ELSEVIER

Journal of Organometallic Chemistry 692 (2007) 1421–1441

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Substituted lithiumtrimethylsiloxysilanides LiSiRR′(OSiMe$_3$) – Investigations of their synthesis, stability and reactivity

Joerg Harloff, Eckhard Popowski *, Helmut Reinke

Institut für Chemie der Universität Rostock, Albert-Einstein-Straße 3a, D-18051 Rostock, Germany

Received 29 August 2006; received in revised form 16 November 2006; accepted 22 November 2006
Available online 1 December 2006

Abstract

The reactions of the trimethylsiloxychlorosilanes (Me$_3$SiO)RR′SiCl (**1a**–**h**: R′ = Ph, **1a**: R = H, **1b**: R = Me, **1c**: R = Et, **1d**: R = ^{i}Pr, **1e**: R = ^{t}Bu, **1f**: R = Ph, **1g**: R = 2,4,6-Me$_3$C$_6$H$_2$ (Mes), **1h**: R = 2,4,6-(Me$_2$CH)$_3$C$_6$H$_2$ (Tip); **1i**: R = R′ = Mes) with lithium metal in tetrahydrofuran (THF) at −78 °C and in a mixture of THF/diethyl ether/*n*-pentane in a volume ratio 4:1:1 at −110 °C lead to mixtures of numerous compounds. Dependent on the substituents silyllithium derivatives (Me$_3$SiO)RR′SiLi (**2b**–**i**), Me$_3$SiO(RR′Si)$_2$Li (**3a**–**g**), Me$_3$SiRR′SiLi (**4a**–**h**), (LiO)RR′SiLi (**12e**, **12g**–**i**), trisiloxanes (Me$_3$SiO)$_2$SiRR′ (**5a**–**i**) and trimethylsiloxydisilanes (**6f***, **6h***, **6i***) are formed. All silyllithium compounds were trapped with Me$_3$SiCl or HMe$_2$SiCl resulting in the following products: (Me$_3$SiO)RR′SiSiMe$_2$R″ (**6b**–**i**: R″ = Me, **7c**–**i**: R″ = H), Me$_3$SiO(RR′Si)$_2$SiMe$_2$R″ (**8a**–**g**: R″ = Me, **9a**–**g**: R″ = H), Me$_3$SiRR′-SiSiMe$_2$R″ (**10a**–**h**: R″ = Me, **11a**–**h**: R″ = H) and (HMe$_2$SiO)RR′SiSiMe$_2$H (**13e**, **13g**–**i**). The stability of trimethylsiloxysilyllithiums **2** depends on the substituents and on the temperature. (Me$_3$SiO)Mes$_2$SiLi (**2i**) is the most stable compound due to the high steric shielding of the silicon centre. The trimethylsiloxysilyllithiums **2a**–**g** undergo partially self-condensation to afford the corresponding trimethylsiloxydisilanyllithiums Me$_3$SiO(RR′Si)$_2$Li (**3a**–**g**). (Me$_3$)Si–O bond cleavage was observed for **2e** and **2g**–**i**. The relatively stable trimethylsiloxysilyllithiums **2f**, **2g** and **2i** react with *n*-butyllithium under nucleophilic butylation to give the *n*-butyl-substituted silyllithiums ^{n}BuRR′SiLi (**15g**, **15f**, **15i**), which were trapped with Me$_3$SiCl. By reaction of **2g** and **2i** with 2,3-dimethylbuta-1,3-diene the corresponding 1,1-diarylsilacyclopentenes **17g** and **17i** are obtained.

X-ray studies of **17g** revealed a folded silacyclopentene ring with the silicon atom located 0.5 Å above the mean plane formed by the four carbon ring atoms.

Keywords: Trimethylsiloxysilyllithiums; Self-condensation; Ambiphilic reactivity; Si–O bond cleavage; Disilanes; Trisilanes

1. Introduction

α-Heteroatom-substituted organolithium compounds LiCRR′(X) show ambiphilic – carbenoid – behaviour, if X is a halogen atom or an OR group [1–14]. The reason for this is the existence of an electropositve metal atom and an electronegative substituent on the same carbon atom. Lithiumcarbenoids react with electrophiles as well as with nucleophiles and in many cases undergo a bimolecular dimerisation (self-condensation), in which one molecule behaves as nucleophile and the other one as electrophile [5,6,11,12]. They can also be used as sources of carbenes [1,7,12,15]. Whether a carbenoid reacts as nucleophile or electrophile, depends mainly on the reaction temperature [1,7,9,14]. The carbanionic character is favoured by very low temperatures. Exclusively, organolithium compounds with a nitrogen atom at α-position only show carbanionic character [9,14,16–18].

Functionalised silyllithium compounds (X)RR′SiLi (X = electronegative leaving group), analogues of the α-heteroatom-substituted organolithium compounds, have been the object of increasing interest in recent years (reviews in [19–22]). Detailed reports are given on syntheses and chemical properties of aminosilyl- [23–28], alkoxysilyl- [24,29,30], allyloxysilyl- [25,31], siloxysilyl- [32,33],

---

* Corresponding author. Tel.: +49 381 498 6380; fax: +49 381 498 6382.
E-mail address: eckhard.popowski@uni-rostock.de (E. Popowski).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.11.033

halogensilyl- [34–37] and mesitylthiosilyllithium compounds [38], which are stable at least at low temperatures. Nucleophilic and electrophilic behaviour, i.e. silylenoid character, were experimentally proved only for the compounds $[(Me_3Si)_2N]MePhSiLi$ [26], $(RO)Ph_2SiLi$ ($R = {}^tBu, {}^iPr, Me$) [24,29], $(Me_3SiO)Me_{2-n}Ph_nSiLi$ ($n = 1, 2$) [32] and $X_2[(Me_3Si)_3C]SiLi$ ($X = Cl, Br$) [37].

Earlier we reported that the bis(trimethylsilyl)amino- and trimethylsiloxy-substituted silyllithium compounds $(X)Me_{2-n}Ph_nSiLi$ ($X = (Me_3Si)_2N, Me_3SiO$; $n = 1, 2$) are available by reaction of the corresponding chlorosilanes with lithium (used as very thin plates) in tetrahydrofuran (THF) at low temperatures [26,32]. The formation of the siloxysilyllithium compounds was accompanied by a Si–O bond cleavage that afforded the silanides $Me_3SiSiMe_{2-n}Ph_nLi$ ($n = 1, 2$).

Bis(trimethylsilyl)aminosilyllithium $[(Me_3Si)_2N]MePhSiLi$ [26] and both trimethylsiloxysilyllithiums $(Me_3SiO)Me_{2-n}Ph_nSiLi$ ($n = 1, 2$) [32] react as alkoxysilyllithiums $(RO)Ph_2SiLi$ ($R = {}^tBu, {}^iPr, Me$) [24,29] under bimolecular self-condensation, which is a characteristic silylenoid behaviour (Eq. (1)) [20,21,24,29].

$$\begin{aligned}&(X)Me_{2-n}Ph_nSiLi + (X)Me_{2-n}Ph_nSiLi\\&\quad \rightarrow (X)Me_{2-n}Ph_nSi\text{–}SiMe_{2-n}Ph_nLi + LiX\\&\qquad X = (Me_3Si)_2N,\ n = 1;\ \ X = Me_3SiO,\ n = 1,2 \qquad (1)\end{aligned}$$

The extent of self-condensation of diphenyl-trimethylsiloxy-silyllithium is considerably smaller than that of methyl-phenyl-trimethylsiloxy-silyllithium [32].

This result as well as the observed Si–O bond cleavage during the preparation of both trimethylsiloxysilyllithiums prompted us to follow the question, how strong substituents influence the synthesis, stability and reactivity of trimethylsiloxysilyllithiums.

In the following, we report the results of our investigations of the preparation of substituted trimethylsiloxysilyllithium compounds $(Me_3SiO)RR'SiLi$ by reaction of siloxychlorosilanes $(Me_3SiO)RR'SiCl$ (**1a**–**i**) with lithium metal (preliminary communication in [33]), and on their reaction behaviour.

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
R	H	Me	Et	${}^iPr$	${}^tBu$	Ph	Mes[a]	Tip[b]	Mes
R′	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Mes

[a] Mes: 2,4,6-$Me_3C_6H_2$.

[b] Tip: 2,4,6-$(Me_2CH)_3C_6H_2$.

2. Results and discussion

2.1. Reaction of the siloxychlorosilanes $(Me_3SiO)RR'SiCl$ (*1a–i*) with lithium metal

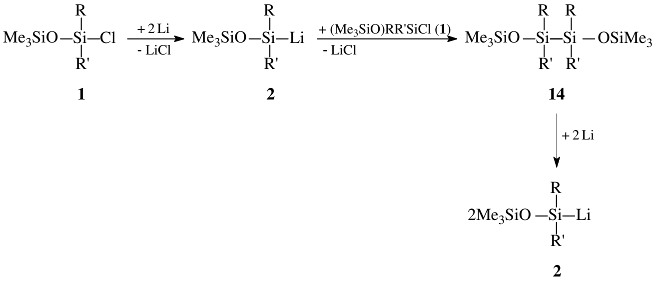
The siloxychlorosilanes **1a**–**i** react with very thin lithium plates in THF at −78 °C and in a Trapp mixture [1] (THF/diethyl ether/n-pentane in volume ratio 4:1:1) at −110 °C to give brown, red and green solutions, respectively, containing never only the expected trimethylsiloxysilyllithium $(Me_3SiO)RR'SiLi$ (**2**). A mixture of several silyllithium compounds **2**–**4**, **12**, trisiloxane **5** as well as siloxydisilane **6*** depending on the substituents R and R′ is obtained (Schemes 1 and 2). The typical reaction behaviour of all siloxychlorosilanes is shown in Scheme 1. Beside the summarised compounds in Scheme 1 more ones are given in Scheme 2, which were additionally formed in the reaction of the siloxychlorosilanes **1e** and **1g**–**i** with lithium.

The silyllithium compounds $(Me_3SiO)RR'SiLi$ (**2b**–**i**), $(Me_3SiO)RR'SiRR'SiLi$ (**3a**–**g**), $Me_3SiRR'SiLi$ (**4a**–**h**) and $(LiO)RR'SiLi$ (**12e**, **12g**–**i**) were trapped with chlorotrimethylsilane and chlorodimethylsilane (Schemes 1 and 2) to give the corresponding trimethylsiloxydisilanes $(Me_3SiO)RR'Si\text{–}SiMe_2R''$ (**6b**–**i**: $R'' = Me$; **7c**–**i**: $R'' = H$), trimethylsiloxytrisilanes $(Me_3SiO)RR'SiRR'Si\text{–}SiMe_2R''$ (**8a**–**g**: $R'' = Me$; **9a**–**g**: $R'' = H$), trisilanes $Me_3SiRR'Si\text{–}SiMe_2R''$ (**10a**–**h**: $R'' = Me$; **11a**–**h**: $R'' = H$) and dimethylsiloxydisilanes $(HMe_2SiO)RR'Si\text{–}SiMe_2H$ (**13e**, **13g**–**i**) (Schemes 1 and 2, Table 1).

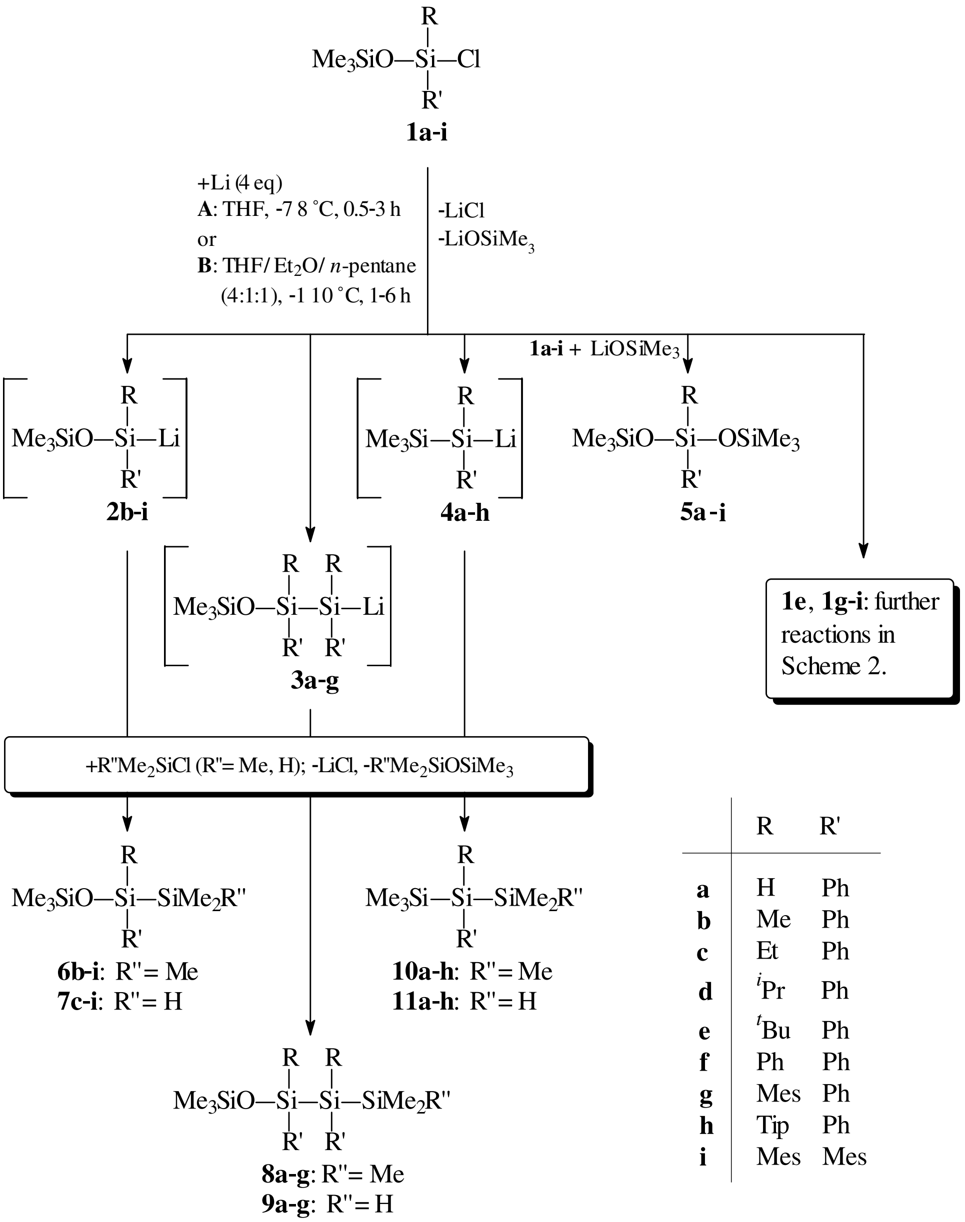
The disilanes $(Me_3SiO)HPhSi\text{–}SiMe_2R''$ ($R'' = Me, H$), trapping products of hydrido-phenyl-trimethylsiloxy-silyllithium $(Me_3SiO)HPhSiLi$ (**2a**), could not be detected in the reaction mixtures. Beside chlorotrimethylsilane as trapping agent chlorodimethylsilane was used to unequivocally prove the compounds in the reaction mixture. So the formation of the lithiumoxysilyllithiums **12e** and **12g**–**i** (Scheme 2) was only noticed with HMe_2SiCl as trapping agent. With Me_3SiCl the lithium derivatives $(Me_3SiO)RR'SiLi$ (**2**) and $(LiO)RR'SiLi$ (**12**) yielded identical products **6**.

As a broad variety of products was observed, a complicated reaction pathway can be assumed, e.g. parallel and multiple step reactions starting from trimethylsiloxysilyllithium **2**. The formation of products such as **3**–**5**, **6*** and **12** (Schemes 1 and 2) already began clearly before the trimethylsiloxychlorosilane **1** was completely consumed evidenced by GC and GC–MS investigations. The samples for the GC and GC–MS measurements were trapped with Me_3SiCl and HMe_2SiCl, respectively.

Presumably, the formation of the siloxysilyllithiums $(Me_3SiO)RR'SiLi$ (**2**) proceeds via a disilane intermediate (Eq. (2)) as described for the synthesis of silyllithium compounds with at least one aryl group on the silicon atom by reaction of a chlorosilane $>$Si(aryl)Cl with lithium metal [19,28,39].



$$Me_3SiO\text{–}SiRR'\text{–}Cl \xrightarrow[-\,LiCl]{+2\,Li} Me_3SiO\text{–}SiRR'\text{–}Li \xrightarrow[-\,LiCl]{+\,(Me_3SiO)RR'SiCl\ (1)} Me_3SiO\text{–}SiRR'\text{–}SiRR'\text{–}OSiMe_3 \xrightarrow{+2\,Li} 2\,Me_3SiO\text{–}SiRR'\text{–}Li \qquad (2)$$

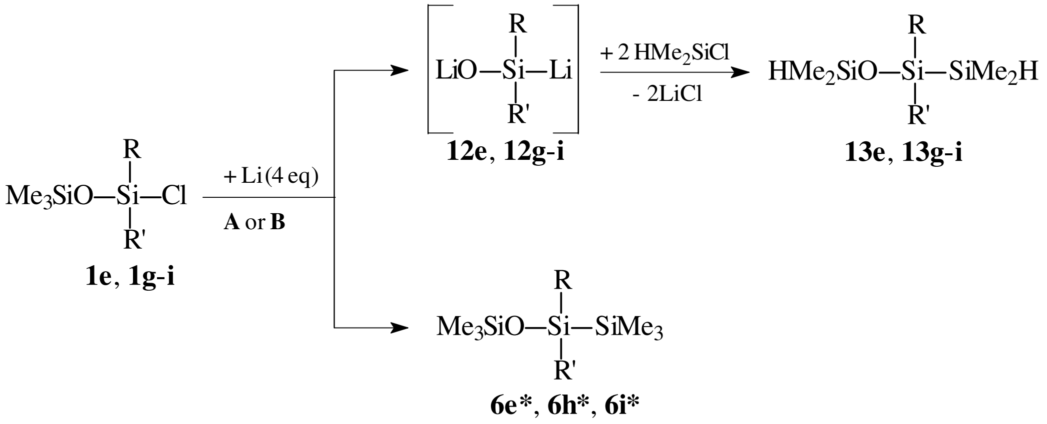


	R	R'
a	H	Ph
b	Me	Ph
c	Et	Ph
d	^{i}Pr	Ph
e	^{t}Bu	Ph
f	Ph	Ph
g	Mes	Ph
h	Tip	Ph
i	Mes	Mes

Scheme 1. Reaction products obtained in the reaction of the siloxychlorosilanes **1a-i** with lithium (**1b**, **1f** in [32]) as well as trapping of the formed lithiumsilanides with Me_3SiCl or HMe_2SiCl.

The initially formed siloxysilyllithium $(Me_3SiO)RR'SiLi$ (**2**) reacts with the excess chlorosilane $(Me_3SiO)RR'SiCl$ (**1**) to give a disilane $(Me_3SiO)RR'Si–SiRR'(OSiMe_3)$ (**14**), which is cleft by lithium to form **2**. In the reactions of the siloxychlorosilanes $(Me_3SiO)^{t}BuPhSiCl$ (**1e**) or $(Me_3SiO)MesPhSiCl$ (**1g**) with lithium the disilanes $[(Me_3SiO)RPhSi]_2$ (**14e**: R = ^{t}Bu, **14g**: R = Mes) can only be isolated, if the reaction is stopped at an early stage by quenching with Me_3SiCl.

According to the data given in Table 2, trimethylsiloxysilyllithiums **2b–i** are more stable at −110 °C than at −78 °C. With exception of $(Me_3SiO)TipPhSiLi$ (**6h**) the trimethylsiloxysilyllithiums $(Me_3SiO)RR'SiLi$ (**2f**: R/R′ = Ph/Ph, **2g**: R/R′ = Mes/Ph, **2i**: R/R′ = Mes/Mes) with two aromatic substituents are considerably more stable than **2b–e** with only one aromatic substituent. The dimesityl-trimethylsiloxy-silyllithium **2i** has the highest stability at both temperatures (−78 °C and −110 °C) because the Si–Li moiety of **2i** is highly shielded. From the proportions of the trimethylsiloxysilyllithiums **2b–i** in the reaction mixtures it is apparent that the substituents R and R′ have an influence on the stability of **2b–i** as especially illustrated by the yields obtained in the reactions at −110 °C. The following order of stability depending on R and R′ could be established: R/R′ = Mes/Mes > Mes/Ph > Ph/Ph > ^{t}Bu/Ph > ^{i}Pr/Ph > Tip/Ph > Et/Ph ~ Me/Ph > H/Ph. The order of stability at −110 °C, observed in the row of compounds $(Me_3SiO)RPhSiLi$ (R = H, Me, Et,



Variant	Yield (%)						
	13e	**13g**	**13h**	**13i**	**6e***	**6h***	**6i***
A	34	4	33	8	9	2	10
B	17	2	31	5	10	28	5

Scheme 2. Continuation of Scheme 1.

Table 1
Yields of the trapping products (Me$_3$SiO)RR′SiSiMe$_2$R″ (**6b**–**i**: R″ = Me; **7c**–**i**: R″ = H), Me$_3$SiO(RR′Si)$_2$SiMe$_2$R″ (**8a**–**g**: R″ = Me; **9a**–**g**: R″ = H) and Me$_3$SiRR′SiSiMe$_2$R″ (**10a**–**h**: R″ = Me; **11a**–**h**: R″ = H) for the respective lithiumsilanides formed in the reaction of trimethylsiloxychlorosilanes (Me$_3$SiO)RR′SiCl (**1a**–**i**) with lithium at −78 °C (variant **A**) and at −110 °C (variant **B**) as well as yields of the trisiloxanes (Me$_3$SiO)$_2$SiRR′ (**5a**–**i**)

Variant	Trapping agent	Compound	Yield (%)								
			a	**b**[a]	**c**	**d**	**e**	**f**[a]	**g**	**h**	**i**
			R = H R′ = Ph	Me Ph	Et Ph	^{i}Pr Ph	^{t}Bu Ph	Ph Ph	Mes Ph	Tip Ph	Mes Mes
A	Me$_3$SiCl	**6**	–[b]	1	7	9	44 [c]	19	51[c]	48[c]	71[c]
B	Me$_3$SiCl	**6**	–[b]	17	16	32	66[c]	47	66[c]	78[c]	75[c]
A	HMe$_2$SiCl	**7**	–[b]	–	3	10	4	18	47	13	54
B	HMe$_2$SiCl	**7**	–[b]	–[d]	15	31	38	45	62	20	67
A	Me$_3$SiCl	**8**	10	71	67	56	5	27	24	–	–
B	Me$_3$SiCl	**8**	47	75	70	36	4	28	20	–	–
A	HMe$_2$SiCl	**9**	7	78	75	63	4	29	28	–	–
B	HMe$_2$SiCl	**9**	45	–[d]	68	46	1	26	18	–	–
A	Me$_3$SiCl	**10**	6	4	6	17	34	22	17	36	–
B	Me$_3$SiCl	**10**	5	1	2	4	7	17	8	2	–
A	HMe$_2$SiCl	**11**	3	3	4	7	31	17	13	31	–
B	HMe$_2$SiCl	**11**	3	–[d]	2	3	11	15	6	2	–
A	Me$_3$SiCl	**5**	10	18	9	7	2	8	3	11	4
A	HMe$_2$SiCl	**5**	9	10	8	7	2	8	2	5	3
B	Me$_3$SiCl	**5**	10	4	9	11	1	8	4	8	3
B	HMe$_2$SiCl	**5**	11	–[d]	5	6	2	8	3	2	3

[a] Yields of **5b**, **6b**, **8b**–**11b**, **5f** and **6f**–**11f** (variant **A**) as well as yields of **5b**, **6b**, **8b**, **10b**, **5f**, **6f**, **8f** and **10f** (variant **B**) from [32].

[b] No trapping products (Me$_3$SiO)HPhSiSiMe$_2$R″ for (Me$_3$SiO)HPhSiLi. In the reaction of **1a** with lithium higher-molecular silanes with Si–Si bonds were also obtained beside **8a**–**11a** and **5a** after trapping.

[c] The yields of **6e**, **6g**–**i** are composed of the yields of the lithium derivatives (Me$_3$SiO)RR′SiLi (**2e**, **2g**–**i**) and (LiO)RR′SiLi (**12e**, **12g**–**i**) trapped with Me$_3$SiCl as well as the disilanes (Me$_3$SiO)RR′SiSiMe$_3$ (**6e***,**6h***,**6i***) formed already before the addition of trapping agent.

[d] The reaction mixture was not trapped with HMe$_2$SiCl.

^{i}Pr, ^{t}Bu), is attributed to steric shielding of the central silicon atom by the substituents R = ^{t}Bu > ^{i}Pr > Et ~ Me > H. The same holds for the stability series of the diaryl-substituted species: **2f** < **2h** < **2i**. Step-by-step substitution of phenyl by mesityl substituents results in an increase of steric shielding of the Si(Li)-atom. Assuming a

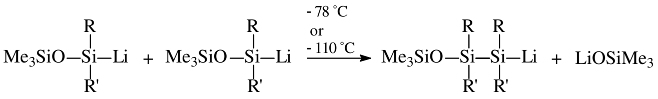
Table 2
Proportions of the silyllithiums (Me$_3$SiO)RR′SiLi (**2b**–**i**), Me$_3$SiO(RR′Si)$_2$Li (**3a**–**g**) and Me$_3$SiRR′SiLi (**4a**–**h**) in the reaction mixture of silanides (formed in the reaction of siloxychlorosilanes (Me$_3$SiO)RR′SiCl (**1a**–**i**) with lithium) determined from yields of the trapping products (Me$_3$SiO)RR′SiSiMe$_2$R″ (**6b**–**d**, **6f**: R″ = Me; **7e**, **7g**–**i**: R″ = H), Me$_3$SiO(RR′Si)$_2$SiMe$_2$R″ (**8a**–**g**: R″ = Me; **9a**–**g**: R″ = H) and Me$_3$SiRR′SiSiMe$_2$R″ (**10a**–**h**: R″ = Me; **11a**–**h**: R″ = H)

Temperature (°C)	a	b	c	d	e	f	g	h	i
	R = H R′ = Ph	Me Ph	Et Ph	^{i}Pr Ph	^{t}Bu Ph	Ph Ph	Mes Ph	Tip Ph	Mes Mes
(Me$_3$SiO)RR′SiLi (**2**) (%)									
−78	–	1[a]	7	9	4	19[a]	47	13	54
−110	–	17[a]	16	32	38	47[a]	62	20	67
Me$_3$SiO(RR′Si)$_2$Li (**3**) (%) from **8a**–**g**/**9a**–**g**									
−78	10/7	71/78[a]	67/75	56/63	5/4	27/29[a]	24/28	–/–	–/–
−110	47/45	75[a]/–[b]	70/68	36/46	4/1	28/26	20/18	–/–	–/–
Me$_3$SiRR′SiLi (**4**) (%) from **10a**–**h**/**11a**–**h**									
−78	6/3	4/3[a]	6/4	17/7	34/31	22/17[a]	17/13	36/31	–/–
−110	5/3	1[a]/–[b]	2/2	4/3	7/11	17[a]/15	8/6	2/2	–/–

[a] Values from [32].
[b] The reaction mixture was not trapped with HMe$_2$SiCl.

considerable steric stabilisation in trimethylsiloxysilyllithium compounds the yields of (Me$_3$SiO)^{t}BuPhSiLi (**2e**) at −78 °C and of (Me$_3$SiO)TipPhSiLi (**2h**) at −78 °C as well as at −110 °C are relatively low (Table 2) and can be attributed to a (Me$_3$)Si–O bond cleavage. For a detailed discussion see below.

The siloxysilyllithiums (Me$_3$SiO)RR′SiLi (**2b**–**g**) undergo bimolecular self-condensation reactions at −78 °C and −110 °C to a different extent (Eq. (3), Table 2) affording the corresponding siloxydisilanyllithiums **3b**–**g**, which were trapped as siloxytrisilanes Me$_3$SiO(RR′Si)$_2$SiMe$_2$R″ (**9b**–**g**: R″ = Me; **10b**–**g**: R″ = H) (Scheme 1, Table 1).



$$\mathrm{Me_3SiO{-}SiRR'{-}Li} + \mathrm{Me_3SiO{-}SiRR'{-}Li} \xrightarrow[-110\,^{\circ}C]{-78\,^{\circ}C\ \text{or}} \mathrm{Me_3SiO{-}SiRR'{-}SiRR'{-}Li} + \mathrm{LiOSiMe_3}$$

2b-g **2b-g** **3b-g**

b: R = Me, **c**: R = Et, **d**: R = ^{i}Pr, **e**: R = ^{t}Bu, **f**: R = Ph, **g**: R = Mes; **b-g**: R′ = Ph

(3)

This type of reaction (Eq. (3)), in which one molecule behaves as an electrophile and the other one as a nucleophile, clearly indicates ambiphilic reactivity, i.e. silylenoid behaviour, of **2b**–**g**.

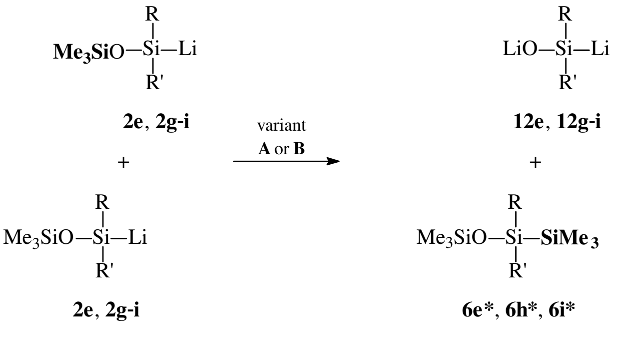
For trimethylsiloxysilyllithium (Me$_3$SiO)HPhSiLi (**2a**), which could neither be trapped at −78 °C nor at −110 °C, the self-condensation product (Me$_3$SiO)HPhSi–HPhSiLi (**3a**) was obtained as well. However, the amount of **3a** in the reaction mixture was relatively small, especially in the reaction of **1a** with lithium at −78 °C. These results and the formation of higher-molecular silanes with Si–Si bonds (only observed in the case of reaction of **1a** with lithium) indicate that self-condensation of **2a** did not stop on the level of **3a**. But starting from **3a** a number of another Si–Si coupling reactions took place according to Eq. (3). The lithiumtrimethylsilanolate formed by self-condensation, reacts with the corresponding siloxychlorosilanes (Me$_3$SiO)RR′SiCl (**1a**–**g**) to give the trisiloxanes (Me$_3$SiO)$_2$SiRR′ (**5a**–**g**), whose formation already took place during the reaction of siloxychlorosilanes with lithium.

The siloxysilyllithiums (Me$_3$SiO)Ph$_2$SiLi (**2f**) and (Me$_3$SiO)MesPhSiLi (**2g**), in which two aromatic substituents are bonded to the central silicon atom, tend far less towards self-condensation than the three alkyl-phenyl-substituted compounds (Me$_3$SiO)RPhSiLi (**2b**: R = Me, **2c**: R = Et, **2d**: R = ^{i}Pr) (Eq. (3), Table 2). (Me$_3$SiO)^{t}BuPhSiLi (**2e**) takes an exceptional position within the list of alkyl-phenyl-substituted compounds because of the (Me$_3$)Si–O bond cleavage tendency as already mentioned.

Both siloxysilyllithiums (Me$_3$SiO)TipPhSiLi (**2h**) and (Me$_3$SiO)Mes$_2$SiLi (**2i**), which bear also two aromatic substituents on the Si(Li)-atom like **2f** and **2g**, do not undergo self-condensation. The reason for this is of steric nature. The higher steric shielding of the central silicon atom compared to **2f** and **2g** suppresses the bimolecular self-condensation process.

The mixtures of products formed in the reaction of siloxychlorosilanes **1a**–**g** with lithium gave no indication for a β-elimination of lithiumtrimethylsilanolate from the trimethylsiloxydisilanyllithiums **3a**–**g**.

The formation of the lithiumoxysilyllithiums (LiO)RR′SiLi (**12e**, **12g**–**i**) and the trimethylsiloxydisilanes (Me$_3$SiO)RR′Si–SiMe$_3$ (**6***), which already existed in the respective reaction mixtures before quenching with Me$_3$SiCl or HMe$_2$SiCl (Scheme 2), may be explained by reaction between two trimethylsiloxysilyllithiums. One molecule of **2** attacks the Me$_3$Si group of another molecule of **2** under (Me$_3$)Si–O bond cleavage and generation of a Si–Si bond (Eq. (4))



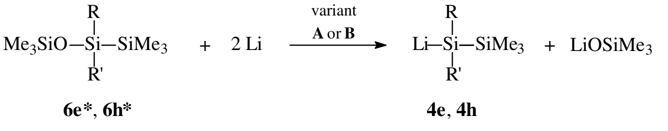
$$\mathrm{Me_3SiO{-}SiRR'{-}Li} + \mathrm{Me_3SiO{-}SiRR'{-}Li} \xrightarrow{\text{variant A or B}} \mathrm{LiO{-}SiRR'{-}Li} + \mathrm{Me_3SiO{-}SiRR'{-}SiMe_3}$$

e: R = ^{t}Bu, R' = Ph; **g**: R = Mes, R' = Ph; **h**: R = Tip, R' = Ph; **i**: R = R' = Mes

(4)

In case of the reaction of the siloxychlorosilane **1g** with lithium a disilane **6g*** according to **6e***, **6h*** and **6i*** could not be detected. Due to the yields of the dimethylsiloxydisilanes $(HMe_2SiO)RR'Si{-}SiMe_2H$ (**13e**: R = ^{t}Bu, R′ = Ph; **13g**: R = Mes, R′ = Ph; **13h**: R = Tip, R′ = Ph; **13i**: R = R′ = Mes) (Scheme 2), trapping products of **12e** and **12g–i**, it is apparent that the $(Me_3)Si{-}O$ bond cleavage in **2e** and **2h** is considerable and significantly greater than that of **2g** and **2i**. Obviously, the high extent of $(Me_3)Si{-}O$ bond cleavage in **2e** and **2h** is the reason for the unexpectedly low yield of **2e** and **2h** (Table 2) in the reaction of **1e** and **1h** with lithium. In the reaction of the siloxychlorosilanes **1e** and **1g–i** with lithium very small amounts of hexamethyl- and pentamethyldisilane as trapping products were obtained, respectively, suggesting the formation of a little $LiSiMe_3$.

Interestingly, for the siloxydisilanes $(Me_3SiO)RR'Si{-}SiMe_3$ (**6e***, **6h***) a $RR'Si{-}O$ bond cleavage by lithium was observed under formation of lithiumtrimethylsilanolate and the trimethylsilylsilyllithiums $Me_3Si{-}RR'SiLi$ (**4e**, **4h**) (Eq. (5)).



$$\mathrm{Me_3SiO{-}SiRR'{-}SiMe_3} + 2\,\mathrm{Li} \xrightarrow{\text{variant A or B}} \mathrm{Li{-}SiRR'{-}SiMe_3} + \mathrm{LiOSiMe_3}$$

e: R = ^{t}Bu, R' = Ph; **h**: R = Tip, R' = Ph

(5)

With the trapping agents Me_3SiCl and HMe_2SiCl the trimethylsilylsilyllithium derivatives **4e** and **4h** yielded the trisilanes $Me_3Si{-}RR'Si{-}SiMe_2R''$ (**10e**, **10h**: R″ = Me; **11e**, **11h**: R″ = H) (Scheme 1). The lithiumsilanolate reacted with the siloxychlorosilanes **1e** and **1h** to give the trisiloxanes $(Me_3SiO)_2SiRR'$ (**5e**, **5h**). The Si–O bond cleavage according to Eq. (5) was confirmed by reaction of the pure disilanes $(Me_3SiO)RR'Si{-}SiMe_3$ (**6e**: R = ^{t}Bu, R′ = Ph; **6f**: R = R′ = Ph; **6h**: R = Tip, R′ = Ph) with lithium in THF at −78 °C. However, the dimesityl-substituted siloxydisilane $(Me_3SiO)Mes_2Si{-}SiMe_3$ (**6i**) did not react with lithium under the same conditions. Hence, no trimethylsilylsilyllithium $Me_3Si{-}Mes_2SiLi$ according to **4e** and **4h** was generated in the reaction of **1i** with lithium (Scheme 1).

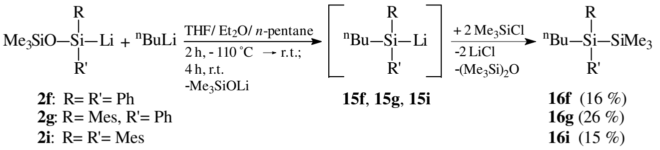
The formation of the trimethylsilylsilyllithium derivatives $Me_3Si{-}RR'SiLi$ (**4a–d**, **4f**, **4g**) remains unclear. Presumably, they are generated in the same way as **4e** and **4h**: (i) reaction of $(Me_3SiO)RR'SiLi$ (**2**) according to Eq. (4) affording lithiumoxysilyllithium $(LiO)RR'SiLi$ (**12**) and siloxydisilane $(Me_3SiO)RR'Si{-}SiMe_3$ (**6***) and (ii) $RR'Si{-}O$ bond cleavage of **6*** with lithium (Eq. (5)). However, the formation of compounds, which could confirm this assumption, was not observed in the reaction of the siloxychlorosilanes **1a–d**, **1f** and **1g** with lithium. According to the yields of **10a–h**, **11a–h** (Table 1) and **4a–h** (Table 2), respectively, it follows that the processes leading to the formation of **4a–h** are suppressed by lowering the reaction temperature from −78 °C to −110 °C.

2.2. Reaction of selected siloxysilyllithium compounds with n-butyllithium and 2,3-dimethylbuta-1,3-diene

To gain further insight into the reactivity of trimethylsiloxysilyllithium compounds the reaction behaviour of relatively stable lithiumsilanides $(Me_3SiO)RR'SiLi$ (**2f**: R = R′ = Ph; **2g**: R = Mes, R′ = Ph; **2i**: R = R′ = Mes) towards *n*-butyllithium and of **2g** and **2i** towards 2,3-dimethylbuta-1,3-diene, respectively, have been studied.

Lithiumcarbenoids $\rangle C(X)Li$ (X = halogen atom, OR) react with organolithium compounds RLi under nucleophilic substitution of the leaving group X by the organic moiety R [1,5–7,9,12,14]. This reaction is regarded to be characteristic of the electrophilic reactivity of carbenoids. Analogously, Tamao and Kawachi [20,24,29] took the nucleophilic butylation of the alkoxysilyllithiums $(RO)Ph_2SiLi$ (R = Me, ^{t}Bu) with *n*-butyllithium as expression of the electrophilic – silylenoid – behaviour of the silicon in these compounds.

The solutions of products (Schemes 1 and 2) with about 60% of the respective trimethylsiloxysilyllithium **2f**, **2g** and **2i** formed in the reaction of the siloxychlorosilanes **1f**, **1g** and **1i** with lithium at −110 °C, respectively, were mixed with *n*-BuLi after separation from excess lithium, then slowly warmed to room temperature (r.t.) and after 4 h stirring quenched with chlorotrimethylsilane at the same temperature. Except for the already known trapping products (Schemes 1 and 2, Table 1) the *n*-butyl-substituted disilanes $^nBuRR'Si{-}SiMe_3$ (**16f**, **16g**, **16i**) were obtained as new compounds indicating the formation of the *n*-butyl-substituted silyllithiums $^nBuRR'SiLi$ (**15f**, **15g**, **15i**) from **2f**, **2g** and **2i**, respectively (Eq. (6)).



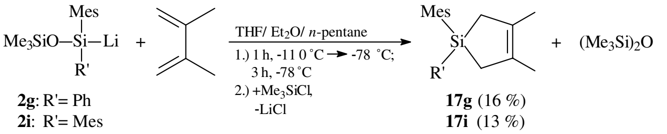
$$\mathrm{Me_3SiO{-}SiRR'{-}Li} + {}^n\mathrm{BuLi} \xrightarrow[\substack{2\,\mathrm{h},\,-110\,^\circ\mathrm{C}\,\to\,\mathrm{r.t.};\\ 4\,\mathrm{h},\,\mathrm{r.t.}\\ -\mathrm{Me_3SiOLi}}]{\mathrm{THF/Et_2O}/n\text{-pentane}} \left[{}^n\mathrm{Bu{-}SiRR'{-}Li}\right] \xrightarrow[\substack{-2\,\mathrm{LiCl}\\ -(\mathrm{Me_3Si})_2\mathrm{O}}]{+2\,\mathrm{Me_3SiCl}} {}^n\mathrm{Bu{-}SiRR'{-}SiMe_3}$$

(6)

Beside self-condensation the nucleophilic butylation of **2f**, **2g** and **2i** is another proof of an electrophilic reactivity of trimethylsiloxysilyllithium compounds. The nucleophilic behaviour was verified in many cases by trapping reactions with the electrophiles Me_3SiCl and HMe_2SiCl. Even **2i**, which does not undergo self-condensation under the chosen reaction conditions, still shows electrophilic behaviour towards the strong nucleophile *n*-butyllithium.

The formation of silacyclopentenes in the reaction of di- and trihalosilanes with lithium in the presence of 2,3-dimethylbuta-1,3-diene is often considered as proof of the formation of silylene intermediates [38,40–42]. However, the silacyclopentene can also be produced by reaction of the diene with a halogen silylenoid $>$Si(X)Li (X = halogen atom) [37,43], a precursor of silylenes. But the alkoxysilylenoid (^{t}BuO)Ph_2SiLi does not react with 2,3-dimethylbuta-1,3-diene [29].

The trimethylsiloxysilyllithiums **2g** and **2i**, which are produced by reaction of the siloxychlorosilanes **1g** and **1i** with lithium (4 equiv.) at −110 °C in THF/Et_2O/*n*-pentane (in addition to **2g** and **2i** further compounds could be found in the solution), react with 2,3-dimethylbuta-1,3-diene within the temperature range from −110 °C to −78 °C to give the silacyclopentenes **17g** and **17i** as well as lithiumtrimethylsilanolate (Eq. (7)). The silanolate was trapped with chlorotrimethylsilane resulting in hexamethyldisiloxane.



(7)

In case of the reaction of **2g** with 2,3-dimethylbuta-1,3-diene the trapping products $Me_3SiO(MesPhSi)_2SiMe_3$ (**8g**) and $Me_3SiMesPhSiSiMe_3$ (**10g**) (Scheme 1) beside **17g** were obtained additionally.

The silacyclopentenes could be produced either by direct reaction between the siloxysilylenoid and the diene or by reaction of a silylene, which is formed by α-elimination of $LiOSiMe_3$ from the siloxysilylenoid, with the diene. The fact that the reaction already takes place at −78 °C is a strong argument for a silylenoid mechanism. Furthermore this assumption is supported by the reaction according to Eq. (7), in which the established trapping agent of silylenes triethylsilane [36,38,41,44–47] was exchanged for the diene (molar ratio of siloxychlorosilane/Et_3SiH = 1:4; slowly warming to 20 °C). A formation of products of a silylene insertion R′Mes(H)Si–$SiEt_3$ could not be proved.

Colourless single crystals of **17g** suitable for the X-ray diffraction analysis were obtained by crystallisation from *n*-pentane. The molecular structure of **17g** is shown in

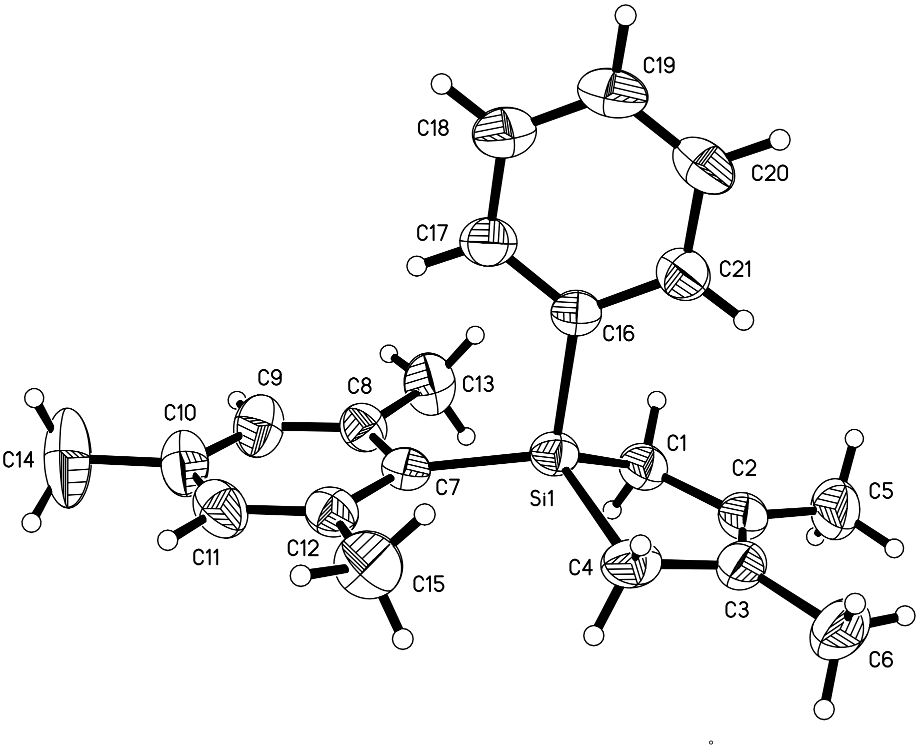


Fig. 1. Molecular structure of **17g** with 30% probability thermal ellipsoids. Selected distances (Å), bond angles and torsion angles (°): Si(1)–C(1) = 1.878(3), Si(1)–C(4) = 1.868(4), C(2)–C(3) = 1.332(5), Si(1)–C(7) = 1.881(3), Si(1)–C(16) = 1.895(3); C(1)–Si(1)–C(4) = 92.7(2), Si(1)–C(1)–C(2) = 103.8 (2), C(1)–C(2)–C(3) = 16.8(4); C(16)–Si(1)–C(7)–C(8) = 85.1(3), C(7)–Si(1)–C(16)–C(17) = 1.6(3), Si(1)–C(1)–C(2)–C(3) = 16.5(4), Si(1)–C(4)–C(3)–C(2) = −15.5(4).

Fig. 1. Crystallographic data and essential parameters of the structure refinement are summarised in Section 3.7.

With exception of the C(1)–Si(1)–C(4) angle the distances and bond angles in the silacyclopentene ring correspond approximately to those of known silacyclopentenes, which were obtained by trapping reactions of silylenes and a lithiumchlorosilylenoid with 2,3-dimethylbuta-1,3-diene, respectively [37,42,48]. In comparison with the compounds described in [37,42,48] the silicon atom is clearly outside the mean plane of the five-membered ring as can be seen from the torsion angles Si–C–C–C ([37]: – 7.4°, 5.6°; [42]: – 1.3°, 2.2°; [48]: – 2.3°, 2.3°; **17g**: – 15.5°, 16.6°). In fact the silicon atom in **17g** is located 0.5 Å above the mean plane formed by the four carbon ring atoms. The four Si–C distances (1.868(4)–1.895(3) Å) in **17g** differ only slightly from each other. They are within the expected range of 1.86–1.91 Å for Si–C distances in organosilicon compounds with low steric strain [49,50]. From the torsion angles C(16)–Si(1)–C(7)–C(8) and C(7)–Si(1)–C(16)–C(17) it can be concluded that the ring planes of both aromatic substituents are nearly perpendicular to each other.

3. Experimental

Mass spectra: Mass spectrometer Intectra AMD 402-3. GC–MS: Coupling gas chromatograph Hewlett–Packard HP-5890-II – Mass spectrometer HP 59827 A. Gas chromatography: Hewlett–Packard HP-5890-II, capillary column HP1 (FS, non-polar) 25 m; Chrompack CP 9002, capillary column WCOT (FS, non-polar) 24 m. Preparative GC: Gerstel HP-5890-II, capillary column HP5 and HP FFAP 30 m. Preparative LPLC: The separation of compounds was carried out under normal pressure with silica gel 60 (63–200 μm) and *n*-heptane as mobile solvent (column: 30 × 3 cm). The separation process was monitored by TLC (precoated TLC foil: silica gel 60, layer 0.2 mm). The compounds on the TLC foil were coloured with iodine. NMR spectra: Bruker ARX 400 (^{1}H/^{13}C/^{29}Si NMR: 400.1/100.6/79.5 MHz), Bruker ARX 250 (^{1}H NMR: 250.1 MHz) or Bruker ARX 300 (^{13}C/^{29}Si NMR: 75.5/59.6 MHz); solutions of 30–50% in C_6D_6, reference C_6D_6, chemical shifts refer to $\delta_{TMS} = 0.0$ ppm. IR spectra: Nicolet 205 FT-IR; liquids as films between KBr disks, solids in nujol between KBr disks or in KBr pellets. Elemental analyses: Leco Modell 932, absolute error ±0.3%.

The trimethylsiloxychlorosilanes **1a**–**i** were synthesised under exclusion from moisture. All other reactions were carried out in dry, degassed solvents under an atmosphere of argon. The solvents used were dried by standard procedures and distilled under argon. Me_3SiCl and HMe_2SiCl were treated with small amounts of CaH_2 to remove traces of dissolved HCl. 2,3-Dimethylbuta-1,3-diene and Et_3SiH were dried over molecular sieves (4 Å) and distilled immediately before use.

The starting compounds Me_2SiCl_2, $MePhSiCl_2$, Ph_2SiCl_2, $HSiCl_3$, $PhSiCl_3$, $SiCl_4$, PhBr, ^{i}PrCl, MesBr, tri-*iso*-propylbenzene, ^{t}BuLi and ^{n}BuLi were commercial products. The dichlorosilanes $R(Ph)SiCl_2$ (R = H [51], Et [52,53], ^{i}Pr [54], ^{t}Bu [55], Tip [56]), Mes_2SiCl_2 [57] and $MesPhSiCl_2$ (analogously to Mes_2SiCl_2 [57] by reaction of $PhSiCl_3$ with MesLi) were prepared according to published procedures.

Dichloro(2,4,6-trimethylphenyl)phenylsilane: Yield: 74%. B.p.: 139–140 °C/0.1 Torr. MS (EI, 70 eV): *m*/*z* (%) = 294 (29) $[M]^+$, 216 (100) $[M-C_6H_6]^+$, 118 (66) $[C_9H_{10}]^+$, 77 (13) $[C_6H_5]^+$, 180 (26). ^{1}H NMR: $\delta = 2.03$ (s, *p*-Me, 3H), 2.37 (s, *o*-Me, 6H), 6.63 (s, HC_{ar}, 2H), 7.08–7.73 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 21.1$ (*p*-Me), 25.3 (*o*-Me); 125.5–145.3 (C_{ar}) ppm. ^{29}Si NMR: $\delta = 4.3$ ppm. Anal. Calc. for $C_{15}H_{16}Cl_2Si$ (295.287): C, 61.01; H, 5.46. Found: C, 60.76; H, 5.44%.

The lithium wire was purchased from Fluka (unknown sodium content) as well as from Aldrich (about 0.01% Na) and converted into very thin plates for the reactions. The lithium from Aldrich was only used in the reactions described in Sections 3.2.8–3.2.10 and 3.4–3.6.

The course of reaction of the siloxychlorosilanes **1a**–**i** with lithium metal was monitored by GC. The compounds **8a**, **9a**, **6c**–**9c**, **6d**–**9d**, **10d**, **6e**, **7e**, **10e**, **11e**, **13e**, **7f**, **9f**, **11f**, **6g**–**9g**, **6h**, **10h**, **11h**, **6i**, **7i** could be isolated by fractional distillation or by recrystallisation, the compounds **10a**, **10c**, **11c**, **11d**, **10g**, **11g** by preparative GC and **17g**, **17i** by preparative LPLC. These compounds were identified and characterised by their elemental analyses (except them isolated by preparative GC) as well as mass, NMR and partially IR spectra. The identification of compounds in mixtures was carried out by GC, GC–MS and spectroscopic investigations as well as in the case of the siloxanes **5a**–**c**, **5f**, **5h**, **5i** and of the disilanes **16f**, **16g**, **16i** additionally by comparison with the data of authentic samples. Well-known compounds are **5a** [58,59], **10a** [60]; **5c**, **10c** [61]; **5f** [62,63], **7f**, **9f**, **11f** [32]; **10g** [44] and **17i** [64,65].

The yields given in Schemes 1 and 2, in Tables 1 and 2 as well as in Eqs. (6) and (7) are based on GC investigations of all fractions (pure and/or mixed fractions), which were obtained by work-up of the quenched reaction mixtures. The yields of the compounds isolated by distillation or recrystallisation are given in the respective procedures together with the analytical data. They are clearly lower than those determined by GC because of the work-up of complex mixtures with very similar compounds.

3.1. Preparation of the trimethylsiloxychlorosilanes (Me_3SiO)RR′SiCl (1a, 1c–e, 1g–i)

The trimethylsiloxychlorosilanes (Me_3SiO)RPhSiCl (**1a**: R = H, **1b**: R = Me, **1c**: R = Et, **1d**: R = ^{i}Pr, **1e**: R = ^{t}Bu, **1f**: R = Ph, **1g**: R = Mes, **1h**: R = Tip) and (Me_3SiO)Mes_2SiCl (**1i**) were synthesised analogously to the preparation of (Me_3SiO)Me_2SiCl in [32,66] by reaction of the dichlorosilanes $R(Ph)SiCl_2$ (R = H, Me, Et, ^{i}Pr, ^{t}Bu, Ph, Mes, Tip) and Mes_2SiCl_2 with $NaOSiMe_3$ in molar ratio 1.1:1 in *n*-pentane/Et_2O (volume ratio 3:2) at −78 °C in yields of 50–85%.

1-Chloro-3,3,3-trimethyl-1-phenyl-disiloxane (**1a**): B.p.: 97–98 °C/15 Torr. ^{1}H NMR: $\delta = 0.16$ (s, Me_3SiO, 9H), 5.75 (s, HSi, 1H), 7.13–7.67 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.5$ (Me_3SiO); 128.4, 131.4, 133.4, 134.4 (Ph) ppm. ^{29}Si NMR: $\delta = -27.2$ (SiCl), 15.0 ($SiMe_3$) ppm; $J(^{29}Si–^1H) = 269.7$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1078, δ(CH_3Si) 1253, $\tilde{\nu}$(SiH) 2186 cm^{-1}. Anal. Calc. for $C_9H_{15}OClSi_2$ (230.841): C, 46.83; H, 6.55. Found: C, 46.63; H, 6.38%.

1-Chloro-1-ethyl-3,3,3-trimethyl-1-phenyl-disiloxane (**1c**): B.p.: 71–72 °C/2.8 Torr. MS (EI, 70 eV): m/z (%) = 258 (1) $[M]^+$, 243 (100) $[M-Me]^+$, 229 (70) $[M-Et]^+$, 214 (63) $[M-Me-Et]^+$, 193 (51) $[M-Cl-C_2H_6]^+$. ^{1}H NMR: $\delta = 0.13$ (s, Me_3SiO, 9H), 0.93 (t, H_3C, 3H), 0.99 (q, H_2C, 2H), 7.14–7.66 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.8$ (Me_3SiO), 6.5 (CH_2), 11.2 ($CH_2\mathit{CH}_3$); 128.3, 130.8, 133.7, 135.2 (Ph) ppm. ^{29}Si NMR: $\delta = -8.3$ (SiCl), 12.8 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1075, δ(CH_3Si) 1253 cm^{-1}. Anal. Calc. for $C_{11}H_{19}OClSi_2$ (258.898): C, 51.03; H, 7.40. Found: C, 51.30; H, 7.59%.

1-Chloro-3,3,3-trimethyl-1-phenyl-*iso*-propyl-disiloxane (**1d**): B.p.: 107–109 °C/5.0 Torr. MS (EI, 70 eV): m/z (%) = 272 (1) $[M]^+$, 229 (100) $[M-{}^iPr]^+$, 193 (51) $[M-Cl-C_3H_8]^+$. ^{1}H NMR: $\delta = 0.13$ (s, Me_3SiO, 9H), 1.01 (d, Me_2C, 6H), 1.27 (sept, HC, 1H), 7.12–7.65 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.8$ (Me_3SiO), 16.5 ($\mathit{C}Me_2$), 17.4 ($C\mathit{Me}_2$); 128.2, 128.5, 131.0, 134.1 (Ph) ppm. ^{29}Si NMR: $\delta = -8.1$ (SiCl), 12.8 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1082, δ(CH_3Si) 1253 cm^{-1}. Anal. Calc. for $C_{12}H_{21}OClSi_2$ (272.921): C, 52.81; H, 7.76. Found: C, 53.08; H, 7.71%.

1-*tert*-Butyl-1-chloro-3,3,3-trimethyl-1-phenyl-disiloxane (**1e**): B.p.: 103–104 °C/3.7 Torr. MS (EI, 70 eV): m/z (%) = 286 (4) $[M]^+$, 271 (6) $[M-Me]^+$, 229 (100) $[M-{}^tBu]^+$, 193 (52) $[M-Cl-C_4H_{10}]^+$, 135 (6). ^{1}H NMR: $\delta = 0.13$ (s, Me_3SiO, 9H), 0.97 (s, Me_3C, 9H), 7.20–7.63 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.9$ (Me_3SiO), 21.1 ($\mathit{C}Me_3$), 25.5 ($C\mathit{Me}_3$); 128.1, 130.7, 133.6, 134.8 (Ph) ppm. ^{29}Si NMR: $\delta = -7.8$ (SiCl), 12.8 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1079, δ(CH_3Si) 1253 cm^{-1}. Anal. Calc. for $C_{13}H_{23}OClSi_2$ (286.953): C, 54.41; H, 8.08. Found: C, 54.32; H, 7.96%.

1-Chloro-3,3,3-trimethyl-1-(2,4,6-trimethylphenyl)-1-phenyl-disiloxane (**1g**): B.p.: 133–134 °C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 348 (17) $[M]^+$, 333 (32) $[M-Me]^+$, 297 (15) $[M-Cl-Me-H]^+$, 270 (39) $[M-C_6H_6]^+$, 255 (100) $[M-C_6H_6-Me]^+$. ^{1}H NMR: $\delta = 0.13$ (s, Me_3SiO, 9H), 2.11 (s, *p*-Me, 3H), 2.47 (s, *o*-Me, 6H), 6.74 (s, HC_{ar}, 2H), 7.10–7.76 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.8$ (Me_3SiO), 21.1 (*p*-Me), 24.7 (*o*-Me); 127.0, 128.4, 130.0, 130.6, 133.5, 138.1, 140.8, 145.4 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -20.9$ (SiCl), 13.1 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1084, δ(CH_3Si) 1253 cm^{-1}. Anal. Calc. for $C_{18}H_{25}OClSi_2$ (349.024): C, 61.94; H, 7.22. Found: C, 61.81; H, 7.26%.

1-Chloro-3,3,3-trimethyl-1-phenyl-1-(2,4,6-tri-*iso*-propylphenyl)disiloxane (**1h**): B.p.: 142–143 °C/0.04 Torr. MS (EI, 70 eV): m/z (%) = 432 (9) $[M]^+$, 417 (17) $[M-Me]^+$, 354 (100) $[M-C_6H_6]^+$, 311 (34), 297 (19), 229 (10) $[M-C_{15}H_{23}]^+$, 193 (23) $[Me_3SiOSiPh]^+$, 135 (10) $[SiMe_2Ph]^+$, 73 (10) $[SiMe_3]^+$, 43 (23) $[C_3H_7]^+$. ^{1}H NMR: $\delta = 0.09$ (s, Me_3SiO, 9H), 1.18, 1.34 (2 × d, H_3C, 12H), 1.45 ((d), H_3C, 6H), 2.78 (sept, $HC(Me)_2$, 1H), 3.83 (sept, $HC(Me)_2$, 2H), 7.10 (s, HC_{ar}, 2H), 7.04–7.71 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 24.1$ (*p*-($\mathit{C}H_3)_2CH$); 24.5, 25.6 (*o*-($\mathit{C}H_3)_2CH$), 32.5 (*o*-$\mathit{C}H(CH_3)_2$), 34.8 (*p*-$\mathit{C}H(CH_3)_2$); 122.1, 125.5, 128.2, 130.3, 133.3, 138.9, 153.1, 157.2 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -20.6$ (SiCl), 13.2 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1080, δ(CH_3Si) 1252 cm^{-1}. Anal. Calc. for $C_{24}H_{37}ClOSi_2$ (433.187): C, 66.55; H, 8.61. Found: C, 66.31; H, 8.74%.

1-Chloro-3,3,3-trimethyl-1,1-bis(2,4,6-trimethylphenyl) disiloxane (**1i**): B.p.: 178–180 °C/0.01 Torr. MS (EI, 70 eV): m/z (%) = 390 (4) $[M]^+$, 375 (16) $[M-Me]^+$, 355 (2) $[M-Cl]^+$, 324 (13), 309 (29), 270 (26) $[M-C_9H_{12}]^+$, 255 (100) $[M-C_9H_{12}-Me]^+$, 120 (51) $[C_9H_{12}]^+$. ^{1}H NMR: $\delta = 0.12$ (s, Me_3SiO, 9H), 2.08 (s, *p*-Me, 6H), 2.47 (s, *o*-Me, 12H), 6.68 (s, HC_{ar}, 4H) ppm. ^{13}C NMR: $\delta = 1.6$ (Me_3SiO), 21.1 (*p*-Me), 24.1 (*o*-Me); 130.1, 132.2, 139.9, 143.4 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -21.2$ (SiCl), 12.6 ($SiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1078, δ(CH_3Si) 1251 cm^{-1}. Anal. Calc. for $C_{21}H_{31}ClOSi_2$ (391.106): C, 64.49; H, 7.99. Found: C, 64.58; H, 8.06%.

3.2. Reaction of the trimethylsiloxychlorosilanes *1a*, *1c–i* with lithium metal in THF at −78 °C or in a Trapp mixture at −110 °C as well as trapping of the formed lithiumsilanides with chlorotrimethyl- and chlorodimethylsilane

On the analogies of the preparative work a general procedure is given for the reactions of the trimethylsiloxychlorosilanes **1a**, **1c–i** with lithium metal and for the following trapping reactions with Me_3SiCl and HMe_2SiCl. The work-up of the crude products is described separately. Some details of reactions are given in Schemes 1 and 2, additionally, the proportions of products in the reaction mixtures, which were determined by GC, are summarised in Tables 1 and 2.

3.2.1. General procedure

A mixture of 0.14 mol very thin lithium plates and 70 ml THF or 70 ml Trapp mixture (THF/Et_2O/*n*-pentane in volume ratio 4:1:1) was cooled down to −78 °C (reactions in THF) and to −110 °C (reactions in a Trapp mixture), respectively. To the respective mixture 0.035 mol trimethylsiloxychlorosilane **1a**, **1c–i**, dissolved in 30 ml THF or Trapp mixture, was added dropwise within 15 min with vigorous stirring. The vigorous stirring was continued at −78 °C or at −110 °C until the siloxychlorosilane **1** was consumed completely and the composition of the reaction mixture was nearly constant. The reaction progress was monitored by GC of samples quenched with Me_3SiCl and HMe_2SiCl, respectively. The reaction times t_{rct} are given in Sections 3.2.2–3.2.9. The solutions turned brown (reactions of **1a**, **1c**, **1d** and **1i**), red (reactions of **1e** and **1h**) and green (reactions of

1f and **1g**). After the reaction times t_{rct} as given below the excess lithium was removed. Then 0.07 mol trapping agent Me_3SiCl or HMe_2SiCl was added to the solution of lithiumsilanides stirred at the respective reaction temperature. The reaction mixture was warmed to room temperature (20 °C) within 30 min and was allowed to react for 24 h at the same temperature. Subsequently, the solvent and excess trapping agent were removed under reduced pressure at room temperature and 50 ml *n*-pentane were added to the residue. The resulting suspension was filtered, and the solvent of the filtrate was evaporated under reduced pressure. The respective residue was distilled in vacuo below 0.5 Torr, and that of the reaction of **1i** with lithium (trapping agent Me_3SiCl) was recrystallised.

In dependence on the trapping agent used the evaporated solvents contained $(Me_3Si)_2O$ or $HMe_2SiOSiMe_3$ as well as from the reactions of **1e** and **1g–i** $Me_3Si–SiMe_3$ or $Me_3Si–SiMe_2H$.

In the case of the reactions of the siloxychlorosilanes **1e** and **1g** with lithium metal in a Trapp mixture at −110 °C the siloxydisilanes $(Me_3SiO)RR'Si–SiRR'(OSiMe_3)$ (**14e**: $R = {}^tBu$, $R' = Ph$; **14g**: R = Mes, $R' = Ph$) could be proved and isolated as intermediates (Section 3.2.10). For this purpose the excess lithium was removed and the respective reaction mixtures were quenched with 0.07 mol Me_3SiCl clearly before the siloxychlorosilanes **1e** and **1g** were consumed completely.

3.2.2. Trapping products of the lithiumsilanides from the reaction of $(Me_3SiO)HPhSiCl$ (*1a*) with lithium and the trisiloxane *5a*

(1) THF, −78 °C, $t_{rct} = 0.5$ h, trapping agent Me_3SiCl.
Distillation of the residue through a small Vigreux column (49–136 °C/0.1 Torr) yielded a fraction (49–56 °C) of **5a** and **10a** as well as two fractions in the temperature range of 56–136 °C, which consisted of mixtures of **8a**, **10a** and small amounts of **5a**. In the distillation residue higher-molecular products with Si–Si groups were found. From the first fraction **10a** was isolated by preparative GC.

(2) Trapp mixture, −110 °C, $t_{rct} = 1$ h, trapping agent Me_3SiCl.
Distillation of the residue through a slit pipe column (Fischer, Mikro-Spaltrohr-System D100) in the temperature range of 50–135 °C/0.1 Torr yielded three fractions, which consisted of **5a** and **10a** (50–55 °C), **5a**, **10a** and **8a** (55–130 °C) as well as of pure **8a** (130–131 °C). The resulting residue contained higher-molecular products with Si–Si groups and minor **8a**.

(3) THF, −78 °C, $t_{rct} = 0.5$ h, trapping agent HMe_2SiCl.
Distillation of the residue through a small Vigreux column (42–130 °C/0.2 Torr) yielded a fraction (42–60 °C) of **5a** and minor **11a** as well as two fractions (60–105 °C, 105–130 °C), which consisted of mixtures of **9a** and small amounts of **5a** as well as **11a**. In the distillation residue higher-molecular products with Si–Si groups were found.

(4) Trapp mixture, −110 °C, $t_{rct} = 1$ h, trapping agent HMe_2SiCl.
Distillation of the residue through a Fischer slit pipe column in the temperature range of 45–125 °C/0.2 Torr yielded four fractions, which consisted of **5a** and minor **11a** (45–50 °C), minor **5a** and **11a** (50–60 °C), **5a**, **11a** and **9a** (60–122 °C) as well as of pure **9a** (122–123 °C). The distillation residue contained higher-molecular products with Si–Si groups and minor **9a**.

1,1,1,5,5,5-Hexamethyl-3-phenyl-trisiloxane (**5a**) [58,59]: $C_{12}H_{24}O_2Si_3$ (284.58). MS (EI, 70 eV): *m/z* (%) = 284 (12) $[M]^+$, 269 (100) $[M-Me]^+$, 206 (15) $[M-C_6H_6]^+$, 191 (19) $[M-C_6H_6-Me]^+$, 135 (62), 73 (15) $[SiMe_3]^+$. ^1H NMR: $\delta = 0.21$ (s, Me_3SiO, 18H), 5.31 (s, HSi, 1H), 7.18–7.73 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.8$ (Me_3SiO); 128.4, 130.1, 134.1, 136.0 (Ph) ppm. ^{29}Si NMR: $\delta = -48.7$ (SiHPh), 10.5 ($OSiMe_3$) ppm; $J(^{29}Si–^1H) = 245.2$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1063, $\delta(CH_3Si)$ 1250, $\tilde{\nu}$(SiH) 2152 cm^{-1}.

3,3,3-Trimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**8a**): Yield: 1.3 g (20%). B.p.: 130–131 °C/0.1 Torr. GC: Diastereomeric ratio 1.2:1. MS (EI, 70 eV): *m/z* (%) = 374 (5) $[M]^+$, 359 (14) $[M-Me]^+$, 300 (32) $[M-SiMe_3-H]^+$, 271 (100) $[M-SiMe_4-Me]^+$, 255 (41) $[M-OSiMe_3-2Me]^+$, 193 (52), 178 (45) $[Me_3SiSiPh]^+$, 135 (52), 73 (40) $[SiMe_3]^+$. ^1H NMR: $\delta = 0.07$, 0.10 (s, Me_3Si, 9H); 0.15, 0.18 (s, Me_3SiO, 9H); 4.29, 4.30 (s, *H*Si-SiMe$_3$, 1H, $J(^{29}Si–^1H) = 171.0$ Hz); 5.98, 5.99 (s, *H*SiO-SiMe$_3$, 1H, $J(^{29}Si–^1H) = 204.1$ Hz); 7.10–7.68 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -0.4$, −0.3 (Me_3Si); 1.7, 1.8 (Me_3SiO); 128.3–138.0 (Ph) ppm. ^{29}Si NMR: $\delta = -65.6$, −65.3 (SiHPh); −15.6, −15.5 (OSiHPh); −15.0, −14.8 ($SiMe_3$); 12.3, 12.5 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1059, $\delta(CH_3Si)$ 1253, 1260; $\tilde{\nu}$(SiH) 2087 cm^{-1}. Anal. Calc. for $C_{18}H_{30}OSi_4$ (374.783): C, 57.69; H, 8.07. Found: C, 57.45; H, 7.92%.

3,3-Dimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**9a**): Yield: 1.0 g (16%). B.p.: 122–123 °C/0.2 Torr. GC: Diastereomeric ratio 1.2:1. MS (EI, 70 eV): *m/z* (%) = 360 (5) $[M]^+$, 345 (11) $[M-Me]^+$, 300 (15) $[M-SiMe_2H-H]^+$, 271 (98) $[M-SiMe_4-H]^+$, 193 (80) $[M-SiMe_4-H-C_6H_6]^+$, 164 (78) $[HMe_2SiSiPh]^+$, 135 (100), 73 (52) $[SiMe_3]^+$, 59 (22) $[SiMe_2H]^+$. ^1H NMR: $\delta = 0.09$, 0.11 (s, Me_3SiO, 9H); 0.16, 0.17, 0.18, 0.19 (2 × d, Me_2HSi, 6H); 4.28, 4.29 (s, *H*SiSi-Me$_2$H, 1H, $J(^{29}Si–^1H) = 171.8$ Hz); 4.40, 4.41 (sept, HMe_2Si, 1H, $J(^{29}Si–^1H) = 175.7$ Hz); 6.03, 6.04 (s, *H*SiO-SiMe$_3$, 1H, $J(^{29}Si–^1H) = 204.3$ Hz); 7.08–7.79 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -5.3$, −5.2, −5.1, − 5.0 (Me_2HSi); 1.6, 1.8 (Me_3SiO); 128.1–138.5 (Ph) ppm. ^{29}Si NMR: $\delta = -66.3$, −66.0 (SiHPh); −37.7, −37.6 ($SiMe_2H$); − 16.6, −16.4 (OSiHPh); 12.6, 12.7 ($OSiMe_3$) ppm. Anal. Calc. for $C_{17}H_{28}OSi_4$ (360.756): C, 56.60; H, 7.76. Found: C, 56.39; H, 7.69%.

1,1,1,3,3,3-Hexamethyl-2-phenyl-trisilane (**10a**) [60]: $C_{12}H_{24}Si_3$ (252.58). MS (EI, 70 eV): m/z (%) = 252 (13) $[M]^+$, 237 (8) $[M-Me]^+$, 178 (68) $[M-SiMe_3-H]^+$, 163 (100) $[M-SiMe_4-H]^+$, 135 (46), 73 (63) $[SiMe_3]^+$. ^1H NMR: $\delta = 0.16$ (s, Me_3Si, 18H), 4.08 (s, HSi, 1H), 7.11–7.56 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.1$ (Me_3Si); 128.3, 130.5, 133.4, 136.1 (Ph) ppm. ^{29}Si NMR: $\delta = -61.1$ (SiHPh), -15.4 ($SiMe_3$) ppm; $J(^{29}Si–^1H) = 165.2$ Hz. IR(film): $\delta(CH_3Si)$ 1253, $\tilde{\nu}$(SiH) 2068 cm^{-1}.

1,1,1,3,3-Pentamethyl-2-phenyl-trisilane (**11a**): $C_{11}H_{22}Si_3$ (238.56). MS (EI, 70 eV): m/z (%) = 238 (4) $[M]^+$, 223 (3) $[M-Me]^+$, 178 (11) $[M-SiMe_2H-H]^+$, 164 (43) $[M-SiMe_3-H]^+$, 135 (100), 73 (14) $[SiMe_3]^+$, 59 (20) $[SiMe_2H]^+$. ^1H NMR: $\delta = 0.17$ (s, Me_3Si, 9H); 0.20, 0.21 (2 × d, Me_2HSi, 6H); 4.18 (s, HSi, 1H, $J(^{29}Si–^1H) = 167.4$ Hz), 4.23 (sept, HMe_2Si, 1H, $J(^{29}Si–^1H) = 176.2$ Hz), 7.10–7.54 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -4.9$, -4.8 (Me_2HSi); 0.5 (Me_3Si); 128.1–136.0 (Ph) ppm. ^{29}Si NMR: $\delta = -63.3$ (SiHPh), -37.9 ($SiMe_2H$), -17.1 ($SiMe_3$) ppm.

*3.2.3. Trapping products of the lithiumsilanides from the reaction of (Me_3SiO)EtPhSiCl (**1c**) with lithium and the trisiloxane **5c***

(1) THF, −78 °C, $t_{rct} = 2$ h, trapping agent Me_3SiCl.
Distillation of the residue through a Fischer slit pipe column (60–140 °C/0.1 Torr) yielded four fractions, which contained **5c**, **6c** and minor **10c** (60–95 °C), **6c** and **10c** (95–120 °C), **10c** and **8c** (120–135 °C) as well as pure **8c** (136–137 °C). In the distillation residue minor **8c** was found beside unknown products. From the second fraction **10c** was isolated by preparative GC.

(2) Trapp mixture, −110 °C, $t_{rct} = 3$ h, trapping agent Me_3SiCl.
Distillation of the residue through a Fischer slit pipe column in the temperature range of 60–120 °C/0.1 Torr yielded three fractions, which contained **5c**, **6c** and small amounts of **10c** (60–96 °C), pure **6c** (97–98 °C) as well as **6c** and minor **10c** (99–120 °C).

(3) THF, −78 °C, $t_{rct} = 2$ h, trapping agent HMe_2SiCl.
Distillation of the residue through a Fischer slit pipe column (50–125 °C/0.1 Torr) yielded four fractions. The first two fractions (50–58 °C, 59–70 °C) contained mixtures of **5c**, **7c** and minor **11c**. The third fraction (70–123 °C) consisted of **7c**, **11c** and minor **9c**. In the last fraction (124–125 °C) pure **9c** was found. From the third fraction **11c** was isolated by preparative GC.

(4) Trapp mixture, −110 °C, $t_{rct} = 3$ h, trapping agent HMe_2SiCl.
Distillation of the residue through a Fischer slit pipe column in the temperature range of 50–123 °C/0.1 Torr yielded three fractions, which consisted of **5c**, **7c** and minor **11c**(50–65 °C), pure **7c** (66–67 °C) as well as of **7c**, **11c** and minor **9c** (68–123 °C).

3-Ethyl-1,1,1,5,5,5-hexamethyl-3-phenyl-trisiloxane (**5c**) [61]: $C_{14}H_{28}O_2Si_3$ (312.64). MS (EI, 70 eV): m/z (%) = 312 (1) $[M]^+$, 297 (25) $[M-Me]^+$, 283 (100) $[M-Et]^+$, 135 (47). ^1H NMR: $\delta = 0.16$ (s, Me_3SiO, 18H), 0.78 (q, H_2C, 2H), 1.04 (t, H_3C, 3H), 7.12–7.70 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 2.0$ (Me_3SiO), 6.9 (CH_2), 8.5 ($CH_2\mathit{CH_3}$); 128.1, 129.9, 133.8, 137.6 (Ph) ppm. ^{29}Si NMR: $\delta = -33.9$ (SiEtPh), 8.0 ($OSiMe_3$) ppm.

1-Ethyl-2,2,2-trimethyl-1-trimethylsiloxy-1-phenyl-disilane (**6c**): Yield: 0.7 g (7%). B.p.: 97–98 °C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 296 (5) $[M]^+$, 281 (4) $[M-Me]^+$, 267 (12) $[M-Et]^+$, 223 (82) $[M-SiMe_3]^+$, 195 (100) $[M-SiMe_3-C_2H_4]^+$, 135 (29), 73 (23) $[SiMe_3]^+$. ^1H NMR: $\delta = 0.15$ (s, Me_3Si, 9H), 0.17 (s, Me_3SiO, 9H), 0.92 (q, H_2C, 2H), 1.07 (t, H_3C, 3H), 7.14–7.60 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -1.7$ (Me_3Si), 2.3 (Me_3SiO), 7.3 (CH_2), 9.8 ($CH_2\mathit{CH_3}$); 128.2, 129.2, 133.4, 139.8 (Ph) ppm. ^{29}Si NMR: $\delta = -23.0$ ($SiMe_3$), -3.0 (SiEtPh), 7.9 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1068, $\delta(CH_3Si)$ 1253, 1261 cm^{-1}. Anal. Calc. for $C_{14}H_{28}OSi_3$ (296.637): C, 56.69; H, 9.51. Found: C, 56.49; H, 9.42%.

1-Ethyl-2,2-dimethyl-1-trimethylsiloxy-1-phenyl-disilane (**7c**): Yield: 0.8 g (8%). B.p.: 66–67 °C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 282 (12) $[M]^+$, 267 (7) $[M-Me]^+$, 253 (8) $[M-Et]^+$, 223 (87) $[M-SiMe_2H]^+$, 195 (100) $[M-SiMe_2H-C_2H_4]^+$, 135 (27), 73 (17) $[SiMe_3]^+$, 59 (9) $[SiMe_2H]^+$. ^1H NMR: $\delta = 0.13$ (s, Me_3SiO, 9H); 0.14, 0.15 (2 × d, Me_2HSi, 6H); 0.90 (q, H_2C, 2H), 1.03 (t, H_3C, 3H), 4.01 (sept, HSi, 1H), 7.13–7.56 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -6.2$, -6.1 (Me_2HSi); 2.3 (Me_3SiO), 7.3 (CH_2), 10.2 ($CH_2\mathit{CH_3}$); 128.2, 129.4, 133.5, 139.3 (Ph) ppm. ^{29}Si NMR: $\delta = -44.4$ ($SiMe_2H$), -2.7 (SiEtPh), 8.7 ($OSiMe_3$) ppm; $J(^{29}Si–^1H) = 174.2$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1066, $\delta(CH_3Si)$ 1244, 1253; $\tilde{\nu}$(SiH) 2090 cm^{-1}. Anal. Calc. for $C_{13}H_{26}OSi_3$ (282.610): C, 55.25; H, 9.27. Found: C, 55.13; H, 9.18%.

1,2-Diethyl-3,3,3-trimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**8c**): Yield: 3.1 g (41%). B.p.: 136–137 °C/0.1 Torr. GC: Diastereomeric ratio 1.3:1. MS (EI, 70 eV): m/z (%) = 430 (12) $[M]^+$, 415 (6) $[M-Me]^+$, 401 (4) $[M-Et]^+$, 357 (11) $[M-SiMe_3]^+$, 223 (100) $[Me_3SiO\text{-}SiEtPh]^+$, 194 (88) $[Me_3SiOSiPh]^+$, 135 (29), 73 (13) $[SiMe_3]^+$. ^1H NMR: $\delta = 0.10$, 0.11 (s, Me_3Si, 9H); 0.13, 0.14 (s, Me_3SiO, 9H); 0.90–1.05 (m, H_2C, 4H); 1.08–1.20 (m, H_3C, 6H); 7.11–7.53 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -0.1$, 0.0 (Me_3Si); 2.4, 2.4 (Me_3SiO); 7.3–7.6 (CH_2); 10.5–11.0 ($CH_2\mathit{CH_3}$); 128.1–140.1 (Ph) ppm. ^{29}Si NMR: $\delta = -43.2$, -43.1 (SiEtPh); -16.7, -16.6 ($SiMe_3$); -1.4, -1.3 (OSiEtPh); 8.4, 8.5 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1059, $\delta(CH_3Si)$ 1253, 1260 cm^{-1}. Anal. Calc. for $C_{22}H_{38}OSi_4$ (430.892): C, 61.33; H, 8.89. Found: C, 61.07; H, 8.86%.

1,2-Diethyl-3,3-dimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**9c**): Yield: 3.5 g (48%). B.p.: 124–125 °C/0.1 Torr. GC: Diastereomeric ratio 1.3:1. MS (EI, 70 eV): m/z (%) = 416 (9) $[M]^+$, 401 (6) $[M-Me]^+$, 357 (4) $[M-SiMe_2H]^+$, 329 (4) $[M-SiMe_2H-C_2H_4]^+$, 223 (87)

$[\mathrm{Me_3SiOSiEtPh}]^+$, 195 (98), 192 (100) $[\mathrm{SiEtPhSiMe_2}]^+$, 135 (32), 73 (11) $[\mathrm{SiMe_3}]^+$, 59 (8) $[\mathrm{SiMe_2H}]^+$. ^{1}H NMR: $\delta = 0.13$, 0.14 (s, Me$_3$SiO, 9H); 0.17, 0.18, 0.19, 0.20 (2 × d, Me$_2$HSi, 6H); 1.01–1.07 (m, H$_2$C, 4H); 1.10–1.14 (m, H$_3$C, 6H); 4.22, 4.23 (sept, HSi, 1H), 7.12–7.56 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -5.13$, -5.10, -5.03, -4.97 (Me$_2$HSi); 2.3, 2.4 (Me$_3$SiO); 7.4–11.0 (CH$_2$CH$_3$); 128.2–139.7 (Ph) ppm. ^{29}Si NMR: $\delta = -42.8$, -42.7 (SiEtPh); -38.4, -38.3 (SiMe$_2$H); -1.92, -1.86 (OSiEtPh); 8.57, 8.62 (OSiMe$_3$) ppm; $J(^{29}\mathrm{Si}\text{–}^1\mathrm{H}) = 176.3$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1065, δ(CH$_3$Si) 1244, 1252; $\tilde{\nu}$(SiH) 2093 cm^{-1}. Anal. Calc. for $C_{21}H_{36}OSi_4$ (416.864): C, 60.51; H, 8.70. Found: C, 60.39; H, 8.77%.

2-Ethyl-1,1,1,3,3,3-hexamethyl-2-phenyl-trisilane (**10c**) [61]: $C_{14}H_{28}Si_3$ (280.637). MS (EI, 70 eV): *m/z* (%) = 280 (28) $[\mathrm{M}]^+$, 265 (6) $[\mathrm{M-Me}]^+$, 251 (3) $[\mathrm{M-Et}]^+$, 207 (50) $[\mathrm{M-SiMe_3}]^+$, 179 (100) $[\mathrm{M-SiMe_3-C_2H_4}]^+$, 135 (56), 73 (40) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.17$ (s, Me$_3$Si, 18H), 0.76 (q, H$_2$C, 2H), 1.12 (t, H$_3$C, 3H), 7.09–7.50 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.21$ (Me$_3$Si), 8.5 (CH$_2$), 10.6 (CH$_2$*CH$_3$*); 128.3, 129.9, 133.8, 135.2 (Ph) ppm. ^{29}Si NMR: $\delta = -40.1$ (SiEtPh), -16.6 (SiMe$_3$) ppm.

2-Ethyl-1,1,1,3,3-pentamethyl-2-phenyl-trisilane (**11c**): $C_{13}H_{26}Si_3$ (266.61). MS (EI, 70 eV): *m/z* (%) = 266 (11) $[\mathrm{M}]^+$, 251 (5) $[\mathrm{M-Me}]^+$, 207 (14) $[\mathrm{M-SiMe_2H}]^+$, 192 (100) $[\mathrm{M-SiMe_3-H}]^+$, 179 (78) $[\mathrm{M-SiMe_2H-C_2H_4}]^+$, 135 (87), 105 (44) $[\mathrm{SiPh}]^+$, 73 (48) $[\mathrm{SiMe_3}]^+$, 59 (24) $[\mathrm{SiMe_2H}]^+$. ^{1}H NMR: $\delta = 0.11$ (s, Me$_3$Si, 9H); 0.14, 0.15 (2 × d, Me$_2$HSi, 6H); 0.72 (q, H$_2$C, 2H), 1.01 (t, H$_3$C, 3H), 4.15 (sept, HSi, 1H), 7.07–7.47 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.30$, -5.27 (Me$_2$HSi); -0.5 (Me$_3$Si), 8.5 (CH$_2$), 10.5 (CH$_2$*CH$_3$*); 128.3, 130.0, 133.9, 135.3 (Ph) ppm. ^{29}Si NMR: $\delta = -39.2$ (SiEtPh), -38.8 (SiMe$_2$H), -16.5 (SiMe$_3$) ppm; $J(^{29}\mathrm{Si}\text{–}^1\mathrm{H}) = 175.2$ Hz.

3.2.4. Trapping products of the lithiumsilanides from the reaction of $(Me_3SiO)^iPrPhSiCl$ (1d) with lithium and the trisiloxane 5d

(1) THF, −78 °C, $t_{\mathrm{rct}} = 2$ h, trapping agent Me$_3$SiCl.
Distillation of the residue through a Fischer slit pipe column (55–145 °C/0.03 Torr) yielded five fractions, which contained **5d** and **6d** (55–65 °C), **5d**, **6d** and **10d** (65–73 °C), pure **10d** (74–77 °C), **10d** and **8d** (80–140 °C) as well as pure **8d** (141–142 °C). In the distillation residue small amounts of **8d** were found beside unknown products.

(2) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 3$ h, trapping agent Me$_3$SiCl.
Distillation of the residue through a Fischer slit pipe column (55–145 °C/0.03 Torr) yielded six fractions, which consisted of **5d** and **6d** (55–61 °C), pure **6d** (62–63 °C), **5d**, **6d** and **10d** (64–73 °C), **10d** (only 25%) and **8d** (74–95 °C), **8d** and small amounts of **10d** (96–140 °C) as well as pure **8d** (141–142 °C).

(3) THF, −78 °C, $t_{\mathrm{rct}} = 2$ h, trapping agent HMe$_2$SiCl.
Distillation of the residue through a Fischer slit pipe column (60–147 °C/0.4 Torr) yielded four fractions, which contained **5d** and **7d** (60–70 °C), **7d** and **11d** (70–85 °C), **11d** beside minor **7d**, **9d** (85–145 °C) as well as pure **9d** (146–147 °C). In the distillation residue small amounts of **9d** were found beside unknown products.

(4) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 3$ h, trapping agent HMe$_2$SiCl.
Distillation of the residue through a Fischer slit pipe column (60–147 °C/0.4 Torr) yielded five fractions, which consisted of **5d** and **7d** (60–71 °C), pure **7d** (72–73 °C), **7d** and **13d** (73–85 °C), **11d** beside minor **7d**, **9d** (85–145 °C) as well as pure **9d** (146–147 °C). From the third fraction **13d** was isolated by preparative GC.

1,1,1,5,5,5-Hexamethyl-3-phenyl-3-*iso*-propyl-trisiloxane (**5d**): B.p.: 97–98 °C/1.1 Torr. MS (EI, 70 eV): *m/z* (%) = 326 (1) $[\mathrm{M}]^+$, 311 (14) $[\mathrm{M-Me}]^+$, 283 (100) $[\mathrm{M-{}^iPr}]^+$, 135 (55), 73 (9) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.16$ (s, Me$_3$SiO, 18H), 0.98 (sept, HC, 1H), 1.05 (d, Me$_2$C, 6H), 7.13–7.68 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 2.1$ (Me$_3$SiO), 15.0 (*C*Me$_2$), 17.5 (C*Me$_2$*); 127.9, 129.8, 134.2, 136.7 (Ph) ppm. ^{29}Si NMR: $\delta = -34.9$ (Si^{i}PrPh), 7.7 (OSiMe$_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1059, δ(CH$_3$Si) 1251 cm^{-1}. Anal. Calc. for $C_{15}H_{30}O_2Si_3$ (326.657): C, 55.15; H, 9.26. Found: C, 54.93; H, 9.16%.

2,2,2-Trimethyl-1-trimethylsiloxy-1-phenyl-1-*iso*-propyl-disilane (**6d**): Yield: 1.0 g (9%). B.p.: 62–63 °C/0.03 Torr. MS (EI, 70 eV): *m/z* (%) = 310 (5) $[\mathrm{M}]^+$, 295 (3) $[\mathrm{M-Me}]^+$, 267 (100) $[\mathrm{M-{}^iPr}]^+$, 237 (39) $[\mathrm{M-SiMe_3}]^+$, 209 (70), 193 (81) $[\mathrm{M-SiMe_3-C_3H_8}]^+$, 135 (77), 73 (49) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.17$ (s, Me$_3$Si, 9H), 0.19 (s, Me$_3$SiO, 9H), 1.04 (d, Me$_2$C, 6H), 1.21 (sept, HC, 1H), 7.14–7.58 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -1.0$ (Me$_3$Si), 2.4 (Me$_3$SiO), 16.9 (*C*Me$_2$), 17.8 (C*Me$_2$*); 128.1, 129.1, 133.5, 134.2 (Ph) ppm. ^{29}Si NMR: $\delta = -23.0$ (SiMe$_3$), -2.4 (Si^{i}PrPh), 7.3 (OSiMe$_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1060, δ(CH$_3$Si) 1253, 1261 cm^{-1}. Anal. Calc. for $C_{15}H_{30}OSi_3$ (310.658): C, 57.99; H, 9.73. Found: C, 58.06; H, 9.64%.

2,2-Dimethyl-1-trimethylsiloxy-1-phenyl-1-*iso*-propyl-disilane (**7d**): Yield: 1.3 g (13%). B.p.: 72–73 °C/0.4 Torr. MS (EI, 70 eV): *m/z* (%) = 296 (5) $[\mathrm{M}]^+$, 281 (3) $[\mathrm{M-Me}]^+$, 253 (44) $[\mathrm{M-{}^iPr}]^+$, 237 (55) $[\mathrm{M-SiMe_2H}]^+$, 209 (59), 193 (53) $[\mathrm{M-SiMe_2H-C_3H_8}]^+$, 135 (100), 73 (73) $[\mathrm{SiMe_3}]^+$, 59 (29) $[\mathrm{SiMe_2H}]^+$, 43 (27) $[\mathrm{C_3H_7}]^+$. ^{1}H NMR: $\delta = 0.15$ (s, Me$_3$SiO, 9H); 0.16, 0.18 (2 × d, Me$_2$SiH, 6H); 1.04 (d, Me$_2$C, 6H), 1.14 (sept, HC, 1H), 4.06 (sept, HSi, 1H), 7.12–7.56 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.9$, -5.8 (Me$_2$SiH); 2.3 (Me$_3$SiO), 17.1 (*C*Me$_2$), 17.6 (C*Me$_2$*); 128.1, 129.4, 133.7, 138.7 (Ph) ppm. ^{29}Si NMR: $\delta = -45.2$ (SiMe$_2$H), -1.9 (Si^{i}PrPh), 8.2 (OSiMe$_3$) ppm; $J(^{29}\mathrm{Si}\text{–}^1\mathrm{H}) = 174.2$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1062, δ(CH$_3$Si) 1245, 1253; $\tilde{\nu}$(SiH) 2091 cm^{-1}. Anal. Calc. for $C_{14}H_{28}OSi_3$ (296.637): C, 56.69; H, 9.51. Found: C, 56.72; H, 9.48%.

3,3,3-Trimethyl-1-trimethylsiloxy-1,2-diphenyl-1,2-di-*iso*-propyl-trisilane (**8d**): Yield: 1.8 g (22%). B.p.: 141–142 °C/0.03 Torr. GC: Diastereomeric ratio 1.4:1. MS (EI, 70 eV): m/z (%) = 458 (7) $[\mathrm{M}]^+$, 443 (5) $[\mathrm{M{-}Me}]^+$, 415 (35) $[\mathrm{M{-}{}^{i}Pr}]^+$, 373 (31) $[\mathrm{M{-}{}^{i}Pr{-}C_3H_6}]^+$, 308 (22), 237 (100) $[\mathrm{Me_3SiOSi{}^{i}PrPh}]^+$, 209 (63), 195 (70), 135 (52), 73 (24) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.17$, 0.18 (s, $\mathrm{Me_3Si}$, 9H); 0.20, 0.21 (s, $\mathrm{Me_3SiO}$, 9H); 0.98–1.30 (m, $\mathrm{Me_2C}$, 12H); 1.50–1.70 (m, HC, 2H); 7.11–7.58 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = 1.0$, 1.1 ($\mathrm{Me_3Si}$); 2.6, 2.7 ($\mathrm{Me_3SiO}$); 17.8, 17.9 ($C\mathrm{Me_2}$); 20.9, 21.0 ($\mathrm{C}Me_2$); 127.9–140.1 (Ph) ppm. ^{29}Si NMR: $\delta = -37.9$, -37.8 ($\mathrm{Si{}^{i}PrPh}$); -16.5, -16.3 ($\mathrm{SiMe_3}$); -0.1, 0.0 ($\mathrm{OSi{}^{i}PrPh}$); 7.7, 7.8 ($\mathrm{OSiMe_3}$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1060, $\delta(\mathrm{CH_3Si})$ 1253, 1261 cm^{-1}. Anal. Calc. for $\mathrm{C_{24}H_{42}OSi_4}$ (458.937): C, 62.81; H, 9.22. Found: C, 62.63; H, 9.10%.

3,3-Dimethyl-1-trimethylsiloxy-1,2-diphenyl-1,2-di-*iso*-propyl-trisilane (**9d**): Yield: 2.1 g (27%). B.p.: 146–147 °C/0.4 Torr. GC: Diastereomeric ratio 1.4:1. MS (EI, 70 eV): m/z (%) = 444 (1) $[\mathrm{M}]^+$, 429 (2) $[\mathrm{M{-}Me}]^+$, 401 (10) $[\mathrm{M{-}{}^{i}Pr}]^+$, 359 (11) $[\mathrm{M{-}{}^{i}Pr{-}C_3H_6}]^+$, 237 (73) $[\mathrm{Me_3SiOSi{}^{i}PrPh}]^+$, 206 (100) $[\mathrm{{}^{i}PrPhSiSiMe_2}]^+$, 164 (59) $[\mathrm{PhSiSiMe_2H}]^+$, 135 (56), 73 (25) $[\mathrm{SiMe_3}]^+$, 59 (10) $[\mathrm{SiMe_2H}]^+$, 43 (14) $[\mathrm{{}^{i}Pr}]^+$. ^{1}H NMR: $\delta = 0.16$, 0.17 (s, $\mathrm{Me_3SiO}$, 9H); 0.204, 0.208, 0.22, 0.24 (2 × d, $\mathrm{Me_2SiH}$, 6H); 0.95–1.21 (m, $\mathrm{Me_2C}$, 12H); 1.44–1.61 (m, HC, 2H); 4.26, 4.31 (sept, HSi, 1H); 7.10–7.56 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -4.21$, -4.18, -4.14, -4.09 ($\mathrm{Me_2SiH}$); 2.6 ($\mathrm{Me_3SiO}$); 13.1, 13.4, 18.2, 18.3 ($C\mathrm{Me_2}$); 17.7, 17.8, 20.8, 21.0 ($\mathrm{C}Me_2$); 128.0–139.7 (Ph) ppm. ^{29}Si NMR: $\delta = -39.0$, -38.6 ($\mathrm{SiMe_2H}$); -37.4, -37.3 ($\mathrm{Si{}^{i}PrPh}$); -0.8, -0.5 ($\mathrm{OSi{}^{i}PrPh}$); 7.9, 8.0 ($\mathrm{OSiMe_3}$) ppm; $J(^{29}\mathrm{Si}{-}^{1}\mathrm{H}) = 176.2$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1061, $\delta(\mathrm{CH_3Si})$ 1244, 1252; $\tilde{\nu}$(SiH) 2090 cm^{-1}. Anal. Calc. for $\mathrm{C_{23}H_{40}OSi_4}$ (444.919): C, 62.09; H, 9.06. Found: C, 61.91; H, 9.14%.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-*iso*-propyl-trisilane (**10d**): Yield: 0.6 g (6%). B.p.: 74–77 °C/0.03 Torr. MS (EI, 70 eV): m/z (%) = 294 (40) $[\mathrm{M}]^+$, 279 (3) $[\mathrm{M{-}Me}]^+$, 251 (51) $[\mathrm{M{-}{}^{i}Pr}]^+$, 221 (26) $[\mathrm{M{-}SiMe_3}]^+$, 179 (100) $[\mathrm{M{-}SiMe_3{-}C_3H_6}]^+$, 135 (79), 102 (53), 73 (51) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.21$ (s, $\mathrm{Me_3Si}$, 18H), 1.17 (d, $\mathrm{Me_2C}$, 6H), 1.55 (sept, HC, 1H), 7.12–7.50 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 0.8$ ($\mathrm{Me_3Si}$), 13.1 ($C\mathrm{Me_2}$), 21.1 ($\mathrm{C}Me_2$); 128.2, 129.1, 135.7, 136.8 (Ph) ppm. ^{29}Si NMR: $\delta = -34.3$ ($\mathrm{Si{}^{i}PrPh}$), -16.8 ($\mathrm{SiMe_3}$) ppm. Anal. Calc. for $\mathrm{C_{15}H_{30}Si_3}$ (294.659): C, 61.14; H, 10.26. Found: C, 60.85; H, 10.08%.

1,1,1,3,3-Pentamethyl-2-phenyl-2-*iso*-propyl-trisilane (**11d**): $\mathrm{C_{14}H_{28}Si_3}$ (280.64). MS (EI, 70 eV): m/z (%) = 280 (7) $[\mathrm{M}]^+$, 265 (1) $[\mathrm{M{-}Me}]^+$, 237 (12) $[\mathrm{M{-}{}^{i}Pr}]^+$, 206 (74) $[\mathrm{{}^{i}PrPhSiSiMe_2}]^+$, 179 (72) $[\mathrm{M{-}SiMe_2H{-}C_3H_6}]^+$, 164 (68) $[\mathrm{PhSiSiMe_2H}]^+$, 135 (100), 73 (62) $[\mathrm{SiMe_3}]^+$, 59 (21) $[\mathrm{SiMe_2H}]^+$, 43 (27) $[\mathrm{{}^{i}Pr}]^+$. ^{1}H NMR: $\delta = 0.18$ (s, $\mathrm{Me_3Si}$, 9H); 0.238, 0.242 (2 × d, $\mathrm{Me_2SiH}$, 6H); 1.05 (d, $\mathrm{Me_2C}$, 6H), 1.15 (sept, HC, 1H), 4.25 (sept, HSi, 1H), 7.11–7.56 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -4.5$, -4.4 ($\mathrm{Me_2SiH}$); 0.3 ($\mathrm{Me_3Si}$), 17.5 ($C\mathrm{Me_2}$), 21.0 ($\mathrm{C}Me_2$); 128.1, 129.4, 133.7, 135.9 (Ph) ppm. ^{29}Si NMR: $\delta = -39.9$ ($\mathrm{SiMe_2H}$), -33.3 ($\mathrm{Si{}^{i}PrPh}$), -16.6 ($\mathrm{SiMe_3}$) ppm; $J(^{29}\mathrm{Si}{-}^{1}\mathrm{H}) = 174.7$ Hz.

3.2.5. *Trapping products of the lithiumsilanides from the reaction of ($\mathrm{Me_3SiO}$)^{t}BuPhSiCl (1e) with lithium and the trisiloxane 5e as well as the siloxydisilane 6e**

(1) THF, −78 °C, $t_{\mathrm{rct}} = 2.5$ h, trapping agent $\mathrm{Me_3SiCl}$.
Distillation of the residue through a Fischer slit pipe column in the temperature range of 65–95 °C/0.05 Torr yielded four fractions, which consisted of **5e** and **6e** (65–77 °C), pure **6e** (78–79 °C), **6e** and **10e** (80–90 °C) as well as of pure **10e** (90–91 °C). The distillation residue contained **10e** and enriched **8e** as well as unknown products.

(2) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 6$ h, trapping agent $\mathrm{Me_3SiCl}$.
The result of the fractional distillation of the residue through a Fischer slit pipe column is in accordance with that under (1). However, **10e** was not isolated but only a mixed fraction of **6e** and **10e** (80–90 °C/0.05 Torr) was obtained.

(3) THF, −78 °C, $t_{\mathrm{rct}} = 2.5$ h, trapping agent $\mathrm{HMe_2SiCl}$.
Distillation of the residue through a Fischer slit pipe column (62–87 °C/0.1 Torr) yielded four fractions, which consisted of **5e** and **13e** (62–77 °C), pure **13e** (78–79 °C), **13e**, **7e**, **11e** and minor **6e*** (79–86 °C) as well as of pure **11e** (86–87 °C). Minor **11e** and **9e** remained in the distillation residue. By distillation of this residue using a ball tube oven (Büchi, Kugelrohrofen GKR-51), **11e** was isolated in the first fraction (<100 °C/0.05 Torr). Both following fractions (100–120 °C, 120–140 °C) and the remaining residue contained **11e** and **9e** in different proportions beside unknown products.

(4) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 6$ h, trapping agent $\mathrm{HMe_2SiCl}$.
Distillation of the residue through a Fischer slit pipe column (62–87 °C/0.1 Torr) yielded five fractions, which contained **5e** and **13e** (62–77 °C), pure **13e** (78–79 °C), **7e**, **13e**, **11e** and minor **6e*** (79–82 °C), pure **7e** (82–83 °C) as well as **7e** and **11e** (84–87 °C). In the distillation residue **11e** and minor **9e** were found.

3-*tert*-Butyl-1,1,1,5,5,5-hexamethyl-3-phenyl-trisiloxane (**5e**): $\mathrm{C_{16}H_{32}O_2Si_3}$ (340.69). MS (EI, 70 eV): m/z (%) = 340 (1) $[\mathrm{M}]^+$, 325 (4) $[\mathrm{M{-}Me}]^+$, 283 (100) $[\mathrm{M{-}{}^{t}Bu}]^+$, 267 (11) $[\mathrm{M{-}SiMe_3}]^+$, 251 (8) $[\mathrm{M{-}OSiMe_3}]^+$, 135 (51), 73 (10) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.08$ (s, $\mathrm{Me_3SiO}$, 18H), 0.88 (s, $\mathrm{Me_3C}$, 9H), 7.18–7.65 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 2.1$ ($\mathrm{Me_3SiO}$), 20.4 ($C\mathrm{Me_3}$), 26.0 ($\mathrm{C}Me_3$); 127.9, 129.7, 134.0, 135.2 (Ph) ppm. ^{29}Si NMR: $\delta = -\ 35.8$ ($\mathrm{Si{}^{t}BuPh}$), 8.5 ($\mathrm{OSiMe_3}$) ppm.

1-*tert*-Butyl-2,2,2-trimethyl-1-trimethylsiloxy-1-phenyl-disilane (**6e**): Yield: 4.1 g (36%). B.p.: 78–79 °C/0.05 Torr. MS (EI, 70 eV): m/z (%) = 324 (4) $[\mathrm{M}]^+$, 309 (9) $[\mathrm{M{-}Me}]^+$, 267 (100) [M−^{t}Bu]$^+$, 193 (39) [M−SiMe$_3$−C$_4$H$_{10}$]$^+$, 135 (41), 73 (25) [SiMe$_3$]$^+$. ^{1}H NMR: $\delta = 0.12$ (s, Me$_3$Si, 9H), 0.16 (s, Me$_3$SiO, 9H), 0.95 (s, Me$_3$C, 9H), 7.11–7.54 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.2$ (Me$_3$Si), 2.6 (Me$_3$SiO), 21.3 (*C*Me$_3$), 26.9 (C*Me*$_3$); 127.9, 129.2, 133.9, 138.9 (Ph) ppm. ^{29}Si NMR: $\delta = -22.9$ (SiMe$_3$), −1.7 (Si^{t}BuPh), 6.9 (OSiMe$_3$) ppm. Anal. Calc. for $C_{16}H_{32}OSi_3$ (324.691): C, 59.19; H, 9.93. Found: C, 59.33; H, 10.08%.

1-*tert*-Butyl-2,2-dimethyl-1-trimethylsiloxy-1-phenyldisilane (**7e**): Yield: 1.3 g (12%). B.p.: 82–83 °C/0.1 Torr. MS (EI, 70 eV): *m*/*z* (%) = 310 (3) [M]$^+$, 295 (4) [M−Me]$^+$, 253 (100) [M−^{t}Bu]$^+$, 251 (15) [M−SiMe$_2$H]$^+$, 209 (48) [M−SiMe$_2$H−C$_4$H$_{10}$]$^+$, 193 (57), 179 (30), 147 (52), 135 (98), 73 (54) [SiMe$_3$]$^+$, 59 (22) [SiMe$_2$H]$^+$. ^{1}H NMR: $\delta = 0.17$ (s, Me$_3$SiO, 9H); 0.22, 0.23 (2 × d, HMe$_2$Si, 6H); 0.99 (s, Me$_3$C, 9H), 4.13 (sept, HSi, 1H), 7.12–7.59 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.3$, −5.2 (HMe$_2$Si); 2.4 (Me$_3$SiO), 21.1 (*C*Me$_3$), 26.5 (C*Me*$_3$); 128.0, 129.4, 134.0, 137.2 (Ph) ppm. ^{29}Si NMR: $\delta = -45.7$ (SiMe$_2$H), −1.1 (Si^{t}BuPh), 7.9 (OSiMe$_3$) ppm; $J(^{29}\text{Si}–^1\text{H}) = 174.2$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1074, δ(CH$_3$Si) 1245, 1254; $\tilde{\nu}$(SiH) 2093 cm^{-1}. Anal. Calc. for $C_{15}H_{30}OSi_3$ (310.664): C, 57.99; H, 9.73. Found: C, 57.87; H, 9.68%.

1,2-Di-*tert*-butyl-3,3,3-trimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**8e**): $C_{26}H_{46}OSi_4$ (486.99). GC: Diastereomeric ratio 1.1:1. MS (EI, 70 eV): *m*/*z* (%) = 486 (1) [M]$^+$, 471 (2) [M−Me]$^+$, 429 (16) [M−^{t}Bu]$^+$, 251 (33) [Me$_3$SiOSi^{t}BuPh]$^+$, 209 (100), 147 (83), 135 (71), 73 (29) [SiMe$_3$]$^+$. ^{1}H NMR: $\delta = 0.17$, 0.18 (s, Me$_3$Si, 9H); 0.21, 0.22 (s, Me$_3$SiO, 9H); 0.83, 0.85, 0.93, 0.95 (2xs, Me$_3$C, 18H), 7.10–7.87 (m, Ph, 10H) ppm. ^{29}Si NMR: $\delta = -32.2$, −32.0 (Si^{t}BuPh); −16.8, −16.7 (SiMe$_3$); 1.8, 2.2 (OSi^{t}BuPh); 7.3, 7.4 (OSiMe$_3$) ppm.

1,2-Di-*tert*-butyl-3,3-dimethyl-1-trimethylsiloxy-1,2-diphenyl-trisilane (**9e**): $C_{25}H_{44}OSi_4$ (472.97). GC: Diastereomeric ratio 1.1:1. MS (EI, 70 eV): *m*/*z* (%) = 472 (0.2) [M]$^+$, 457 (1) [M−Me]$^+$, 415 (24) [M−^{t}Bu]$^+$, 359 (8) [M−^{t}Bu−C$_4$H$_8$]$^+$, 251 (22) [Me$_3$SiOSi^{t}BuPh]$^+$, 209 (81), 147 (100), 135 (84), 73 (51) [SiMe$_3$]$^+$, 59 (19) [SiMe$_2$H]$^+$. ^{1}H NMR: $\delta = 0.16$, 0.17 (s, Me$_3$SiO, 9H); 0.24, 0.25, 0.26, 0.27 (2 × d, HMe$_2$Si, 6H); 0.81, 0.83, 0.90, 0.91 (2xs, Me$_3$C, 18H); 4.47, 4.50 (sept, HSi, 1H); 7.11–7.85 (m, Ph, 10H) ppm. ^{29}Si NMR: $\delta = -37.3$, −37.0 (SiMe$_2$H); −32.8, −32.7 (Si^{t}BuPh); 0.9, 1.1 (OSi^{t}BuPh); 7.5, 7.6 (OSiMe$_3$) ppm; $J(^{29}\text{Si}–^1\text{H}) = 175.7$ Hz.

2-*tert*-Butyl-1,1,1,3,3,3-hexamethyl-2-phenyl-trisilane (**10e**): Yield: 1.4 g (13%). B.p.: 90–91 °C/0.05 Torr. MS (EI, 70 eV): *m*/*z* (%) = 308 (14) [M]$^+$, 293 (3) [M−Me]$^+$, 251 (100) [M−^{t}Bu]$^+$, 135 (81), 73 (49) [SiMe$_3$]$^+$. ^{1}H NMR: $\delta = 0.30$ (s, Me$_3$Si, 18H), 1.11 (s, Me$_3$C, 9H), 7.14–7.68 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.8$ (Me$_3$Si), 21.2 (*C*Me$_3$), 30.7 (C*Me*$_3$); 128.1, 128.6, 136.8, 137.2 (Ph) ppm. ^{29}Si NMR: $\delta = -26.8$ (Si^{t}BuPh), −17.0 (SiMe$_3$) ppm. Anal. Calc. for $C_{16}H_{32}Si_3$ (308.691): C, 62.26; H, 10.45. Found: C, 62.05; H, 10.38%.

2-*tert*-Butyl-1,1,1,3,3-pentamethyl-2-phenyl-trisilane (**11e**): Yield: 1.2 g (12%). B.p.: 86–87 °C/0.1 Torr. MS (EI, 70 eV): *m*/*z* (%) = 294 (10) [M]$^+$, 279 (2) [M−Me]$^+$, 237 (85) [M−^{t}Bu]$^+$, 235 (22) [M−SiMe$_2$H]$^+$, 220 (56) [M−SiMe$_3$−H]$^+$, 177 (37) [Me$_3$SiSiPh−H]$^+$, 164 (39) [SiPhSiMe$_2$H]$^+$,163 (33) [SiPhSiMe$_2$]$^+$, 135 (100), 73 (54) [SiMe$_3$]$^+$, 59 (13) [SiMe$_2$H]$^+$. ^{1}H NMR: $\delta = 0.24$ (s, Me$_3$Si, 9H); 0.27, 0.28 (2 × d, Me$_2$HSi, 6H); 1.08 (s, Me$_3$C, 9H), 4.36 (sept, HSi, 1H), 7.10–7.64 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -3.8$ (Me$_2$HSi), 1.3 (Me$_3$Si), 20.7 (*C*Me$_3$), 30.3 (C*Me*$_3$); 128.1, 128.7, 136.1, 137.2 (Ph) ppm. ^{29}Si NMR: $\delta = -39.6$ (SiMe$_2$H), −26.4 (Si^{t}BuPh), −16.7 (SiMe$_3$) ppm; $J(^{29}\text{Si}–^1\text{H}) = 174.2$ Hz. IR(film): δ(CH$_3$Si) 1246, 1260; $\tilde{\nu}$(SiH) 2088 cm^{-1}. Anal. Calc. for $C_{15}H_{30}Si_3$ (294.664): C, 61.14; H, 10.26. Found: C, 60.98; H, 10.12%.

1-*tert*-Butyl-2,2-dimethyl-1-dimethylsiloxy-1-phenyl-disilane (**13e**): Yield: 1.7 g (16%). B.p.: 78–79 °C/0.1 Torr. MS (EI, 70 eV): *m*/*z* (%) = 296 (3) [M]$^+$, 281 (3) [M−Me]$^+$, 239 (100) [M−^{t}Bu]$^+$, 237 (22) [M−SiMe$_2$H]$^+$, 209 (17) [M−^{t}Bu−2Me]$^+$, 195 (28), 179 (30), 135 (48), 73 (48) [SiMe$_3$]$^+$, 59 (17) [SiMe$_2$H]$^+$. ^{1}H NMR: $\delta = 0.14$, 0.15 (2 × d, Me$_2$HSiSi, 6H); 0.17, 0.18 (2 × d, Me$_2$HSiO, 6H); 0.95 (s, Me$_3$C, 9H), 4.09 (sept, HSiMe$_2$, 1H), 5.04 (sept, HSiMe$_2$O, 1H), 7.09–7.53 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -$ 5.3 (Me$_2$HSi), 1.3 (Me$_2$HSiO), 21.2 (*C*Me$_3$), 26.5 (C*Me*$_3$); 128.1, 129.5, 134.0, 137.2 (Ph) ppm. ^{29}Si NMR: $\delta = -45.7$ (SiMe$_2$H), −5.0 (OSiMe$_2$H), 1.0 (Si^{t}BuPh) ppm; $J(^{29}\text{Si}–^1\text{H}) = 174.7$ (HMe$_2$Si), 204.2 (HMe$_2$SiO) Hz. IR(film): $\tilde{\nu}$(SiOSi) 1075; δ(CH$_3$Si) 1253, 1260; $\tilde{\nu}$(HSi$_{\text{Si}}$) 2094, $\tilde{\nu}$(HSi$_{\text{O}}$) 2121 cm^{-1}. Anal. Calc. for $C_{14}H_{28}OSi_3$ (296.637): C, 56.69; H, 9.51. Found: C, 56.93; H, 9.45%.

*3.2.6. Trapping products of the lithiumsilanides from the reaction of (Me$_3$SiO)Ph$_2$SiCl (**1f**) with lithium and the trisiloxane **5f***

Trapp mixture, −110 °C, $t_{\text{rct}} = 4$ h, trapping agent HMe$_2$SiCl.

Distillation of the residue through a Fischer slit pipe column (80–120 °C/0.3 Torr) yielded four fractions, which contained **5f** and **7f** (85–89 °C), pure **7f** (89–91 °C), **7f** and **11f** (91–109 °C) as well as pure **11f** (109–111 °C). In the distillation residue **9f** crystallised out, which could be purified by recrystallisation from *n*-hexane. Yields: **7f** 2.4 g (21%), **9f** 0.9 g (10%) and **11f** 0.8 g (7%). The analytical data of the compounds obtained from the reaction of **1f** with lithium are in accordance with those in [32].

*3.2.7. Trapping products of the lithiumsilanides from the reaction of (Me$_3$SiO)MesPhSiCl (**1g**) with lithium and the trisiloxane **5g***

(1) THF, −78 °C, $t_{\text{rct}} = 2$ h, trapping agent Me$_3$SiCl. Distillation of the residue through a Fischer slit pipe column (120–170 °C/0.1 Torr) yielded three fractions, which contained **5g** and **6g** (120–155 °C), pure **6g** (159–160 °C) as well as **6g** and **10g** (160–170 °C). From the third fraction **10g** was isolated by preparative GC. In the distillation residue trimethylsiloxytrisilane **8g** crystallised out, which could be purified and

isolated by distillation using a Büchi ball tube oven (180–220 °C/0.06 Torr) and by recrystallisation from *n*-hexane.

(2) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 4.5$ h, trapping agent $\mathrm{Me_3SiCl}$.
The fractional distillation of the residue through a Fischer slit pipe column gave the same result as under (1). However, the proportion of **10g** in the mixed fraction is smaller.

(3) THF, −78 °C, $t_{\mathrm{rct}} = 2$ h, trapping agent $\mathrm{HMe_2SiCl}$.
Distillation of the residue through a Fischer slit pipe column (110–150 °C/0.1 Torr) yielded three fractions, which contained **7g**, minor **5g** and **13g** (110–127 °C), pure **7g** (128–130 °C) as well as **7g** and **11g** (130–150 °C). From the third fraction the trisilane **11g** was isolated by preparative GC. In the distillation residue **9g** was mainly found, which was isolated by distillation using a Büchi ball tube oven (195–202 °C/0.07 Torr).

(4) Trapp mixture, −110 °C, $t_{\mathrm{rct}} = 4.5$ h, trapping agent $\mathrm{HMe_2SiCl}$.
Distillation of the residue through a Fischer slit pipe column gave the same result as under (3). However, the proportion of **11g** in the third fraction is smaller.

1,1,1,5,5,5-Hexamethyl-3-(2,4,6-trimethylphenyl)-3-phenyl-trisiloxane (**5g**): $\mathrm{C_{21}H_{34}O_2Si_3}$ (402.76). MS (EI, 70 eV): m/z (%) = 402 (2) $[\mathrm{M}]^+$, 387 (7) $[\mathrm{M{-}Me}]^+$, 324 (26) $[\mathrm{M{-}C_6H_6}]^+$, 309 (100) $[\mathrm{M{-}C_6H_6{-}Me}]^+$, 283 (39) $[\mathrm{M{-}Mes}]^+$, 267 (69), 135 (23). ^{1}H NMR: $\delta = 0.15$ (s, $\mathrm{Me_3SiO}$, 18H), 2.05 (s, *p*-Me, 3H), 2.38 (s, *o*-Me, 6H), 6.65 (s, $\mathrm{HC_{ar}}$, 2H), 7.08–7.82 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 2.1$ ($\mathrm{Me_3SiO}$), 21.1 (*p*-Me), 25.3 (*o*-Me); 127.9–145.4 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -45.2$ (SiMesPh), 9.0 ($\mathrm{OSiMe_3}$) ppm.

2,2,2-Trimethyl-1-(2,4,6-trimethylphenyl)-1-trimethylsiloxy-1-phenyl-disilane (**6g**): Yield: 3.5 g (26%). B.p.: 159–160 °C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 386 (2) $[\mathrm{M}]^+$, 371 (5) $[\mathrm{M{-}Me}]^+$, 313 (100) $[\mathrm{M{-}SiMe_3}]^+$, 193 (21) $[\mathrm{M{-}C_9H_{12}{-}SiMe_3}]^+$, 73 (5) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.04$ (s, $\mathrm{Me_3Si}$, 9H), 0.26 (s, $\mathrm{Me_3SiO}$, 9H), 2.13 (s, *p*-Me, 3H), 2.35 (s, *o*-Me, 6H), 6.77 (s, $\mathrm{HC_{ar}}$, 2H), 7.10–7.60 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.7$ ($\mathrm{Me_3Si}$), 2.2 ($\mathrm{Me_3SiO}$), 21.1 (*p*-Me), 24.9 (*o*-Me); 127.8, 128.3, 129.3, 131.5, 133.9, 139.0, 140.6, 144.6 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -20.7$ ($\mathrm{SiMe_3}$), −9.8 (SiMesPh), 8.6 ($\mathrm{OSiMe_3}$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1037, δ($\mathrm{CH_3Si}$) 1250, 1258 cm^{-1}. Anal. Calc. for $\mathrm{C_{21}H_{34}OSi_3}$ (386.763): C, 65.22; H, 8.86. Found: C, 65.51; H, 8.73%.

2,2-Dimethyl-1-(2,4,6-trimethylphenyl)-1-trimethylsiloxy-1-phenyl-disilane (**7g**): Yield: 2.7 g (21%). B.p.: 128–130°C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 372 (1) $[\mathrm{M}]^+$, 357 (13) $[\mathrm{M{-}Me}]^+$, 313 (100) $[\mathrm{M{-}SiMe_2H}]^+$, 235 (16), 193 (24) $[\mathrm{M{-}C_9H_{12}{-}SiMe_2H}]^+$, 73 (2) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.10$ (s, $\mathrm{Me_3SiO}$, 9H); 0.24, 0.26 (2 × d, $\mathrm{Me_2HSi}$, 6H); 2.14 (s, *p*-Me, 3H), 2.40 (s, *o*-Me, 6H), 4.27 (sept, HSi, 1H), 6.75 (s, $\mathrm{HC_{ar}}$, 2H), 7.13–7.63 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.6$, −5.5 ($\mathrm{Me_2HSi}$); 2.2 ($\mathrm{Me_3SiO}$), 21.2 (*p*-Me), 24.8 (*o*-Me); 128.3, 129.3, 129.6, 131.2, 133.7, 135.1, 138.4, 144.7 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -39.1$ ($\mathrm{SiMe_2H}$), −10.8 (SiMesPh), 9.3 ($\mathrm{OSiMe_3}$) ppm; $J(^{29}\mathrm{Si}{-}^1\mathrm{H}) = 176.8$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1039, δ($\mathrm{CH_3Si}$) 1251, 1261; $\tilde{\nu}$(SiH) 2092 cm^{-1}. Anal. Calc. for $\mathrm{C_{20}H_{32}OSi_3}$ (372.735): C, 64.45; H, 8.65. Found: C, 64.54; H, 8.42%.

3,3,3-Trimethyl-1,2-bis(2,4,6-trimethylphenyl)-1-trimethylsiloxy-1,2-diphenyl-trisilane (**8g**): Yield: 0.5 g (5%). M.p.: 148–151 °C. GC: Diastereomeric ratio 1.4:1. MS (EI, 70 eV): m/z (%) = 610 (0.2) $[\mathrm{M}]^+$, 595 (2) $[\mathrm{M{-}Me}]^+$, 537 (1) $[\mathrm{M{-}SiMe_3}]^+$, 460 (3), 313 (100) $[\mathrm{Me_3SiOSiMesPh}]^+$, 297 (4) $[\mathrm{Me_3SiSiMesPh}]^+$, 237 (9), 193 (14) $[\mathrm{Me_3SiOSiPh\ {-}H}]^+$, 177 (3) $[\mathrm{Me_3SiSiPh\ {-}H}]^+$. ^{1}H NMR: $\delta = -0.05$, 0.05 (s, $\mathrm{Me_3Si}$, 9H); 0.18 (s, $\mathrm{Me_3SiO}$, 9H); 2.11, 2.13, 2.14 (s, *p*-Me, 6H); 2.29, 2.31, 2.32 (s, *o*-Me, 12H); 6.71, 6.76, 6.77 (s, $\mathrm{HC_{ar}}$, 4H); 7.08–7.84 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = 0.8$, 1.1 ($\mathrm{Me_3Si}$); 2.1, 2.4 ($\mathrm{Me_3SiO}$); 21.0, 21.1 (*p*-Me); 25.4, 25.5, 27.0, 27.2 (*o*-Me); 127.9–146.0 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -45.8$, −45.3 (SiMesPh); −12.3, −12.0 ($\mathrm{SiMe_3}$); −8.5, −7.7 (OSiMesPh); 9.6, 10.2 ($\mathrm{OSiMe_3}$) ppm. IR(KBr): $\tilde{\nu}$(SiOSi) 1065, δ($\mathrm{CH_3Si}$) 1250, 1259 cm^{-1}. Anal. Calc. for $\mathrm{C_{36}H_{50}OSi_4}$ (611.143): C, 70.75; H, 8.25. Found: C, 70.59; H, 8.14%.

3,3-Dimethyl-1,2-bis(2,4,6-trimethylphenyl)-1-trimethylsiloxy-1,2-diphenyl-trisilane (**9g**): Yield: 1.1 g (11%). B.p.: 195–202 °C/0.07 Torr. GC: Diastereomeric ratio 1.4:1. MS (EI, 70 eV): m/z (%) = 596 (1) $[\mathrm{M}]^+$, 581 (3) $[\mathrm{M{-}Me}]^+$, 537 (2) $[\mathrm{M{-}SiMe_2H}]^+$, 313 (100) $[\mathrm{Me_3SiOSiMesPh}]^+$, 282 (14) $[\mathrm{Me_2SiSiMesPh}]^+$, 237 (8), 193 (12) $[\mathrm{Me_3SiOSiPh\ {-}H}]^+$. ^{1}H NMR: $\delta = 0.03$, 0.05 (s, $\mathrm{Me_3SiO}$, 9H); 0.09, 0.11, 0.12, 0.13 (2 × d, $\mathrm{Me_2HSi}$, 6H); 2.08, 2.09, 2.10, 2.12 (s, *p*-Me, 6H); 2.25, 2.28, 2.32, 2.33 (s, *o*-Me, 12H); 4.44, 4.58 (sept, HSi, 1H); 6.69, 6.73, 6.74 (s, $\mathrm{HC_{ar}}$, 4H); 7.07–7.82 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -4.8$, −4.4, −4.1, −3.9 ($\mathrm{Me_2SiH}$); 2.2, 2.4 ($\mathrm{Me_3SiO}$); 20.9–21.2 (*p*-Me); 25.3–26.9 (*o*-Me); 127.9–146.2 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -47.3$, −45.7 (SiMesPh); −29.2, −28.7 ($\mathrm{SiMe_2H}$); −9.1, −7.8 (OSiMesPh); 9.9, 10.3 ($\mathrm{OSiMe_3}$) ppm; $J(^{29}\mathrm{Si}{-}^1\mathrm{H}) = 182.1$ Hz. IR(film): $\tilde{\nu}$(SiOSi) 1066, δ($\mathrm{CH_3Si}$) 1252, 1260; $\tilde{\nu}$(SiH) 2114 cm^{-1}. Anal. Calc. for $\mathrm{C_{35}H_{48}OSi_4}$ (597.116): C, 70.40; H, 8.10. Found: C, 70.13; H, 7.92%.

1,1,1,3,3,3-Hexamethyl-2-(2,4,6-trimethylphenyl)-2-phenyl-trisilane (**10g**) [44]: $\mathrm{C_{21}H_{34}Si_3}$ (370.76). MS (EI, 70 eV): m/z (%) = 370 (9) $[\mathrm{M}]^+$, 355 (3) $[\mathrm{M{-}Me}]^+$, 297 (69) $[\mathrm{M{-}SiMe_3}]^+$, 237 (32), 220 (100) $[\mathrm{M{-}Ph{-}SiMe_3}]^+$, 205 (72) $[\mathrm{M{-}SiMe_4{-}Ph}]^+$, 73 (14) $[\mathrm{SiMe_3}]^+$. ^{1}H NMR: $\delta = 0.22$ (s, $\mathrm{Me_3Si}$, 18H), 2.13 (s, *p*-Me, 3H), 2.27 (s, *o*-Me, 6H), 6.75 (s, $\mathrm{HC_{ar}}$, 2H), 7.14–7.48 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 0.7$ ($\mathrm{Me_3Si}$), 21.0 (*p*-Me), 26.7 (*o*-Me); 127.6, 128.3, 129.6, 130.4, 135.1, 138.2, 142.4, 145.1 ($\mathrm{C_{ar}}$) ppm. ^{29}Si NMR: $\delta = -43.5$ (SiMesPh), −15.0 ($\mathrm{SiMe_3}$) ppm.

1,1,1,3,3-Pentamethyl-2-(2,4,6-trimethylphenyl)-2-phenyl-trisilane (**11g**): $\mathrm{C_{20}H_{32}Si_3}$ (356.74). MS (EI, 70 eV): m/z (%) = 356 (15) $[\mathrm{M}]^+$, 341 (5) $[\mathrm{M{-}Me}]^+$, 297 (22) $[\mathrm{M{-}SiMe_2H}]^+$, 282 (100) $[\mathrm{M{-}SiMe_3{-}H}]^+$, 267 (14), 237

(28), 205 (44) [M$-$SiMe$_3$$-H-$Ph]$^+$, 73 (11) [SiMe$_3$]$^+$. ^{1}H NMR: $\delta = 0.21$, 0.22 (2 × d, Me$_2$SiH, 6H); 0.26 (s, Me$_3$Si, 9H), 2.13 (s, *p*-Me, 3H), 2.31 (s, *o*-Me, 6H), 4.40 (sept, HSi, 1H), 6.77 (s, HC$_{ar}$, 2H), 7.09–7.51 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -4.5$, -4.4 (Me$_2$SiH); 0.5 (Me$_3$Si), 21.0 (*p*-Me), 26.5 (*o*-Me); 127.9–145.3 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -44.0$(SiMesPh), -33.5 (SiMe$_2$H), -15.2 (SiMe$_3$) ppm; $J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 178.4$ Hz.

2,2-Dimethyl-1-(2,4,6-trimethylphenyl)-1-dimethylsiloxy-1-phenyl-disilane (**13g**): C$_{19}$H$_{30}$OSi$_3$ (358.71). MS (EI, 70 eV): *m*/*z* (%) = 358 (2) [M]$^+$, 343 (21) [M$-$Me]$^+$, 299 (100) [M$-$SiMe$_2$H]$^+$, 221 (23) [M$-$SiMe$_2$H$-$C$_6$H$_6$]$^+$, 179 (26) [PhSiOSiMe$_2$]$^+$, 135 (6), 59 (4) [SiMe$_2$H]$^+$. ^{1}H NMR: $\delta = 0.17$, 0.18 (2 × d, Me$_2$HSiSi, 6H); 0.23, 0.24 (2 × d, Me$_2$HSiO, 6H); 2.13 (s, *p*-Me, 3H), 2.42 (s, *o*-Me, 6H), 4.29 (sept, HSiSi, 1H), 5.03 (sept, HSiO, 1H), 6.76 (s, HC$_{ar}$, 2H), 7.11–7.65 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.4$ (Me$_2$HSi), 1.0 (Me$_2$HSiO), 21.1 (*p*-Me), 24.7 (*o*-Me); 128.1–145.0 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -$ 38.7 (SiMe$_2$H), -8.9 (SiMesPh), -4.9 (OSiMe$_2$H) ppm; $J(^{29}\mathrm{Si}–^{1}\mathrm{H}) =$ 176.3 (SiMe$_2$H), 204.7 (OSiMe$_2$H) Hz.

3.2.8. *Trapping products of the lithiumsilanides from the reaction of (Me$_3$SiO)TipPhSiCl (**1h**) with lithium and the trisiloxane **5h** as well as the siloxydisilane **6h****

(1) THF, -78 °C, $t_{\mathrm{rct}} = 2.5$ h, trapping agent Me$_3$SiCl. Distillation of the residue through a Fischer slit pipe column (120–160 °C/0.03 Torr) yielded four fractions, which contained **5h** and **6h** (120–141 °C), pure **6h** (141–143 °C), **6h** and **10h** (143–159 °C) as well as pure **10h** (159–160 °C).

(2) Trapp mixture, -110 °C, $t_{\mathrm{rct}} = 4.5$ h, trapping agent Me$_3$SiCl.
The residue was fractionated as under (1) and at first mixed fractions of **5h** and **6h** (120–141 °C/0.03 Torr) and after that a pure fraction of **6h** (141–142 °C/0.03 Torr) were obtained. In the distillation residue **10h** was found beside minor amounts of **6h**.

(3) THF, -78 °C, $t_{\mathrm{rct}} = 2.5$ h, trapping agent HMe$_2$SiCl. Distillation of the residue through a Fischer slit pipe column (115–149 °C/0.04 Torr) yielded five fractions, which contained mainly **13h** beside **5h**, **7h** and small amounts of **6h*** (115–135 °C). It followed a mixed fraction of **7h**, **11h**, minor **13h** and **6h*** (135–148 °C) as well as a fraction of pure **11h** (148–149 °C).

(4) Trapp mixture, -110 °C, $t_{\mathrm{rct}} = 4.5$ h, trapping agent HMe$_2$SiCl.
Distillation of the residue through a Fischer slit pipe column (115–145 °C/0.04 Torr) yielded several mixed fractions, which consisted of **13h** beside **7h**, **6h*** and small amounts of **5h** (115–130 °C) and of **13h**, **7h**, **6h*** beside small amounts of **11h** (130–145 °C), respectively.

1,1,1,5,5,5-Hexamethyl-3-phenyl-3-(2,4,6-tri-*iso*-propylphenyl)-trisiloxane (**5h**): C$_{27}$H$_{46}$O$_2$Si$_3$ (486.92). MS (EI, 70 eV): *m*/*z* (%) = 486 (2) [M]$^+$, 471 (7) [M$-$Me]$^+$, 408 (100) [M$-$C$_6$H$_6$]$^+$, 393 (33), 283 (20), 283 (20) [M$-$C$_{15}$H$_{23}$]$^+$, 207 (20), 135 (28) [SiMe$_2$Ph]$^+$, 73 (10) [SiMe$_3$]$^+$, 43 (4) [C$_3$H$_7$]$^+$. ^{1}H NMR: $\delta = 0.17$ (s, Me$_3$SiO, 18H); 1.33 (d, H$_3$C, 12H); 1.37 (d, H$_3$C, 6H), 2.82 (sept, HC(Me)$_2$, 1H), 3.76 (sept, HC(Me)$_2$, 2H), 7.13 (s, HC$_{ar}$, 2H), 7.05–7.72 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 2.2$ (Me$_3$SiO), 24.5 (*p*-(*C*H$_3$)$_2$CH); 25.3, 25.9 (*o*-(*C*H$_3$)$_2$CH), 31.9 (*o*-*C*H(CH$_3$)$_2$), 34.7 (*p*-*C*H(CH$_3$)$_2$); 121.6–157.4 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -$ 45.2 (SiTipPh), 9.1 (OSiMe$_3$) ppm.

2,2,2-Trimethyl-1-trimethylsiloxy-1-phenyl-1-(2,4,6-tri-*iso*-propylphenyl)-disilane (**6h**): Yield: 7.9 g (47%). B.p.: 141–142 °C/0.03 Torr. MS (EI, 70 eV): *m*/*z* (%) = 470 (<1) [M]$^+$, 455 (2) [M$-$Me]$^+$, 397 (100) [M$-$SiMe$_3$]$^+$, 355 (3), 320 (4), 277 (10), 245 (4), 193 (4) [Me$_3$SiOSiPh]$^+$, 135 (3) [SiMe$_2$Ph]$^+$, 73 (5) [SiMe$_3$]$^+$, 43 (2) [C$_3$H$_7$]$^+$. ^{1}H NMR: $\delta = 0.11$ (s, Me$_3$Si, 9H), 0.30 (s, Me$_3$SiO, 9H); 1.17, 1.18 (2 × d, H$_3$C, 12H); 1.22 ((d), H$_3$C, 6H), 2.80 (sept, HC(Me)$_2$, 1H), 3.60 (sept, HC(Me)$_2$, 2H), 7.12 (s, HC$_{ar}$, 2H), 7.06–7.54 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.7$ (Me$_3$Si), 2.5 (Me$_3$SiO), 24.1 (*p*-(*C*H$_3$)$_2$CH); 25.3, 25.8 (*o*-(*C*H$_3$)$_2$CH), 33.2 (*o*-*C*H(CH$_3$)$_2$), 34.6 (*p*-*C*H(CH$_3$)$_2$); 121.8, 127.9, 128.8, 131.1, 133.8, 143.4, 150.6, 156.6 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -19.7$ (SiMe$_3$), -11.7 (SiTipPh), 8.5 (OSiMe$_3$) ppm. Anal. Calc. for C$_{27}$H$_{46}$OSi$_3$ (470.925): C, 68.86; H, 9.85. Found: C, 68.74; H, 9.81%.

2,2-Dimethyl-1-trimethylsiloxy-1-phenyl-1-(2,4,6-tri-*iso*-propylphenyl)-disilane (**7h**): C$_{26}$H$_{44}$OSi$_3$ (456.90). MS (EI, 70 eV): *m*/*z* (%) = 456 (<1) [M]$^+$, 441 (3) [M$-$Me]$^+$, 397 (100) [M$-$SiMe$_2$H]$^+$, 277 (13) [M$-$SiPhOSiMe$_2$]$^+$, 193 (9) [Me$_3$SiOSiPh]$^+$, 135 (5) [SiMe$_2$Ph]$^+$, 73 (7) [SiMe$_3$]$^+$, 59 (8) [SiMe$_2$H]$^+$, 43 (4) [C$_3$H$_7$]$^+$. ^{1}H NMR: $\delta = 0.13$ (s, Me$_3$SiO, 9H); 0.26, 0.28 (2 × d, Me$_2$HSi, 6H); 1.15, 1.16 (2 × d, H$_3$C, 12H); 1.23 ((d), H$_3$C, 6H), 2.78 (sept, HC(Me)$_2$, 1H), 3.87 (sept, HC(Me)$_2$, 2H), 4.22 (sept, HSi, 1H), 7.09 (s, HC$_{ar}$, 2H), 7.02–7.66 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.6$, -5.3 (Me$_2$HSi); 2.2 (Me$_3$SiO), 24.6 (*p*-(*C*H$_3$)$_2$CH); 25.3, 25.5 (*o*-(*C*H$_3$)$_2$CH), 33.1 (*o*-*C*H(CH$_3$)$_2$), 34.5 (*p*-*C*H(CH$_3$)$_2$); 121.8, 127.9, 129.0, 130.0, 134.1, 139.9, 150.1, 156.6 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -38.8$ (SiMe$_2$H), -12.1 (SiTipPh), 9.3 (OSiMe$_3$) ppm; $J(^{29}\mathrm{Si}–^{1}\mathrm{H}) = 177.7$ Hz.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(2,4,6-tri-*iso*-propylphenyl)-trisilane (**10h**): Yield: 2.4 g (14%). B.p.: 159–160 °C/0.03 Torr. MS (EI, 70 eV): *m*/*z* (%) = 454 (<1) [M]$^+$, 439 (3) [M$-$Me]$^+$, 381 (56) [M$-$SiMe$_3$]$^+$, 304 (37) [M$-$SiMe$_3$$-C_6H_5$]$^+$, 245 (100), 230 (92), 187 (17), 145 (11), 135 (28) [SiMe$_2$Ph]$^+$, 73 (25) [SiMe$_3$]$^+$, 43 (5) [C$_3$H$_7$]$^+$. ^{1}H NMR: $\delta = 0.27$ (s, Me$_3$Si, 18H); 1.12 (d, H$_3$C, 12H); 1.28 (d, H$_3$C, 6H), 2.79 (sept, HC(Me)$_2$, 1H), 3.37 (sept, HC(Me)$_2$, 2H), 7.10 (s, HC$_{ar}$, 2H), 7.04–7.43 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 1.0$ (Me$_3$Si), 24.1 (*p*-(*C*H$_3$)$_2$CH); 25.3, 25.9 (*o*-(*C*H$_3$)$_2$CH), 34.6 (*o*-*C*H(CH$_3$)$_2$), 35.9 (*p*-*C*H(CH$_3$)$_2$); 122.0, 127.8, 128.9, 130.3, 135.8, 140.8, 150.1, 156.8 (C$_{ar}$) ppm. ^{29}Si NMR: $\delta = -45.4$ (SiTipPh), -14.7 (SiMe$_3$) ppm. Anal. Calc. for C$_{27}$H$_{46}$Si$_3$

(454.926): C, 71.29; H, 10.19. Found: C, 71.05; H, 10.28%.

1,1,1,3,3-Pentamethyl-2-phenyl-2-(2,4,6-tri-*iso*-propylphenyl)trisilane (**11h**): Yield: 1.5 g (9%). B.p.: 148–149 °C/0.04 Torr. MS (EI, 70 eV): m/z (%) = 440 (1) $[M]^+$, 425 (6) $[M-Me]^+$, 381 (31) $[M-SiMe_2H]^+$, 367 (28) $[M-SiMe_3]^+$, 307 (34) $[M-SiMe_3-SiMe_2H-H]^+$, 245 (78), 230 (100), 187 (21), 135 (26) $[SiMe_2Ph]^+$, 73 (17) $[SiMe_3]^+$, 59 (8) $[SiMe_2H]^+$. ^{1}H NMR: $\delta = 0.25$ (d, Me_2HSi, 6H), 0.27 (s, Me_3Si, 9H); 1.13, 1.14 (2 × d, H_3C, 12H); 1.21 ((d), H_3C, 6H), 2.80 (sept, $HC(Me)_2$, 1H), 3.40 (sept, $HC(Me)_2$, 2H), 4.34 (sept, HSi, 1H), 7.12 (s, HC_{ar}, 2H), 7.02–7.41 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -4.1$, -3.6 (Me_2HSi); 0.6 (Me_3Si), 24.2 (p-(CH$_3$)$_2$CH); 25.6, 25.8 (o-(CH$_3$)$_2$CH), 34.5 (o-CH(CH$_3$)$_2$), 36.1 (p-CH(CH$_3$)$_2$); 122.0, 127.9, 129.5, 133.8, 135.6, 140.2, 150.0, 156.7 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -46.6$ (SiTipPh), -33.6 ($SiMe_2H$), -13.8 ($SiMe_3$) ppm; $J(^{29}Si-^1H) = 178.7$ Hz. Anal. Calc. for $C_{26}H_{44}Si_3$ (440.899): C, 70.83; H, 10.06. Found: C, 70.69; H, 9.95%.

2,2-Dimethyl-1-dimethylsiloxy-1-phenyl-1-(2,4,6-tri-*iso*-propylphenyl)-disilane (**13h**): $C_{25}H_{42}OSi_3$ (442.87). MS (EI, 70 eV): m/z (%) = 442 (1) $[M]^+$, 427 (3) $[M-Me]^+$, 383 (100) $[M-SiMe_3]^+$, 263 (21) $[M-SiPhOSiMe_2]^+$, 179 (7) $[SiPhOSiMe_2]^+$, 59 (6) $[SiMe_2H]^+$. ^{1}H NMR: $\delta = 0.21$, 0.22 (2 × d, Me_2HSiO, 6H); 0.25, 0.26 (2 × d, Me_2HSiSi, 6H); 1.12, 1.13 (2 × d, H_3C, 12H); 1.18 ((d), H_3C, 6H), 2.78 (sept, $HC(Me)_2$, 1H), 3.61 (sept, $HC(Me)_2$, 2H), 4.23 (sept, HSiSi, 1H), 5.02 (sept, HSiO, 1H), 7.13 (s, HC_{ar}, 2H), 7.06–7.53 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -5.4$ (Me_2HSi), 1.4 (Me_2HSiO), 24.5 (p-(CH$_3$)$_2$CH); 25.3, 25.5 (o-(CH$_3$)$_2$CH), 33.4 (o-CH(CH$_3$)$_2$), 34.7 (p-CH(CH$_3$)$_2$); 122.3, 128.1, 129.1, 133.7, 135.7, 142.0, 149.0, 156.8 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -38.1$ ($SiMe_2H$), -10.7 (SiTipPh), -4.6 ($OSiMe_2H$) ppm; $J(^{29}Si-^1H) = 177.6$ ($SiMe_2H$), 204.9 ($OSiMe_2H$) Hz. IR(film): $\tilde{\nu}$(SiOSi) 1076, δ(CH_3Si) 1251, 1261; $\tilde{\nu}$(HSi_{Si}) 2094, $\tilde{\nu}$(HSi_O) 2122 cm^{-1}.

*3.2.9. Trapping products of the lithiumsilanides from the reaction of (Me$_3$SiO)Mes$_2$SiCl (**1i**) with lithium and the trisiloxane **5i** as well as the siloxydisilane **6i****

(1) THF, −78 °C, $t_{rct} = 3$ h, trapping agent Me_3SiCl.
The solid residue contained the siloxydisilane **6i** and minor **5i**. Recrystallisation from *n*-heptane yielded pure **6i**.

(2) Trapp mixture, −110 °C, $t_{rct} = 6$ h, trapping agent Me_3SiCl.
The residue was recrystallised from *n*-heptane as under (1) and the compound **6i** was isolated.

(3) THF, −78 °C, $t_{rct} = 3$ h, trapping agent HMe_2SiCl.
Distillation of the residue using a Büchi ball tube oven (145–190 °C/0.3 Torr) yielded two fractions in the temperature range of 145–176 °C, which consisted of mixtures of **5i**, **13i** and **7i**, a fraction of nearly pure **7i** with very small amounts of **6i*** (176–178 °C) and a mixed fraction of **7i** and **6i*** (178–190 °C). By recrystallisation of the third fraction from *n*-hexane the disilane **7i** was isolated.

(4) Trapp mixture, −110 °C, $t_{rct} = 6$ h, trapping agent HMe_2SiCl.
Distillation of the residue using a Büchi ball tube oven gave the same result as under (3). However, the yield of pure **7i** was higher.

1,1,1,5,5,5-Hexamethyl-3,3-bis(2,4,6-trimethylphenyl)-trisiloxane (**5i**): $C_{24}H_{40}O_2Si_3$ (444.84). MS (EI, 70 eV): m/z (%) = 444 (3) $[M]^+$, 429 (8) $[M-Me]^+$, 324 (47) $[M-C_9H_{12}]^+$, 309 (100) $[M-C_9H_{12}-Me]^+$. ^{1}H NMR: $\delta = 0.10$ (s, Me_3SiO, 18H), 2.11 (s, p-Me, 6H), 2.45 (s, o-Me, 12H), 6.72 (s, HC_{ar}, 4H) ppm. ^{13}C NMR: $\delta = 1.9$ (Me_3SiO), 21.2 (p-Me), 23.2 (o-Me); 129.7, 130.8, 138.9, 143.6 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -43.7$ ($SiMes_2$), 8.6 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$(SiOSi) 1036, δ(CH_3Si) 1250 cm^{-1}.

2,2,2-Trimethyl-1,1-bis(2,4,6-trimethylphenyl)-1-trimethylsiloxy-disilane (**6i**): Yield: 8.0 g (53%). M.p.: 109–110 °C. MS (EI, 70 eV): m/z (%) = 428 (2) $[M]^+$, 413 (5) $[M-Me]^+$, 355 (100) $[M-SiMe_3]^+$. ^{1}H NMR: $\delta = 0.07$ (s, Me_3SiO, 9H), 0.26 (s, Me_3SiSi, 9H), 2.11 (s, p-Me, 6H), 2.41 (s, o-Me, 12H), 6.72 (s, HC_{ar}, 4H) ppm. ^{13}C NMR: $\delta = -0.6$ (Me_3SiSi), 2.0 (Me_3SiO), 21.1 (p-Me), 24.4 (o-Me); 129.5, 135.8, 138.5, 142.8 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -17.5$ ($SiMe_3$), -10.8 ($SiMes_2$), 8.3 ($OSiMe_3$) ppm. IR(nujol): $\tilde{\nu}$(SiOSi) 1032, δ(CH_3Si) 1251, 1260 cm^{-1}. Anal. Calc. for $C_{24}H_{40}OSi_3$ (428.844): C, 67.22; H, 9.40. Found: C, 67.27; H, 9.42%.

2,2-Dimethyl-1,1-bis(2,4,6-trimethylphenyl)-1-trimethylsiloxy-disilane (**7i**): Yield: 6.0 g (41%). M.p.: 69–70 °C, b.p.: 176–178 °C/0.3 Torr. MS (EI, 70 eV): m/z (%) = 414 (2) $[M]^+$, 399 (11) $[M-Me]^+$, 355 (100) $[M-SiMe_2H]^+$, 235 (26), 133 (30), 73 (8) $[SiMe_3]^+$, 59 (7) $[SiMe_2H]^+$. ^{1}H NMR: $\delta = 0.08$ (s, Me_3SiO, 9H), 0.26 (d, Me_2HSi, 6H), 2.12 (s, p-Me, 6H), 2.44 (s, o-Me, 12H), 4.25 (sept, HSi, 1H), 6.73 (s, HC_{ar}, 4H) ppm. ^{13}C NMR: $\delta = -5.0$ (Me_2HSi), 1.9 (Me_3SiO), 21.1 (p-Me), 24.0 (o-Me); 129.6, 134.9, 138.7, 143.0 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -34.3$ ($SiMe_2H$), -10.8 ($SiMes_2$), 9.1 ($OSiMe_3$) ppm; $J(^{29}Si-^1H) = 177.3$ Hz. IR(nujol): $\tilde{\nu}$(SiOSi) 1030, δ(CH_3Si) 1250, 1260; $\tilde{\nu}$(SiH) 2100 cm^{-1}. Anal. Calc. for $C_{23}H_{38}OSi_3$ (414.817): C, 66.60; H, 9.23. Found: C, 66.54; H, 9.27%.

2,2-Dimethyl-1,1-bis(2,4,6-trimethylphenyl)-1-dimethylsiloxy-disilane (**13i**): $C_{22}H_{36}OSi_3$ (400.79). MS (EI, 70 eV): m/z (%) = 400 (2) $[M]^+$, 385 (8) $[M-Me]^+$, 341 (100) $[M-SiMe_2H]^+$, 266 (38) $[SiMes_2]^+$, 147 (61) $[SiMes]^+$, 59 (28) $[SiMe_2H]^+$. ^{1}H NMR: $\delta = 0.09$ (d, Me_2HSiSi, 6H), 0.24 (d, Me_2HSiO, 6H), 2.11 (s, p-Me, 6H), 2.41 (s, o-Me, 12H), 4.34 (sept, HSiSi, 1H), 4.97 (sept, HSiO, 1H), 6.72 (s, HC_{ar}, 4H) ppm. ^{13}C NMR: $\delta = -4.4$ (Me_2HSi), 0.7 (Me_2HSiO), 21.2 (p-Me), 24.1 (o-Me); 129.1–144.4 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -33.2$ ($SiMe_2H$), -9.1 ($SiMes_2$), -5.3 ($OSiMe_2H$) ppm; $J(^{29}Si-^1H) = 181.6$ ($SiMe_2H$), 204.3 ($OSiMe_2H$) Hz.

*3.2.10. Isolation of the intermediates (Me_3SiO)RR′Si–SiRR′($OSiMe_3$) (**14e**: R = ^{t}Bu, R′ = Ph; **14g**: R = Mes, R′ = Ph)*

Isolation of the siloxydisilane **14e** from the reaction of **1e** with lithium.

Distillation of the residue through a Fischer slit pipe column (60–95 °C/0.05 Torr) yielded three fractions (60–75 °C, 75–85 °C, 85–95 °C), which contained **1e**, **5e**, **6e** and **10e** in different proportions. Additionally, **14e** and minor **8e** remained in the distillation residue. By distillation of this residue using a Büchi ball tube oven nearly pure **14e** (160–180 °C/0.05 Torr) was obtained. Recrystallisation from *n*-hexane yielded pure **14e**.

1,2-Di-*tert*-butyl-1,2-bis(trimethylsiloxy)-1,2-diphenyl-disilane (**14e**): Yield: 0.3 g (3%). M.p.: 215–218 °C. MS (EI, 70 eV): m/z (%) = 502 (7) $[M]^+$, 487 (31) $[M-Me]^+$, 445 (100) $[M-{}^tBu]^+$, 251 (41) $[Me_3SiOSi^tBuPh]^+$, 209 (30), 147 (17), 135 (58), 73 (22) $[SiMe_3]^+$. ^{1}H NMR: $\delta = 0.12$ (s, Me_3SiO, 18H), 1.09 (s, Me_3C, 18H), 7.15–7.69 (m, Ph, 10H) ppm. ^{29}Si NMR: $\delta = -15.1$ (Si^tBuPh), 8.4 ($OSiMe_3$) ppm. Anal. Calc. for $C_{26}H_{46}O_2Si_4$ (502.999): C, 62.09; H, 9.22. Found: C, 62.27; H, 9.13%.

Isolation of the siloxydisilane **14g** from the reaction of **1g** with lithium.

Distillation of the residue through a Fischer slit pipe column in the temperature range of 105–155 °C/0.05 Torr yielded two fractions (105–130 °C, 130–155 °C), which consisted of **1g**, **5g**, **6g** and **10g** in different proportions. Additionally, **14g** and **8g** remained in the distillation residue. Distillation of this residue using a Büchi ball tube oven yielded the pure siloxydisilane **14g** (210–215 °C/0.02 Torr).

1,2-Bis(2,4,6-trimethylphenyl)-1,2-bis(trimethylsiloxy)-1,2-diphenyl-disilane (**14g**): Yield: 0.6 g (5%). B.p.: 210–215 °C/0.02 Torr. GC: Diastereomeric ratio 1:1.4. MS (EI, 70 eV): m/z (%) = 626 (0.2) $[M]^+$, 611 (1) $[M-Me]^+$, 537 (3) $[M-OSiMe_3]^+$, 313 (100) $[M/2]^+$, 235 (9), 193 (14) $[M/2-C_9H_{12}]^+$. ^{1}H NMR: $\delta = 0.15$, 0.17 (s, Me_3SiO, 18H); 2.08, 2.18 (s, *p*-Me, 6H); 2.21, 2.47 (s, *o*-Me, 12H); 6.63, 6.80 (s, HC_{ar}, 4H); 7.07–7.94 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = 2.0$, 2.3 (Me_3SiO); 21.0, 21.1 (*p*-Me); 25.2, 25.3 (*o*-Me); 128.1–145.4 (C_{ar}) ppm. ^{29}Si NMR: $\delta = -15.6$, -14.4 (SiMesPh); 9.4, 9.6 ($OSiMe_3$) ppm. Anal. Calc. for $C_{36}H_{50}O_2Si_4$ (627.143): C, 68.95; H, 8.04. Found: C, 68.83; H, 7.96%.

*3.3. Reaction of the pure siloxydisilanes **6e**, **6f** and **6h** with lithium metal in THF and trapping with HMe_2SiCl – formation of the trisilanes $Me_3Si–Si^tBuPh–SiMe_2H$ (**11e**), $Me_3Si–SiPh_2–SiMe_2H$ (**11f**) and $Me_3Si–SiTipPh–SiMe_2H$ (**11h**)*

On the analogies of the preparative work a general procedure is given for the reactions of **6e**, **6f** and **6h** with lithium in THF and for the following trapping with HMe_2SiCl. The trisilanes formed were identified by comparison with the data of the pure compounds, which are described in Sections 3.2.5, 3.2.6 and 3.2.8

General procedure. To 4 equivalents (4 equiv.) of very thin lithium plates in 70 ml THF the siloxydisilane **6e** (4.2 mmol), **6f** (2.8 mmol) and **6h** (1.1 mmol), dissolved in 30 ml THF, was added dropwise within 5 min at −78 °C with vigorous stirring. For completion of the reaction the mixture was stirred for 24 h at −78 °C and for 4 h at room temperature (reaction of **6e**), for 3.5 h at −78 °C (reaction of **6f**) and for 20 h at −78 °C (reaction of **6h**). The solutions turned brown (reactions of **6e** and **6h**) and green (reaction of **6f**). Afterwards the excess lithium was removed. Then 2.5 equiv. HMe_2SiCl were added to the solution of lithiumsilanides at the respective reaction temperature. The reaction mixture was allowed to react for 24 h at room temperature. The reaction progress could be observed by the colour change of the solution from brown or green to colourless. After completion of quenching the work-up of the reaction mixture was carried out in analogy to Section 3.2.1. All three distillates of solvent contained $Me_3SiOSiMe_2H$. The residues were distilled using a Büchi ball tube oven. The respective main fractions contained the trisilanes **11e** (80–95 °C/0.1 Torr, yield: 0.91 g (74%)), **11f** (100–120 °C/0.3 Torr, yield: 0.70 g (79%)) and **11h** (150–170 °C/0.1 Torr, yield: 0.31 g (64%)). The analytical data of **11f** are given in [32].

*3.4. Reaction of the mixtures of lithiumsilanides from reaction of **1f**, **1g**, **1i** and lithium metal at −110 °C with ^{n}BuLi and trapping with Me_3SiCl – formation of the disilanes $^nBuPh_2SiSiMe_3$ (**16f**), $^nBuMesPhSiSiMe_3$ (**16g**) and $^nBuMes_2SiSiMe_3$ (**16i**)*

On the analogies of the preparative work a general procedure is given for the reactions of **1f**, **1g** and **1i** with lithium at – 110 °C and for the following ones of the mixtures of the lithiumsilanides with ^{n}BuLi as well as for the trapping with Me_3SiCl. The work-up of the crude products is described separately. Some details of reactions are shown in Eq. (6). The formed *n*-butyl-substituted disilanes were identified by comparison with the data of authentic compounds (Section 3.5).

General procedure. To 0.14 mol very thin lithium plates (4 equiv.) in 70 ml Trapp mixture (THF/Et_2O/*n*-pentane in volume ratio 4:1:1) 0.035 mol trimethylsiloxychlorosilane **1f**, **1g** and **1i**, dissolved in 30 ml Trapp mixture, was added dropwise within 15 min at −110 °C with vigorous stirring. For completion of the reaction the mixture was stirred for 4 h at −110 °C (reaction of **1f**), for 4.5 h at −110 °C (reaction of **1g**) and for 6 h at −110 °C (reaction of **1i**). The solutions turned green (reactions of **1f** and **1g**) and brown (reaction of **1i**). Afterwards the excess lithium was removed. Then to the respective solution of lithiumsilanides 0.175 mol ^{n}BuLi (1.6 M in *n*-hexane, cooled down to −78 °C) were added dropwise within 30 min at −110 °C with vigorous stirring. Subsequently, the reaction solution was warmed to room temperature within 2 h, stirred further for 4 h and quenched with 0.245 mol (7 equiv.) Me_3SiCl at the same temperature. The reaction mixture was allowed to react for 24 h at room temperature. The reaction progress could be observed by the colour change of the solution from green or brown to colourless. After completion of quenching the work-up of the reaction mixture was carried out in analogy to Section 3.2.1. The obtained residues were distilled in vacuo.

Reaction of the solution of lithiumsilanides, formed from **1f** and lithium, with ^{n}BuLi.

Distillation of the residue through a Fischer slit pipe column (90–130 °C/0.03 Torr) yielded three fractions (90–100 °C, 100–110 °C, 110–130 °C), which consisted of mixtures of **5f**, **10f**, **16f** and minor **6f** in different proportions. In the second fraction (100–110 °C) the disilane **16f** was enriched to 25%. In the distillation residue **8f** crystallised out.

Reaction of the solution of lithiumsilanides, formed from **1g** and lithium, with ^{n}BuLi.

Distillation of the residue through a Fischer slit pipe column (105–160 °C/0.3 Torr) yielded three fractions (105–120 °C, 120–140 °C, 140–160 °C), which contained mixtures of **5g**, **10g**, **16g** and small amounts of **6g** in different proportions. Especially, the second fraction (120–140 °C) consisted of the disilane **16g** enriched to 36%. In the distillation residue the trimethylsiloxytrisilane **8g** was found.

Reaction of the solution of lithiumsilanides, formed from **1i** and lithium, with ^{n}BuLi.

Distillation of the residue using a Büchi ball tube oven (130–175 °C/0.5 Torr) yielded four fractions (130–150 °C, 150–165 °C, 165–170 °C, 170–175 °C), which contained mixtures of **6i**, **16i** and minor **5i** in different proportions. Especially, in the second fraction (150–165 °C) the disilane **16i** was enriched to 21%.

*3.5. Preparation of the n-butyl-substituted disilanes ^{n}BuPh$_2$SiSiMe$_3$ (**16f**), ^{n}BuMesPhSiSiMe$_3$ (**16g**) and ^{n}BuMes$_2$SiSiMe$_3$ (**16i**)*

General procedure

(i) Syntheses of chlorosilanes ^{n}BuRR′SiCl (R = Ph, R′ = Ph, Mes; R = R′ = Mes).
To a solution of 7.6 mmol dichlorosilane RR′SiCl$_2$ (R = Ph, R′ = Ph, Mes; R = R′ = Mes) and 50 ml *n*-hexane 7.6 mmol ^{n}BuLi in 50 ml *n*-hexane were added dropwise within 1 h at −78 °C with vigorous stirring. For completion of the reaction the mixture was stirred for 3 h at room temperature (reaction with R = R′ = Ph), for 2 h at reflux (reaction with R = Mes, R′ = Ph) and for 24 h at reflux (reaction with R = R′ = Mes), respectively. After the respective reaction times LiCl was filtered off. The solvent was distilled from the filtrate under reduced pressure. The resulting colourless chlorosilanes were used without purification in the next procedure.

(ii) Reductive coupling of chlorosilanes ^{n}BuRR′SiCl with Me$_3$SiCl.
To the crude chlorosilanes ^{n}BuRR′SiCl 15.2 mmol Me$_3$SiCl and 20 ml THF were added. The solution of chlorosilanes was added dropwise to a mixture of 30.4 mmol of very thin lithium plates and 50 ml THF at room temperature with vigorous stirring. After a reaction time of 2 h at room temperature (reactions with ^{n}BuPh$_2$SiCl or ^{n}BuMesPhSiCl) or of 4 h (reaction with ^{n}BuMes$_2$SiCl) at room temperature the excess lithium was removed. Work-up of the reaction mixtures analogously to Section 3.2.1. yielded residues, which were distilled in vacuo using a Büchi ball tube oven.

1-*n*-Butyl-2,2,2-trimethyl-1,1-diphenyl-disilane (**16f**): Yield: 0.7 g (28%). B.p.: 109–110 °C/0.3 Torr. MS (EI, 70 eV): m/z (%) = 312 (20) [M]$^+$, 297 (2) [M−Me]$^+$, 255 (10) [M−^{n}Bu]$^+$, 239 (29) [M−SiMe$_3$]$^+$, 183 (100) [M−SiMe$_3$−C$_4$H$_8$]$^+$, 135 (10), 105 (14) [SiPh]$^+$, 73 (5) [SiMe$_3$]$^+$. ^{1}H NMR: $\delta = 0.21$ (s, Me$_3$Si, 9H); 0.85 (t, H$_3$C, 3H); 1.23, 1.34, 147 (3xm, H$_2$C, 6H); 7.13–7.58 (m, Ph, 10H) ppm. ^{13}C NMR: $\delta = -1.1$ (Me$_3$Si), 12.9 (CH$_3$ (^{n}Bu)); 13.8, 27.0, 27.2 (CH$_2$ (^{n}Bu)); 128.2, 129.0, 135.5, 136.7 (Ph) ppm. ^{29}Si NMR: $\delta = -$ 19.6 (SiMe$_3$), −19.1 (Si^{n}BuPh$_2$) ppm. Anal. Calc. for C$_{19}$H$_{28}$Si$_2$ (312.607): C, 73.00; H, 9.03. Found: C, 72.83; H, 8.92%.

1-*n*-Butyl-2,2,2-trimethyl-1-(2,4,6-trimethylphenyl)-1-phenyl-disilane (**16g**): Yield: 1.1 g (41%). B.p.: 81–82 °C/0.06 Torr. MS (EI, 70 eV): m/z (%) = 354 (11) [M]$^+$, 339 (2) [M−Me]$^+$, 297 (6) [M−^{n}Bu]$^+$, 281 (80) [M−SiMe$_3$]$^+$, 225 (100) [M−SiMe$_3$−C$_4$H$_8$]$^+$, 73 (7) [SiMe$_3$]$^+$. MS (CI, *iso*-butane): m/z (%) = 354 (7) [M]$^+$, 339 (28) [M−Me]$^+$, 307 (12), 281 (15) [M−SiMe$_3$]$^+$, 277 (11), 235 (100) [M−C$_9$H$_{11}$]$^+$, 179 (20) [M−C$_9$H$_{11}$−C$_4$H$_8$]$^+$, 175 (25), 157 (12) [M−C$_9$H$_{11}$−C$_6$H$_6$]$^+$. ^{1}H NMR: $\delta = 0.20$ (s, Me$_3$Si, 9H), 0.84 (t, H$_3$C, 3H), 1.37 (m, H$_2$C, 6H), 2.13 (s, *p*-Me, 3H), 2.32 (s, *o*-Me, 6H), 6.76 (s, HC$_{\text{ar}}$, 2H), 7.12–7.47 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = -0.2$ (Me$_3$Si), 13.9 (CH$_3$ (^{n}Bu)); 14.8, 27.1, 27.8 (CH$_2$ (^{n}Bu)); 21.0 (*p*-Me), 25.7 (*o*-Me); 128.2, 129.4, 134.4 (C$_{\text{ar}}$H); 130.7, 138.7, 140.9, 145.3 (C$_{\text{ar}}$) ppm. ^{29}Si NMR: $\delta = -$ 22.0 (Si^{n}BuMesPh), −16.5 (SiMe$_3$) ppm. Anal. Calc. for C$_{22}$H$_{34}$Si$_2$ (354.688): C, 74.50; H, 9.66. Found: C, 74.45; H, 9.62%.

1-*n*-Butyl-2,2,2-trimethyl-1,1-bis(2,4,6-trimethylphenyl)-disilane (**16i**): Yield: 1.8 g (60%). B.p.: 133–134 °C/0.1 Torr. MS (EI, 70 eV): m/z (%) = 396 (3) [M]$^+$, 381 (1) [M−Me]$^+$, 339 (3) [M−^{n}Bu]$^+$, 323 (33) [M−SiMe$_3$]$^+$, 267 (100) [M−SiMe$_3$−C$_4$H$_8$]$^+$, 73 (8) [SiMe$_3$]$^+$. MS (CI, *iso*-butane): m/z (%) = 397 (12) [M+H]$^+$, 396 (8) [M]$^+$, 381 (55) [M−Me]$^+$, 339 (10) [M−^{n}Bu]$^+$, 323 (86) [M−SiMe$_3$]$^+$, 277 (100) [M−C$_9$H$_{11}$]$^+$, 221 (19) [M−C$_9$H$_{11}$−C$_4$H$_8$]$^+$. ^{1}H NMR: $\delta = 0.25$ (s, Me$_3$Si, 9H), 0.82 (t, H$_3$C, 3H), 1.28 (m, H$_2$C, 6H), 2.13 (s, *p*-Me, 6H), 2.31 (s, *o*-Me, 12H), 6.72 (s, HC$_{\text{ar}}$, 4H) ppm. ^{13}C NMR: $\delta = 0.5$ (Me$_3$Si), 13.9 (CH$_3$ (^{n}Bu)); 18.7, 27.2, 28.5 (CH$_2$ (^{n}Bu)); 21.1 (*p*-Me), 25.1 (*o*-Me), 129.4 (C$_{\text{ar}}$H); 134.6, 137.8, 143.3 (C$_{\text{ar}}$) ppm.

^{29}Si NMR: $\delta = -22.4$ (Si^{n}BuMes$_2$), -13.9 (SiMe$_3$) ppm. Anal. Calc. for $C_{25}H_{40}Si_2$ (396.770): C, 75.68; H, 10.16. Found: C, 75.53; H, 10.31%.

3.6. Reaction of the mixtures of lithiumsilanides from reaction of **1g**, **1i** and lithium metal at −110 °C with 2,3-dimethylbuta-1,3-diene – formation of 3,4-dimethyl-1-(2,4,6-trimethylphenyl)-1-phenyl-silacyclopent-3-ene **17g** and 3,4-dimethyl-1,1-bis(2,4,6-trimethylphenyl)-silacyclopent-3-ene **17i**

On the analogies of the preparative work a general procedure is given for the reactions of **1g** and **1i** with lithium metal at −110 °C and the following ones of the mixtures of the lithiumsilanides with 2,3-dimethylbuta-1,3-diene as well as for the quenching with Me$_3$SiCl. The work-up of the crude products is described separately. Some details of reactions are shown in Eq. (7).

General procedurze. To 0.14 mol (4 equiv.) very thin lithium plates in 70 ml Trapp mixture (THF/Et$_2$O/*n*-pentane in volume ratio 4:1:1) 0.035 mol trimethylsiloxychlorosilane **1g** or **1i**, dissolved in 30 ml Trapp mixture, was added dropwise within 15 min at −110 °C with vigorous stirring. For completion of the reaction the mixture was stirred vigorously for 4.5 h at −110 °C (reaction of **1g**) and for 6 h at −110 °C (reaction of **1i**). The solutions turned green (reaction of **1g**) and brown (reaction of **1i**). Afterwards the excess lithium was removed. Then to the respective solution of lithiumsilanides 0.105 mol (3 equiv.) 2,3-dimethylbuta-1,3-diene were added with stirring. The reaction solution was warmed from −110 °C to −78 °C within 1 h, stirred further 3 h at −78 °C and quenched with 0.07 mol (2 equiv.) trapping agent Me$_3$SiCl at the same temperature. The reaction mixture was allowed to react for 24 h at room temperature. The reaction progress could be observed by the colour change of the solution from green or brown to colourless. After completion of quenching the work-up of the reaction mixture was carried out in analogy to Section 3.2.1. The respective residues obtained were distilled in vacuo using a Büchi ball tube oven.

Reaction of the solution of lithiumsilanides, formed from **1g** and lithium, with 2,3-dimethylbuta-1,3-diene.

Distillation of the residue in the temperature range of 120–210 °C/0.1 Torr yielded several fractions. In the fraction (170–180 °C), **17g** was enriched to 50%. Preparative LPLC of this fraction yielded pure **17g**. Subsequently, single crystals of **17g** could be obtained by crystallisation from *n*-pentane.

3,4-Dimethyl-1-(2,4,6-trimethylphenyl)-1-phenyl-silacyclopent-3-ene (**17g**): Yield: 0.35 g (3%, referring to **1g**). M.p.: 76 °C. MS (EI, 70 eV): m/z (%) = 306 (87) [M]$^+$, 228 (33) [M$-$C$_6$H$_6$]$^+$, 224 (23) [M$-$C$_6$H$_{10}$]$^+$, 186 (100) [M$-$C$_9$H$_{12}$]$^+$, 105 (33) [PhSi]$^+$. ^{1}H NMR: $\delta = 1.78$ (s, H$_3$CC=, 6H), 2.11, 2.13 (2xs, H$_2$CC=, 4H); 2.18 (s, *p*-Me, 3H), 2.29 (s, *o*-Me, 6H), 6.81 (s, HC$_{ar}$, 2H), 7.10–7.54 (m, Ph, 5H) ppm. ^{13}C NMR: $\delta = 19.1$ (Me), 21.2 (*p*-Me), 24.5 (*o*-Me), 29.1 (CH$_2$), 127.9–145.1 (C$_{ar}$ and C=C) ppm. ^{29}Si NMR: $\delta = -0.7$ ppm. Anal. Calc. for $C_{21}H_{26}Si$ (306.527): C, 82.29; H, 8.55. Found: C, 82.05; H, 8.72%.

Reaction of the solution of lithiumsilanides, formed from **1i** and lithium, with 2,3-dimethylbuta-1,3-diene.

The residue consisted of a mixture of **5i**, **17i** and unknown compounds. Distillation of the residue using a Büchi ball tube oven (120–240 °C/0.07 Torr) yielded a fraction (160–195 °C), which contained **17i** enriched to about 30%. From this fraction **17i** was isolated as an amorphous compound by preparative LPCP.

3,4-Dimethyl-1,1-bis(2,4,6-trimethylphenyl)-silacyclopent-3-ene [64,65] (**17i**): Yield: 0.25 g (2%, referring to **1i**). MS (EI, 70 eV): m/z (%) = 348 (2) [M]$^+$, 266 (3) [M$-$C$_6$H$_{10}$]$^+$, 228 (100) [M$-$C$_9$H$_{12}$]$^+$, 147 (28) [SiMes]$^+$, 119 (13) [C$_9$H$_{11}$]$^+$. ^{1}H NMR: $\delta = 1.74$ (s, H$_3$CC=, 6H), 2.11 (s, H$_2$CC=, 4H), 2.11 (s, *p*-Me, 6H), 2.37 (s, *o*-Me, 12H), 6.71 (s, HC$_{ar}$, 4H) ppm. ^{13}C NMR: $\delta = 19.3$ (Me), 21.0 (*p*-Me), 24.1 (*o*-Me), 30.6 (CH$_2$); 129.5, 131.2, 134.5, 138.3, 143.9 (C$_{ar}$ and C=C) ppm. ^{29}Si NMR: $\delta = -2.6$ ppm. Anal. Calc. for $C_{24}H_{32}Si$ (348.609): C, 82.69; H, 9.25. Found: C, 82.44; H, 9.37%.

3.7. Single crystal X-ray diffraction analysis of **17g**

Empirical formula: $C_{21}H_{26}Si$; formula weight: 306.51; crystal size: $0.52 \times 0.38 \times 0.24$ mm^3; crystal system: monoclinic; space group: *C*2/*c*; $a = 23.300(4)$ Å, $b = 13.080(4)$ Å, $c = 14.908(3)$ Å, $\beta = 124.61(1)°$; $V = 3739(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.089$ g cm^{-3}, $\mu = 0.121$ mm^{-1}, $F(000) = 1328$, $T = 293(2)$ K, $\lambda = 0.71073$ Å; scan range (θ): 2.07–23.00°; *hkl* ranges: −1/25, −1/14, −16/13; number of collected reflections = 3134, number of independent reflections = 2611, reflections with $I > 2\sigma(I) = 1666$, refined parameters = 204, GOOF = 1.015, R_1 $[I > 2\sigma(I)] = 0.0603$, R_1 (all data) = 0.0986, wR_2 (all data) = 0.1718; largest diff. peak and hole: 0.16/−0.29 e Å^{-3}. The data collection was done on a Bruker P4 diffractometer by means of Mo Kα radiation (graphite monochromator), performing ω-scan for each frame. The structure was solved by direct methods (Bruker SHELXTL [67]), and for the refinement against F^2 a full-matrix least-squares target was used (SHELXL-97 [68]). The hydrogen atoms were placed at geometrically calculated positions and refined by means of a riding model.

4. Supplementary material

CCDC 610626 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

We thank the Fonds der Chemischen Industrie for the material support of this work.

References

[1] G. Köbrich, Angew. Chem. 84 (1972) 557;
G. Köbrich, Angew. Chem., Int. Ed. Engl. 11 (1972) 473.
[2] D. Seebach, H. Siegel, J. Gabriel, R. Hässig, Helv. Chim. Acta 63 (1980) 2046.
[3] H. Siegel, Top. Curr. Chem. 106 (1982) 55.
[4] G. Boche, M. Marsch, A. Müller, K. Harms, Angew. Chem. 105 (1993) 1081;
G. Boche, M. Marsch, A. Müller, K. Harms, Angew. Chem., Int. Ed. Engl. 32 (1993) 1032.
[5] G. Boche, F. Bosold, J.C.W. Lohrenz, A. Opel, R. Zulauf, Chem. Ber. 126 (1993) 1873.
[6] A. Maercker, Angew. Chem. 105 (1993) 1072;
A. Maercker, Angew. Chem., Int. Ed. Engl. 32 (1993) 1023.
[7] M. Topolski, M. Duraisamy, J. Rachon, J. Gawronski, K. Gawronska, V. Goedken, H.M. Walborsky, J. Org. Chem. 58 (1993) 546.
[8] M. Shimizu, T. Hata, T. Hiyama, Tetrahedron Lett. 38 (1997) 4591.
[9] M. Braun, Angew. Chem. 110 (1998) 444;
M. Braun, Angew. Chem., Int. Ed. Engl. 37 (1998) 430.
[10] H. Hermann, J.C.W. Lohrenz, A. Kühn, G. Boche, Tetrahedron 56 (2000) 4109.
[11] Y. Naruse, A. Hayashi, S. Sou, H. Ikeda, S. Inagaki, Bull. Chem. Soc. Jpn. 74 (2001) 245.
[12] G. Boche, J.C.W. Lohrenz, Chem. Rev. 101 (2001) 697.
[13] Th. Baumgartner, P. Moors, M. Nieger, H. Hupfer, E. Niecke, Organometallics 21 (2002) 4919.
[14] M. Braun, in: Z. Rappoport, I. Marek (Eds.), The Chemistry of Organolithium Compounds, vol. 2, Wiley, Chichester, 2004, p. 829.
[15] P.J. Stang, Chem. Rev. 78 (1978) 383.
[16] A.F. Burchat, J.M. Chong, S.B. Park, Tetrahedron Lett. 34 (1993) 51.
[17] A.R. Katrizky, M. Qi, Tetrahedron 54 (1998) 2647.
[18] R.E. Gawley, E. Low, Q. Zhang, R. Haris, J. Am. Chem. Soc. 122 (2000) 3344.
[19] K. Tamao, A. Kawachi, Adv. Organomet. Chem. 38 (1995) 1.
[20] A. Kawachi, K. Tamao, Bull. Chem. Soc. Jpn. 70 (1997) 945.
[21] K. Tamao, A. Kawachi, M. Asahara, A. Toshimitsu, Pure Appl. Chem. 71 (1999) 393.
[22] J. Belzner, U. Dehnert, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 779.
[23] K. Tamao, A. Kawachi, Y. Ito, J. Am. Chem. Soc. 114 (1992) 3989.
[24] K. Tamao, A. Kawachi, Organometallics 14 (1995) 3108.
[25] A. Kawachi, N. Doi, K. Tamao, J. Am. Chem. Soc. 119 (1997) 233.
[26] I. Rietz, E. Popowski, H. Reinke, M. Michalik, J. Organomet. Chem. 556 (1998) 67.
[27] A. Kawachi, K. Tamao, J. Am. Chem. Soc. 122 (2000) 1919.
[28] C. Strohmann, O. Ulbrich, D. Auer, Eur. J. Inorg. Chem. (2001) 1013.
[29] K. Tamao, A. Kawachi, Angew. Chem. 107 (1995) 886;
K. Tamao, A. Kawachi, Angew. Chem., Int. Ed. Engl. 34 (1995) 818.
[30] A. Kawachi, K. Tamao, Organometallics 15 (1996) 4653.
[31] A. Kawachi, H. Maeda, H. Nakamura, N. Doi, K. Tamao, J. Am. Chem. Soc. 123 (2001) 3143.
[32] J. Harloff, E. Popowski, H. Fuhrmann, J. Organomet. Chem. 592 (1999) 136.
[33] J. Harloff, E. Popowski, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry V – From Molecules to Materials, Wiley–VCH, Weinheim, 2003, p. 175.
[34] N. Tokitoh, K. Hatano, T. Sadahiro, R. Okazaki, Chem. Lett. (1999) 931.
[35] M.E. Lee, H.M. Cho, M.S. Ryu, Ch.H. Kim, W. Ando, J. Am. Chem. Soc. 123 (2001) 7732.
[36] N. Wiberg, W. Niedermayer, J. Organomet. Chem. 628 (2001) 57.
[37] M.E. Lee, H.M. Cho, Y.M. Lim, J.K. Choi, Ch.H. Park, S.E. Jeong, U. Lee, Chem. Eur. J. 10 (2004) 377.
[38] A. Kawachi, Y. Oishi, T. Kataoka, K. Tamao, Organometallics 23 (2004) 2949.
[39] P.D. Lickiss, C.M. Smith, Coord. Chem. Rev. 145 (1995) 75.
[40] J. Grobe, T. Schierholdt, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry II – From Molecules to Materials, Wiley–VCH, Weinheim, 1996, p. 317.
[41] P.P. Gaspar, R. West, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 2463.
[42] M.E. Lee, H.M. Cho, C.H. Kim, W. Ando, Organometallics 20 (2001) 1472.
[43] R. Corriu, G. Lanneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin, C. Tan, J. Organomet. Chem. 466 (1994) 55.
[44] M.J. Michalczyk, M.J. Fink, D.J. De Young, C.W. Carlson, K.M. Welsh, R. West, J. Michl, Silicon, Germanium, Tin Lead Compd. 9 (1986) 75.
[45] P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrisciel, K.R. Anderson, Angew. Chem. 100 (1988) 1406;
P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrisciel, K.R. Anderson, Angew. Chem., Int. Ed. Engl. 27 (1988) 1355.
[46] N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, J. Am. Chem. Soc. 119 (1997) 1456.
[47] N. Wiberg, W. Niedermayer, Z. Naturforsch. B 55 (2000) 406.
[48] M. Haaf, T.A. Schmedake, B.J. Paradise, R. West, Can. J. Chem. 78 (2000) 1526.
[49] W.S. Sheldrick, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, vol. 1, Wiley, Chichester, 1989, p. 227.
[50] M. Kaftory, M. Kapon, M. Botoshansky, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1998, p. 181.
[51] H.J. Emeleus, S.R. Robinson, J. Chem. Soc. (1947) 1592.
[52] F.S. Kipping, J. Chem. Soc. 91 (1907) 215.
[53] G.V. Motsarev, V.T. Inshakova, V.I. Kolbasov, R.V. Dshagaipanjan, Zh. Obshch. Khim. 41 (1971) 1573.
[54] K.A. Andrianov, G.V. Kotrelev, L.I. Nosova, Zh. Obshch. Khim. 42 (1972) 854.
[55] L.H. Sommer, L.J. Tyler, J. Am. Chem. Soc. 76 (1954) 1030.
[56] C.N. Smit, F. Bickelhaupt, Phosphorus, Sulfur, Silicon Rel. Elem. 30 (1987) 357.
[57] N. Wiberg, B. Neruda, Chem. Ber. 99 (1966) 740.
[58] U. Scheim, H. Grosse-Ruyken, K. Rühlmann, G. Schmidt, GDR-Pat. DD226567 (1984); CA (1984) 267446.
[59] R. Wagner, L. Richter, Y. Wu, J. Weissmüller, J. Reiners, E. Hengge, Appl. Organomet. Chem. (1997) 645.
[60] M. Nanjo, A. Sekiguchi, H. Sakurai, Bull. Chem. Soc. Jpn. 71 (1998) 741.
[61] Z.-E. Lin, S.-H. Wu, Z.-P. Yao, Org. Mass Spectrom. 26 (1991) 24.
[62] P.E. Lebedev, A.D. Fedorov, V.O. Reichsfeld, Zh. Obshch. Khim. 46 (1976) 931.
[63] R.E. Swaim, W.P. Weber, J. Am. Chem. Soc. 101 (1979) 5703.
[64] H. Sakurai, K. Oharu, Y. Nakadaira, Chem. Lett. (1986) 1797.
[65] S. Zhang, R.T. Conlin, J. Am. Chem. Soc. 113 (1991) 4272.
[66] R. West, P. Nowakowski, P. Boudjouk, J. Am. Chem. Soc. 98 (1976) 5620.
[67] Bruker SHELTX Version 5.10 SGI/IRIX 5.3, Copyright ©, Bruker Analytical X-ray Systems, 1997.
[68] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1997.