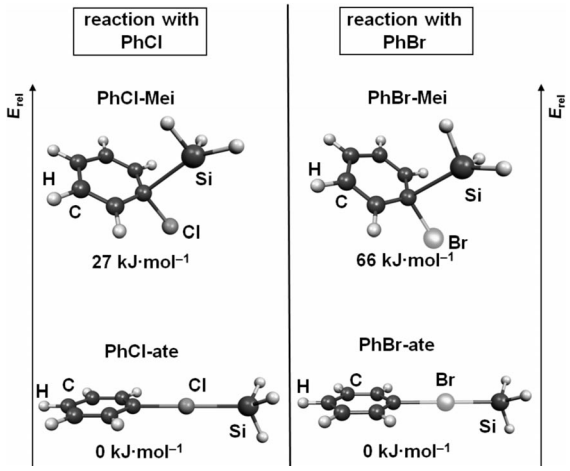


Figure 3. Calculated stationary points for the studied model systems H_3Si^-/PhCl (left) and H_3Si^-/PhBr (right) [B3LYP/6-31+G(d), CPCM]; in both cases, an ate complex and a reaction via an intermediate analogous to a Meisenheimer complex were optimized; *Molekel* plots.[36]

case of PhCl as the aromatic system should, in general, stabilize radicals (also for chloride). Consistent with the less-preferred reaction of chlorides through a radical mechanism, PhCl yielded a better *er* than PhBr. The *er* for PhI [(*R*)/(*S*) = 56:44] can be explained as a result of the almost equal importance of the ate complex and the silyl radical, thus the product is obtained almost in racemic form. The slightly higher amount of the (*R*)-enantiomer (retention) could be the result of a small preference of the mechanism via the silyl radical.

Conclusion

We have presented the reaction of enantiomerically pure lithiosilanes with both aliphatic and aromatic halo electrophiles to gain a better understanding of the reaction mechanisms involved. Based on the stereochemical probe encoded on silicon, we were able to systematically study the influences of the organic and halide groups of the trapping reagents on product compositions and enantiomeric ratios (depending on the dominating reaction mechanism, different stereoisomers were obtained). In all cases, high stereoselectivities and product yields are only obtained if there is one distinct, dominating reaction mechanism. In case of aliphatic trapping reagents (R–CH_2–X; X = Cl, Br, I; R = Me_3Si, Me_3C, PhS, Ph), experimental and quantum chemical studies support the preferred reaction of chlorides through an S_N2 mechanism under retention of configuration on silicon, whereas bromides tend to react under inversion on silicon through a halide–lithium exchange (ate complex). The corresponding iodides led to the almost complete loss of stereoinformation due to the growing importance of silyl radicals. Thus, the stereochemical purity decreases as follows: *er*(RCl) > *er*(RBr) >> *er*(RI). Another interesting observation could be made concerning the used organic groups: The higher the ability of the used organyl to stabi-

lize the negative charge of the respective transition state (pentacoordinate for the S_N2 mechanism, ate complex for the halide–lithium exchange), the higher the obtained *er* in the main product. For aromatic trapping reagents (PhX, X = Cl, Br, I), these relationships change: chlorides and bromides both favor reaction through an ate complex over nucleophilic aromatic substitution, leading to inversion of configuration. Again, the formation of a silyl radical becomes more important for iodobenzene resulting in the almost complete racemization of the product. At the moment we are trying to elucidate the influence of further functional groups on the preferred reaction mechanism especially for the reaction of enantiomerically pure lithiosilanes and aromatic halo electrophiles.

Experimental Section

General: All experiments were carried out under a dry, argon atmosphere using standard Schlenk techniques. All solvents – excluding NMR solvents – were dried with sodium and distilled prior to use. NMR spectra were recorded on DRX-300, Avance-400, and AMX-500 *Bruker* spectrometers at 22 °C. Assigning the signals was supported by additional DEPT-135, and C,H- and H,H-COSY experiments. Elemental CHN analysis was performed on a Leco Elemental Analyser CHNS 932. GC/MS analysis were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); Column: Zebron, Capillary GC Column, ZB-1.

Synthesis: All chlorosilanes were obtained from ABCR or Wacker Chemie AG. Aliphatic and aromatic trapping reagents were purchased from Acros Organics or Sigma–Aldrich. Elemental lithium used for the synthesis of **2** and **21** was obtained from Chemetall.

(*R*)-**1** was synthesized according to a literature procedure.[12d] All spectroscopic data can be found in this reference.

Synthesis of *rac*-5, *rac*-6, and *rac*-7: *rac*-**1** was added to lithium (2 equiv.) in thf and cooled to 0 °C at the first occurrence of a color change. After 6 h, the dark solution of lithiosilane **2** was added to the respective chloro electrophile (2.2 equiv.) dissolved in thf (15 mL). The solution was warmed to room temperature and all volatiles were removed in vacuo. The residue was suspended in NaOH (2 M, 20 mL) and extracted (5×) with diethyl ether (20 mL). The combined organic layers were extracted (5×) with HCl (2 M, 15 mL) and afterwards set to pH 12 with KOH. Finally the aqueous layer was extracted (5×) with diethyl ether (20 mL) and the combined organic layers were dried with Na_2SO_4. After removal of all volatile compounds in vacuo, the crude product was subjected to kugelrohr distillation; pressure: 10^{-3} mbar; boiling point (b.p.). Table 6 includes explicit information concerning the amounts of involved reactants, volume of solvents, yields, and distillation temperatures. The analytical data of the synthesized silanes are given below.

Table 6. Synthesis of *rac*-**5**, *rac*-**6,** and *rac*-**7**: amounts of involved reactants and volume of solvents as well as yields and distillation temperatures.

Product	*m* (*rac*-**1**) [mg, mmol]	*m* (Li) [mg, mmol]	*V* (thf) [mL]	*m* (RCl) [mg, mmol]	Yield [g, mmol, %]	B.p. [°C]
rac-**5**	5.45, 13.1	182, 6.2	10	3.54, 8.9	3.41, 1.2, 86	161
rac-**6**	4.85, 11.7	162, 3.3	8	2.74, 5.7	1.31, .53, 39	155
rac-**7**	3.32, 8.00	111, 6	6	2.79, 7.6	0.81, .36, 28	190

Spectroscopic Data

1A) *rac*-Methylphenyl(piperidinomethyl)[(trimethylsilyl)methyl]silane (*rac*-5): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.14 [s, 9 H, Si(CH_3)$_3$], 0.13–0.15 (AB system, not fully resolved, 2 H, SiCH_2Si), 0.53 (s, 3 H, SiCH_3), 1.33–1.40 (m, 2 H, NCCCH_2), 1.55–1.61 (m, 4 H, NCCH_2C), 2.23 (s, 2 H, SiCH_2N), 2.35–2.44 (m, 4 H, NCH_2CC), 7.29–7.37 (m, 3 H, H^m and H^p), 7.67–7.71 (m, 2 H, H^o) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = –1.84 (1 C, NCSiCH_3), 1.21 (1 C, SiCH_2Si), 1.54 [3 C, Si(CH_3)$_3$], 24.3 (1 C, NCCCH_2), 26.7 (2 C, NCCH_2C), 51.6 (1 C), (SiCH_2N), 58.9 (2 C, NCH_2CC), 127.9 (2 C, C^m, C_6H_5Si), 129.0 (1 C, C^p, C_6H_5Si), 134.1 (2 C, C^o, C_6H_5Si), 140.4 (1 C, C^i, C_6H_5Si) ppm. ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = –6.62 (1 Si, NC*Si*), 0.67 [1 Si, SiCH$_2$*Si*(CH$_3$)$_3$] ppm. GC/EI-MS: t_R = 8.16 min [80 °C (2 min) – 10 °C min^{-1} – 280 °C (5 min)] *m*/*z* (%): 305 (7) [M$^+$], 290 (10) [M$^+$ – CH$_3$], 207 (6) [M$^+$ – (H$_2$C=NC$_5$H$_{10}$)], 98 (100) [(H$_2$C=NC$_5$H$_{10}$)$^+$]. $C_{17}H_{31}NSi_2$ (305.61): calcd. C 66.8, H 10.2, N 4.58; found C 66.9, H 10.2, N 5.29.

1B) *rac*-Methylphenyl(neopentyl)(piperidinomethyl)silane (*rac*-6): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.40 (s, 3 H, SiCH_3), 0.82 [s, 9 H, C(CH_3)$_3$], 0.91–0.93 [m, 2 H, SiCH_2C(CH$_3$)$_3$], 1.21–1.28 (m, 2 H, NCCCH_2), 1.38–1.45 (m, 4 H, NCCH_2C), 2.02, 2.08 (AB system, $^2J_{AB}$ = 14.59 Hz, 2 H, SiCH_2N), 2.13–2.24 (m, 4 H, NCH_2CC), 7.19–7.27 (m, 3 H, Ar*H*), 7.47–7.52 (m, 2 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = –2.61 (1C, SiCH_3), 19.7 [3 C, SiCH$_2$C(CH_3)$_3$], 23.7 (1 C, NCCCH$_2$), 26.1 (2 C, NCCH_2C), 31.1 [1 C, SiCH_2C(CH$_3$)$_3$], 33.1 [1 C, C(CH$_3$)$_3$], 50.6 (1 C, SiCH_2N), 58.5 (2 C, NCH_2CC), 127.6 (2 C, C^m, C_6H_5Si), 128.6 (1 C, C^p, C_6H_5Si), 133.9 (2 C, C^o, C_6H_5Si), 127.9 (1 C, C^i, C_6H_5Si) ppm. ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = –8.39 (1 Si, NC*Si*) ppm. GC/EI-MS: t_R = 8.18 min [80 °C (2 min) – 10 °C min^{-1} – 280 °C (5 min)] *m*/*z* (%): 289 (7) [M$^+$], 218 (29) [M$^+$ – CH$_2$C(CH$_3$)$_3$], 98 (100) [(H$_2$C=NC$_5$H$_{10}$)$^+$]. $C_{18}H_{31}NSi$ (289.54): calcd. C 74.7, H 10.8, N 4.84; found C 74.5, H 10.7, N 5.2.

1C) *rac*-Methylphenyl(piperidinomethyl)[(thiophenyl)methyl]silane (*rac*-7): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.50 (s, 3 H, SiCH_3), 1.25–1.37 (m, 2 H, NCCCH_2), 1.44–1.55 (m, 4 H, NCCH_2C), 2.25–2.30 (m, 2 H, SiCH_2N), 2.31–2.39 (m, 4 H, NCH_2CC), 2.41–2.46 (m, 2 H, SCH_2Si), 7.17–7.70 (m, 10 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = –4.74 (1C, SiCH_3), 16.4 (1 C, SCH_2Si), 23.6 (1 C, NCCCH$_2$), 26.1 (2 C, NCCH_2C), 48.4 (1 C, SiCH_2N), 58.5 (2 C, NCH_2CC), 127.8 (2 C, C^m, C_6H_5Si), 128.6 (2 C, C^m, C_6H_5S), 129.2 (1 C, C^p, C_6H_5Si), 129.6 (1 C, C^p, C_6H_5S), 134.0 (2 C, C^o, C_6H_5Si), 134.6 (2 C, C^o, C_6H_5S), 136.2 (1 C, C^i, C_6H_5Si), 140.1 (1 C, C^i, C_6H_5S) ppm. ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ = –7.31 (1 Si, NC*Si*) ppm. GC/EI-MS:t_R = 9.18 min [80 °C (2 min) – 10 °C min^{-1} – 280 °C (5 min)] *m*/*z* (%): 341 (3) [M$^+$], 243 (1) [*M*$^+$ – H$_2$CNC$_5$H$_{10}$], 218 (35) [*M*$^+$ – C$_6$H$_5$SCH$_2$], 98 (100) [(H$_2$C=NC$_5$H$_{10}$)$^+$].

The determination of the enantiomeric ratios was determined in the presence of 3 equiv. of (*R*)-mandelic acid (for *rac*-**5** and *rac*-**7**) or 1.5 equiv. of (2*R*,3*R*)-di-*O*-benzoyltartaric acid (for *rac*-**6**) in $CDCl_3$ (500 μL).

2A) *rac*-5 with (*R*)-Mandelic Acid: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = –0.17, –0.16 [s, 9 H each; Si(CH_3)$_3$, D1 and D2], 0.00, 0.07 (AB system, $^2J_{AB}$ = 13.97 Hz, 4 H, SiCH_2Si, D1 and D2), 0.39, 0.43 (s, 3 H each; SiCH_3, D1 and D2), 0.91–1.13 (m, 2 H, NCCCH_2, D1/D2), 1.29–1.49 (m, 6 H, NCCH_2CH_2, D1/D2), 1.50–1.69 (m, 4 H, NCCH_2CH_2, D1/D2), 2.09–2.35 (m, 4 H, NCH_2CC, D1/D2), 2.40–2.60 (AB system, not fully resolved, 4 H, SiCH_2N), 2.95–3.15, 3.16–3.35 (m, 2 H each; NCH_2CC, D1/D2), 4.98 (s, 2 H, C*H*OH), 7.14–7.48 (m, 20 H, aromat. H) ppm. The NH, OH signals were not

clearly localized. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = –3.89, –3.85 (1 C each, NCSi*C*H$_3$, D1 and D2), 0.12, 0.16 (1 C each, Si*C*H$_2$Si, D1 and D2), 0.81 [6 C, Si(*C*H$_3$)$_3$, D1 and D2], 20.9 (2 C, NCC*C*H$_2$, D1 and D2), 22.12, 22.15 (2 C each, NC*C*H$_2$C, D1 and D2), 49.1 (2 C, Si*C*H$_2$N, D1 and D2), 55.2, 56.6 (2 C each, N*C*H$_2$CC, D1 and D2), 73.4 (2 C, *C*HOH, D1 and D2), 126.2 (4 C, C^m, $C_6H_5CHOHCO_2$, D1 and D2), 126.9 (2 C, C^p, $C_6H_5CHOHCO_2$, D1 and D2), 127.7 (4 C, C^o, $C_6H_5CHOHCO_2$, D1 and D2), 127.9 (4 C, C^m, C_6H_5Si, D1 and D2), 129.6 (2 C, C^p, C_6H_5Si, D1 and D2), 133.3 (4 C, C^o, C_6H_5Si, D1 and D2), 135.6 (2 C, C^i, C_6H_5Si, D1 and D2), 140.9 (2 C, C^i, C_6H_5CHOH, D1 and D2), 176.64 (2 C, *C*OO, D1 and D2) ppm. $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = –6.62, –6.60 (1 Si each, NC*Si*, D1 and D2), 0.94 [2 Si, *Si*(CH$_3$)$_3$, D1 and D2] ppm.

2B) *rac*-6 with (2*R*,3*R*)-Di-*O*-benzoyltartaric Acid: ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.49, 0.57 (s, 3 H each; SiC*H*$_3$, D1 and D2), 0.66, 0.72 [s, 9 H each; C(C*H*$_3$)$_3$, D1 and D2], 0.76–0.89 (AB system, not fully resolved, 4 H, SiC*H*$_2$C, D1 and D2), 1.03–1.32 (m, 6 H, NCC*H*$_2$C*H*$_2$, D1/D2), 1.33–1.71 (m, 6 H, NCC*H*$_2$C*H*$_2$, D1/D2), 1.86–2.25 (m, 4 H, NC*H*$_2$CC, D1/D2), 2.31, 2.35 (AB system, $^2J_{AB}$ = 14.90 Hz, 2 H, SiC*H*$_2$N, D1/D2), 2.58, 2.67 (AB system, $^2J_{AB}$ = 14.90 Hz, 2 H, SiC*H*$_2$N, D2/D1), 2.72–3.09, 3.10–3.54 (m, 2 H each; NC*H*$_2$CC, D1/D2), 5.94 (s, 4 H, C*H*CO$_2$ H), 7.03–7.52 (m, 25 H, Ar*H*), 8.02–8.18 (m, 5 H, Ar*H*) ppm. The N*H* and CO$_2$*H* signals were not clearly localized. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = –3.67, –3.66 (1 C each, NCSi*C*H$_3$, D1 and D2), 19.79, 19.84 [3 C each, C(*C*H$_3$)$_3$, D1 and D2], 21.44, 21.46 (1 C each, NCC*C*H$_2$, D1 and D2), 22.46, 22.50 (2 C each, NC*C*H$_2$C, D1 and D2), 29.87, 29.96 (1 C each, Si*C*H$_2$C, D1 and D2), 30.98, 31.04 [1 C each, *C*(CH$_3$)$_3$, D1 and D2], 47.7 (2 C, Si*C*H$_2$N, D1 and D2), 55.8, 58.0 (2 C each, N*C*H$_2$CC, D1 and D2), 73.8 (4 C, *C*HCO$_2$ H, D1 and D2), 127.9 (4 C, C^m, C_6H_5Si, D1 and D2), 128.1 (4 C, C^p, $C_6H_5CO_2C$, D1 and D2), 129.51, 129.54 (1C each, C^p, C_6H_5Si, D1 and D2), 130.1 (8 C, C^o, $C_6H_5CO_2C$, D1 and D2), 130.7 (2 C, C^i, C_6H_5Si, D1 and D2), 132.3 (8 C, C^m, $C_6H_5CO_2C$, D1 and D2), 133.72, 133.75 (2 C each, C^o, C_6H_5Si, D1 and D2), 136.46, 136.61 (2 C each, C^i, $C_6H_5CO_2C$, D1 and D2), 165.7 (4 C, $C_6H_5CO_2C$, D1 and D2), 171.4 (4 C, *C*O$_2$ H, D1 and D2) ppm. $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ = –8.63, –8.61 (1 Si each, NC*Si*, D1 and D2) ppm.

2C) *rac*-7 with (*R*)-Mandelic Acid: ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.49, 0.50 (s, 3 H each; SiC*H*$_3$, D1 and D2), 1.02–1.13 (m, 2 H, NCCC*H*$_2$, D1/D2), 1.38–1.53 (m, 6 H, NCC*H*$_2$C*H*$_2$, D1/D2), 1.54–1.66 (m, 4 H, NCC*H*$_2$C, D1/D2), 2.24–2.45 (m, 4 H, NC*H*$_2$CC, D1/D2), 2.25–2.52 (m, 4 H, SC*H*$_2$Si, D1 and D2), 2.70, 2.73 (AB system,$^2J_{AB}$ = 3.24 Hz, 2 H, SiC*H*$_2$N, D1 and D2), 2.79, 2.82 (AB system,$^2J_{AB}$ = 3.71 Hz, 2 H, SiC*H*$_2$N, D2 and D1), 3.16–3.25, 3.27–3.35 (m, 2 H each; NC*H*$_2$CC, D1/D2), 5.03 (s, 2 H, C*H*OH, D1 and D2), 7.20–7.53 (m, 30 H, Ar*H*) ppm. The N*H*, O*H* signals were not clearly localized. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = –5.22, –5.18 (1 C each, NCSi*C*H$_3$, D1 and D2), 15.1, 15.7 (1 C each, Si*C*H$_2$S, D1 and D2), 21.18, 21.22 (1 C each, NCC*C*H$_2$, D1 and D2), 22.5 (4 C, NC*C*H$_2$C, D1 and D2), 46.7, 46.8 (1 C each, Si*C*H$_2$N, D1 and D2), 56.4 (1 C), 56.6 (2 C), 56.8 (1 C, N*C*H$_2$CC, D1 and D2), 73.2 (2 C, *C*HOH, D1 and D2), 126.6 (4 C, C^m, $C_6H_5CHOHCO_2$, D1 and D2), 127.8 (2 C, C^p, $C_6H_5CHOHCO_2$, D1 and D2), 128.2 (4 C, C^o, $C_6H_5CHOHCO_2$, D1 and D2), 128.35 (4 C, C^m, C_6H_5Si, D1 and D2), 128.44 (4 C, C^m, C_6H_5S, D1 and D2), 128.84, 128.85 (1 C each, C^p, C_6H_5Si, D1 and D2), 130.35, 130.37 (2 C each, C^o, C_6H_5Si, D1 and D2), 132.96, 132.97 (1 C each, C^i, C_6H_5Si, D1 and D2), 133.9 (2 C, C^p, C_6H_5S, D1 and D2), 134.4 (4 C, C^o, C_6H_5S, D1 and D2), 138.27, 138.28 (1 C each, C^i, C_6H_5S, D1 and D2), 139.6 (2 C, C^i, C_6H_5CHOH, D1 and D2), 176.7 (2 C, *C*OO, D1 and D2) ppm. $^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$): δ = –7.93, (2 Si, NC*Si*, D1 and D2) ppm.

General Specification for the Reaction of Enantiomerically Pure 2 with (Halomethyl)trimethylsilanes, Neopentyl Halides and (Chloromethyl)phenyl Sulfide: (*R*)-**1** was added to lithium (2 equiv.) in thf and cooled to –78 °C at the first occurrence of color change. After a reaction time of 8 h, the dark solution of lithiosilane **2** was separated into three parts and added at –78 °C to the respective halo electrophile (RCl, RBr, RI; 2.2 equiv.) in thf (2 mL). Afterwards, the solution was warmed to room temperature and all volatiles were removed in vacuo. The residue was suspended in a minimum amount of *n*-pentane and separated from all salts. The mixtures of the products were investigated with GC/MS and NMR spectroscopy without further purification. The following Table 7 includes explicit information concerning the amounts of involved reactants and volume of solvents.

Table 7. Reaction of enantiomerically pure **2** with (halomethyl)trimethylsilanes, neopentyl halides and (chloromethyl)phenyl sulfide: amounts of involved reactants and volume of solvents; n.i.: not investigated.

	m (*R*)-**1** [mg, mmol]	*m* (Li) [mg, mmol]	*V* (thf) [mL]	*m* (RCl) [mg, mmol]	*m* (RBr) [mg, mmol]	*m* (RI) [mg, mmol]
Me_3SiCH_2	1.00, 2.41	33.5, 4.82	4	217, .77	295, .77	378, .77
Me_3CCH_2	1.07, 2.57	35.7, 5.14	4	201, .89	285, .89	373, .89
$PhSCH_2$	0.36, 0.87	12.1, 1.74	2	304, .89	n.i.	n.i.

The analytical data are in agreement with those given above.

Synthesis of *rac*-20 and (*R*)-20

The synthesis of *rac*-**20** and (*R*)-**20** used for the subsequent, selective cleavage of the Si–C bond has been carried out according to the literature.[12e] All spectroscopic data can be found in this reference. Yet, as the ^1H NMR spectroscopic data of **20** are of crucial necessity for the determination of the enantiomeric ratio in the reaction of enantiomerically pure **21** with halobenzenes, these data are listed below.

***rac*-21:** ^1H NMR (300.1 MHz, C_6D_6): δ = 0.28 [s, 9 H, Si(C*H*$_3$)$_3$], 0.54 (s, 3 H, SiC*H*$_3$), 1.30–1.40 (m, 2 H, NCCC*H*$_2$), 1.50–1.62 (m, 4 H, NCC*H*$_2$C), 2.35–2.45 (m, 4 H, NC*H*$_2$CC), 2.29, 2.51 (AB system, $^2J_{AB}$ = 14.4 Hz, 2 H, SiC*H*$_2$N), 7.25–7.40 (m, 3 H, Ar*H*), 7.45–7.55 (m, 2 H, Ar*H*) ppm.

***rac*-21 with Three Equivalents of (*R*)-Mandelic Acid:** ^1H NMR (300.1 MHz, C_6D_6): δ = 0.20 [s, 9 H, Si(C*H*$_3$)$_3$, D2], 0.21 [s, 9 H, Si(C*H*$_3$)$_3$, D1], 0.47 (s, 3 H, SiC*H*$_3$, D1), 0.53 (s, 3 H, SiC*H*$_3$, D2), 0.90–1.15 (m, 2 H, NCCC*H*$_2$, D1/D2), 1.30–1.80 (m, 10 H, NCC*H*$_2$C*H*$_2$, D1 and D2), 2.10–2.50 (m, 4 H, NC*H*$_2$CC, D1 and D2), 2.40, 3.02 (AB system, $^2J_{AB}$ = 14.6 Hz, 4 H, SiC*H*$_2$N, D1 and D2), 3.05–3.60 (m, 4 H, NC*H*$_2$CC, D1 and D2), 5.48 (s, 2 H, C*H*OH, D1 and D2), 7.20–7.50 (m, 20 H, Ar*H*) ppm. The O*H* and N*H* signals were not clearly localized.

Reaction of Enantiomerically Pure 21 with Halobenzenes: (*R*)-**20** (0.25 g, 0.86 mmol) was added to a suspension of lithium (11.9 mg, 1.72 mmol) in thf (2 mL) and cooled to –50 °C at the first occurrence of color change. After 6.5 h, the dark solution of lithiosilane **21** was separated into three parts and added at –78 °C to i) chlorobenzene (70.8 mg, 0.63 mmol), ii) bromobenzene (98.7 mg, 0.63 mmol) and iii) iodobenzene (128 mg,0.63 mmol) in of thf (2 mL). The solution was warmed to room temperature and all volatiles were removed in vacuo. The residue was suspended in a

minimum amount of *n*-pentane and separated from all salts. The obtained product mixtures were investigated with GC/MS and NMR spectroscopy without further purification. The analytical data comply with those given above.

Determination of the Product Composition: The product compositions of all described reactions have been determined through a combination of GC/MS and NMR spectroscopic analysis. The GC/MS measurements were used to determine the various products, whereas product ratios were determined by the integration of relevant groups in the ^{1}H NMR spectra.

Computational Details: All calculations were done without symmetry restrictions. Starting coordinates were obtained with Chem3-DUltra 10.0. Optimization and additional harmonic vibrational frequency analyses (to establish the nature of stationary points on the potential energy surface) were performed with the software package Gaussian 03 (rev. E.01) on the B3LYP/6-31+G(d) level.[35] The stationary points were energy optimized in thf solution (ε = 7.58 for thf) by means of the self-consistent reaction field (SCRF) method. The energies for the structures obtained were calculated with the polarizable conductor calculation model (CPCM). The calculated stationary points exhibited exactly one imaginary frequency in the direction of the expected reaction coordinate in each case. The total (SCF) and zero-point energies (ZPE) of all systems can be found in Table 8. All coordinates of the investigated systems are available in the Supporting Information.

Table 8. Total (SCF) and zero-point energies (ZPE) of the calculated model systems.

Optimized system	SCF [Hartree]	ZPE [Hartree]
S_N2-Cl	–1082.168985	–1082.095785
ate-Cl	–1082.155393	–1082.083454
S_N2-Br	–3193.696841	–3193.623446
ate-Br	–3193.697703	–3193.625500
TS-PhCl-ate	–983.197581	–983.087307
TS-PhCl-Mei	–983.187544	–983.077039
TS-PhBr-ate	–3094.745311	–3094.634502
TS-PhBr-Mei	–3094.719164	–3094.609352

Supporting Information (see footnote on the first page of this article): Extracts of relevant NMR spectra, computational data.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support. Furthermore we acknowledge Wacker Chemie AG and Chemetall GmbH for providing chemicals. C. D. thanks the Studienstiftung des deutschen Volkes for a doctoral scholarship. S. O. B. thanks the Fonds der chemischen Industrie for an undergraduate scholarship.

[1] For some general articles and reviews concerning organolithium compounds, see: a) D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2282–2316; b) P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acc. Chem. Res.* **1996**, *29*, 552–556; c) M. C. Whisler, S. MacNeil, V. Snieckus, P. Beak, *Angew. Chem.* **2004**, *116*, 2256; *Angew. Chem. Int. Ed.* **2004**, *43*, 2206–2225; d) T. Stey, D. Stalke, in: *The Chemistry of Organolithium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, Chichester, U.K., **2004**, vol. 1, pp. 47–120; e) V. H. Gessner, C. Däschlein, C. Strohmann, *Chem. Eur. J.* **2009**, *15*, 3320–3334.

[2] For some of the countless articles including such trapping reactions, see: a) C. Strohmann, V. H. Gessner, *Angew. Chem.* **2007**, *119*, 8429–8432; *Angew. Chem. Int. Ed.* **2007**, *46*, 8281–8284; b) S. T. Kerrick, P. Beak, *J. Am. Chem. Soc.* **1991**, *113*, 9709–9710; c) D. Hoppe, F. Hintze, P. Tebben, *Angew. Chem.* **1990**, *102*, 1457–1459; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1422–1424; d) A. Hameau, F. Guyon, M. Knorr, C. Däschlein, C. Strohmann, N. Avarvari, *Dalton Trans.* **2008**, 4866; e) M. J. McGrath, J. L. Bilke, P. O'Brien, *Chem. Commun.* **2006**, 2607–2609; f) J.-C. Kizirian, *Chem. Rev.* **2008**, *108*, 140–205; g) A. Basu, S. Thayumanavan, *Angew. Chem.* **2002**, *114*, 740–763; *Angew. Chem. Int. Ed.* **2002**, *41*, 716–738.

[3] There are three general methods for the stabilization of a lithiated carbon center: i) introduction of a strongly electronegative substituent, ii) introduction of a coordinating side arm, and iii) introduction of an organosulfur substituent in the α-position to the negative charge; for a current example dealing with these three effects, see: H. Ott, C. Däschlein, D. Leusser, D. Schildbach, T. Seibel, D. Stalke, C. Strohmann, *J. Am. Chem. Soc.* **2008**, *130*, 11901–11911.

[4] For some examples concerning the introduction of a strongly electronegative substituent for the stabilization of a lithiated carbon center in reactions with halo electrophiles, see: a) W. C. Still, C. Sreekumar, *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202; b) H. A. Bent, *Chem. Rev.* **1961**, *61*, 275–311.

[5] For some examples concerning the introduction of a coordinating side arm for the stabilization of a lithiated carbon center in reactions with halo electrophiles, see: a) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1–21; b) T. H. Chan, P. J. Pellon, *J. Am. Chem. Soc.* **1989**, *111*, 8737–8738; c) T. H. Chan, S. Lamonthe, *Tetrahedron Lett.* **1991**, *32*, 1847–1850; d) C. Strohmann, K. Lehmen, K. Wild, D. Schildbach, *Organometallics* **2002**, *21*, 3079–3081; e) C. Strohmann, B. C. Abele, K. Lehmen, F. Villafane, L. Sierra, S. Martín-Barrios, D. Schildbach, *J. Organomet. Chem.* **2002**, *661*, 149–158; f) C. Strohmann, B. C. Abele, K. Lehmen, D. Schildbach, *Angew. Chem.* **2005**, *117*, 3196-3199; *Angew. Chem. Int. Ed.* **2005**, *44*, 3136–3139; g) C. Däschlein, V. H. Gessner, C. Strohmann, *Chem. Eur. J.* **2010**, *16*, 4048–4062.

[6] For some examples concerning the introduction of an organosulfur substituent to the α-position to the negative charge for the stabilization of a lithiated carbon center in reactions with halo electrophiles, see: a) R. K. Dress, T. Rölle, R. W. Hoffmann, *Chem. Ber.* **1995**, *128*, 673–677; b) A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434–1445; c) U. Salzner, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 10231–10236; d) J. A. Dobado, H. Martínez-Garzía, J. M. Molina, M. R. Sundberg, *J. Am. Chem. Soc.* **1998**, *120*, 8461–8471; e) T. Stefan, R. Janoschek, *J. Mol. Model.* **2000**, *6*, 282–288.

[7] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262–286; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272–295.

[8] For studies on silyl anions, see: a) J. B. Lambert, M. Urdaneta-Perez, H.-N. Sun, *J. Chem. Soc., Chem. Commun.* **1976**, 806–807; b) J. B. Lambert, M. Urdaneta-Perez, *J. Am. Chem. Soc.* **1978**, *100*, 157–162; c) M. Flock, C. Marschner, *Chem. Eur. J.* **2002**, *8*, 1024–1030; d) M. Flock, C. Marschner, *Chem. Eur. J.* **2005**, *11*, 4635–4642.

[9] For some selected pioneer works on functionalized lithiosilanes, see: a) L. H. Sommer, J. E. Lyons, H. Fujimoto, *J. Am. Chem. Soc.* **1969**, *91*, 7051–7061; b) E. Colomer, R. J. P. Corriu, *J. Chem. Soc., Chem. Commun.* **1976**, 176–177.

[10] For selected works on lithiosilanes, see: a) C. Strohmann, M. Bindl, V. C. Vraaß, J. Hörnig, *Angew. Chem.* **2004**, *116*, 1029–1032; *Angew. Chem. Int. Ed.* **2004**, *43*, 1011–1014; b) D. Auer, M. Kaupp, C. Strohmann, *Organometallics* **2004**, *23*, 3647–3655; c) M. Nanjo, M. Masayuki, Y. Ushida, Y. Awamura, K. Mochida, *Tetrahedron Lett.* **2005**, *46*, 8945–8947; d) D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Botoshansky, B. Tumanskii, Y. Apeloig, *Angew. Chem.* **2005**, *117*, 749–753; *Angew. Chem. Int. Ed.* **2005**, *44*, 739–743; e) T. I. Kückmann, F. Dornhaus, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Eur. J. Inorg. Chem.* **2007**, 1989–2003; f) D. Scheschke-

witz, *Angew. Chem.* **2004**, *116*, 3025–3028; *Angew. Chem. Int. Ed.* **2004**, *43*, 2965–2967; g) H.-W. Lerner, *Coord. Chem. Rev.* **2005**, *249*, 781–798; h) H.-W. Lerner, S. Scholz, M. Bolte, M. Wagner, *Z. Anorg. Allg. Chem.* **2004**, *630*, 443–451.

[11] For some of our studies on lithiosilanes, see: a) C. Strohmann, C. Däschlein, D. Auer, *J. Am. Chem. Soc.* **2006**, *128*, 704–705; b) C. Strohmann, C. Däschlein, *Chem. Commun.* **2008**, 2791–2793; c) C. Däschlein, V. H. Gessner, C. Strohmann, *Acta Crystallogr., Sect. E* **2008**, *64*, o1950; d) C. Däschlein, C. Strohmann, *Eur. J. Inorg. Chem.* **2009**, 43–52.

[12] To date, six enantiomerically enriched or enantiomerically pure lithiosilanes can be found in the literature: a) L. H. Sommer, R. Mason, *J. Am. Chem. Soc.* **1965**, *87*, 1619–1620; b) E. Colomer, R. J. P. Corriu, *J. Organomet. Chem.* **1977**, *133*, 159–168; c) M. Omote, T. Tokita, Y. Shimizu, I. Imae, E. Shirakawa, Y. Kawakami, *J. Organomet. Chem.* **2000**, *611*, 20–25; d) C. Strohmann, J. Hörnig, D. Auer, *Chem. Commun.* **2002**, 766–767; e) C. Strohmann, C. Däschlein, M. Kellert, D. Auer, *Angew. Chem.* **2007**, *119*, 4864–4866; *Angew. Chem. Int. Ed.* **2007**, *46*, 4780–4782; f) M. Oestreich, G. Auer, M. Keller, *Eur. J. Org. Chem.* **2005**, 184–195.

[13] Recently, we have reported new details about the reactivity of disilanes and elemental lithium for the formation of lithioisilanes; this manuscript also includes the synthesis of the seventh enantiomerically pure lithiosilane, although not isolated in pure form; for details see: C. Däschlein, C. Strohmann, *Dalton Trans.* **2010**, *39*, 2062–2069.

[14] For another recent example, see: C. Strohmann, C. Däschlein, *Organometallics* **2008**, *27*, 2499–2504.

[15] For some examples, see: a) A. Sekiguchi, M. Nanjo, C. Cabuto, H. Sakurai, *Organometallics* **1995**, *14*, 2630–2632; b) I. Fleming, R. S. Robert, S. C. Smith, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1209–1214.

[16] For selected examples concerning an S_N2 mechanism in the reaction with other nucleophiles: Y. Fang, Y. Gao, P. Ryberg, J. Eriksson, M. Kolodziejska-Huben, A. Dybala-Defratyka, S. Madhavan, R. Danielsson, P. Paneth, O. Matsson, K. C. Westaway, *Chem. Eur. J.* **2003**, *9*, 2696–2709, and references cited therein.

[17] Quantum chemical studies of Boche et al. on methyl ate-complexes suggested that ate complexes are pivotal intermediates in halogen–lithium exchange reactions with alkyllithium compounds: G. Boche, M. Schimeczek, J. Cioslowski, P. Piskorz, *Eur. J. Org. Chem.* **1998**, 1851–1860.

[18] For selected examples concerning discussions of the mechanism of halide–lithium exchange reactions, see: a) R. W. Hoffmann, M. Brönstrup, M. Müller, *Org. Lett.* **2003**, *5*, 313–316; b) M. Müller, M. Brönstrup, O. Knopff, V. Schulze, R. W. Hoffmann, *Organometallics* **2003**, *22*, 2931–2937; c) V. P. W. Böhm, V. Schulze, M. Brönstrup, M. Müller, R. W. Hoffmann, *Organometallics* **2003**, *22*, 2925–2930; d) K. B. Wiberg, S. Sklenak, W. F. Bailey, *J. Org. Chem.* **2000**, *65*, 2014–2021; e) P. Beak, D. J. Allen, *J. Am. Chem. Soc.* **1992**, *114*, 3420–3425; f) W. F. Bailey, J. J. Patricia, *J. Organomet. Chem.* **1988**, *352*, 1–46; g) H. Gilman, G. D. Lichtenwalter, *J. Am. Chem. Soc.* **1958**, *80*, 608–611; h) K.-W. Lee, J. S. Filippo Jr, *Organometallics* **1983**, *2*, 906–908; i) J. S. Filippo Jr, J. Silbermann, *J. Am. Chem. Soc.* **1982**, *104*, 2831–2836, and references cited therein.

[19] The absolute configuration of lithiosilane (*S*)-**2** is not experimentally confirmed. Yet, although no enantiomerically pure lithiosilane could be isolated as single crystal for the determination of the absolute configuration until today, it is in general supposed, that the Si–Si bond cleavage proceeds under retention of configuration, e.g., see: K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1–58.

[20] Important remark: Although the synthesis of the lithiosilane starting with disilane (*R*)-**1** is supposed to proceed under retention of the stereoinformation, lithiosilane (*S*)-**2** has the (*S*)-configuration due to the change of the priority of the CIP nomenclature. This change of the priority of the CIP nomenclature has to be kept in mind in all of these transformations.

[21] G. T. Notte, J. L. Leighton, *J. Am. Chem. Soc.* **2008**, *130*, 6676–6677.

[22] S. Shirakawa, P. J. Lombardi, J. L. Leighton, *J. Am. Chem. Soc.* **2005**, *127*, 9974–9975.

[23] S. Shirakawa, R. Berger, J. L. Leighton, *J. Am. Chem. Soc.* **2005**, *127*, 2858–2859.

[24] For some other examples concerning the application of Si-chiral silanes, see: a) B. H. Lipshutz, N. Tanaka, B. R. Taft, C.-T. Lee, *Org. Lett.* **2006**, *8*, 1963–1966; b) B. Zhu, J. S. Panek, *Eur. J. Org. Chem.* **2001**, 1701–1714; c) S. Rendler, G. Auer, M. Oestreich, *Angew. Chem.* **2005**, *117*, 7793–7797; *Angew. Chem. Int. Ed.* **2005**, *44*, 7620–7624; d) S. E. Denmark, G. L. Beutner, *J. Am. Chem. Soc.* **2003**, *125*, 7800–7801; e) P. J. Stang, A. E. Learned, ***J. Org. Chem.*** **1989**, *54*, 1779–1981.

[25] The low temperature (–78 °C) in the synthesis of lithiosilane (*S*)-**2** is necessary to prevent the racemization process, which occurs at temperatures above –30 °C; for a detailed description, see: D. Auer, J. Hörnig, C. Strohmann, in: *Organosilicon Chemistry V: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, Germany, **2003**, pp. 167.

[26] The reaction of **2** and Me_3SiCl is known to proceed selectively under full preservation of the stereoinformation (retention) yielding the corresponding disilane. All relevant NMR spectroscopic data can be found in ref.[12e].

[27] In all cases, the product composition has been determined by GC/MS analysis whereas ^1H NMR spectroscopic studies have been used to determine the ratios between identified products.

[28] In case of the racemic disilane *rac*-**1**, the reaction time can be decreased due to the higher reaction temperature.

[29] Treatment of the corresponding racemic silane with (*R*)-mandelic or (2*R*,3*R*)-di-*O*-benzoyltartaric acid results in the formation of diastereomeric salts, which can be differentiated in the ^1H NMR spectroscopic studies. In all cases, the signal of at least one group of these diastereomers (e.g., one of the methyl groups) was separated fully in the spectrum and therefore independent integration of the different diastereomers was possible. These diastereomeric ratios comply with enantiomeric ratios.

[30] The formed compounds have been identified by GC/MS spectroscopy, their ratio has been determined by NMR spectroscopy.

[31] For some selected examples, see: a) C. Strohmann, S. Lüdtke, E. Wack, *Chem. Ber.* **1996**, *129*, 799–805; b) C. Strohmann, S. Lüdtke, O. Ulbrich, *Organometallics* **2000**, *19*, 4223–4227.

[32] There is one slight exception to this trend: as displayed in Table 4, Me_3SiCH_2Cl has a slightly higher *er* value than $PhCH_2Cl$.

[33] Currently, we are performing quantum chemical calculations on the reactivity of lithiumorganyls and cloro-/bromosilanes; all results show that the negatively charged carbanionic center of the carbon attacks selectively under inversion of configuration at silicon; publication in preparation.

[34] For some recent theoretical studies on hypervalent (pentacoordinate)silicon atoms in substitution reactions, see: a) S. C. A. H. Pierrefixe, C. F. Guerra, F. M. Bickelhaupt, *Chem. Eur. J.* **2008**, *14*, 819–828; b) M. A. van Bochove, F. M. Bickelhaupt, *Eur. J. Org. Chem.* **2008**, 649–654; c) A. P. Bento, F. M. Bickelhaupt, *J. Org. Chem.* **2007**, *72*, 2201–2207.

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dap-

prich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, rev. E.01, Gaussian, Inc., Wallingford CT, **2004**.

[36] P. Flükinger, H. P. Lüthi, S. Portmann, J. Weber, *Molekel 4.3*, Swiss Center for Scientific Computing, Manno, Switzerland, **2000**–**2002**.

[37] J. Hörnig, Dissertation, University of Würzburg, **2004**.

[38] For examples, see: a) T. Linker, M. Schmittel, *Radikale und Radikalionen in der Organischen Synthese*, Wiley-VCH, Weinheim, Germany, **1998**, pp. 129–133; b) P. Dowd, W. Zhang, *Chem. Rev.* **1993**, *93*, 2091–2115; c) A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, A. K. Serelis, *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.

[39] P. J. Krusic, P. J. Fagan, J. S. Filippo Jr, *J. Am. Chem. Soc.* **1977**, *99*, 250–252.

[40] Contrary to some textbook opinions, silyl radicals should – like "silyl anions" – have a stable configuration at least at low temperatures. These low temperatures were present in the performed reactions.

[41] The higher reaction temperature (–50 °C) in the synthesis of lithiosilane **21** (in comparison with lithiosilane **2**) is necessary due to the decreased reactivity of the Si–C bond against elemental lithium in (*R*)-**20**.

[42] The reaction of **21** and $Me_3SiSiMe_2Cl$ is known to proceed selectively under full preservation of the stereoinformation (retention) yielding the corresponding tetrasilane, see Scheme 8.

[43] Under these conditions, the resonances of the methyl groups of the SiMe moiety could be integrated separately in the ^1H NMR spectra.

[44] The absolute configuration of **20** can be determined through the corresponding hydrochloride, see ref.[12e]

Received: August 3, 2010
Published Online: February 18, 2011

