The competition between Si–Si and Si–C cleavage in functionalised oligosilanes: their reactivity with elemental lithium†

Christian Däschlein and Carsten Strohmann*

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The reaction of aryl-substituted disilanes with elemental lithium is a common method for the preparation of lithiosilanes and the subsequent synthesis of functionalised oligosilanes, especially of enantiomerically pure compounds. A series of alkyl- and arylsubstituted di- and trisilanes has been investigated with respect to their reactivity against elemental lithium. Thereby, depending on the substituents, silicon–silicon bond cleavage of the central Si–Si unit and/or silicon–carbon bond cleavage to arenes are observed. Quantum chemical studies provide a deeper insight into the ongoing processes. The reactive centre can be estimated by both, bond elongation after electron transfer and frontier orbital interactions (π-bonding and σ-antibonding part). Aromatic substituents at the silicon atoms proved to be necessary for the processing of any cleavage reaction in the studied systems by stabilising the radical anion after electron transfer at the corresponding di- or trisilane. Yet, selective cleavage reactions do not depend on the number of arenes.

Introduction

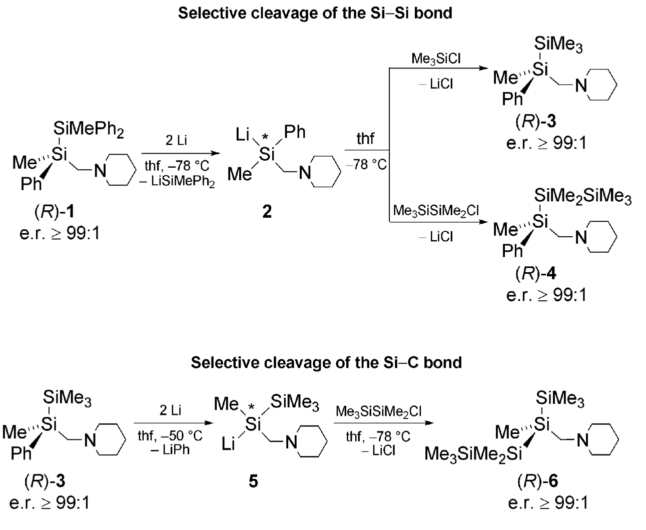
Functionalised lithiosilanes[1,2] are versatile reagents in organic and organometallic chemistry, *e.g.* for the nucleophilic introduction of protecting groups, synthesis of silyl substituted transition metal complexes or silicon based polymers.[3,4] Besides the synthesis of lithiosilanes *via* the reaction of chlorosilanes with elemental lithium,[5] their preparation *via* selective silicon–silicon bond cleavage with lithium has become the method of choice as no disrupting lithium chloride is formed.[2c,3b,3c,6] According to a general formulation of the reactivity of simple disilanes by Tamao and Kawachi,[3c] systems possessing at least one aromatic substituent at silicon can be cleaved selectively at their central Si–Si unit using lithium in polar solvents such as thf. Contrary to solely alkyl substituted disilanes, they referred the electron transfer (ET) from the metal to the disilane (the first step of the cleavage reaction) and therefore the following cleavage of the Si–Si bond in aryl substituted systems to the decrease of the energy of the lowest unoccupied molecular orbital (LUMO). Nevertheless, this has mainly been studied for simple and often symmetric disilanes whereas investigations concerning the reactivity of more complex systems are rare.

As part of our studies on aminomethyl and amino substituted silanes,[4b–4f,7] we herein report the synthesis of a series of functionalised di- and trisilanes and their reactivity against elemental lithium. A combination of experimental and theoretical studies has been used to elucidate the preferred centre of reactivity and the reasons for the observed competing Si–Si and Si–C cleavage reactions.

Results and discussion

Experimental studies

In 2002 and 2007 we reported the selective synthesis of the enantiomerically pure lithiosilanes **2** and **5** *via* selective cleavage of the Si–Si unit (for the synthesis of **2**)[4c] and selective cleavage of the Si–C unit (for the synthesis of **5**),[4e] respectively, in the functionalised disilanes (*R*)-**1** and (*R*)-**3** (see Scheme 1).[8,9]



Scheme 1 Synthesis of the enantiomerically pure lithiosilanes **2** and **5** *via* selective Si–Si (upper row) and Si–C (lower row) cleavage in the disilanes (*R*)-**1** and (*R*)-**3**.[4c,4e]

Most recently, we realised that the related trisilane (*R*)-**4** yields a product mixture consisting of the trapping products of a Si–Si cleavage and of a Si–C cleavage to the aromatic substituent (see Scheme 2). Thus, the reactivity of (*R*)-**4** against lithium represents a transition from the selective Si–Si in **1** to the Si–C

Anorganische Chemie, Technische Universität Dortmund, Otto-Hahn-Straße 6, 44227 Dortmund, Germany. E-mail: mail@carsten-strohmann.de; Fax: (+) 49-231-755-7062; Tel: (+) 49-231-755-3807

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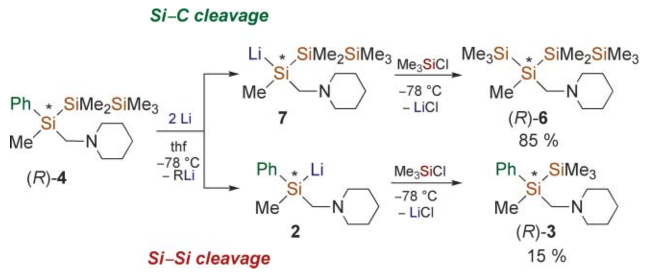
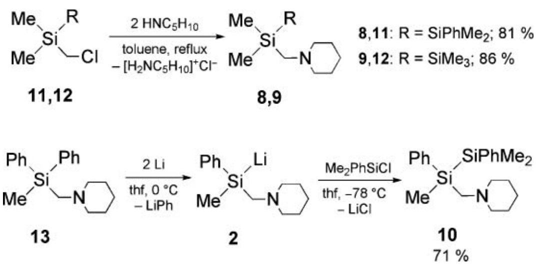


Scheme 2 Reaction of the enantiomerically pure trisilane (*R*)-**4** with elemental lithium.

cleavage in **3**. Thereby, the thermodynamically stronger Si–C bond is preferential cleaved at −78 °C.[9,10]

Based on these results, we wondered about the cause for the different reactivity of the three reactants (*R*)-**1**, (*R*)-**3** and (*R*)-**4**, and if we can estimate the observed reactive centre in functionalised oligosilanes in general.

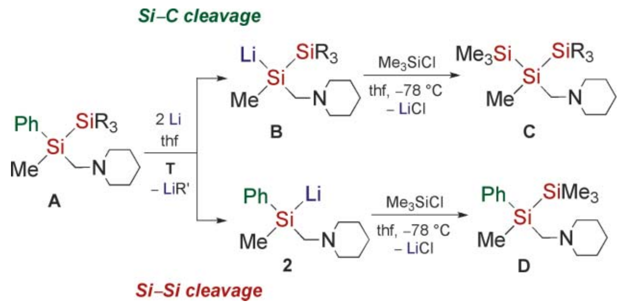
For a systematic study of the reactivity of di- and trisilanes against elemental lithium, we first synthesised – in addition to the already known compounds (*R*)-**1**,[4c] (*R*)-**3**[4e] and (*R*)-**4**[4b] – the three disilanes **8**, **9** and **10** (see Scheme 3).



Scheme 3 Synthesis of the disilanes **8**, **9** and **10**.

8 and **9** have been synthesised according to the previously reported method for **1**[4c] starting with the (chloromethyl) substituted disilanes **11** (for **8**) and **12** (for **9**) *via* an amination reaction with a twofold excess of piperidine in toluene. **10** was synthesised *via* selective cleavage of the Si–C bond with elemental lithium in diphenylmethyl(piperidinomethyl)silane (**13**) and subsequent trapping reaction of the formed lithiosilane with dimethylphenylchlorosilane.[11] The newly synthesised disilanes have been chosen as additional systems for our investigations, as this series of functionalised silanes feature a gradual decrease of the number of aromatic substituents at silicon atoms. Starting with the triphenyl substituted disilane **1** to the solely alkyl substituted compound **9**, we were now able to investigate the impact of the aromatic substituents on the cleavage reactions. It has to be noted that silane **10** has been synthesised in its racemic form, as the stereo information is not of relevance for these reactivity studies.

To examine the reactivity of the shown compounds against elemental lithium, each silane was added to lithium (granals) in thf.[12] After a reaction time of 6 h at 0 °C,[13] each solution was trapped with a twofold excess of Me_3SiCl. In each case, we expected a silicon–silicon and/or a silicon–carbon bond cleavage to the aromatic substituent of the central silicon (see Scheme 4).



Scheme 4 Expected reactions (Si–Si *vs.* Si–C cleavage) in functionalised di- and trisilanes; R = Me or Ph; R′ = Ph or SiR_3; *T* = temperature.

Afterwards, the product mixtures were analysed *via* GC/MS analysis and NMR spectroscopy. Based on the obtained results the investigated silanes can be separated into four different categories: (i) systems reacting under selective Si–Si cleavage, (ii) systems reacting under selective Si–C cleavage, (iii) systems resulting in a mixture of both possible reactions and (iv) systems without any reaction. Fig. 1 and Table 1 summarise the described reactions

Table 1 Experimentally investigated silanes, reaction temperatures and observed reactions

System	Reaction temperature	Observed reaction	Ratio Si–Si : Si–C cleavage
1	−78 °C/0 °C[a]	Selective Si–Si cleavage	100 : 0
8	0 °C	Selective Si–Si cleavage	100 : 0
4	−78 °C[b]	Mixture of Si–Si and Si–C cleavage	15 : 85
10	0 °C[b]	Mixture of Si–Si and Si–C cleavage	58 : 42
3	−50 °C/0 °C[a]	Selective Si–C cleavage	0 : 100
9	0 °C	No reaction	—

[a] Both reaction temperatures are known in literature. [b] Detailed investigations follow below.

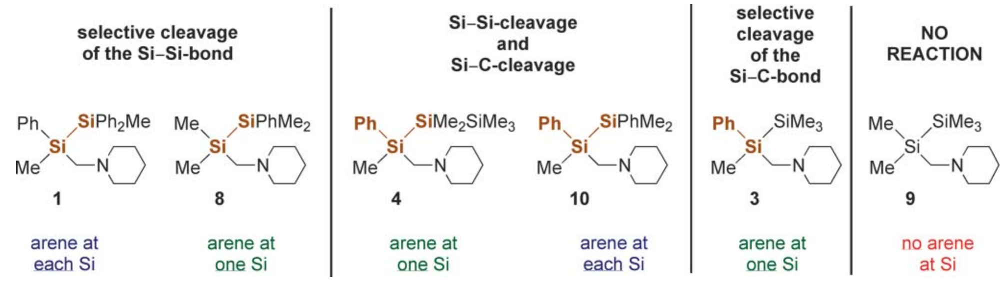


Fig. 1 Experimentally investigated silanes and their experimentally determined reactivity against elemental lithium [the reactive bond(s) is(are) labelled in dark red].

(for Fig. 1: reactive centres are indicated in dark red; blue, green and red refers to the number of aromatic substituents in each compound).

The obtained results allow the following conclusions: (i) there is no distinct trend between the number of aromatic substituents at the silicon atoms and the observed reactive centre; (ii) yet, the aromatic substituents are obviously necessary for the procedure of any reaction (no transformation takes place in case of the solely alkyl substituted disilane **9**). Most remarkably, silane **10** undergoes no selective cleavage of its Si–Si bond despite its phenyl substituent. Instead, a product mixture resulting from both possible reactions could be determined. Contrary, the mono phenyl substituted disilane **8** shows selective cleavage of the silicon–silicon bond, although it is strongly related to the disilane **3**, reacting under selective Si–C cleavage. Hence, albeit very useful for simple disilanes, the above mentioned postulate of Tamao and Kawachi[3c] obviously has to be modified for more complex systems.

Theoretical studies

To get a deeper insight into the experimentally observed reactivities of the silanes against elemental lithium, we performed quantum chemical calculations for all investigated molecules. The geometries of the stationary points were initially optimised by using density functional theory with the hybrid B3LYP functional and the 6-31+G(d) basis set.[14] Harmonic vibrational frequency analyses – to establish the nature of the global minima – were performed on the same level showing no imaginary frequencies. The starting structural parameters for the systems were taken from the X-ray data of (*S*)-**1**·HCl[7b] and (*R*)-**3**·HCl.[4e] All other compounds were constructed based thereon with *Chem3D*.

The cleavage of element–element bonds with lithium (alkali metals, respectively) is supposed to proceed *via* double electron transfer from the metal to the investigated system, creating a radical anion after the first ET before the second ET induces the bond cleavage.[3c,4b,15] Thus, each molecule was optimised both, as a neutral compound and as a radical anion. Possible interactions between the radical anion and the metal have not been considered in these calculations. According to the postulate of Tamao and Kawachi,[3c] additional aromatic substituents should result in a decrease of the energy of the LUMO. Thus, we first examined the energy of the frontier orbitals of the neutral systems as well as their HOMO–LUMO gap (LUMO = lowest unoccupied molecular orbital; HOMO = highest occupied molecular orbital; SOMO = single occupied molecular orbital). The results can be found in Table 2.

Both, HOMO and LUMO of all investigated silanes as well as the HOMO–LUMO gap have comparable energy. Similar values for HOMO and LUMO and the HOMO–LUMO gap have already been reported for other functionalised silanes.[16] Astonishingly, the lowest energy of the LUMO is not found for disilane **1** (selective Si–Si cleavage) – as expected – but for disilane **10**, which showed both possible reactions in the experiment. The highest value is observed for the solely alkyl substituted disilane **9**. Altogether, no clear tendency can be found for the energy of the frontier orbitals.

Table 2 HOMO and LUMO energies as well as the HOMO–LUMO gap of all optimised silanes

Optimised system	HOMO/a.u.	LUMO/a.u.	Gap/a.u.	Gap/eV
1	−0.21490	−0.02754	−0.18736	−5.10
8	−0.20960	−0.02343	−0.18617	−5.07
4	−0.21380	−0.02384	−0.18996	−5.17
10	−0.21331	−0.02962	−0.18369	−4.99
3	−0.21396	−0.02262	−0.19134	−5.21
9	−0.21774	−0.01371	−0.20403	−5.55

Table 3 Lengths of the Si–Si and Si–C bonds of all investigated silanes

Optimised system	Observed reaction	Bond length Si–Si/Å	Bond length Si–C_i/Å
1	Si–Si cleavage	2.388	1.896
1$^{\cdot-}$	Si–Si cleavage	2.442	1.874
8	Si–Si cleavage	2.378	—
8$^{\cdot-}$	Si–Si cleavage	2.380	—
4	Mixture	2.380	1.898
4$^{\cdot-}$	Mixture	2.413	1.865
10	Mixture	2.381	1.897
10$^{\cdot-}$	Mixture	2.415	1.869
3	Si–C cleavage	2.377	1.898
3$^{\cdot-}$	Si–C cleavage	2.389	1.872
9	None	2.377	—
9$^{\cdot-}$	None	2.376	—

“$^{\cdot-}$” indicates the corresponding radical anion.

How can the reactivity of these silanes against elemental lithium be understood? One common feature of all reactions is the fact, that the bond cleavage always takes place between the central, (piperidinomethyl) substituted silicon and one of its substituents (SiR_3 or Ph). In almost all cases, the electron transfer results in an elongation of the Si–Si bond. The highest change is found between disilane **1** and its radical anion (Δd = 0.054 Å) which undergoes selective cleavage of this bond. In fact, there is an almost continuous decrease of the bond elongation over the disilane **10** and the trisilane **4** (showing Si–Si and Si–C cleavage in the experiment) with values of 0.034 Å and 0.033 Å until only an elongation of 0.012 Å in the disilane **3** (which shows no Si–Si cleavage in the experiment anymore). Finally, silane **9** – without any reaction – actually shows a slight shortening of this bond of 0.001 Å. The only exception of this trend is disilane **8** (0.002 Å, Si–Si cleavage). Contrary, the Si–C distances show no clear tendency. Although the electron transfer does result in a shortened bond in all cases, the smallest bond shortening was observed in disilane **1** and not – as expected – in the trimethyl substituted system **3** showing the cleavage of this bond in the experiment (Si–C bond shortenings: **1**: 0.022 Å; **4**: 0.033 Å; **10**: 0.028 Å; **3**: 0.026 Å). Thus, although the change of the bond lengths is already indicating a difference between the investigated silanes, it can not be the only reason for the diverse reactivities. Table 3 summarises the described bond elongations and shortenings.

Recognising the frontier orbitals (HOMO, LUMO and SOMO) of all investigated silanes one similarity can be seen (see Fig. 2): the LUMO of all compounds are located with almost the same shape at the aromatic substituents, except of disilane **9** without any reaction. This observation confirms the statement of Tamao and Kawachi[3c] concerning the necessity of the arenes for a successful cleavage reaction. Obviously, an orbital of suitable energy and shape is required in the first step of the bond cleavage (the electron transfer), to stabilise the transferred electron and initiate the subsequent cleavage reaction. Although the frontier orbitals are in general comparable, some significant differences with respect

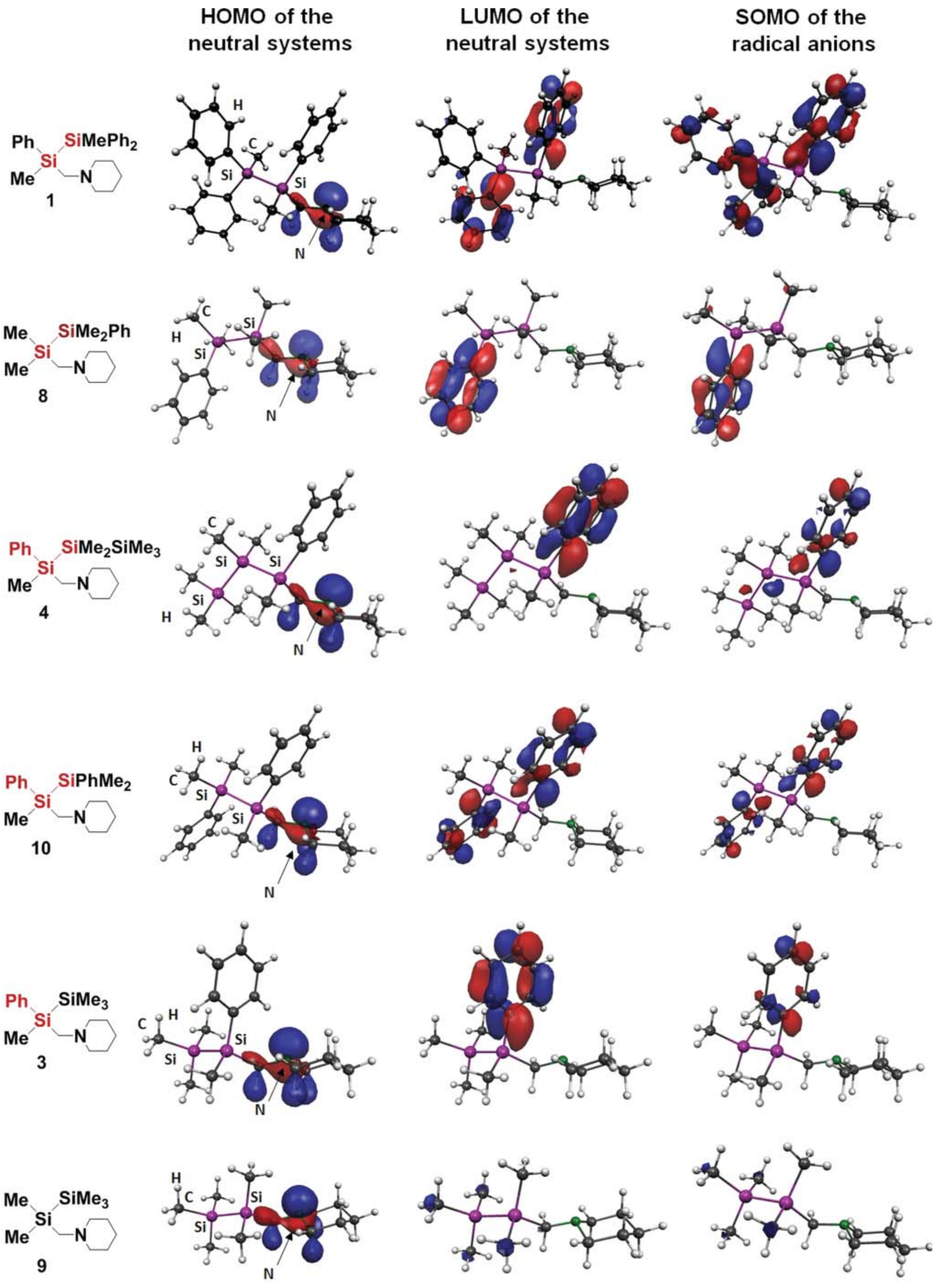


Fig. 2 HOMO (second from the left) and LUMO (second from the right) of the neutral systems as well as the SOMO (right) of the radical anions; *Molekel plots*;[17] threshold values: cutoff 0.04. In the schematic drawing (left), the reactive bond(s) are indicated in red.

to π-bonding and σ-antibonding parts of the relevant bonds can be found in all cases. The SOMO is almost exclusively located at the aromatic substituent. In disilane **1** with selective Si–Si bond cleavage as well as in **4** and **10** with partly Si–Si cleavage, a significant π-bonding part can be found between the silicon and the phenyl group (also present in **8**, but to the arene at the other silicon). This π-bonding part leads to the stabilising of the corresponding bond. Thereby, this π-bonding part is mostly pronounced in **1** where no cleavage of this bond was observed in the experiment. Together with the present σ-antibonding part (destabilising; most pronounced in disilane **1**) between the two silicon atoms, this is consistent with the experimental reactivity. This is confirmed by the trimethylsilyl substituted disilane **3** (selective Si–C cleavage): on the one hand, **3** exhibits no σ-antibonding part between the two silicon atoms and on the other hand, it shows the less distinct π-bonding part to the arene. None of these effects is visible in **9** (no reaction). Fig. 3 shows (simplified) the described orbital interactions.

Based on these observations, the reactivity of all compounds investigated can be understood:

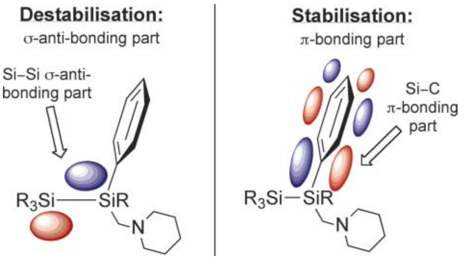


Fig. 3 (Strongly) Simplified ChemDraw picture showing destabilising σ-antibonding part between the two silicon atoms (left) and stabilising π-bonding part to the arene (right).

1 (selective cleavage of the Si–Si bond): the electron transfer results in the weakening of the silicon–silicon bond due to the bond elongation and the σ-antibonding part between both silicon atoms. The cleavage of the Si–C bond is not observed due to the significant π-bonding part.

3 (selective cleavage of the Si–C bond): although the electron transfer does also result in an elongated Si–Si bond, the SOMO doesn't possess any σ-antibonding part. Together with the weakest π-bonding part to the arene, the ET finally results in the cleavage of the most weakened bond, the Si–C bond.

4 and **10** (Si–Si as well as Si–C cleavage): the ET results in an elongation of the central Si–Si bond in both compounds weakening this bond, which is further amplified by a σ-antibonding part (although not as distinct as in **1**). Moreover, the π-bonding part to the arene (stabilising the bond to the phenyl group) is less pronounced compared to **1**. This finally results in the cleavage of both possible bonds. It should be noted, that the SOMO of **4** also possesses a σ-antibonding part between Si2 and Si3. Anyhow, as it is less pronounced than between Si1 and Si2, no competing cleavage between both Si–Si bonds does occur.

8 (selective cleavage of the Si–Si bond): the ET only results in a slight elongation of the Si–Si bond in disilane **8**, yet, no σ-antibonding part is effected. Contrary, the strong π-bonding part to the aromatic substituent obviously amplifies this bond so much, that no Si–C cleavage can occur. As a result, the thermodynamically weakest Si–Si bond is cleaved after the electron transfer.

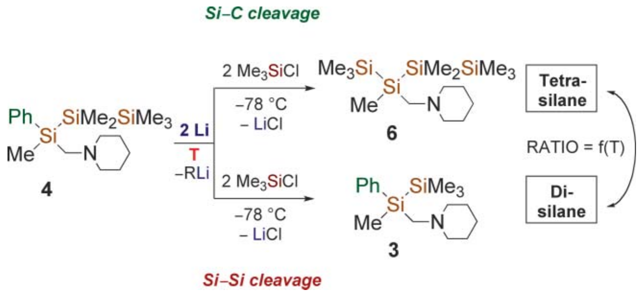
Temperature-dependence of the reactive centre in trisilane 4 and disilane 10 in the experiment

As described above, reactions of trisilane **4** as well as disilane **10** with elemental lithium lead to product mixtures of both possible cleavage reactions (Si–Si and Si–C) at the chosen temperature (−78 °C for **4**, 0 °C for **10**). Often, the strict control of temperature is the method of choice to distinguish between two possible reaction pathways. To investigate a possible influence of the chosen reaction temperature on the product composition of the cleavage reactions (see Scheme 4) of **4** and **10**, respectively, with elemental lithium, we investigated both reactions at different temperatures.

At first, **4** was treated as described with elemental lithium and subsequently trapped with Me_3SiCl (see Scheme 5; see also Scheme 2) at five different temperatures, starting with +45 °C (thf)[18] until ~ −90 °C (n-pentane/N_2).[19] The crude products were again investigated *via* GC/MS and NMR spectroscopy.

Table 4 Product distribution between the tetrasilane **6** (Si–C cleavage) and the disilane **3** (Si–Si cleavage), depending on the reaction temperature

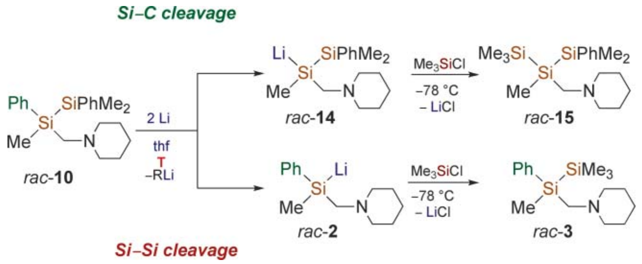
Entry	*T*/°C	Si–C cleavage (tetrasilane **6**)	Si–Si cleavage (disilane **3**)
1	+ 45	60	40
2	RT (~20)	68	32
3	−50	76	20
4	−78	85	15
5	~ −90	87	13



Scheme 5 Reaction of trisilane **4** with elemental lithium to tetrasilane **6** (Si–C cleavage) and disilane **3** (Si–Si cleavage); *T* = temperature.

Increasing the temperature from −90 °C to +45 °C resulted in an increase of the Si–Si bond cleavage, whereas low temperatures led to the preferred cleavage of the thermodynamically stronger Si–C bond (see Table 4). The ratio between **6** and **3** varies between 60 : 40 at +45 °C and a considerable preference of the tetrasilane **6** at −90 °C (87 : 13). A further decrease of the temperature is limited due to the melting point of thf and the difficulty to maintain the low temperature.

Afterwards, disilane **10** was reacted likewise with lithium for 6 h at three different temperatures (~15 °C, 0 °C and −78 °C) and subsequently trapped with two equivalents of Me_3SiCl (see Scheme 6). Finally, the crude products were investigated *via* GC/MS and NMR spectroscopy.



Scheme 6 Reaction of racemic disilane *rac*-**10** with elemental lithium to silanes *rac*-**15** (Si–C cleavage) and *rac*-**3** (Si–Si cleavage); *T* = temperature.

As anticipated, the product composition between Si–C cleavage (trisilane **15**) and Si–Si cleavage (disilane **3**) is also influenced by the reaction temperature (see Table 5). Yet, contrary to trisilane **4**, the weaker Si–Si bond is cleaved preferentially in disilane **10** at lower temperatures, what is in agreement with the chemical expectations. Nevertheless, this temperature dependency is less pronounced than in the trisilane **4**. Table 5 summarises the experimentally obtained ratios between both products.

Thus, simple variation of the temperature in the reaction of trisilane **4** and disilane **10** with elemental lithium, respectively, leads to a preference of one of both possible reactions. In both

Table 5 Product distribution between Si–Si and Si–C bond cleavage in disilane **10** depending on the reaction temperature

Entry	*T*/°C	Si–C cleavage	Si–Si cleavage
1	RT (~15)	44	56
2	0	42	58
3	−78	33	67

cases, the amount of the preferred cleavage product at room temperature is increased at lower temperatures (Si–C cleavage for **3**; Si–Si cleavage for **10**). This preference of the main product at low temperatures is the expected course for two competing, kinetically controlled reaction pathways (with different reaction barriers). Further effects influencing or regulating these different reaction barriers are not clear at the moment.

Conclusions

We herein presented the synthesis of a series of alkyl and aryl substituted di- and trisilanes and their reactivity against elemental lithium. Depending on the substituents at silicon selective Si–Si and Si–C cleavages as well as mixtures of both possible reactions have been observed. Aromatic substituents at the silicon atoms proved to be necessary for the viability of any cleavage reaction as they are stabilising the radical anion after electron transfer to the corresponding di- or trisilane. Yet, selective cleavage reactions do not depend on the number of arenes. The observed reactivity in the respective silane can be understood *via* bond elongation, σ-antibonding and π-bonding of involved bonds. Si–Si bond elongation in combination with σ-antibonding between the silicon atoms and π-bonding between silicon and the aromatic substituents results in the selective cleavage of the thermodynamically weakest Si–Si bond (*e.g.* disilane **1**). Weakened π-bonding and missing σ-antibonding topple the reactivity towards a selective Si–C bond cleavage (disilane **3**).

Furthermore, if both possible cleavage reactions – Si–Si and Si–C – occur in the experiment (silanes **4** and **10**), the observed ratio between Si–Si and Si–C cleavage feature a reaction temperature dependency in favour of the kinetic product. Thereby, decreasing the temperature resulted in cleavage of the thermodynamically stronger Si–C bond in trisilane **4**, whereas the weaker Si–Si bond was cleaved in the disilane **10**.

At the moment we are trying to elucidate the reactivity of further functionalised silanes against elemental lithium and the effects of electron-withdrawing substituents at silicon to the preferred reactive centre.

Experimental

General details

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium and distilled prior to use. NMR spectra were recorded on an AMX-400 Bruker spectrometer at 22 °C. Assigning the signals was supported by additional DEPT-135, C,H- and H,H-COSY experiments. GC/MS analysis were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); Column; Zebron, Capillary GC Column, ZB-1.

Synthesis

(*R*)-**1**,[4c] (*R*)-**3**[4e] and (*R*)-**4**[4b] have been synthesised according to literature procedures.

Synthesis of 1,1,2,2-tetramethyl-1-phenyl-1-(piperidinomethyl)-disilane (8). The synthesis of **8** was performed analogue to the synthesis of **1**.[4c] Therefore, a solution of 10.0 g (41.2 mmol) 1-(chloromethyl)-1,2,2-trimethyl-1,2-diphenyldisilane and 8.06 g (94.7 mmol) piperidine, dissolved in 50 ml toluene, was heated under reflux for 18 h. After removal of all volatile compounds *in vacuo*, the crude product was dissolved again in 80 ml n-pentane, separated from all salts and finally cleaned through bulb-to-bulb distillation (oven temperature: 132 °C; pressure 3.2 10^{-4} mbar). Yield: 9.72 g (33.3 mmol, 81%); ^{1}H-NMR (400.1 MHz, $CDCl_3$): $\delta = 0.06$ [s, 6H; $Si(CH_3)_2$], 0.34 [s, 6H; $Si(CH_3)_2$], 1.25–1.35 (m, 2H; $NCCCH_2$), 1.45–1.50 (m, 4H; $NCCH_2C$), 1.91 (s 2H; $SiCH_2$), 2.15–2.25 (m, 4H; NCH_2CC), 7.25–7.35 (m, 3H; aromat. H), 7.45–7.50 (m, 2H; aromat. H); {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$): $\delta = -3.7, -3.4$ (2C each) [$Si(CH_3)_2$], 23.9 (1C) ($NCCCH_2$), 26.3 (2C) ($NCCH_2$), 50.4 (1C) ($SiCH_2N$), 58.5 (2C) (NCH_2C), 127.6 (2C) (*C*-m), 128.2 (1C) (*C*-p), 133.9 (2C) (*C*-o), 139.6 (1C) (*C*-i); {^{1}H}^{29}Si-NMR (59.6 MHz, $CDCl_3$): $\delta = -21.0$ (1Si) (NC*Si*), −19.8 (1Si) (NCSi*Si*).

Synthesis of 1,1,2,2,2-pentamethyl-1-(piperidinomethyl)disilane (9). The synthesis of **9** was performed analogue to the synthesis of **8**. Yield: 8.73 g (38.1 mmol, 86%); ^{1}H-NMR (400.1 MHz, $CDCl_3$): $\delta = 0.07$ [s, 9H; $Si(CH_3)_3$], 0.42 [s, 6H; $Si(CH_3)_2$], 1.25–1.35 (m, 2H; $NCCCH_2$), 1.45–1.55 (m, 4H; $NCCH_2C$), 1.89 (s 2H; $SiCH_2$), 2.15–2.25 (m, 4H; NCH_2CC); {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$): $\delta = -3.9$ (2C) [$Si(CH_3)_2$], −2.1 (3C) [$Si(CH_3)_3$], 23.7 (1C) ($NCCCH_2$), 26.1 (2C) ($NCCH_2$), 49.6 (1C) ($SiCH_2N$), 58.3 (2C) (NCH_2C); {^{1}H}^{29}Si-NMR (59.6 MHz, $CDCl_3$): $\delta = -21.5$ (1Si) (NC*Si*), −20.2 (1Si) (NCSi*Si*).

Synthesis of 1,2,2-trimethyl-1,2-diphenyl-1-(piperidinomethyl)-disilane (10). 235 mg (33.9 mmol) lithium in 10 ml thf were combined with 5.00 g (16.9 mmol) diphenylmethyl(piperidinomethyl)silane (**13**) at 0 °C and stirred at this temperature for 5 h. Afterwards, the brown solution of the lithiosilane was added at −78 °C to 6.36 g (37.2 mmol) dimethylphenylchlorosilane, resulting in the immediate decolouration of the mixture, before it was allowed to warm to room temperature. After removal of all volatiles *in vacuo* the residue was suspended in 15 ml of 2M NaOH and extracted 5 times with 15 ml diethyl ether. The combined organic layers were extracted 5 times with 10 ml of 2M HCl and afterwards set to pH 12 with NaOH. Finally the aqueous layer was extracted 5 times with 15 ml of diethyl ether and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds *in vacuo*, the crude product was cleaned through bulb-to-bulb distillation (oven temperature: 220 °C; 1.0 10^{-3} mbar). Yield: 3.97 g (11.2 mmol, 71%); ^{1}H-NMR (400.1 MHz, $CDCl_3$): $\delta = 0.34, 0.36, 0.37$ (s, 3H each; $SiCH_3$), 1.25–1.35 (m, 2H; $NCCCH_2$), 1.40–1.50 (m, 4H; $NCCH_2C$), 2.15–2.30 (m, 4H; NCH_2CC), 2.16, 2.27 (AB-system, $^2J_{AB} =$ 14.3 Hz, 2H; $SiCH_2$), 7.20–7.55 (m, 10H; aromat. H); {^{1}H}^{13}C-NMR (100.6 MHz, $CDCl_3$): $\delta = -5.4$ (1C) ($NCSiCH_3$), −3.5, −3.4 (1C each) [$Si(CH_3)_2$], 23.8 (1C) ($NCCCH_2$), 26.3 (2C) ($NCCH_2$), 48.9 (1C) ($SiCH_2N$), 58.5 (2C) (NCH_2C), 127.56, 127.61 (2C each) (all *C*-m), 128.34, 128.37 (1C each) (all *C*-p), 134.07, 134.16 (2C

Table 6 Total (SCF) and zero-point energies (ZPE) of all calculated systems

Compound	SCF/Hartree	ZPE/Hartree
1	−1644.467099	−1643.940472
$\mathbf{1}^{\cdot-}$	−1644.459014	−1643.938856
8	−1260.987489	−1260.569191
$\mathbf{8}^{\cdot-}$	−1260.972001	−1260.557901
4	−1629.846083	−1630.339755
$\mathbf{4}^{\cdot-}$	−1629.836490	−1630.324531
10	−1452.728037	−1452.255706
$\mathbf{10}^{\cdot-}$	−1452.717959	−1452.251796
3	−1260.569402	−1260.987286
$\mathbf{3}^{\cdot-}$	−1260.557420	−1260.971240
9	−1069.246902	−1068.883119
$\mathbf{9}^{\cdot-}$	−1069.227136	−1068.865497

each) (all *C*-o), 138.2, 139.0 (1C each) (all *C*-i); $\{^1H\}^{29}$Si-NMR (59.6 MHz, $CDCl_3$): $\delta = -23.3$ (1Si) (NC*Si*), −21.2 (1Si) (NCSi*Si*).

General specification for the cleavage of the Si–Si and Si–C bonds with elemental lithium in silanes 4 and 10. For the reactivity studies, 100 mg (**10**: 283 μmol; **4**: 286 μmol) of the corresponding silane were dissolved in 1 ml of thf and reacted with two equivalents of elemental lithium (granals) for 6 h at the temperature given in Table 4 (for **4**) and Table 5 (for **10**). Afterwards, 2.2 equivalents of trimethylchlorosilane was added at −78 °C resulting in the decolouration of the corresponding mixture, before it was allowed to warm to room temperature. After removal of all volatiles *in vacuo* the residue was suspended in a minimum amount of n-pentane and separated from all salts. Finally, the obtained product mixtures were investigated *via* GC/MS and NMR spectroscopy without further purification. The obtained product ratios are given in Table 4 (for **4**) and Table 5 (for **10**), respectively.

Determination of the product distribution

The product distributions between Si–Si and Si–C cleavage have been determined *via* a combination of GC/MS and NMR spectroscopic analysis. Thereby, the results obtained from the GC/MS measurements have been used to determine the obtained products, whereas their ratios have been determined *via* integration of relevant methyl groups in the ^{1}H NMR spectra.

Computational details

All calculations were done without symmetry restrictions. Starting coordinates were obtained with *Chem3D Ultra 10.0*. Optimisation 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 (Revision D.01 and Revision E.01) on the B3LYP/6-31+G(d) level.[14] Thereby, no imaginary frequencies were obtained. The starting structural parameters for the systems were taken from the X-ray data of (*S*)-**1**·HCl[7b] and (*R*)-**3**·HCl.[4e] All other compounds were constructed based thereon with *Chem3D Ultra 10.0*. The total (SCF) and zero-point energies (ZPE) of all systems can be found in Table 6. All coordinates are available in the ESI.†

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Notes and references

1 For some selected pioneer works on functionalised lithiosilanes, see: (*a*) L. H. Sommer and R. Mason, *J. Am. Chem. Soc.*, 1965, **87**, 1619; (*b*) L. H. Sommer, J. E. Lyons and H. Fujimoto, *J. Am. Chem. Soc.*, 1969, **91**, 7051; (*c*) E. Colomer and R. J. P. Corriu, *J. Chem. Soc., Chem. Commun.*, 1976, 176; (*d*) E. Colomer and R. J. P. Corriu, *J. Organomet. Chem.*, 1977, **133**, 159.

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

3 (*a*) I. Fleming, R. S. Roberts and S. C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1215; (*b*) U. Schubert and A. Schenkel, *Transition Met. Chem.*, 1985, **10**, 210; (*c*) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, 1995, **38**, 1; (*d*) H.-S. Oh, L.-S. Park and Y. Kawakami, *Chirality*, 2003, **15**, 646; (*e*) W. Uhlig, *J. Organomet. Chem.*, 2003, **685**, 70; (*f*) I. Fleming in *Organocopper Reagents*, ed. R. J. K. Taylor, Oxford University Press, Oxford, U.K., 1994, pp 257.

4 For other selected works on lithiosilanes, see: (*a*) M. Omote, T. Tokita, Y. Shimizu, I. Imae, E. Shirakawa and Y. Kawakami, *J. Organomet. Chem.*, 2000, **611**, 20; (*b*) C. Strohmann and C. Däschlein, *Organometallics*, 2008, **27**, 2499; (*c*) C. Strohmann, J. Hörnig and D. Auer, *Chem. Commun.*, 2002, 766; (*d*) C. Strohmann, M. Bindl, V. C. Vraaß and J. Hörnig, *Angew. Chem.*, 2004, **116**, 1029; C. Strohmann, M. Bindl, V. C. Vraaß and J. Hörnig, *Angew. Chem., Int. Ed.*, 2004, **43**, 1011; (*e*) C. Strohmann, C. Däschlein, M. Kellert and D. Auer, *Angew. Chem.*, 2007, **119**, 4864; C. Strohmann, C. Däschlein, M. Kellert and D. Auer, *Angew. Chem., Int. Ed.*, 2007, **46**, 4780; (*f*) D. Auer, M. Kaupp and C. Strohmann, *Organometallics*, 2004, **23**, 3647; (*g*) M. Nanjo, M. Masayuki, Y. Ushida, Y. Awamura and K. Mochida, *Tetrahedron Lett.*, 2005, **46**, 8945; (*h*) D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Botoshansky, B. Tumanskii and Y. Apeloig, *Angew. Chem.*, 2005, **117**, 749; D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Botoshansky, B. Tumanskii and Y. Apeloig, *Angew. Chem., Int. Ed.*, 2005, **44**, 739; (*i*) T. I. Kückmann, F. Dornhaus, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Eur. J. Inorg. Chem.*, 2007, 1989; (*j*) D. Scheschkewitz, *Angew. Chem.*, 2004, **116**, 3025; D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2004, **43**, 2965; (*k*) H.-W. Lerner, *Coord. Chem. Rev.*, 2005, **249**, 781.

5 For some examples, see: (*a*) M. Oestreich, G. Auer and M. Keller, *Eur. J. Org. Chem.*, 2005, 184; (*b*) C. Strohmann, O. Ulbrich and D. Auer, *Eur. J. Inorg. Chem.*, 2001, 1013; (*c*) H.-W. Lerner, S. Scholz, M. Bolte and M. Wagner, *Z. Anorg. Allg. Chem.*, 2004, **630**, 443.

6 For some examples, see: (*a*) H. Gilman, D. J. Peterson and D. Wittenberg, *Chem. Ind. (London)*, 1958, 1479; (*b*) A. G. Brook and H. G. Gilman, *J. Am. Chem. Soc.*, 1954, **76**, 278; (*c*) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, 1951, **73**, 4031.

7 For more examples concerning our studies, see: (*a*) C. Däschlein and C. Strohmann, *Eur. J. Inorg. Chem.*, 2009, 43; (*b*) C. Däschlein, V. H. Gessner and C. Strohmann, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, o1950; (*c*) C. Strohmann and C. Däschlein, *Chem. Commun.*, 2008, 2791; (*d*) H. Ott, C. Däschlein, D. Leusser, D. Schildbach, T. Seibel, D. Stalke and C. Strohmann, *J. Am. Chem. Soc.*, 2008, **130**, 11901; (*e*) A. Hameau, F. Guyon, M. Knorr, C. Däschlein, C. Strohmann and N. Avarvari, *Dalton Trans.*, 2008, 4866; (*f*) C. Strohmann, C. Däschlein and D. Auer, *J. Am. Chem. Soc.*, 2006, **128**, 704; (*g*) V. H. Gessner, C. Däschlein and C. Strohmann, *Chem.–Eur. J.*, 2009, **15**, 3320; (*h*) C. Däschlein, J. O. Bauer and C. Strohmann, *Angew. Chem.*, 2009, **121**, 8218; C. Däschlein, J. O. Bauer and C. Strohmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 8074; (*i*) C. Däschlein and C. Strohmann, *Z. Naturforsch.*, 2009, **64b**, 1558.

8 The selective cleavage of the Si–C bond in functionalised silanes is a desired reaction. Yet, this reaction type was hithereto mainly observed as an unwanted side reaction, *e.g.* see: (*a*) M. Porchia, N. Brianese, U. Casellato, F. Ossola, G. Rossetto, P. Zanella and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1989, 677; (*b*) A. L. Allred, R.T. Smart and D. A. Van Beek Jr., *Organometallics*, 1992, **11**, 4225; (*c*) H. Tsuji, A. Toshimitsu and K. Tamao, *Chem. Heterocycl. Compd.*, 2001, **37**, 1369.

9 The low temperature (−78 °C/−50 °C) in the synthesis of the shown lithiosilanes is necessary to prevent the racemisation process occurring at temperatures above −30 °C; for a detailed description, see: D. Auer, J. Hörnig and C. Strohmann in *Organosilicon Chemistry V: From Molecules to Materials*, ed. N. Auner and J. Weis, Wiley-VCH, Weinheim, 2003, pp. 167.

10 Although not isolated in pure form, the intermediate lithiosilane **7** is only the seventh highly enantiomerically enriched lithiosilane known in literature so far.

11 C. Strohmann, D. Schildbach and D. Auer, *J. Am. Chem. Soc.*, 2005, **127**, 7968.

12 The beginning of a reaction is indicated by a change of the colour: the formation of any lithiosilane results in the change of the previously colourless solution to a dark red, dark green or dark brown solution.

13 0 °C have been chosen as reaction temperature to minimized by-products caused by ether-cleavage.

14 (*a*) *Gaussian 03, Revision D.01*, 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. Dapprich, 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 and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004; (*b*) *Gaussian 03, Revision E.01*, 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. Dapprich, 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 and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

15 For some selected work dealing with element-element bond cleavage reactions, see: (*a*) J.-M. Savéant, *Advances in Electron Transfer Chemistry*, 1994, **4**, 53; (*b*) L. Eberson, *Acta Chem. Scand.*, 1999, **53**, 751; (*c*) F. Maran, D. D. M. Wayner and M. S. Workentin, *Adv. Phys. Org. Chem.*, 2001, **36**, 85; (*d*) R. O. Al-Kaysi and J. L. Goodman, *J. Am. Chem. Soc.*, 2005, **127**, 1620; (*e*) Z. Grobelny, *Eur. J. Org. Chem.*, 2004, 2973; (*f*) E. D. Lorance, W. H. Kramer and I. R. Gould, *J. Am. Chem. Soc.*, 2004, **126**, 14071; (*g*) S. Jakobsen, H. Jensen, S. U. Pedersen and K. Daasbjerg, *J. Phys. Chem. A*, 1999, **103**, 4141; (*h*) S. Antonello, K. Daasbjerg, H. Jensen, F. Taddei and F. Maran, *J. Am. Chem. Soc.*, 2003, **125**, 14905; (*i*) A. B. Meneses, S. Antonello, M. C. Arevalo and F. Maran, *Electrochim. Acta*, 2005, **50**, 1207; (*j*) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.

16 For one example, see: D.-R. Bai and S. Wang, *Organometallics*, 2004, **23**, 5958.

17 P. Flükinger, H. P. Lüthi, S. Portmann and J. Weber, Molekel 4.3, Swiss Center for Scientific Computing, Manno, Switzerland, 2000-2002.

18 Due to the relatively high reaction temperature, several byproducts caused by ether cleavage could be obtained in the reaction mixture. Yet, we were able to focus on the desired tetra- and disilane.

19 The average temperature in this entry was about −90 °C; yet, intermittent, slightly higher or lower temperatures were existent.