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Electrochemical synthesis of symmetrical difunctional disilanes as precursors for organofunctional silanes

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Abstract

Difunctional disilanes of the general type XR_2SiSiR_2X (**1–5**) (X = OMe, H; R = Me, Ph, H) have been synthesized by electrolysis of the appropriate chlorosilanes XR_2SiCl in an undivided cell with a constant current supply and in the absence of any complexing agent. Reduction potentials of the chlorosilane starting materials derived from cyclic voltammetry measurements were used to rationalize the results of preparative electrolyses. Organofunctional silanes of the general formula $MeO(Me_2)SiC_6H_4Y$ (**6a–c**, **7**) were subsequently obtained by the reaction of *sym*-dimethoxytetramethyldisilane (**1**) with NaOMe in the presence of p-functional aryl bromides BrC_6H_4Y (Y = OMe, NEt_2, NH_2).
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1. Introduction

Due to their widespread applications, e.g. in rubber, coatings, thermoplastics and adhesives, silanes of the general formula X–(R_2)Si–R′Y, with X and Y meaning two functional groups, are of great industrial interest [1]. With their functionality Y bound to an organic spacer they can undergo chemical bond formation to organic substrates, whereas the functional group X at the inorganic side of the molecule provides a possible linkage to inorganic substrates. Thus, a hybrid character is obtained for these so-called organofunctional silanes (OFS). Usually, very specific synthesis routes have been developed and patented for the large scale production of OFS, e.g. aminopropyltriethoxysilane [2]. The aim of our work in this field is to explore new, simple and more general methods for the synthesis of OFS.

There exists a wide variety of methods for the formation of silicon–carbon bonds involving the cleavage of Si–Si bonds, such as the metathesis reaction of disilanes with organic halides [3,4] or acid halides [5,6], the addition of disilanes to unsaturated systems [7] or reactions via the formation of silylenes [8] or silyl radicals [9]. Furthermore, Si–Si bonds can be cleaved with strong bases such as F^- [10] or sodium methoxide. Sakurai and Kondo [11] reported the cleavage of hexamethyldisilane with NaOMe in strongly coordinating solvents such as HMPA, 1,3-dimethyl-2-imidazolione or THF/crown ethers. Based on this work, Watanabe et al. [12] cleaved 1,2-dimethoxytetramethyldisilane with NaOMe and reacted the postulated silyl anion intermediate with aromatic and aliphatic halides, thus yielding phenyl or butyl substituted silanes (Eqs. (1) and (2)).

$$MeOMe_2SiSiMe_2OMe \xrightarrow{NaOMe} MeOMe_2Si^-Na^+ + (MeO)_2SiMe_2 \quad (1)$$

$$MeOMe_2Si^-Na^+ \xrightarrow[-NaX]{RX} MeOMe_2SiR \quad [R = Ph, n\text{-}Bu; X = Cl, Br] \quad (2)$$

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In order to utilize this approach for the synthesis of OFS starting from commercially available precursors we were seeking for convenient methods for the direct formation of difunctional disilanes from chlorosilanes. Compounds like H–(Si_2R_4)–H or MeO–(Si_2R_4)–OMe are usually made by substituent exchange starting from the appropriate 1,2-dichloro precursors [13]. Et_2N–(Si_2Me_4)–NEt_2 and Me_3SiO–(Si_2R_4)–$OSiMe_3$ can be prepared by coupling Et_2N–$SiMe_2Cl$ or Me_3SiO–$SiMe_2Cl$, respectively, with Li in THF [14,15]. Due to our own experience in the electrochemical formation of silyl compounds [16] and based on a Japanese patent [17] we expected the electrochemical coupling of appropriate chlorosilanes to be a reasonable alternative.

2. Results and discussion

2.1. Electrochemical synthesis of 1,2-difunctional disilanes

Although there exist several papers in the literature dealing with the electrochemical formation of methylated or phenylated disilanes [18–21], much less attempts have been made to reduce chlorosilanes bearing one or more functional groups on the silicon atom. Besides a patent claiming the formation of 1,2-difunctional disilanes by the electrolysis of chlorosilanes $R'R_2SiCl$ ($R' = Me$, Ph, MeO, allyl, octyl) in THF with various supporting electrolytes and two metal electrodes [17], to the best of our knowledge only one publication exists dealing with the electrohemical Si–Si bond formation starting from a functional chlorosilane: the formation of 1,3-dihydrotrisilanes by co-electrolysis of HMe_2SiCl and Ph_2SiCl_2 with Mg electrodes in THF/$LiClO_4$ [19].

Based on this literature, we electrolyzed several functional chlorosilanes in THF in a simple undivided cell equipped with a stainless steel cathode and a sacrificial Mg anode (Eq. (3)).

$$2X{-}SiMe_2{-}Cl \xrightarrow[\text{stainless steel cathode } 0.15 \text{ mA/cm}^2]{\text{Mg-anode}} X{-}SiMe_2SiMe_2{-}X + MgCl_2$$
$$X = Cl, MeO, NR_2, H \qquad (3)$$

The results are summarized in Table 1. Not unexpectedly product distribution and yield obtained after electrolysis strongly depend on the nature of the functional group attached to the silicon atom. Methoxy and amino substituted chlorosilanes turned out to be nearly unreactive under the reaction conditions applied. $MeOMe_2SiCl$ affords only traces of $MeOMe_2SiSiMe_2OMe$ (**1**), while in the case of Et_2NMe_2SiCl and $(Me_3Si)_2NMe_2SiCl$, respectively, the unreacted starting materials were recovered nearly quantitatively even after prolonged electrolysis times (4F instead of 2). The attempt to couple Me_2SiCl_2 selectively to the corresponding disilane also failed. Insoluble poly(dimethyl)silane is formed as the major product, $ClMe_2SiSiMe_2Cl$ or soluble oligomers $Cl(Me_2Si)_nCl$ could not be detected at all.

H-Si functional chlorosilanes were finally found to be suitable substrates for the electrochemical conversion to the corresponding 1,2-dihydrodisilanes, although the choice of the supporting electrolyte turned out to be crucial in order to avoid extended side reactions. When HMe_2SiCl is electrolyzed in THF solution in the presence of Bu_4NBr as supporting electrolyte, not only the desired tetramethyldisilane (**2**) but also significant amounts of hexamethyltrisilane and octamethyltetrasilane are formed (Table 2). At first sight rather inexplicable, the formation of these products is easy to understand taking into account that quaternary ammonium salts are known to catalyze the equilibration reaction of HMe_2SiCl to Me_2SiH_2 and Me_2SiCl_2 (Eq. (4)) [20], which is an ideal co-substrate in the electroreduction giving rise to the formation of oligosilanes (Eq. (5)).

$$HSiMe_2Cl \xrightarrow{THF/Bu_4NBR} H_2SiMe_2 + Cl_2SiMe_2 \qquad (4)$$

$$2HSiMe_2Cl + mCl_2SiMe_2 \xrightarrow{\text{electrolysis}} HSiMe_2[SiMe_2]_mSiMe_2H \qquad (5)$$

To overcome this undesired side reaction we tested several other supporting electrolytes. Bu_4NBF_4, LiCl and even $LiClO_4$ also favored the formation of tri- and tetrasilanes, but finally we found $MgCl_2$ to be most suitable (compare Table 2).

Table 1
Electrolysis products and cyclovoltammetric data of functional chlorosilanes

Starting material	E_p[a]	Disilane (% yield)[b]	Other detected products (% yield)[b]
Me_2SiCl_2	−3.03/−3.23	–	$(Me_2Si)_n$ (30)[c] [16a]
$MeOMe_2SiCl$	−3.3	**1** (traces)[d]	Starting mat. (>90)[d]
HMe_2SiCl	−3.24	**2** (92)[e]	–
HPhMeSiCl	−2.99	**3** (74)[e]	HPhMeSiOSiPhMeH (15)[d]
HPh_2SiCl	−3.14	**4** (29)[e]	$HPh_2SiSiPh_2SiPh_2H$ (14), Ph_3SiH (traces) Ph_2SiH_2 (49)[d]
$H_2PhSiCl$	−2.95	**5** (38)[e]	$PhSiH_3$ (8), H_2SiPh_2 (12), $HPh_2SiOSiPh_2H$ (2) $H_2PhSiSiHPhSiPhH_2$ (7)[d]
Et_2NMe_2SiCl	No signal	–	Starting mat. (>90)[d]
$(Me_3Si)_2NMe_2SiCl$	No signal	–	Starting mat. (>90)[d]

[a] In CH_3CN/Bu_4NBPh_4 at $v = 100$ mV/s, referenced to ferrocene.
[b] After electrolysis in THF/$MgCl_2$.
[c] Isolated yield.
[d] Determined by GC/MS of crude product mixture.
[e] Compare Section 4.

Table 2
Product distribution obtained after electrolysis of HMe_2SiCl using different supporting electrolytes

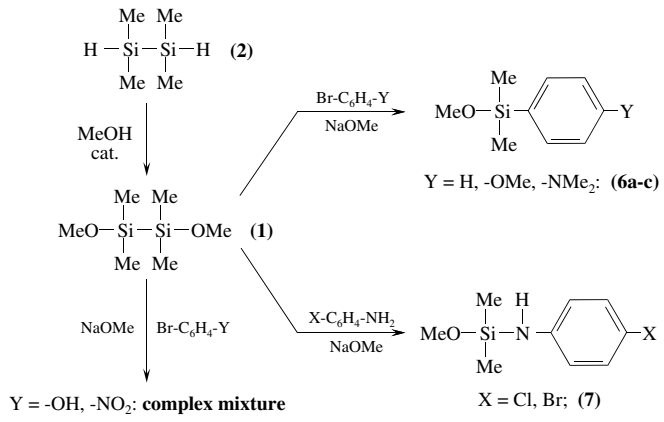
Supporting salt	Products (% yield)[a]		
	Disilane	Trisilane	Others
Bu_4NBr	40	50	Me_2SiH_2 (10)
Bu_4NBF_4	20	25	Me_2SiH_2 (5), HMe_2SiF (50)
LiCl	60	32	Me_2SiH_2 (8)
$LiClO_4$	10	40	$HMe_2SiOSiMe_2H$ (50)
$MgCl_2$	100	–	–

[a] Yields determined by ^1H NMR of crude product mixture.

Although less soluble than conventional supporting electrolytes this low cost salt provides sufficient conductivity and prevents the equilibration reaction of HMe_2SiCl most effectively. Thus, tetramethyldisilane (**2**) was formed in yields up to 90%. As can be seen in Tables 1 and 2, other hydrogen containing chlorosilanes can also be successfully coupled electrochemically in the above mentioned THF/$MgCl_2$ electrolyte to get the corresponding disilanes **3**–**5**. Regarding product distribution, however, it is evident that substituent scrambling and oligosilane formation becomes more important in the presence of additional hydrogen and phenyl substituents at the silicon atom (Table 1). Nevertheless, compared to other methods for the preparation of 1,2-dihydrodisilanes, electrolysis provides a versatile, simple and successful alternative pathway.

2.2. Synthesis of OFS from 2 by anionic cleavage

Although **2** itself like $Me_3SiSiMe_3$ does not react properly with NaOMe according to Eq. (1) it can be easily converted to the 1,2-dimethoxy derivative **1** by methanolysis in the presence of a catalyst [21]. **1** and several p-substituted phenyl bromides were subsequently subjected to the reaction sequence depicted in Eqs. (1) and (2) in order to investigate the tolerance of the method to various functional groups attached to the phenyl ring. The results are summarized in Scheme 1.



Scheme 1.

Only with bromoanisole and bromodimethylaniline the desired difunctional silyl substrates **6b** and **6c** could be obtained in satisfying quantities. When *p*-chloro- or *p*-bromoaniline are reacted with NaOMe the preferred reaction is H abstraction at the unprotected amino group thus leading to the *N*-silylated product **7**. *p*-$BrC_6H_4NO_2$ as well as *p*-BrC_6H_4OH afford complex mixtures of unidentified reaction products arising from the electrochemical instability of the NO_2 or OH group, respectively. The reactions with *p*-$BrC_6H_4OSiMe_2^tBu$ and *p*-$BrC_6H_4CH{=}CH_2$ also gave only poor yields of the corresponding organofunctional silanes. In the case of *p*-$BrC_6H_4OSiMe_2^tBu$ the TBDMS protecting group is split off preferentially by the extremely basic alkoxide, whereas with *p*-bromostyrene large quantities of styrene are formed along with the OFS. In general it needs to be stated that yields strongly depend on the quality of the sodium methoxide used.

Watanabe et al. [12] also reported, that *n*-butyl halides react according to Eqs. (1) and (2) to the corresponding butylsilanes in rather good yields. In contrast to his work, we found that butyl bromide and NaOMe give butylmethyl ether (Eq. (6)), thus following the reaction pathway of the well known Williamson ether synthesis [22].

$$MeOMe_2SiBu \xleftarrow[n\text{-buBr}]{NaOMe} MeOMe_2SiSiMe_2OMe \xrightarrow[n\text{-buBr}]{NaOMe} MeOBu \qquad (6)$$

2.3. Cyclic voltammetry

In order to obtain some information on the reduction potentials and to better understand the results from preparative electrolyses, a cyclic voltammetry study of the starting chlorosilanes was performed. As the THF/$MgCl_2$ solution which was used for the electrolyses did not give any proper voltammograms due to insufficient conductivity, an alternative electrolyte had to be used. Thus, all measurements were carried out in a CH_3CN/Bu_4NBPh_4 electrolyte. At the end of each measurement, ferrocene (FcH) was added as an internal standard and the reduction potentials of the studied chlorosilanes were referenced to $E^\circ_{FcH} = (E_{ox} + E_{red})/2 = 0$. It has to be taken into consideration that the solvent and especially the supporting electrolyte has some influence on the reduction potentials of chlorosilanes [23]. The data from the cyclic voltammetry study and the preparative electrolyses, nevertheless, look consistent, although the absolute values for the reduction potentials in CH_3CN/Bu_4NBPh_4 may be actually different from those in THF/$MgCl_2$.

As expected, all substrates exhibit a reduction wave in the very cathodic region not reversible at scan rates in the range of 20–500 mV/s (compare Table 1). The aminosilanes Et_2NMe_2SiCl and $(Me_3Si)_2NMe_2SiCl$ do not give any products as they obviously cannot be reduced electrochemically in the applied systems. $MeOMe_2SiCl$ is reduced at a very cathodic potential, already

within the limit of electrolyte degradation. As a consequence, the corresponding disilane **1** is formed only in very low yields. In contrast to this, the hydrochlorosilanes have reduction potentials placed conveniently within the electrochemical window, although slightly more negative compared to the corresponding dichlorosilanes. Therefore, if a dichlorosilane such as Me_2SiCl_2 or Ph_2SiCl_2 is formed due to equilibration reactions from the corresponding hydrochlorosilanes (HMe_2SiCl or HPh_2SiCl, respectively) it will be reduced preferentially, thus leading to the formation of oligosilanes as depicted in Eqs. (4) and (5).

3. Conclusions

The electrochemical coupling of monochlorosilanes was shown to be a versatile method for the direct synthesis of difunctional disilanes [24]. Especially 1,2-dihydrodisilanes are easily accessible in good yields using $MgCl_2$ as supporting electrolyte in THF. The results of preparative electrolyses are very well reflected by the reduction potentials of the chlorosilane starting materials derived from cyclic voltammetry measurements. The merit of 1,2-difunctional disilanes for the synthesis of organofunctional silanes, however, turned out to be rather limited by the low tolerance of the subsequent Si–Si-bond cleavage reaction to many functional groups. Further studies concerning the application of electrochemical methods for the synthesis of OFS are currently under investigation.

4. Experimental

4.1. General procedures

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. All solvents were dried and distilled under nitrogen prior to use. Commercial grade Me_2SiCl_2 and HMe_2SiCl (Wacker) as well as HPhMeSiCl, HPh_2SiCl and $H_2PhSiCl$ (Aldrich) were distilled prior to use. $MeOMe_2SiCl$ [25], Et_2NMe_2SiCl [26], $(Me_3Si)_2NMe_2SiCl$ [27] and **1** [28] were synthesized according to the literature procedures. Bu_4NBr, $MgCl_2$ and LiCl (Fluka "puriss. electrochem. grade") were dried in vacuum at 50 °C for several hours. NMR spectra were recorded on a Bruker 300-MSL spectrometer; ^1H NMR: 300.13 MHz; ^{13}C NMR: 75.47 MHz; ^{29}Si NMR: 59.62 MHz. GC/MS analyses were made on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm polydimethylsiloxane).

4.2. Cyclic voltammetry

All voltammograms were performed under an inert atmosphere at room temperature with a Wenking LB 95M potentiostat/Wenking POS 73 scan generator and recorded with a Kipp and Zonen BD8 flatbed recorder. The three electrode system consisted of a platinum disk microelectrode (500 μm), a Pt counter electrode and a Ag/AgCl reference electrode. 25 ml of a 0.1 M solution of Bu_4NBPh_4 in THF were introduced into the cell and the silane was added in a concentration of 10^{-3} M. Ferrocene was added at the end of each experiment and used as an internal standard. Thus, all potentials are quoted relative to the ferrocene/ferrocenium redox couple [29].

4.3. General electrolysis procedure

Constant current supply was afforded by a Wenking STP 84 potentiostat. Electrolysis was carried out in an undivided cell equipped with a magnesium anode in the center and a cylindrical cathode, made of stainless steel, around it. The supporting salt was dissolved in a concentration of 0.2–0.5 mol/L in THF, and this solution was introduced into the cell under a dry nitrogen atmosphere. After addition of the silane, electrolysis was carried out at a constant current density of 0.25 mA/cm^2 until no more starting material could be detected. The reaction was monitored by ^{29}Si NMR and GC/MS.

4.4. 1,2-Dimethoxytetramethyldisilane (*1*)

5.0 g (40 mmol) of $(MeO)Me_2SiCl$ were electrolyzed at 15 mA for 7 days (2,4 F). All volatile compounds were stripped off in vacuum (1 mbar), leaving a grayish white residue which was completely soluble in water. NMR analysis of the volatile fraction showed, that only traces of **1** were formed and most of the starting material remained unreacted.

$MeOMe_2SiSiMe_2OMe$: ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = 11.8$. ^1H NMR ($CDCl_3$, ext. TMS, ppm): $\delta = 0.20$ (s, 12H, $SiCH_3$), 3.40 (s, 6H $SiOCH_3$), both consistent with the literature [30]. MS *m/z* 178 $[M]^+$, 163 $[M - CH_3]^+$, 133 $[M - 3CH_3]^+$ 89 $[SiMe_2OMe]^+$.

4.5. Tetramethyldisilane (*2*)

7.3 g (78 mmol) of HMe_2SiCl were electrolyzed at 15 mA for 8 days (2,75 F). All volatile compounds were stripped off in vacuum (1 mbar), leaving a grayish white residue which is completely soluble in water. To remove excess THF the mixture was distilled with a 1 m rotating strip column until 7.55g of the crude product (including some residual THF) remained. ^1H- and ^{29}Si NMR analysis showed $HMe_2SiSiMe_2H$ to be the only reaction product. Thus, integration and calculation of the THF/disilane ratio allowed to calculate the yield of **2** to be 4.27 g (92%).

$HMe_2SiSiMe_2H$: ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = -39.0$. ^1H NMR ($CDCl_3$, ext. TMS, ppm): $\delta = 0.17$ (12H, $SiCH_3$), 3.75 (2H, SiH), both consistent with the literature [31]. MS *m/z* 118 $[M]^+$, 103 $[M - CH_3]^+$,73 $[Si(CH_3)_3]^+$, 59 $[M - Si(CH_3)_2H]^+$.

4.6. 1,2-Dimethyl-1,2-diphenyldisilane (**3**)

5.0 g (31.9 mmol) of HMePhSiCl were electrolyzed for 6 days at 15 mA (5 F). After removal of all volatile compounds the gray residue was extracted with pentane applying ultrasound. Filtration and subsequent evaporation of pentane yielded 2.85 g of the crude product containing **3** (85%) and HPhMeSiOSiPhMeH (15%) according to GC/MS-, ^{1}H- and ^{29}Si NMR analysis. (The high content of siloxane was due to insufficiently dried $MgCl_2$) This corresponds to a yield of 74 % of **3** based on HMePhSiCl.

HPhMeSiSiPhMeH: ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = -36.4, -36.8$, consistent with the literature [32]. MS *m/z* 242 $[M]^+$, 197 $[Si(C_6H_5)_2(CH_3)]^+$, 121 $[M - Si(C_6H_5)(CH_3)H]^+$, 105 $[Si(C_6H_5)]^+$.

4.7. 1,1,2,2-Tetraphenyldisilane (**4**)

5.1 g (23.3 mmol) of HPh_2SiCl were electrolyzed for 10 days (11,7 F) at 15 mA until all chlorosilane was consumed (reaction control by GC/MS). After removal of all volatile compounds the gray residue was extracted with pentane applying ultrasound. Filtration and subsequent evaporation of the solvent yielded 3.92 g of an oily residue containing **4** (37%), $HPh_2SiSiPh_2SiPh_2H$ (14%), Ph_3SiH (traces) and Ph_2SiH_2 (49 %) according to GC/MS-, ^{1}H- and ^{29}Si NMR analysis. Thus, an overall yield of **4** of 29% based on HPh_2SiCl was obtained.

$HPh_2SiSiPh_2H$: ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = -34.4$; consistent with the literature [33]. MS *m/z* 366 $[M]^+$,259 $[Si(C_6H_5)_3]^+$, 183 $[M - Si(C_6H_5)_2H]$.

4.8. 1,2-Diphenyldisilane (**5**)

4.28 g (19,5 mmol) of $H_2PhSiCl$ were electrolyzed at 20 mA. After 29 h (2.2 F) electrolysis was stopped and all volatile compounds were removed. The resulting gray residue was extracted with pentane applying ultrasound. Filtration and subsequent evaporation of pentane yielded 1.73 g of an oily mixture containing **5** (71%), $PhSiH_3$ (8%), H_2SiPh_2 (12%), $HPh_2SiOSiPh_2H$ (2%) and $H_2PhSiSiHPhSiPhH_2$ (7%) according to GC/MS-, ^{1}H- and ^{29}Si NMR analysis. This corresponds to a yield of 38% of **5** based on $H_2PhSiCl$.

$H_2PhSiSiPhH_2$: ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = -61.2$; consistent with the literature [33]. MS *m/z* 214 $[M]^+$, 183 $[Si(C_6H_5)_2H]^+$, 105 $[Si(C_6H_5)]^+$.

4.9. Attempts to electrolyze N,N-dimethylaminodimethylchlorosilane and N,N-bis(trimethylsilyl)aminodimethylchlorosilane

18 mmol of Et_2NMe_2SiCl or $(Me_3Si)_2NMe_2SiCl$, respectively, were electrolyzed at 20 mA for 60 h (4 F). Reaction control with GC/MS and ^{29}Si NMR showed, that the starting materials remained unreacted and no traces of the wanted disilanes were formed. After distillation of the electrolysis solution, approximately 90% of the starting materials could be recovered.

4.10. General procedure for the reaction of the difunctional disilanes with sodium methoxide

A solution of 0.50 g (2.8 mmol) of **1** in 10 ml of THF was added drop wise to a suspension of 0.15 g (2.8 mmol) of sodium methoxide and the equivalent amount of the organic halide in 20 ml of THF. As sodium halide precipitated the reaction mixture became more and more turbid. After no further conversion could be detected by GC/MS, the reaction mixture was filtered, the solvent was evaporated and the resulting residue was analyzed using GC/MS and NMR.

4.11. Methoxydimethylphenylsilane (**6a**)

0.44 g (2.8 mmol) of bromobenzene gave a mixture of 40% of unreacted bromobenzene and 60% of **6a** according to GC/MS and ^{1}H NMR.

$MeOMe_2SiPh$: ^{1}H NMR ($CDCl_3$, ext. TMS, ppm): $\delta = 0.52$ (s, 6H, $Si(CH_3)_2$), 3.55 (s, 3H, $SiOCH_3$), 7.21 (m, 5H, C_6H_5). ^{29}Si NMR (THF/ext. lock D_2O, ext. TMS, ppm): $\delta = 8.4$, consistent with the literature [34]. MS *m/z* 166 $[M]^+$, 151 $[M - CH_3]^+$, 121 $[M - 3CH_3]^+$.

4.12. p-(Methoxyphenyl)methoxydimethylsilane (**6b**)

0.52 g (2.8 mmol) of 4-bromoanisole gave 0.54 g of a mixture of unreacted 4-bromoanisole (40%) and **6b** (60%) after a reaction time of 3 days according to GC/MS and ^{1}H NMR.

$MeOMe_2SiPhOMe$: ^{1}H NMR ($CDCl_3$, ext.TMS, ppm): $\delta = 0.38$ (s, 6H, $Si(CH_3)_2$), 3.44 (s, 3H, $SiOCH_3$), 3,84 (s, 3H, OCH_3), 7.24 (dd, 4H, C_6H_4). ^{29}Si NMR (ext. lock D_2O, ext. TMS, ppm): $\delta = 8.9$. MS *m/z* 196 $[M]^+$, 181 $[M - CH_3]^+$, 151 $[M - 3CH_3]^+$.

4.13. p-N,N-Dimethylaminophenylmethoxydimethylsilane (**6c**)

0.56 g (2.8 mmol) of 4-bromo-N,N-dimethylaniline gave 0.55 g of a mixture of unreacted 4-bromo-N,N-dimethylaniline (35%) and **6c** 65%) after a reaction time of 4 days according to GC/MS and ^{1}H NMR.

$MeOMe_2SiPhNMe_2$: ^{1}H NMR ($CDCl_3$, ext. TMS, ppm): $\delta = 0.45$ (s, 6H, $Si(CH_3)_2$), 3.05 (s, 6H, $N(CH_3)_2$), 3.55 (s, 3H, $SiOCH_3$), 7.20 (dd, 4H, C_6H_4). MS *m/z* 209 $[M]^+$, 194 $[M - CH_3]^+$, 164 $[M - 3CH_3]^+$ 134 $[Si(CH_3)_2C_6H_4]^+$.

4.14. Attempted synthesis of methoxydimethylsilylaniline

0.48 g (2.8 mmol) of 4-bromoaniline gave 0.63 g of a mixture of 40% of unreacted 4-bromoaniline and 60% of (*N*-4-bromophenylamino)methoxydimethylsilane (**7**) after

a reaction time of 22 h according to GC-MS and ^{1}H NMR.

$MeOMe_2SiNHPhBr$: ^{1}H NMR ($CDCl_3$, ext. TMS, ppm): $\delta = 0.35$ (bd, 6H, $Si(CH_3)_2$), 3.45 (s, 3H, $SiOCH_3$), 6.95 (dd, 4H, C_6H_4) MS m/z 261 $[M]^+$, 246 $[M - CH_3]^+$, 229 $[M - CH_3(OCH_3)]^+$ 165$[M - CH_3\ Br]^+$.

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