

Reactions of trimethylsilyloxychlorosilanes with lithium metal – On the mechanism of the formation of trimethylsilyloxydisilyllithium compounds $\text{LiSiRR}'(\text{OSiMe}_3)$

Joerg Harloff, Eckhard Popowski *

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

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Abstract

The reaction pathway for the formation of the trimethylsilyloxydisilyllithium compounds ($\text{Me}_3\text{SiO}(\text{RR}')\text{SiLi}$ (**2a**: $\text{R} = \text{Et}$, **2b**: $\text{R} = {}^i\text{Pr}$, **2c**: $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (Mes); **2a–c**: $\text{R}' = \text{Ph}$; **2d**: $\text{R} = \text{R}' = \text{Mes}$) starting from the conversion of the corresponding trimethylsilyloxychlorosilanes ($\text{Me}_3\text{SiO}(\text{RR}')\text{SiCl}$ (**1a–d**)) in the presence of excess lithium in a mixture of THF/diethyl ether/*n*-pentane at -110°C was investigated.

The trimethylsilyloxychlorosilanes ($\text{Me}_3\text{SiO}(\text{RPhSiCl})$ (**1a**: $\text{R} = \text{Et}$, **1b**: $\text{R} = {}^i\text{Pr}$, **1c**: $\text{R} = \text{Mes}$) react with lithium to give initially the trimethylsilyloxydisilyllithium compounds ($\text{Me}_3\text{SiO}(\text{RPhSiLi})$ (**2a–c**)). These siloxydisilyllithiums **2** couple partially with more trimethylsilyloxychlorosilanes **1** to produce the siloxydisilanes ($\text{Me}_3\text{SiO}(\text{RPhSi-SiPhR}(\text{OSiMe}_3))$ (**1a–c**)), and they undergo bimolecular self-condensation affording the trimethylsilyloxydisilyllithium compounds ($\text{Me}_3\text{SiO}(\text{RPhSi-RPhSiLi})$ (**3a–c**)). The siloxydisilanes **1** are cleaved by excess of lithium to give the trimethylsilyloxydisilyllithiums ($\text{Me}_3\text{SiO}(\text{RPhSiLi})$ (**2**)). In the case of the two trimethylsilyloxydisilyllithiums ($\text{Me}_3\text{SiO}(\text{RPhSi-RPhSiLi})$ (**3a**: $\text{R} = \text{Et}$, **3b**: $\text{R} = {}^i\text{Pr}$)) a reaction with more trimethylsilyloxychlorosilanes ($\text{Me}_3\text{SiO}(\text{RPhSiCl})$ (**1a**, **1b**)) takes place under formation of siloxytrisilanes ($\text{Me}_3\text{SiO}(\text{RPhSi-RPhSi-SiPhR}(\text{OSiMe}_3))$ (**11a**: $\text{R} = \text{Et}$, **11b**: $\text{R} = {}^i\text{Pr}$)) which are cleaved by lithium to yield the trimethylsilyloxydisilyllithiums ($\text{Me}_3\text{SiO}(\text{RPhSiLi})$ (**2a**, **2b**)) and the trimethylsilyloxydisilyllithiums ($\text{Me}_3\text{SiO}(\text{RPhSi-RPhSiLi})$ (**3a**, **3b**)). The dimethyl-trimethylsilyloxy-silyllithium ($\text{Me}_3\text{SiO}(\text{Mes}_2\text{SiLi})$ (**2d**)) was obtained directly by reaction of the trimethylsilyloxychlorosilane ($\text{Me}_3\text{SiO}(\text{Mes}_2\text{SiCl})$ (**1d**)) and lithium without formation of the siloxydisilane intermediate. Both silyllithium compounds **2** and **3** were trapped with HMe_2SiCl giving the products ($\text{Me}_3\text{SiO}(\text{RR}')\text{Si-SiMe}_2\text{H}$) and ($\text{Me}_3\text{SiO}(\text{RPhSi-RPhSi-SiMe}_2\text{H})$). © 2008 Elsevier B.V. All rights reserved.

Keywords: Disilanes; Trisilanes; Si–Si bond cleavage; Trimethylsilyloxydisilyllithiums; Mechanism of formation

1. Introduction

Organosilyllithium compounds are versatile reagents in synthetic organic and organometallic chemistry. Syntheses, properties and reactivity of the organosilyllithium compounds and of the other alkali metal derivatives of organosilicon compounds have been subject of several reviews [1–12]. The most convenient method for the preparation of triorganosilyllithium compounds $\text{RR}'(\text{aryl})\text{SiLi}$

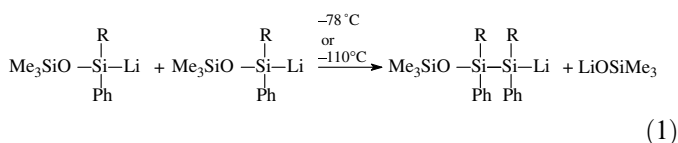
with at least one aryl substituent on the silicon atom is the reaction of the corresponding chlorosilanes $\text{RR}'(\text{aryl})\text{SiCl}$ with lithium metal [1,6,10,11,13–15]. The functionalised silyllithium compounds $(\text{H})\text{Ph}_2\text{SiLi}$ [16], $(\text{H})\text{Mes}_2\text{SiLi}$ [17,18]; $(\text{Et}_2\text{N})_n\text{-Ph}_{3-n}\text{SiLi}$ ($n = 1, 2$), $(\text{Et}_2\text{N})\text{MePhSiLi}$ [7,9–11,19,20]; $({}^i\text{BuO})_2\text{PhSiLi}$ [7,9–11,21], $[(\text{Me}_3\text{Si})_2\text{N}]\text{-Me}_{2-n}\text{Ph}_n\text{SiLi}$ ($n = 1, 2$) [22]; $(\text{Me}_3\text{SiO})\text{RPhSiLi}$ ($\text{R} = \text{Me}$, Et , ${}^i\text{Pr}$, ${}^i\text{Bu}$, Ph , Mes , Tip ; $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $\text{Tip} = 2,4,6\text{-(Me}_2\text{CH)}_3\text{C}_6\text{-H}_2$) and $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiLi}$ [23,24] can be also synthesised by this method.

In the reactions of the trimethylsilyloxychlorosilanes ($\text{Me}_3\text{SiO}(\text{RPhSiCl})$ ($\text{R} = \text{Me}$, Et , ${}^i\text{Pr}$, ${}^i\text{Bu}$, Ph , Mes)) with lithium metal in THF at -78°C and in a mixture of

* Corresponding author. Tel.: + 49 381 498 6380; fax: + 49 381 498 6382.

E-mail address: eckhard.popowski@uni-rostock.de (E. Popowski).

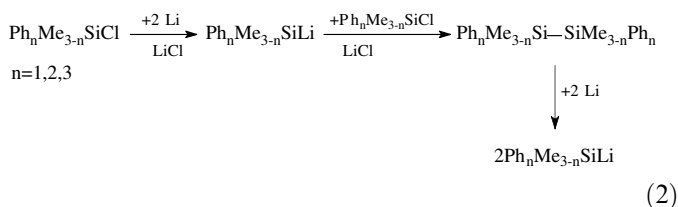
THF/diethyl ether/*n*-pentane (volume ratio 4:1:1) at $-110\text{ }^{\circ}\text{C}$ (Trapp mixture) the silyllithium derivatives $(\text{Me}_3\text{SiO})\text{RPhSiLi}$, $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{Li}$ and $\text{Me}_3\text{SiRPhSiLi}$ have been obtained [23,24]. The stability of the trimethylsilyloxysilyllithiums $(\text{Me}_3\text{SiO})\text{RPhSiLi}$ is higher at $-110\text{ }^{\circ}\text{C}$ than at $-78\text{ }^{\circ}\text{C}$. The trimethylsilyoxydisilyllithiums $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{RPhSiLi}$ are formed by bimolecular self-condensation of trimethylsilyloxysilyllithiums (Eq. (1)).



The trimethylsilyloxysilyllithiums $(\text{Me}_3\text{SiO})\text{TipPhSiLi}$ and $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiLi}$ do not undergo such a self-condensation.

Except for ${}^t\text{Bu}_3\text{SiLi}$ [8,25] the peralkylated silyllithium compounds cannot be prepared by reaction of the corresponding chlorosilanes with lithium metal [6,7,10,11]. The attack of the chlorosilanes R_3SiCl ($\text{R} = \text{alkyl}$ except ${}^t\text{Bu}$) on lithium metal affords the homocoupling products only, i.e. the disilanes $\text{R}_3\text{Si}-\text{SiR}_3$. Similarly, the alkyl(amino) chlorosilanes $(\text{Et}_2\text{N})_n\text{R}_{3-n}\text{SiCl}$ ($n = 1, 2$; $\text{R} = \text{alkyl}$) [26] and $[(\text{Me}_3\text{Si})_2\text{N}]\text{Me}_2\text{SiCl}$ [22] as well as the trimethylsilyoxychlorosilane $(\text{Me}_3\text{SiO})\text{Me}_2\text{SiCl}$ [23] undergo only homocoupling reactions with lithium to give the corresponding symmetrical disilanes.

Although the reductive lithiation of chlorosilanes is widely used for the synthesis of aryl-containing silyllithium compounds [overview in Refs. 2,6,7,10,11], the course of reaction has been investigated only occasionally [1,13–15,20]. For the formation of phenyl-substituted silyllithiums $\text{Ph}_n\text{Me}_{3-n}\text{SiLi}$ ($n = 1, 2, 3$) the following reaction pathway is discussed [1,6,7,10,11,13,14]: (i) rapid formation of the silyllithium, (ii) reaction of the silyllithium with more chlorosilane to give the disilane and (iii) symmetrical cleavage of the Si–Si bond of the disilane by lithium (Eq. (2)).



The disilanes can be isolated when the reactions are stopped at an appropriate stage. The corresponding disilane intermediates are also formed in the lithiation of 1-chloro-1,2,3,4-tetrahydro-1-phenyl-1-silanaphthalene [15] and the diethylamino-substituted chlorosilane $(\text{Et}_2\text{N})\text{Ph}_2\text{SiCl}$ [20]. High steric shielding of the Si(Cl) atom in the chlorosilane can inhibit the formation of the disilane [13–15]. Thus, the reaction of chloro-tri(*o*-tolyl)silane with lithium yields the silyllithium compound without formation of a disilane [1,13].

In Ref. [24] we have assumed that the generation of the trimethylsilyloxysilyllithiums $(\text{Me}_3\text{SiO})\text{RPhSiLi}$ ($\text{R} = \text{Me}$,

Et , ${}^i\text{Pr}$, ${}^t\text{Bu}$, Ph , Mes , Tip) and $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiLi}$ by reductive lithiation of the corresponding trimethylsilyoxychlorosilanes proceeds via a disilane intermediate. This assumption is supported by the results of the reactions of the trimethylsilyoxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ ($\text{R} = {}^t\text{Bu}$, Mes) with lithium in a Trapp mixture at $-110\text{ }^{\circ}\text{C}$. When the reactions have been stopped at an early stage, the disilanes $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{SiPhR}(\text{OSiMe}_3)$ ($\text{R} = {}^t\text{Bu}$, Mes) could be isolated. In many cases the trimethylsilyloxysilyllithiums undergo self-condensation reactions affording the trimethylsilyoxydisilyllithiums (see above). These compounds could also be involved in the process of forming the trimethylsilyloxysilyllithiums.

In this paper we describe the results of our studies on the mechanism of formation of the trimethylsilyloxysilyllithium compounds $(\text{Me}_3\text{SiO})\text{RR}'\text{SiLi}$ (**2a–d**) by reductive lithiation of trimethylsilyoxychlorosilanes with lithium metal in a Trapp mixture at $-110\text{ }^{\circ}\text{C}$.

| | a | b | c | d |
|----|----------|-----------------|------------------|----------|
| R | Et | ${}^i\text{Pr}$ | Mes ^a | Mes |
| R' | Ph | Ph | Ph | Mes |

^a Mes: 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$.

2. Results and discussion

For the investigations of the mechanism of forming the trimethylsilyloxysilyllithiums $(\text{Me}_3\text{SiO})\text{RR}'\text{SiLi}$ by reaction of the corresponding trimethylsilyoxychlorosilanes $(\text{Me}_3\text{SiO})\text{RR}'\text{SiCl}$ (**1a–d**) with lithium metal the reaction temperature $-110\text{ }^{\circ}\text{C}$ was chosen because both the yield and the stability of the trimethylsilyloxysilyllithium compounds $(\text{Me}_3\text{SiO})\text{RR}'\text{SiLi}$ (**2a–d**) are relatively high at this temperature [23,24]. Furthermore, investigations are limited to those transformations of the trimethylsilyoxychlorosilanes **1** with lithium in which the yields of compounds from ambiguous chemical pathways are very small [24]. That are the trimethylsilylsilyllithium derivatives $\text{Me}_3\text{SiRPhSiLi}$ ($\text{R} = \text{Et}$, ${}^i\text{Pr}$) for the reactions of the trimethylsilyoxychlorosilanes $(\text{Me}_3\text{SiO})\text{EtPhSiCl}$ (**1a**) and $(\text{Me}_3\text{SiO}){}^i\text{PrPhSiCl}$ (**1b**) with lithium as well as the lithiumoxysilyllithiums $(\text{LiO})\text{RMesSiLi}$ ($\text{R} = \text{Ph}$, Mes) and the disilane $(\text{Me}_3\text{SiO})\text{Mes}_2\text{Si}-\text{SiMe}_3$ for the reactions of $(\text{Me}_3\text{SiO})\text{MesPhSiCl}$ (**1c**) and $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiCl}$ (**1d**) with lithium [24].

For monitoring the reactions after the reaction start samples of the reaction mixture were taken out at certain time intervals and quenched with dimethylchlorosilane. The identification of the trapped products of lithiumsilanides as well as intermediates was carried out by spectroscopic methods and by using authentic compounds. The changes in amounts of various species in the reaction mixtures were determined by GC. The peak areas in the gas chromatograms serve as relative measure for the changes in amounts of the several compounds.

The reaction leading during the transformation of the two alkyl-substituted trimethylsilyloxychlorosilanes (Me_3SiO)RPhSiCl (**1a**: R = Et, **1b**: R = *i*Pr), of the mesitylphenyl-trimethylsilyloxy-chlorosilane (Me_3SiO)MesPhSiCl (**1c**) and of the dimesityl-trimethylsilyloxy-chlorosilane (Me_3SiO)-Mes₂SiCl (**1d**) with lithium (molar ratio Li: chlorosilane = 4:1) are clearly different from each other. It is most

complex in the case of the reactions of the siloxychlorosilanes (Me_3SiO)RPhSiCl (**1a**: R = Et, **1b**: R = *i*Pr) with lithium. Beside the well-known trapping products (Me_3SiO)RPhSi-SiMe₂H (**4a**: R = Et, **4b**: R = *i*Pr) and (Me_3SiO)RPhSi-RPhSi-SiMe₂H (**5a**: R = Et, **5b**: R = *i*Pr) [24], formed by the reaction of the lithiumsilanides (Me_3SiO)RPhSiLi (**2a**: R = Et, **2b**: R = *i*Pr) and (Me_3SiO)RPhSi-

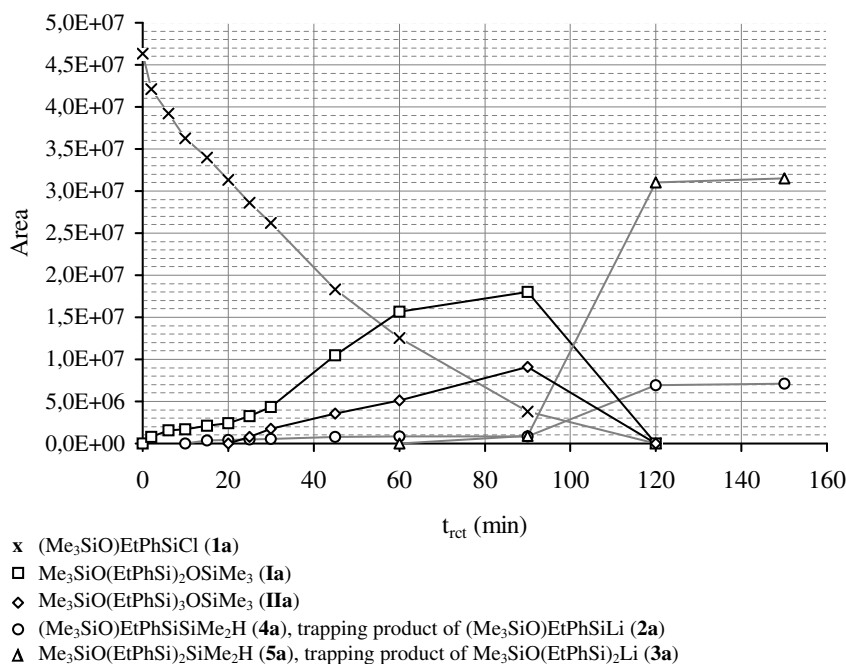


Fig. 1. Course of reaction of the siloxychlorosilane (Me_3SiO)EtPhSiCl (**1a**) with lithium metal in a Trapp mixture at -110°C monitored by GC. For GC measurements samples of the reaction mixture were quenched with HMe_2SiCl .

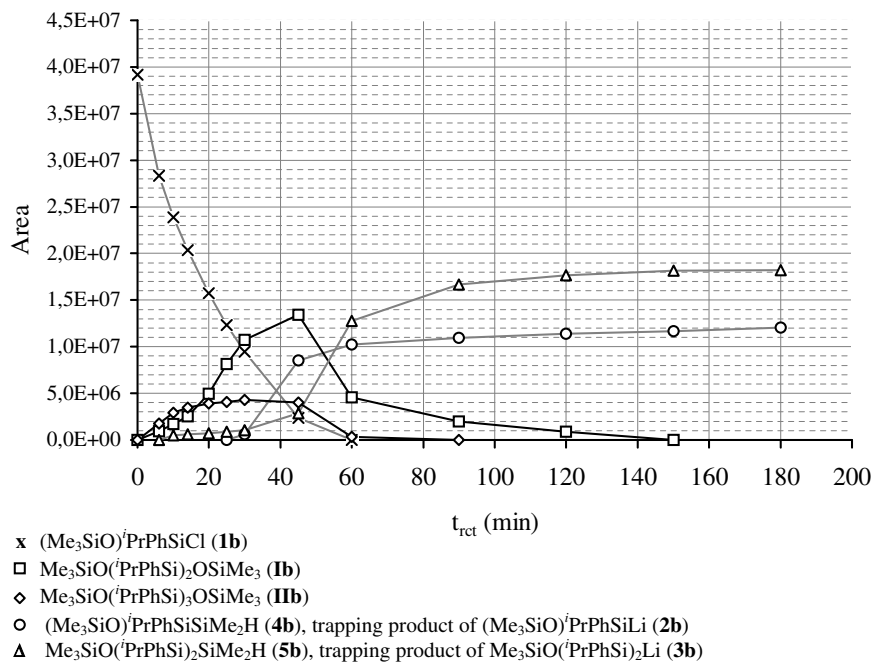


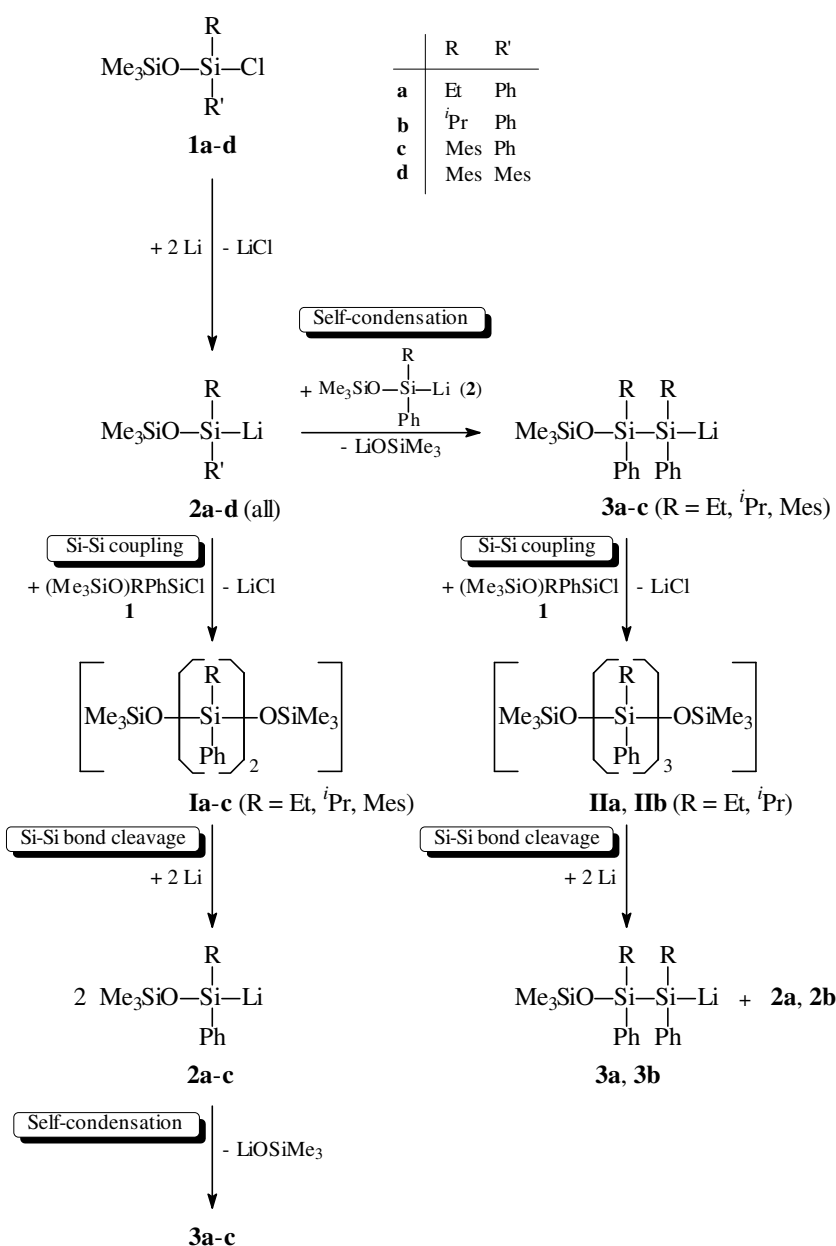
Fig. 2. Course of reaction of the siloxychlorosilane (Me_3SiO)*i*PrPhSiCl (**1b**) with lithium metal in a Trapp mixture at -110°C monitored by GC. For GC measurements samples of the reaction mixture were quenched with HMe_2SiCl .

RPhSiLi (**3a**: R = Et, **3b**: R = *i*Pr) with HMe₂SiCl, respectively, the disilanes (Me₃SiO)RPhSi–SiPhR(OSiMe₃) (**1a**: R = Et, **1b**: R = *i*Pr) and trisilanes (Me₃SiO)RPhSi–SiPhR–SiPhR(OSiMe₃) (**IIa**: R = Et, **IIb**: R = *i*Pr) were found in the quenched reaction mixtures.

In the Figs. 1 and 2 the changes of peak areas of the trimethylsilyloxychlorosilanes (Me₃SiO)RPhSiCl (**1a**: R = Et, **1b**: R = *i*Pr), the trapping products (Me₃SiO)RPhSi–SiMe₂H (**4a**, **4b**) of trimethylsilyloxydilithiums (Me₃SiO)RPhSiLi (**2a**, **2b**), the trapping products (Me₃SiO)RPhSi–SiMe₂H (**5a**, **5b**) of trimethylsilyloxydisilanylithiums Me₃SiO(RPhSi)₂Li (**3a**, **3b**) as well as the disilanes Me₃SiO(RPhSi)₂OSiMe₃ (**Ia**, **Ib**) and the trisilanes Me₃SiO

(RPhSi)₃OSiMe₃ (**IIa**, **IIb**) are shown in dependence of the reaction time *t*_{reac}.

The amount of the siloxychlorosilanes (Me₃SiO)RPhSiCl (**1a**: R = Et, **1b**: R = *i*Pr) decreases continuously. Until an approximately 90% consumption of the chlorosilanes **1a**, **1b** the amounts of the trapping products (Me₃SiO)RPhSi–SiMe₂H (**4a**, **4b**) of (Me₃SiO)RPhSiLi (**2a**, **2b**) and the trapping products (Me₃SiO)RPhSi–RPhSiLi (**3a**, **3b**) are constantly low. Only at a level of about 10% for the chlorosilanes **1** (peak area in gas chromatogram) a considerable increase of the amounts of **4** and **5**, trapping products of the silyllithium derivatives **2** and **3**, is observed.



Scheme 1. Courses of reactions when the trimethylsilyloxychlorosilanes (Me₃SiO)RR'SiCl (**1**) (R = Et, *i*Pr, Mes, R' = Ph; R = R' = Mes) are treated with lithium metal (4 equiv.) in THF/Et₂O/*n*-pentane (volume ratio 4:1:1) at –110 °C.

Immediately from the beginning of the reaction of the chlorosilanes **1** with lithium the formation of the disilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**Ia**, **Ib**) and the trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**Ia**, **Ib**) occurs. In the course of reaction the amounts of the di- and trisilanes **I** and **II** increase slowly, pass through maxima still before the siloxychlorosilanes **1** are consumed completely and fall off then relatively fast. With the decrease of amounts of the intermediates **I** and **II** a clear increase of the amounts of the trapping products $(\text{Me}_3\text{SiO})\text{RPhSi-SiMe}_2\text{H}$ (**4**) of trimethylsilyloxydisilanylolithiums **2** and $(\text{Me}_3\text{SiO})\text{RPhSi-RPhSi-SiMe}_2\text{H}$ (**5**) of trimethylsilyloxydisilanylolithiums **3** is connected. After complete transformation of the disilanes **I** and trisilanes **II** the amounts of the trapping products **4** and **5** of **2** and **3** do not change any longer within the monitoring period considerably. These results are arguments for the reaction pathways during the attack of excess lithium metal on the trimethylsilyloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (**1a**: R = Et, **1b**: R = *i*Pr) summarised in Scheme 1.

The trimethylsilyloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (**1**) react with lithium metal to give the corresponding trimethylsilyloxydisilanylolithiums $(\text{Me}_3\text{SiO})\text{RPhSiLi}$ (**2a**, **2b**) initially. Afterwards the trimethylsilyloxydisilanylolithiums **2** react partially with more siloxychlorosilanes **1** to give the disilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**Ia**, **Ib**) as well as react under bimolecular self-condensation affording the siloxydisilanylolithiums $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{Li}$ (**3a**, **3b**). The trimethylsilyloxydisilanylolithiums **3** then couple with the unconsumed siloxychlorosilanes **1** to give the trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**Ia**, **Ib**). The disilanes and trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_n\text{OSiMe}_3$ (**I**: $n = 2$, **II**: $n = 3$) are cleaved by lithium to form the trimethylsilyloxydisilanylolithiums $(\text{Me}_3\text{SiO})\text{RPhSiLi}$ (**2a**, **2b**), and the trimethylsilyloxydisilanylolithiums $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{Li}$ (**3a**, **3b**) as well as the trimethylsilyloxydisilanylolithiums **2a**, **2b**, respectively. The trimethylsilyloxydisilanylolithiums **2** undergo partially self-condensation to yield the trimethylsilyloxydisilanylolithiums **3** [24].

Presumably, the respective disilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (R = Me, Ph) and trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (R = Me, Ph) are also involved as intermediates in the formation of the trimethylsilyloxydisilanylolithiums

$(\text{Me}_3\text{SiO})\text{RPhSiLi}$ (R = Me, Ph) and the trimethylsilyloxydisilanylolithiums $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{Li}$ (R = Me, Ph), which were obtained beside other compounds in the reaction of the corresponding trimethylsilyloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (R = Me, Ph) with lithium at -110°C in a Trapp mixture [23,24]. Both types of compounds were clearly proved in the reaction mixture before the trimethylsilyloxychlorosilanes **1** were consumed completely. In Table 1 the yields of the disilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**I**) and the respective reaction times $t_{\text{ret}}(\mathbf{I}_{\text{max}})$ between trimethylsilyloxychlorosilanes **1** and lithium metal when the peak areas of the siloxydisilane intermediates **I** have maxima in the gas chromatograms as well as the yields of the trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**II**) and of the trimethylsilyloxychlorosilanes **1** at these reaction times $t_{\text{ret}}(\mathbf{I}_{\text{max}})$ are given. Extended reaction times lead to complete decomposition of the di- and trisilanes **I** and **II** (Table 1).

The reaction leading during the transformation of mesityl-phenyl-trimethylsilyloxy-chlorosilane $(\text{Me}_3\text{SiO})\text{MesPhSiCl}$ (**1c**) with lithium metal corresponds to that of the transformation of the trimethylsilyloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (**1a**: R = Et, **1b**: R = *i*Pr) with lithium (see Fig. 3; Table 1, Scheme 1) with the exception, that no formation of a trisilane intermediate $\text{Me}_3\text{SiO}(\text{MesPhSi})_3\text{OSiMe}_3$ and no cleavage by lithium take place.

The bimolecular reaction of the trimethylsilyloxydisilanylolithium $\text{Me}_3\text{SiO}(\text{MesPhSi})_2\text{Li}$ (**3c**) and the trimethylsilyloxychlorosilane **1c** is most probably suppressed by high steric hindrance about the Si(Li) and Si(Cl) atom.

The dimesityl-trimethylsilyloxy-chlorosilane $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiCl}$ (**1d**) reacts with lithium to give the silyllithium compound $(\text{Me}_3\text{SiO})\text{Mes}_2\text{SiLi}$ (**2d**) without formation of the disilane intermediate $\text{Me}_3\text{SiO}(\text{Mes}_2\text{Si})_2\text{OSiMe}_3$ (Scheme 1). Contrary to the reactions of the trimethylsilyloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (**1a**: R = Et, **1b**: R = *i*Pr, **1c**: R = Mes; also R = Me, Ph) with lithium (see above) the coupling reaction of the formed silylanion **2** with more chlorosilane **1** does not take place. The reason for that is the high steric hindrance at the silicon centre of **1d** and **2d**. The chlorosilanes $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SiCl}$ [1,13]

Table 1

Yields of the 1,2-bis(trimethylsilyloxy)disilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**I**) and 1,3-bis(trimethylsilyloxy)trisilanes $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**II**) in the reaction mixture (formed in the reaction of siloxychlorosilanes $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (**1a-c** and R = Me, Ph) with lithium in a Trapp mixture at -110°C) at the reaction times $t_{\text{ret}}(\mathbf{I}_{\text{max}})$ when the peak area of the respective siloxydisilane intermediate **I** has a maximum in the gas chromatogram

| Compound | a | b | c | | |
|---|--------|-------------|------|-------|------|
| | R = Et | <i>i</i> Pr | Mes | Me | Ph |
| $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (I) (%) | 8 | 6 | 16 | 9 | 26 |
| $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (I) (%) | 39/15 | 34/12 | 22/5 | 12/5 | 33/9 |
| $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (II) (%) | 20/10 | 10/7 | – | 29/14 | 10/7 |
| Reaction time, t_{ret} | | | | | |
| $t_{\text{ret}}(\mathbf{I}_{\text{max}})$ (min) | 90 | 45 | 150 | 65 | 16 |
| $t_{\text{ret}}(\mathbf{I}/\mathbf{II}_{\text{end}})^{\text{a}}$ (min) | 120 | 150 | 270 | 120 | 60 |

Yield determined by GC/yield of the isolated substance.

^a Reaction time when the intermediates **I** and **II** were consumed completely.

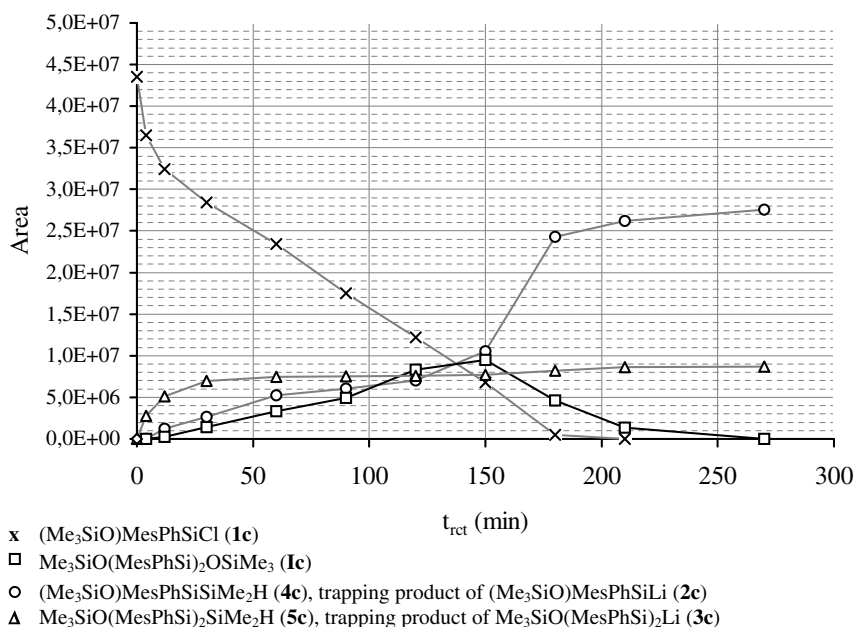


Fig. 3. Course of reaction of the siloxychlorosilane $(\text{Me}_3\text{SiO})\text{MesPhSiCl}$ (**1e**) with lithium metal in a Trapp mixture at -110°C monitored by GC. For GC measurements samples of the reaction mixture were quenched with HMe_2SiCl .

and $(\text{Et}_2\text{N})_2\text{PhSiCl}$ [20] with high steric shielding of the silicon centre react directly with lithium as well to yield exclusively the corresponding silyllithium compounds.

The intermediates $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**1a**: $\text{R} = \text{Et}$, **1b**: $\text{R} = ^i\text{Pr}$, **1c**: $\text{R} = \text{Mes}$; also $\text{R} = \text{Me}$, Ph) and $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**IIa**: $\text{R} = \text{Et}$, **IIb**: $\text{R} = ^i\text{Pr}$; also $\text{R} = \text{Me}$, Ph) could be isolated, if the reactions of the siloxychlorosilanes **1a–c**, and $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ ($\text{R} = \text{Me}$, Ph) with lithium in a Trapp mixture at -110°C were stopped at an early stage, i.e. at the reaction times $t_{\text{ret}}(\mathbf{I}_{\text{max}})$, when the respective siloxydisilane intermediate $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{OSiMe}_3$ (**I**) had a maximum of peak area in the gas chromatogram.

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. NMR spectra: Bruker ARX 400 ($^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ NMR: 400.1/100.6/79.5 MHz), Bruker ARX 250 (^1H NMR: 250.1 MHz) or Bruker ARX 300 ($^{13}\text{C}/^{29}\text{Si}$ NMR: 75.5/59.6 MHz); solutions of 30–50% in C_6D_6 , reference C_6D_6 , chemical shifts refer to $\delta_{\text{TMS}} = 0.0$ ppm. IR spectra: Nicolet 205 FT-IR, liquids as films between KBr disks. Elemental analyses: Leco Modell 932, absolute error $\pm 0.3\%$.

The syntheses of the trimethylsilyloxychlorosilanes **1a–d** and $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ ($\text{R} = \text{Me}$, Ph) are described in Ref. [23] and [24]. All reactions were carried out in dry, degassed solvents under an atmosphere of argon. The sol-

vents 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.

The lithium wire was purchased from Aldrich (about 0.01% Na) and converted into very thin plates for the reactions.

The course of reaction of the siloxychlorosilanes **1a–d** with lithium metal was monitored by GC. Samples of the reaction mixture (1.0 ml for GC and GC-MS, 2.0 ml for NMR) were taken out at certain time intervals and quenched with HMe_2SiCl . Then the received reaction mixtures were analysed by GC and additionally, selected samples of quenched mixtures by GC-MS and NMR. For the identification and determination of reaction products the trimethylsilyloxydisilanes $(\text{Me}_3\text{SiO})\text{RR}'\text{Si}-\text{SiMe}_2\text{H}$ (**4a**: $\text{R} = \text{Et}$, **4b**: $\text{R} = ^i\text{Pr}$, **4c**: $\text{R} = \text{Mes}$; **4a–c**: $\text{R}' = \text{Ph}$; **4d**: $\text{R} = \text{R}' = \text{Mes}$), trapping products of the trimethylsilyloxytrilyllithiums $(\text{Me}_3\text{SiO})\text{RR}'\text{SiLi}$ (**2a–d**); the trimethylsilyloxytrisilanes $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{RPhSi}-\text{SiMe}_2\text{H}$ (**5a**: $\text{R} = \text{Et}$, **5b**: $\text{R} = ^i\text{Pr}$, **5c**: $\text{R} = \text{Mes}$), trapping products of trimethylsilyloxydisilanylithiums $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{RPhSiLi}$ (**3a–c**) as well as the 1,2-bis(trimethylsilyloxy)disilanes $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{SiPhR}(\text{OSiMe}_3)$ (**1a**: $\text{R} = \text{Et}$, **1b**: $\text{R} = ^i\text{Pr}$, **1c**: $\text{R} = \text{Mes}$; also $\text{R} = \text{Me}$, Ph) and the 1,3-bis(trimethylsilyloxy)trisilanes $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{RPhSi}-\text{SiPhR}(\text{OSiMe}_3)$ (**IIa**: $\text{R} = \text{Et}$, **IIb**: $\text{R} = ^i\text{Pr}$; also $\text{R} = \text{Me}$, Ph) were available as pure substances [24, Section 3.2].

The compounds **1a–c**, $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{SiPhR}(\text{OSiMe}_3)$ ($\text{R} = \text{Me}$, Ph), **IIa**, **IIb** and $(\text{Me}_3\text{SiO})\text{RPhSi}-\text{RPhSi}-\text{SiPhR}(\text{OSiMe}_3)$ ($\text{R} = \text{Me}$, Ph) could be isolated by fractional distillation and were identified and characterised by their elemental analyses; mass, NMR and partially by IR spectra.

The GC yields given in Table 1 are based on GC investigations of all fractions (pure and/or mixed fractions), which were obtained by work-up of the quenched reaction mixtures, under using the pure compounds $\text{Me}_3\text{SiO}(\text{RPhSi})_2\text{-OSiMe}_3$ (**Ia**: R = Et, **Ib**: R = ⁱPr, **Ic**: R = Mes; also R = Me, Ph) and $\text{Me}_3\text{SiO}(\text{RPhSi})_3\text{OSiMe}_3$ (**Iia**: R = Et, **Iib**: R = ⁱPr; also R = Me, Ph) as standards. The yields of the compounds isolated by distillation are clearly lower than those determined by GC because of the work-up of complex mixtures with very similar compounds.

3.1. Investigations of the course of reactions of the trimethylsilyloxychlorosilanes **1a–1d** with lithium metal in a Trapp mixture at -110°C quenching of the reaction mixtures with chlorodimethylsilane

On the analogies of the preparative work a general procedure is given for the reactions of the trimethylsilyloxychlorosilanes **1a–d** with lithium metal and for the quenching of samples with HMe_2SiCl . The time intervals of sampling and the peak areas of selected products in the gas chromatograms of the reaction mixtures are given in Figs. 1–3.

General procedure. A mixture of 0.14 mol very thin lithium plates and 100 ml Trapp mixture (THF/ Et_2O /*n*-pentane in volume ratio 4:1:1) was cooled down to -110°C . To the mixture 0.035 mol trimethylsilyloxychlorosilane **1a–1d** without solvent was added within a few seconds with vigorous stirring. The vigorous stirring was continued at -110°C . After the start of reaction samples of the reaction mixture (in most cases 1 ml per sample) were taken out at certain time intervals and quenched with HMe_2SiCl . The changes in amounts of the obtained compounds in the reaction mixtures were determined by GC. The changes in amounts of selected products (peak areas in the gas chromatograms as measure) in dependence of the reaction time t_{ret} are shown in Figs. 1–3. After the end of reaction monitoring by GC the excess lithium was removed. Then 0.07 mol trapping agent HMe_2SiCl was added to the reaction solution stirred at -110°C . The reaction mixture was warmed to room temperature (20°C) and was allowed to react for 24 h at this temperature. After completion of quenching the work-up of the reaction mixture was carried out as described in Ref. [24]. The respective spectrum of products obtained is also given in Ref. [24].

3.2. Isolation of the intermediates $(\text{Me}_3\text{SiO})\text{RPhSi-SiPhR}(\text{OSiMe}_3)$ (**Ia**: R = Et, **Ib**: R = ⁱPr, **Ic**: R = Mes; also R = Me, Ph) and $(\text{Me}_3\text{SiO})\text{RPhSi-RPhSi-SiPhR}(\text{OSiMe}_3)$ (**Iia**: R = Et, **Iib**: R = ⁱPr; also R = Me, Ph)

On the analogies of the preparative work a general procedure is given for the reactions of the trimethylsilyloxychlorosilanes **1a–c** and $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (R = Me, Ph) with

lithium metal and for the following trapping reactions with Me_3SiCl . By quenching with HMe_2SiCl (see Section 3.1) it could clearly be proved that the intermediates **I**, **II** and $\text{Me}_3\text{SiO}(\text{RPhSi})_n\text{OSiMe}_3$ ($n = 2, 3$; R = Me, Ph) are bis(trimethylsilyloxy)-substituted di- and trisilanes and are not possible silanolates such as $\text{Me}_3\text{SiO}(\text{RPhSi})_n\text{OLi}$ ($n = 2, 3$) or $\text{LiO}(\text{RPhSi})_n\text{OLi}$ ($n = 2, 3$). The corresponding trapping products $\text{Me}_3\text{SiO}(\text{RPhSi})_n\text{OSiMe}_2\text{H}$ ($n = 2, 3$) or $\text{HMe}_2\text{SiO}(\text{RPhSi})_n\text{OSiMe}_2\text{H}$ ($n = 2, 3$) were not found in the reaction mixtures. Thus Me_3SiCl could also be used as trapping agent. The work-up of the crude products is described separately. Some details of the reactions are given in Scheme 1 and in Table 1. About the isolation of the siloxydisilane $(\text{Me}_3\text{SiO})\text{MesPhSi-SiPhMes}(\text{OSiMe}_3)$ (**Ic**) from the reaction of the trimethylsilyloxychlorosilane $(\text{Me}_3\text{SiO})\text{MesPhSiCl}$ (**1c**) with lithium was reported in Ref. [24].

3.2.1. General procedure

A mixture of 0.14 mol very thin lithium plates and 70 ml Trapp mixture (THF/ Et_2O /*n*-pentane in volume ratio 4:1:1) was cooled down to -110°C . To the respective mixture 0.035 mol trimethylsilyloxychlorosilane **1a–c** and $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (R = Me, Ph), dissolved in 30 ml Trapp mixture, was added dropwise within 15 min with vigorous stirring. The reaction progress was monitored by GC of samples quenched with HMe_2SiCl . The vigorous stirring was continued at -110°C until the peak areas of the siloxydisilane intermediates **I** and $(\text{Me}_3\text{SiO})\text{RPhSi-SiR-Ph}(\text{OSiMe}_3)$ (R = Me, Ph) in the gas chromatograms of the reaction mixture had a maximum. After the reaction times $t_{\text{ret}}(\mathbf{I}_{\text{max}})$ as given in Table 1 the excess lithium was removed. Then 0.07 mol trapping agent Me_3SiCl was added to the solution of lithium silanides stirred at -110°C . The reaction mixture was warmed to room temperature 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 0.3 Torr. Beside the di- and trisilanes **I**, **II** and $\text{Me}_3\text{SiO}(\text{RPhSi})_n\text{OSiMe}_3$ ($n = 2, 3$; R = Me, Ph) also the compounds were obtained, which are given for the corresponding reactions of trimethylsilyloxychlorosilanes **1** and $(\text{Me}_3\text{SiO})\text{RPhSiCl}$ (R = Me, Ph) with lithium in Ref. [24] and [23].

3.2.2. Isolation of the siloxydisilanes **Ia** and **Iia** from the reaction of **1a** with lithium

Distillation of the residue through a slit pipe column (Fischer, Mikro-Spaltrohr-System D100) ($30\text{--}144^\circ\text{C}/0.05$ Torr) yielded three fractions ($30\text{--}45^\circ\text{C}$, $45\text{--}85^\circ\text{C}$, $85\text{--}142^\circ\text{C}$), which contained mixtures of **Ia**, $(\text{Me}_3\text{SiO})_2\text{SiEtPh}$, $\text{Me}_3\text{SiO}(\text{EtPhSi})_n\text{SiMe}_3$ ($n = 1, 2$), $\text{Me}_3\text{SiEtPhSiSiMe}_3$ [24] and **Ia** in different proportions. In the fourth fraction

(143–144 °C/0.05 Torr) pure disilane **1a** was found. In the distillation residue the trisilanes **IIa** and minor **1a** remained. By distillation of the residue using a ball tube oven (Büchi, Kugelrohrföfen GKR-51) the trisilane **IIa** was isolated (185–190 °C/0.06 Torr).

1,2-Bis(trimethylsiloxy)-1,2-diethyl-1,2-diphenyl-disilane (1a): Yield: 1.2 g (15%). B.p.: 143–144 °C/0.05 Torr. GC: Diastereomeric ratio 1.2:1. MS (EI, 70 eV): m/z (%) = 446 (5) $[M]^+$, 431 (3) $[M-Me]^+$, 417 (31) $[M-Et]^+$, 373 (91) $[M-SiMe_3]^+$, 223 (66) $[Me_3SiOSiEtPh]^+$, 195 (100), 135 (34), 73 (16) $[SiMe_3]^+$. 1H NMR: δ = 0.05, 0.07 (s, Me_3SiO , 18H); 0.80, 0.82 (q, H_2C , 4H); 1.04, 1.07 (t, H_3C , 6H); 7.10–7.67 (m, Ph, 10H) ppm. ^{13}C NMR: δ = 2.1, 2.1 (Me_3SiO); 7.3, 7.3 (CH_3); 10.1, 10.1 (CH_2); 128.1, 128.1, 129.4, 129.4, 133.8, 133.9, 139.3, 139.5 (Ph) ppm. ^{29}Si NMR: δ = -8.54, -8.51 ($SiEtPh$); 8.6, 8.7 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$ ($SiOSi$) 1058, $\delta(CH_3Si)$ 1251 cm^{-1} . Anal. Calc. for $C_{22}H_{38}O_2Si_4$ (446.891): C, 59.13; H, 8.57. Found: C, 58.94; H, 8.62%.

1,3-Bis(trimethylsiloxy)-1,2,3-triethyl-1,2,3-triphenyl-trisilane (IIa): Yield: 0.7 g (10%). B.p.: 185–190 °C/0.06 Torr. GC: Diastereomeric ratio 2:1:1. MS (EI, 70 eV): m/z (%) = 580 (0.5) $[M]^+$, 565 (3) $[M-Me]^+$, 491 (8) $[M-OSiMe_3]^+$, 357 (6) $[Me_3SiO(EtPhSi)_2]^+$, 223 (94) $[Me_3SiOSiEtPh]^+$, 195 (100), 135 (23), 73 (8) $[SiMe_3]^+$. 1H NMR: δ = 0.02, 0.03, 0.04 (s, Me_3SiO , 18H); 0.76–1.19 (H_3CH_2C , 15H); 7.08–7.55 (m, Ph, 15H) ppm. ^{13}C NMR: δ = 2.2, 2.2, 2.3 (Me_3SiO); 3.1, 3.3, 3.7, 11.0, 11.1, 11.2 (CH_2); 7.3, 7.3, 7.4, 10.3, 10.4, 10.6 (CH_3); 127.9–139.8 (Ph) ppm. ^{29}Si NMR: δ = -46.3, -46.2, -46.1 ($SiEt-SiPhSi$); -1.6, -1.42, -1.39 ($EtSiPhO$); 8.4, 8.4, 8.5 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$ ($SiOSi$) 1058, $\delta(CH_3Si)$ 1251 cm^{-1} . Anal. Calc. for $C_{30}H_{48}O_2Si_5$ (581.143): C, 62.00; H, 8.33. Found: C, 61.87; H, 8.41%.

3.2.3. Isolation of the siloxydisilanes **1b** and **1b** from the reaction of **1b** with lithium

Distillation of the residue through a Fischer slit pipe column (45–158 °C/0.05 Torr) yielded three fractions (45–60 °C, 60–80 °C, 80–156 °C), which consisted of mixtures of **1b**, $(Me_3SiO)_2Si^iPrPh$, $Me_3SiO(^iPrPhSi)_nSiMe_3$ ($n = 1, 2$), $Me_3Si^iPrPhSiSiMe_3$ [24] and **1b** in different proportions. The fourth fraction (157–158 °C/0.05 Torr) contained pure disilane **1b**. In the distillation residue the trisilanes **IIb** and minor **1b** remained. Distillation of the residue using a Büchi ball tube oven (195–200 °C/0.02 Torr) yielded pure trisilane **IIb**.

1,2-Bis(trimethylsiloxy)-1,2-di-iso-propyl-1,2-diphenyl-disilane (1b): Yield: 1.0 g (12%). B.p.: 157–158 °C/0.05 Torr. GC: Diastereomeric ratio 1.3:1. MS (EI, 70 eV): m/z (%) = 474 (7) $[M]^+$, 459 (4) $[M-Me]^+$, 431 (100) $[M-^iPr]^+$, 401 (16) $[M-SiMe_3]^+$, 237 (52) $[Me_3SiOSi^iPrPh]^+$, 193 (44) $[M/2-C_3H_8]^+$, 135 (78), 73 (30) $[SiMe_3]^+$. 1H NMR: δ = 0.18, 0.19 (s, Me_3SiO , 18H); 0.87, 0.89 (d, Me_2C , 12H); 1.06, 1.22 (sept, HC, 2H); 7.13–7.70 (m, Ph, 10H) ppm. ^{29}Si NMR: δ = -7.9, -7.4 (Si^iPrPh); 7.9, 8.0 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$ ($SiOSi$) 1053, $\delta(CH_3Si)$ 1252 cm^{-1} .

Anal. Calc. for $C_{24}H_{42}O_2Si_4$ (474.943): C, 60.69; H, 8.91. Found: C, 60.56; H, 8.78%.

1,3-Bis(trimethylsiloxy)-1,2,3-tri-iso-propyl-1,2,3-triphenyl-trisilane (IIb): Yield: 0.5 g (7%). B.p.: 195–200 °C/0.02 Torr. GC: Diastereomeric ratio 2:1:1. MS (EI, 70 eV): m/z (%) = 622 (4) $[M]^+$, 607 (17) $[M-Me]^+$, 579 (26) $[M-^iPr]^+$, 533 (68) $[M-OSiMe_3]^+$, 237 (100) $[Me_3SiOSi^iPrPh]^+$, 193 (52) $[Me_3SiOSi^iPrPh-C_3H_8]^+$, 135 (35), 73 (11) $[SiMe_3]^+$. 1H NMR: δ = 0.14, 0.16, 0.19 (s, Me_3SiO , 18H); 0.84–1.81 (Me_2C and HC, 21H); 7.11–7.76 (m, Ph, 15H) ppm. ^{29}Si NMR: δ = -41.2, -41.0, -40.4 ($Si^iPrSiPhSi$); -0.1, -0.3, -0.6 (iPrSiPhO); 8.0, 8.1, 8.2 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$ ($SiOSi$) 1055, $\delta(CH_3Si)$ 1252 cm^{-1} . Anal. Calc. for $C_{33}H_{54}O_2Si_5$ (623.224): C, 63.60; H, 8.73. Found: C, 63.69; H, 8.67%.

3.2.4. Isolation of the siloxydisilanes $(Me_3SiO)MePhSi-SiPhMe(OSiMe_3)$ and $(Me_3SiO)MePhSi-MePhSi-SiPhMe(OSiMe_3)$ from the reaction of $(Me_3SiO)MePhSiCl$ with lithium

Distillation of the residue through a Fischer slit pipe column in the temperature range of 50–150 °C/0.2 Torr yielded four fractions (50–75 °C, 75–90 °C, 90–120 °C, 120–148 °C), which consisted of mixtures of $(Me_3SiO)MePhSiCl$, $(Me_3SiO)_2SiMePh$, $Me_3SiO(MePhSi)_nSiMe_3$ ($n = 1, 2$), $Me_3SiMePhSiSiMe_3$ [23] and $Me_3SiO(MePhSi)_2OSiMe_3$ in different proportions. The fifth fraction (149–150 °C/0.2 Torr) contained pure disilane $Me_3SiO(MePhSi)_2OSiMe_3$. In the distillation residue the trisilanes $Me_3SiO(MePhSi)_3OSiMe_3$ and small amounts of $Me_3SiO(MePhSi)_2OSiMe_3$ remained. By distillation of the residue using a Büchi ball tube oven the trisilane $Me_3SiO(MePhSi)_3OSiMe_3$ was isolated (150–153 °C/0.05 Torr).

1,2-Bis(trimethylsiloxy)-1,2-dimethyl-1,2-diphenyl-disilane: Yield: 0.4 g (5%). B.p.: 149–150 °C/0.2 Torr. GC: Diastereomeric ratio 1.1:1. MS (EI, 70 eV): m/z (%) = 418 (1) $[M]^+$, 403 (2) $[M-Me]^+$, 345 (39) $[M-SiMe_3]^+$, 209 (100) $[Me_3SiOSiMePh]^+$, 193 (43) $[Me_3SiOSiMePh-CH_4]^+$, 135 (39), 73 (20) $[SiMe_3]^+$. 1H NMR: δ = 0.08, 0.09 (s, Me_3SiO , 18H); 0.508, 0.511 (s, MeSi, 6H); 7.14–7.61 (m, PhSi, 10H) ppm. ^{13}C NMR: δ = 0.9, 1.0 (MeSi); 2.20, 2.24 (Me_3SiO); 128.07, 128.10, 129.42, 129.44, 133.63, 133.63, 140.1, 140.2 (Ph) ppm. ^{29}Si NMR: δ = -10.0, -9.9 (SiMePh); 9.3, 9.4 ($OSiMe_3$) ppm. IR(film): $\tilde{\nu}$ ($SiOSi$) 1048; $\delta(CH_3Si)$ 1252, 1261 cm^{-1} . Anal. Calc. for $C_{20}H_{34}O_2Si_4$ (418.837): C, 57.35; H, 8.18. Found: C, 57.46; H, 8.36%.

1,3-Bis(trimethylsiloxy)-1,2,3-trimethyl-1,2,3-triphenyl-trisilane: Yield: 0.9 g (14%). B.p.: 150–153 °C/0.05 Torr. GC: Diastereomeric mixture. MS (EI, 70 eV): m/z (%) = 538 (2) $[M]^+$, 523 (3) $[M-Me]^+$, 465 (2) $[M-SiMe_3]^+$, 329 (9) $[Me_3SiOSiMePhSiMePh]^+$, 313 (24) $[M-SiMePhOSiMe_3-CH_4]^+$, 252 (35) $[M-SiMePhOSiMe_3-Ph]^+$, 209 (93) $[Me_3SiOSiMePh]^+$, 193 (100) $[Me_3SiOSiMePh-CH_4]^+$, 135 (39), 73 (11) $[SiMe_3]^+$. 1H NMR: δ = 0.04, 0.06, 0.08 (s, Me_3SiO , 18H); 0.48, 0.49, 0.50, 0.53, 0.54, 0.57 (s, MeSiPh, 9H); 7.10–7.58 (m, PhSi,

15H) ppm. ^{13}C NMR: $\delta = -8.5, -8.2, -7.9$ (SiMeSiPhSi); 1.8, 1.9, 2.0 (MeSiPhO); 2.2, 2.3, 2.3 (Me₃SiO); 128.0–140.7 (Ph) ppm. ^{29}Si NMR: $\delta = -52.2, -51.9, -51.7$ (SiMeSiPhSi); $-3.1, -3.0, -2.7$ (MeSiPhO); 9.3, 9.4, 9.5 (OSiMe₃) ppm. IR(film): $\tilde{\nu}(\text{SiOSi})$ 1049; $\delta(\text{CH}_3\text{Si})$ 1248, 1252, 1261 cm^{-1} . Anal. Calc. for C₂₇H₄₂O₂Si₅ (539.065): C, 60.16; H, 7.85. Found: C, 60.20; H, 8.02%.

3.2.5. Isolation of the siloxydisilanes (Me₃SiO)Ph₂Si–SiPh₂(OSiMe₃) and (Me₃SiO)Ph₂Si–Ph₂Si–SiPh₂(OSiMe₃) from the reaction of (Me₃SiO)Ph₂SiCl with lithium

Distillation of the residue through a Fischer slit pipe column (70–140 °C/0.03 Torr) yielded several fractions (70–140 °C), which obtained mixtures of (Me₃SiO)Ph₂SiCl, (Me₃SiO)₂SiPh₂, Me₃SiO(Ph₂Si)_nSiMe₃ ($n = 1, 2$), Me₃SiPh₂SiSiMe₃ [23] and Me₃SiO(Ph₂Si)₂OSiMe₃ in different proportions. In the distillation residue Me₃SiO(Ph₂Si)₂OSiMe₃, Me₃SiO(Ph₂Si)₃OSiMe₃ and small amounts of Me₃SiO(Ph₂Si)₂SiMe₃ remained. By distillation of the residue using a Büchi ball tube oven (180–250 °C/0.05 Torr) the disilane Me₃SiO(Ph₂Si)₂OSiMe₃ (200–205 °C/0.05 Torr) and the trisilane Me₃SiO(Ph₂Si)₃OSiMe₃ (245–250 °C/0.05 Torr) were isolated.

1,2-Bis(trimethylsiloxy)-1,1,2,2-tetraphenyl-disilane: Yield: 0.9 g (9%). B.p.: 200–205 °C/0.05 Torr. MS (EI, 70 eV): m/z (%) = 542 (8) [M]⁺, 527 (2) [M–Me]⁺, 469 (34) [M–SiMe₃]⁺, 271 (80) [Me₃SiOSiPh₂]⁺, 193 (100) [M/2–C₆H₆]⁺, 135 (20), 73 (6) [SiMe₃]⁺. ^1H NMR: $\delta = 0.11$ (s, Me₃SiO, 18H), 7.12–7.76 (m, Ph, 20H) ppm. ^{13}C NMR: $\delta = 2.2$ (Me₃SiO); 128.1, 129.9, 135.1, 138.4 (Ph) ppm. ^{29}Si NMR: $\delta = -18.7$ (SiPh₂), 10.5 (OSiMe₃) ppm. IR (film): $\tilde{\nu}(\text{SiOSi})$ 1041, $\delta(\text{CH}_3\text{Si})$ 1253 cm^{-1} . Anal. Calc. for C₃₀H₃₈O₂Si₄ (542.977): C, 66.36; H, 7.05. Found: C, 66.30; H, 7.17%.

1,3-Bis(trimethylsiloxy)-1,1,2,2,3,3-hexaphenyl-trisilane: Yield: 0.6 g (7%). B.p.: 245–250 °C/0.05 Torr. MS (EI, 70 eV): m/z (%) = 724 (5) [M]⁺, 709 (2) [M–Me]⁺, 574 (2) [M–SiMe₃–Ph]⁺, 453 (9) [Me₃SiOSiPh₂SiPh₂]⁺, 376 (45) [Me₃SiOSiPh₂SiPh]⁺, 271 (100) [Me₃SiOSiPh₂]⁺, 193 (92) [Me₃SiOSiPh₂–C₆H₆]⁺, 135 (9), 73 (5) [SiMe₃]⁺. ^1H NMR: $\delta = 0.06$ (s, Me₃SiO, 18H), 7.11–7.82 (m, Ph, 30H) ppm. ^{13}C NMR: $\delta = 2.3$ (Me₃SiO); 128.0, 128.1, 129.1, 129.7, 134.6, 135.2, 137.5, 138.5 (Ph) ppm. ^{29}Si NMR: $\delta = -48.5$ (SiSiPh₂Si), -12.0 (OSiPh₂), 10.8 (OSiMe₃) ppm. IR(film): $\tilde{\nu}(\text{SiOSi})$ 1043, $\delta(\text{CH}_3\text{Si})$

1251 cm^{-1} . Anal. Calc. for C₄₂H₄₈O₂Si₅ (725.275): C, 69.55; H, 6.67. Found: C, 69.79; H, 6.83%.

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