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Tailor-made synthesis of functional substituted oligo- and polysilanes from silyl triflates and (aminosilyl)lithium compounds

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Abstract

Diethylamino substituted silyllithium compounds have been prepared in situ from the corresponding phenylchlorosilanes and lithium. These reagents undergo coupling reactions with triflate derivatives of silanes and oligosilanes. Exchange processes analogous to metal–halogen exchange and Si–Si bond cleavage, which are side reactions with chlorosilanes, were not observed. Based on the coupling reaction and the amino-to-triflate transformation, functionalized tri-, tetra-, penta- and hexasilanes have been synthesized. α,ω -Triflate substituted oligosilanes containing π -systems have also been obtained. These compounds are useful building blocks for new organosilicon polymers. The formation of the silicon polymers at low temperatures, in short reaction times, and with high yields is reported. The ^{29}Si -NMR spectra indicate a regular, alternating arrangement of the building blocks in the polymer backbone.

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Keywords: Aminosilanes; Oligosilanes; Silyl triflates

1. Introduction

Polysilanes have received much attention due to their interesting chemical and physical properties [1,2]. To investigate these properties, synthetic methodologies for structurally well-defined oligosilanes have been developed. The standard method for the Si–Si chain elongation is based on a combination of two steps: (1) coupling of (organosilyl)lithium compounds with silanes bearing good leaving groups (halogen, triflate) and (2) conversion of the organic groups (phenyl, *para*-tolyl, *para*-anisyl, allyl) on the silicon atoms in good leaving groups [3–5]. Based on this methodology, several groups were successful in the syntheses of dendric polysilanes with regular three-dimensional structures [6–10].

Synthetically useful silyl anions have long been limited to only several simple triorganosilyl anions such as Ph_3Si^- , Ph_2MeSi^- , PhMe_2Si^- [11], Me_3Si^- [12–14] and $(\text{Me}_3\text{Si})_3\text{Si}^-$ [15]. Although three functional silyl anions, Cl_3Si^- [16], $(\text{RO})_n\text{Me}_{3-n}\text{Si}^-$ [17], and

HPh_2Si^- [18] have been reported. The first two derivatives are postulated active species generated in situ in the presence of quenching agents, and the last is obtained in about 10% yield and tends to polymerize readily.

Stable, functional substituted silyl anions are firstly described by the groups of Tamao [19,20] and Roewer and coworkers [21]. (Dialkylamino)phenyl substituted chlorosilanes are able to form silyllithium compounds. Because the generated lithium species have an unusually high stability, compared with the other known silyllithium compounds, they are useful synthons for the synthesis of oligosilane structures. (Aminosilyl)lithium compounds readily react with chlorosilanes to yield a variety of aminosubstituted oligosilanes. By treatment with acyl chloride [19,22] or hydrogen chloride [23,24], these amino-oligosilanes can be converted into chloro-oligosilanes, which work as precursors for further Si–Si chain elongation. In the reaction of (aminosilyl)lithium compounds with chloro-oligosilanes, however, cleavage of the Si–Si bond often occurs to lower the yields of the coupling products. Moreover, metal–halogen exchange processes cannot be suppressed. Therefore, Tamao proposed the use of the mixed reagent $(\text{R}_2\text{N})\text{R}_2\text{SiLi}$ –

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R^1MgBr [25]. The authors assume the in situ formation of (aminosilyl)alkylmagnesium species. The selectivity of the silylation increases as the alkyl group R^1 became bulkier. Side reactions were completely suppressed in the case of $R^1 = i$ -propyl. This method is highly effective, if the chloro-oligosilane does not contain any other functional groups. However, i -PrMgBr is regenerated during the silylation process and can attack functional groups, for instance Si–H bonds. Our investigations in the field of silyl triflates [26–28] have shown that organolithium and organomagnesium compounds react rapidly and completely with silyl triflates at low temperatures. Interestingly, it was found that no exchange processes analogous to metal–halogen exchange occur. Therefore we investigated systematic, stepwise syntheses of oligosilanes and organosilicon polymers from silyl triflates and (aminosilyl)lithium anions.

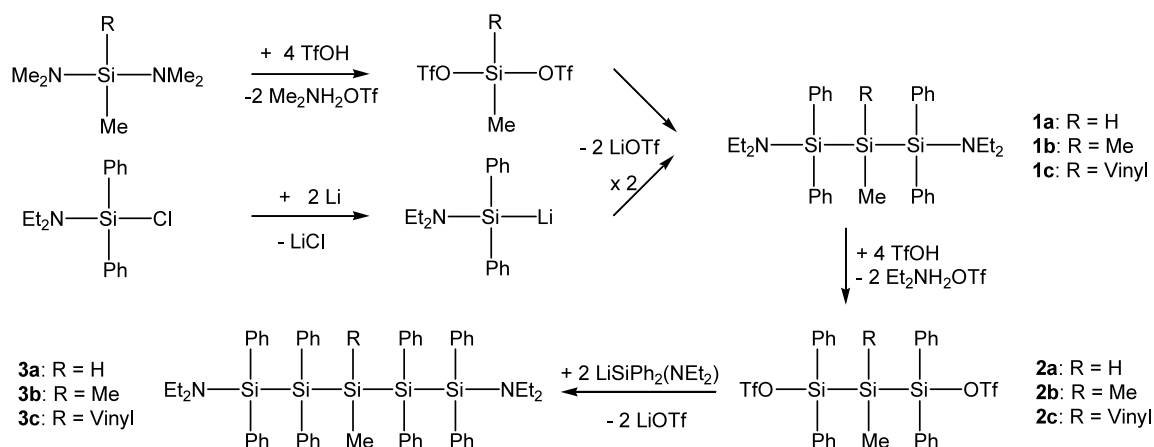
2. Results and discussion

The highly reactive silyl triflates and silyl bis(triflates) are obtained by reaction of the corresponding aminosilanes with triflic acid in diethyl ether as shown in Schemes 1 and 2 [29]. The substitution patterns at the silicon atoms are variable. Functional substituted silanes, e.g. vinyl, allyl or hydrogen derivatives, can also be obtained. [(Diethylamino)diphenylsilyl]lithium is formed from (diethylamino)diphenylchlorosilane with lithium in THF. Yields of both reactions are high (90–95%). Therefore, the products are used for following reaction without further purification. Silyl triflates and (aminosilyl)lithium compounds react to give aminosubstituted trisilanes **1a–1c** (Scheme 1) and disilanes **4a–4c** (Scheme 2). It must be considered, that silyl triflates are not stable in THF for an extended time, because they can initiate the cationic ring-opening polymerization (ROP) of cyclic ethers [30]. Therefore, the silyl triflate (in diethyl ether) is added in drops to the (aminosi-

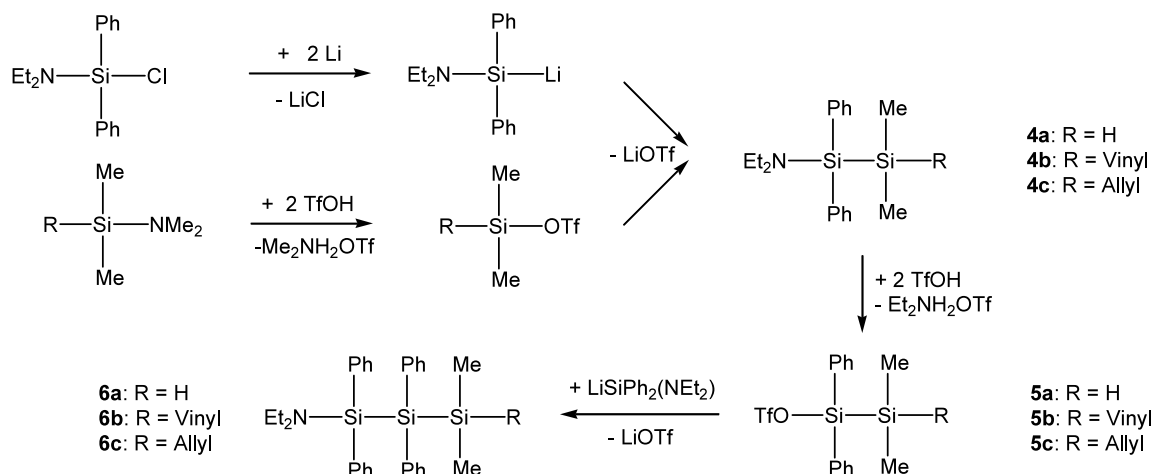
lyl)lithium compound dissolved in THF. The reaction proceed very quickly and ROP of THF is not observed under these conditions. The trisilanes **1a–1c** as well as the disilanes **4a–4c** can be converted by reaction with triflic acid into the trisilanyl bis(triflates) **2a–2c** and disilanyl triflates **5a–5c**, respectively. These compounds are precursors for further chain elongation. The reaction with [(diethylamino)diphenylsilyl]lithium leads to the pentasilanes **3a–3c** and the trisilanes **6a–6c**.

The reaction of [bis(diethylamino)phenylsilyl]lithium [21] with silyl triflates proceeds analogously. The formation of the disilane **7** is shown in Scheme 3 as an example. Conversion with triflic acid and chain elongation with $LiSiPh_2(NEt_2)$ lead to the branched tetrasilane **9**.

The described reaction pathways are useful for the synthesis of new structurally well-defined organosilicon polymers. Recently, we reported on the synthesis of hydrogen-rich organosilicon polymers from α,ω -bis(trifluoromethylsulfonyloxy)-substituted organosilicon compounds and organometallic dinucleophiles [31,32]. The polymers were obtained in excellent yields. Exchange processes analogous to metal–halogen exchange or other side reaction were not observed. Consequently, a regular alternating arrangement of organosilicon and organic groups was found in the polymeric backbone, indicated by narrow signals in the ^{29}Si -NMR spectra. The terminal triflate substituted disilanes, disilylalkynes and 1,4-disilylbenzenes can be modified by reaction with [(diethylamino)diphenylsilyl]lithium. We obtained the tetrasilane **10**, the 1,2-bis(disilanyl)ethyne **11** and 1,4-bis(disilanyl)benzene **12** (Scheme 4). This compounds contain terminal amino groups, which can be exchanged by triflic acid. It should be emphasized that compounds **10–12** contain several different bonds, which can be easily cleaved by triflic acid, e.g. Si–Ph, and Si–H. But the amino substituent is the best leaving group [26]. We obtained selectively the triflate substituted derivatives



Scheme 1.



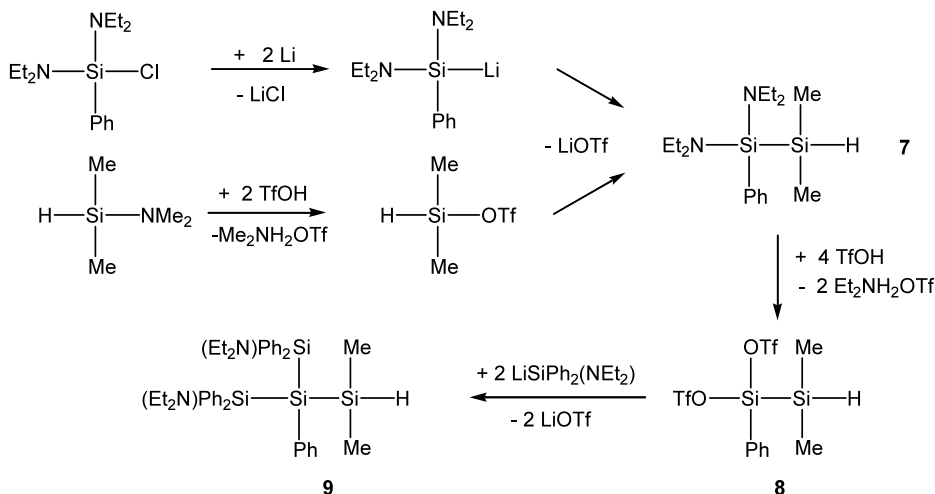
Scheme 2.

13–15 (Scheme 5). These compounds are new useful precursors for organosilicon polymers.

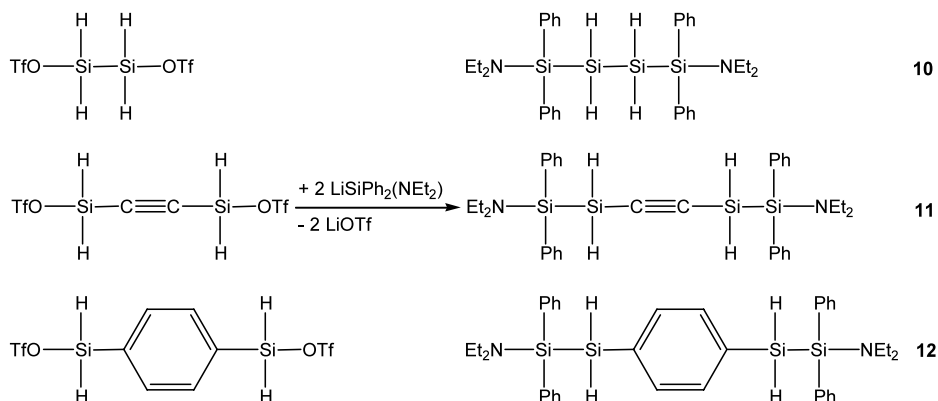
Further synthetic modifications of **13** and **14** are summarized in Schemes 6 and 7. Conversions of **15** are described in [33]. The reaction with $\text{LiSiPh}_2(\text{NEt}_2)$ leads to the elongation of the silicon chain (**16,20**). The reduction with the graphite intercalation compound C_8K gave the copolysilane **18** and the copolymer **22**, which contains an alternating arrangement of tetrasilane units and ethyne groups in the backbone. The best results were obtained using the ‘inverse reducing method’ (addition of C_8K in portions to the silyl triflate solution). Otherwise, an excess of the strong reducing agent C_8K leads to Si–Si bond cleavage and reduction of triflate ions. The organometallic dinucleophiles 1,2-dilithioethyne $\text{LiC}\equiv\text{CLi}$ and 2,5-dilithiothienylene $\text{LiC}_4\text{H}_2\text{SLi}$ react with **13** and **14** to give the copolymers **17, 19, 21, 23**. These compounds are characterized by a regular alternating arrangement of oligosilane units and

unsaturated organic groups. The syntheses are carried out using a small excess of the organolithium compound. Under these conditions we obtained polymers containing terminal ethyne or thienylene groups after hydrolysis of the reaction mixture. Contrary, a small excess of the bis(triflate) derivative leads to copolymers with terminal triflate groups. After hydrolysis these polymers always involve small proportions of undesired siloxy units in the backbone.

We could confirm the formation of **16–23** at low temperatures, in short reaction times, and with high yields. The structural characterization was mainly based on NMR spectroscopy. ^{29}Si -NMR chemical shifts are particularly useful. The ^1H -, ^{13}C -, and ^{29}Si -NMR spectra of all compounds are consistent with the proposed structures of the polymer chain. As expected, one observes relatively broad signals, which are typical for organosilicon polymers. However, the half-band widths of the ^{29}Si -NMR signals, 80–150 Hz, are



Scheme 3.



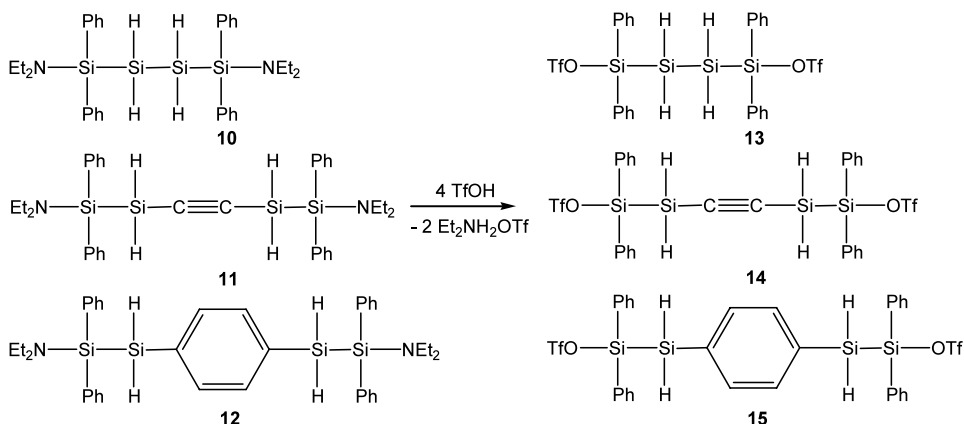
Scheme 4.

narrower than those in the case of organosilicon polymers prepared from chlorosilanes (100–250 Hz). The narrower signals of **17–19** and **21–23** indicate the regular alternating arrangement of the building blocks in the polymer backbone resulting from the fact that the condensation reactions are not accompanied by exchange processes analogous to metal–halogen exchange. The ^{13}C -NMR data also support this view. Thus, only isolated ethynyl groups ($\delta^{13}\text{C}$: 112 ppm) are detectable in the spectra of **17**, and **21**. Diethynyl units $-\text{C}^* \equiv \text{C}^{\circ}-\text{C} \equiv \text{C}-$ ($\delta^{13}\text{C}$: 82 ppm $^{\circ}$; 90 ppm $^{\circ}$), which are produced in variable yields (5–15%) by the reaction of Li_2C_2 with dihalogenosilanes, are not observed. Weight-average molecular weights in the range of $M_w = 8000$ – 16000 , relative to polystyrene standards, were found by GPC. They correspond to polymerization degrees of $n = 15$ – 30 . The polydispersities (M_w/M_n) were found in the range 2.5–3.1. It must be emphasized, that the molecular weights are strongly determined by the reaction conditions. Higher values of M_w were obtained using more concentrated solutions of the reactants. The exact compliance with the stoichiometric ratio of 1:1 is another important requirement. It is therefore necessary

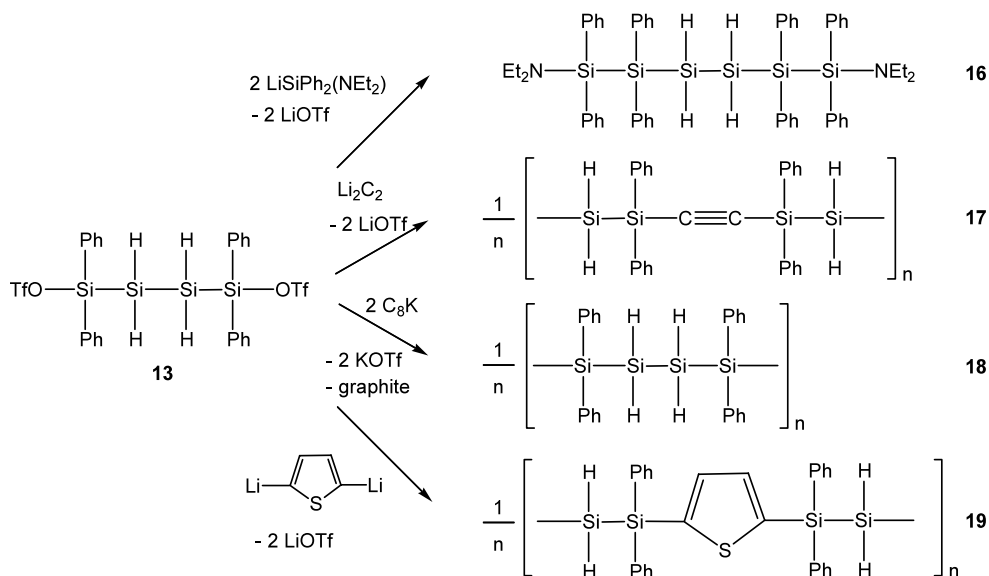
to determine the content of the organometallic compounds quantitatively before use. However, molecular weights can also fall below 5000 when diluted solutions are used. Other changes such as the use of different solvents and reaction temperatures are being currently investigated. Thus, molecular weights reported in the experimental section are those found under the conditions specified there.

The described polymers are solids. They are soluble in the usual organic solvents such as toluene, chloroform, and THF. Defined melting points are not observed. The solids become highly viscous fluids, with concentration of volume, at temperatures between 170 and 220 °C. These conversions occur within temperature intervals of about 20°. Moreover, decomposition (hydrogen elimination) is observed during the melting process. Further work will be directed to investigations of the thermal behaviour of the compounds.

In general, polymers composed of alternating silylene units and π -electron systems are insulators. However, when the polymers are treated with an oxidizing agent, they became conducting. Preliminary doping studies showed, when cast films of selected polymers were



Scheme 5.



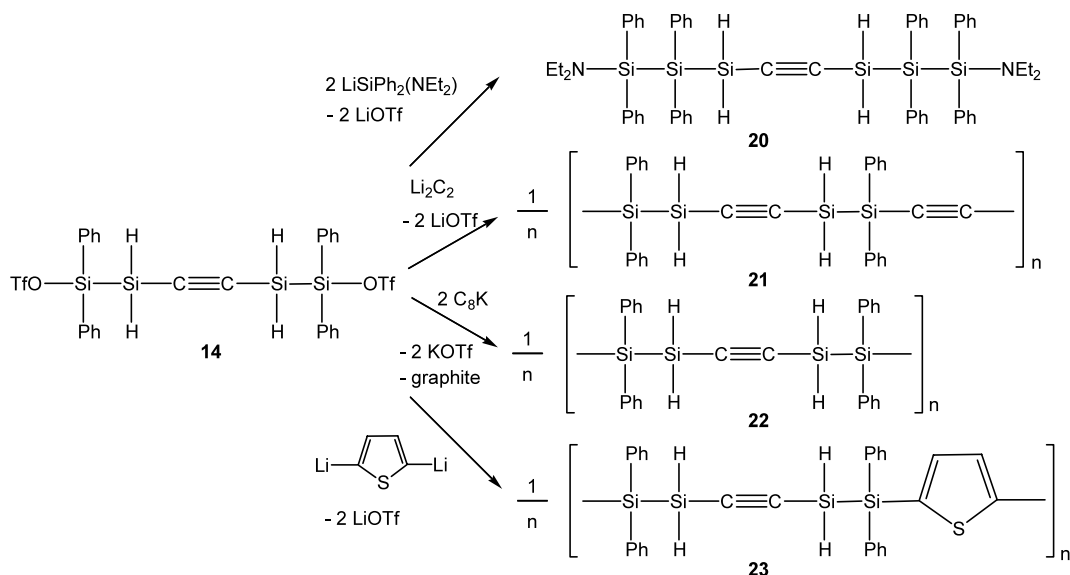
exposed to iodine vapor under reduced pressure, that the conductivity of the films increased and reached almost constant values after 10 h. The conductivity at this point was found to be 3.6×10^{-5} (**19**) and 8.9×10^{-5} S cm⁻¹ (**23**).

Obviously, the synthetic methods described here may currently appear to be too expensive for technical application. However, the essential advantage of the silyl triflate chemistry consists of the possibility of preparing, with relatively little efforts, small amounts of numerous differently structured organosilicon polymers for investigations in the field of materials and surface science.

3. Experimental

3.1. General

All reactions were carried out under nitrogen or argon using Schlenk tubes. Solvents were dried and distilled before use. *The strongly hygroscopic triflic acid must be distilled before use and should be kept under nitrogen. Traces of moisture in CF₃SO₃H always led to undesired formation of siloxanes during the protodeamination reaction.* Detailed information about the purification is included in [34], chapter 7. The ¹H-, ¹³C-, and ²⁹Si-NMR spectra are obtained on a Bruker AC-250



spectrometer; the chemical shifts are relative to tetramethylsilane. The ^{29}Si -NMR spectra were measured for solutions containing 0.1 mol.% of the relaxation reagent $\text{Cr}(\text{acac})_3$. The average molecular weights of the polymers were determined by GPC. Solutions of silyl triflates in THF are not stable for an extended time, because they can initiate the cationic ROP of cationic ethers. However, reactions of silyl triflates with organolithium or organomagnesium compounds dissolved in THF can be carried out, because these reactions proceed very quickly. The following derivatives were prepared by published methods: Li_2C_2 [35], C_8K [36], $(\text{TfO})_2\text{Si}-\text{X}-\text{SiH}_2(\text{OTf})$ [31], $(\text{Et}_2\text{N})\text{Ph}_2\text{SiCl}$ [20], $(\text{Et}_2\text{N})_2\text{PhSiCl}$ [21], $\text{MeRSi}(\text{OTf})_2$ [26,29], $\text{Li}-\text{C}_4\text{H}_2\text{S}-\text{Li}$ [37,38].

3.2. Synthesis of [(diethylamino)diphenylsilyl]lithium [19]

To a suspension of 0.7 g (0.1 mol) lithium in THF (50 ml) was added at 0 °C a solution of 2.9 g (0.01 mol) $(\text{Et}_2\text{N})\text{Ph}_2\text{SiCl}$ dissolved in THF (50 ml). After 5 min the start of the reaction was indicated by a greenish coloured solution. After stirring for 4 h the lithiation was completed and the solution was separated from the lithium for using in further reactions. From NMR spectroscopic measurements we conclude, that the reaction proceeds quantitatively.

3.3. Synthesis of [bis(diethylamino)phenylsilyl]lithium [21]

To a suspension of 0.7 g (0.1 mol) lithium in THF (50 ml) was added at 0 °C a solution of 2.85 g (0.01 mol) $(\text{Et}_2\text{N})_2\text{PhSiCl}$ dissolved in THF (50 ml). After 5 min the start of the reaction was indicated by a greenish coloured solution. After stirring for 4 h the lithiation was completed and the dark red solution was separated from the lithium for using in further reactions. The ^{29}Si -NMR spectrum of the solution shows only one signal ($\delta = +27.5$ ppm).

3.4. Formation of Si–Si bonds by reaction of silyl triflates with (aminosilyl)lithium compounds (general procedure)

The corresponding silyl triflate (0.005 mol of silyl bis(triflate) or 0.01 mol of silyl triflate) dissolved in 50 ml of diethyl ether was added to a solution of the (aminosilyl)lithium compound (0.01 mol), in 100 ml of a THF, at 0 °C within 10 min. The reaction mixture was stirred at room temperature for 2 h. After that time the solution became colourless. The solvent was removed under reduced pressure and replaced by 100 ml of toluene. Lithium triflate precipitated as a white solid and was filtered off. Toluene was removed under vacuum leaving the oligosilanes as yellow, highly viscous

oils in high yields (90–95%). The desired coupling products were obtained in higher than 95% chemoselectivity as indicated from NMR measurements. The disilanes **4a–4c** and **7** can be purified by distillation. Attempts to distillate the higher oligosilanes were not successful. The compounds were decomposed. **1a–c**, **3a–c**, **6a–c**, **9**, **10**, **16**, **20** can be recrystallized from dichloromethane to give the oligosilanes as white crystals (25–30%). Because of the substantial loss of yield during distillation and recrystallization it is recommended to use the raw products for further reactions without purification.

1a: M.p.: 143–146 °C. ^1H -NMR (C_6D_6): $\delta = 0.21$ (d, MeSi), 0.96 (t, CH_3), 2.97 (q, NCH_2), 3.77 (q, SiH), 7.22–7.53 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -3.7$ (MeSi), 14.4 (CH_3), 40.6 (CH_2N), 126.8, 128.3, 134.7, 140.6 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -14.7$ (SiN); -63.0 (SiH). Anal. Calc. for $\text{C}_{33}\text{H}_{44}\text{N}_2\text{Si}_3$ (553.0): C, 71.68; H, 8.02; N, 5.07. Found: C, 71.44; H, 7.77; N, 4.80.

1b: M.p.: 157–161 °C. ^1H -NMR (C_6D_6): $\delta = 0.53$ (s, Me_2Si), 0.92 (t, CH_3), 2.94 (q, NCH_2), 7.19–7.56 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -3.1$ (MeSi), 15.1 (CH_3), 39.8 (CH_2N), 126.5, 127.9, 135.2, 141.3 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -15.7$ (SiN); -37.4 (SiMe). Anal. Calc. for $\text{C}_{34}\text{H}_{46}\text{N}_2\text{Si}_3$ (567.0): C, 72.02; H, 8.18; N, 4.94. Found: C, 71.56; H, 8.11; N, 5.13.

1c: M.p.: 149–153 °C. ^1H -NMR (C_6D_6): $\delta = 0.64$ (s, MeSi), 0.95 (t, CH_3), 3.00 (q, NCH_2), 5.67–6.43 (m, Vi), 7.15–7.61 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -3.9$ (MeSi), 15.7 (CH_3), 40.9 (CH_2N), 127.1, 128.0, 135.0, 140.9 (Ph), 133.6, 136.1 (Vi). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -15.0$ (SiN); -40.6 (SiVi). Anal. Calc. for $\text{C}_{35}\text{H}_{46}\text{N}_2\text{Si}_3$ (579.0): C, 72.60; H, 8.01; N, 4.84. Found: C, 72.27; H, 7.68; N, 5.11.

3a: M.p.: > 200 °C (dec.). ^1H -NMR (C_6D_6): $\delta = 0.23$ (d, MeSi), 0.99 (t, CH_3), 3.04 (q, NCH_2), 3.67 (q, SiH), 7.16–7.66 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -3.3$ (MeSi), 14.6 (CH_3), 39.5 (CH_2N), 127.0–141.5 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -15.9$ (SiN), -36.8 (SiPh), -62.5 (SiH). Anal. Calc. for $\text{C}_{57}\text{H}_{64}\text{N}_2\text{Si}_5$ (917.6): C, 74.61; H, 7.03; N, 3.05. Found: C, 75.02; H, 6.86; N, 2.80.

3b: M.p.: > 200 °C (dec.). ^1H -NMR (C_6D_6): $\delta = 0.57$ (s, Me_2Si), 0.98 (t, CH_3), 3.00 (q, NCH_2), 7.13–7.72 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -2.9$ (MeSi), 14.7 (CH_3), 40.4 (CH_2N), 126.0–141.5 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -14.0$ (SiN); -34.3 (SiMe); -37.6 (SiPh). Anal. Calc. for $\text{C}_{58}\text{H}_{66}\text{N}_2\text{Si}_5$ (931.6): C, 74.78; H, 7.14; N, 3.01. Found: C, 75.19; H, 7.30; N, 2.85.

3c: M.p.: > 200 °C (dec.). ^1H -NMR (C_6D_6): $\delta = 0.68$ (s, MeSi), 0.99 (t, CH_3), 2.89 (q, NCH_2), 5.71–6.54 (m, Vi), 7.02–7.80 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -4.1$ (MeSi), 16.0 (CH_3), 41.4 (CH_2N), 126.5–140.5 (Ph), 132.9, 137.0 (Vi). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -14.8$ (SiN), -37.1 (SiPh), -40.0 (SiVi). Anal. Calc. for

$C_{59}H_{66}N_2Si_5$ (943.6): C, 75.10; H, 7.05; N, 2.97. Found: C, 74.66; H, 6.77; N, 3.09.

4a: B.p. 115–118 °C/0.5 mbar. 1H -NMR (C_6D_6): δ = 0.27 (d, MeSi), 0.94 (t, CH_3), 2.93 (q, NCH_2), 3.81 (sept, SiH), 7.21–7.57 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –3.0 (MeSi), 14.8 (CH_3), 40.9 (CH_2N), 127.0, 128.9, 135.0, 140.4 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –16.0 (SiN); –39.5 (SiH). IR (film): ν = 2142 (SiH) cm^{-1} . Anal. Calc. for $C_{18}H_{27}NSi_2$ (313.6): C, 68.94; H, 8.68; N, 4.47. Found: C, 69.25; H, 8.35; N, 4.42.

4b: B.p. 128–132 °C/0.8 mbar. 1H -NMR (C_6D_6): δ = 0.61 (s, MeSi), 0.99 (t, CH_3), 2.89 (q, NCH_2), 5.72–6.51 (m, Vi), 7.12–7.66 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –4.1 (MeSi), 14.0 (CH_3), 39.5 (CH_2N), 126.8, 128.2, 134.2, 140.1 (Ph), 132.6, 135.1 (Vi). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –17.0 (SiN), –21.7 (SiVi). Anal. Calc. for $C_{20}H_{29}NSi_2$ (339.6): C, 70.73; H, 8.61; N, 4.12. Found: C, 71.14; H, 8.30; N, 3.87.

4c: B.p. 130–134 °C/0.5 mbar. 1H -NMR (C_6D_6): δ = 0.38 (s, MeSi), 0.91 (t, CH_3), 2.96 (q, NCH_2), 1.54 (d, $SiCH_2$), 4.92 (m, CH_2), 5.98 (m, CH), 7.12–7.66 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –3.0 (MeSi), 15.2 (CH_3), 40.0 (CH_2N), 126.5, 127.9, 134.8, 141.0 (Ph), 12.4, 115.7, 136.7 (Allyl). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –16.5 (SiN), –18.1 (SiAllyl). Anal. Calc. for $C_{21}H_{31}NSi_2$ (353.7): C, 71.32; H, 8.84; N, 3.96. Found: C, 70.95; H, 8.56; N, 4.13.

6a: M.p.: 161–165 °C. 1H -NMR (C_6D_6): δ = 0.31 (d, MeSi), 0.97 (t, CH_3), 2.96 (q, NCH_2), 3.88 (sept, SiH), 7.06–7.88 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –4.1 (MeSi), 16.0 (CH_3), 42.7 (CH_2N), 127.0–141.5 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –14.9 (SiN), –36.5 (SiPh), –39.5 (SiH). IR (film): ν = 2139 (SiH) cm^{-1} . Anal. Calc. for $C_{30}H_{37}NSi_3$ (495.9): C, 72.66; H, 7.52; N, 2.82. Found: C, 72.97; H, 7.53; N, 2.70.

6b: M.p.: 170–174 °C. 1H -NMR (C_6D_6): δ = 0.65 (s, MeSi), 1.01 (t, CH_3), 2.87 (q, NCH_2), 5.66–6.55 (m, Vi), 7.08–7.81 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –3.6 (MeSi), 14.8 (CH_3), 41.4 (CH_2N), 126.5–140.5 (Ph), 132.6, 135.1 (Vi). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –17.0 (SiN), –21.7 (SiVi), –37.9 (SiPh). Anal. Calc. for $C_{32}H_{39}NSi_3$ (521.9): C, 73.64; H, 7.53; N, 2.68. Found: C, 73.35; H, 7.47; N, 2.65.

6c: M.p.: 162–167 °C. 1H -NMR (C_6D_6): δ = 0.33 (s, MeSi), 0.95 (t, CH_3), 2.99 (q, NCH_2), 1.61 (d, $SiCH_2$), 4.99 (m, CH_2), 6.02 (m, CH), 7.04–7.75 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –3.6 (MeSi), 14.8 (CH_3), 40.9 (CH_2N), 126.5–141.0 (Ph), 12.9, 116.5, 137.7 (Allyl). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –16.5 (SiN), –18.1 (SiAllyl), –36.2 (SiPh). Anal. Calc. for $C_{33}H_{41}NSi_3$ (535.9): C, 73.95; H, 7.71; N, 2.61. Found: C, 74.19; H, 7.90; N, 2.49.

7: B.p. 111–114 °C/0.3 mbar. 1H -NMR (C_6D_6): δ = 0.28 (d, MeSi), 1.02 (t, CH_3), 2.87 (q, NCH_2), 3.76 (sept, SiH), 7.22–7.53 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –2.4 (MeSi), 15.1 (CH_3), 40.9 (CH_2N), 126.3, 128.0, 135.6,

139.9 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –11.8 (SiN), –39.1 (SiH). IR (film): ν = 2149 (SiH) cm^{-1} . Anal. Calc. for $C_{16}H_{32}N_2Si_2$ (308.6): C, 62.27; H, 10.45; N, 9.08. Found: C, 61.98; H, 10.37; N, 8.88.

9: M.p.: > 200 °C (dec.). 1H -NMR (C_6D_6): δ = 0.25 (d, MeSi), 1.06 (t, CH_3), 2.91 (q, NCH_2), 3.84 (sept, SiH), 7.03–7.91 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = –3.5 (MeSi), 15.6 (CH_3), 42.1 (CH_2N), 128.0–140.0 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –14.7 (SiN), –40.4 (SiH), –75.6 (PhSiSi₃). IR (film): ν = 2151 (SiH) cm^{-1} . Anal. Calc. for $C_{40}H_{52}N_2Si_4$ (672.3): C, 71.37; H, 7.79; N, 4.16. Found: C, 71.09; H, 7.88; N, 4.00.

10: M.p.: > 200 °C (dec.). 1H -NMR (C_6D_6): δ = 0.98 (t, CH_3), 2.97 (q, NCH_2), 3.91 (s, SiH), 7.22–7.56 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = 16.0 (CH_3), 42.3 (CH_2N), 127.2, 128.4, 135.8, 140.4 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –17.8 (SiN), –81.5 (SiH). IR (film): ν = 2147 (SiH) cm^{-1} . Anal. Calc. for $C_{32}H_{44}N_2Si_4$ (569.1): C, 67.54; H, 7.79; N, 4.92. Found: C, 67.13; H, 7.48; N, 5.19.

11: 1H -NMR (C_6D_6): δ = 0.93 (t, CH_3), 2.87 (q, NCH_2), 3.98 (s, SiH), 7.21–7.58 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = 15.5 (CH_3), 39.8 (NCH_2), 111.2 ($C\equiv C$), 126.5, 127.9, 135.1, 141.2 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –16.2 (SiN), –74.9 ($SiC\equiv C$). IR (film): ν = 2144 (SiH), 2034 ($C\equiv C$) cm^{-1} . Anal. Calc. for $C_{34}H_{44}N_2Si_4$ (593.1): C, 68.86; H, 7.48; N, 4.72. Found: C, 68.56; H, 7.36; N, 4.55.

12: 1H -NMR (C_6D_6): δ = 0.97 (t, CH_3), 2.95 (q, NCH_2), 4.17 (s, SiH), 7.04–7.67 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = 14.6 (CH_3), 40.3 (NCH_2), 127.0–142.5 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –18.8 (SiN), –60.9 (SiH). IR (film): ν = 2152 (SiH) cm^{-1} . Anal. Calc. For $C_{38}H_{48}N_2Si_4$ (645.1): C, 70.75; H, 7.50; N, 4.34. Found: C, 71.02; H, 7.28; N, 4.29.

16: M.p.: > 200 °C (dec.). 1H -NMR (C_6D_6): δ = 0.91 (t, CH_3), 2.88 (q, NCH_2), 3.93 (s, SiH), 7.15–7.67 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = 14.7 (CH_3), 41.9 (CH_2N), 127.0–140.5 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –16.5 (SiN), –37.1 (SiPh), –82.7 (SiH). IR (film): ν = 2149 (SiH) cm^{-1} . Anal. Calc. for $C_{56}H_{64}N_2Si_6$ (932.6): C, 72.04; H, 6.91; N, 3.00. Found: C, 71.84; H, 7.10; N, 2.92.

20: M.p.: > 200 °C (dec.). 1H -NMR (C_6D_6): δ = 0.94 (t, CH_3), 2.95 (q, NCH_2), 4.01 (s, SiH), 7.11–7.83 (Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6): δ = 14.5 (CH_3), 40.1 (CH_2N), 112.3 ($C\equiv C$), 128.0–142.0 (Ph). $^{29}Si\{^1H\}$ -NMR (C_6D_6): δ = –14.9 (SiN), –36.8 (SiPh), –79.7 (SiH). IR (film): ν = 2139 (SiH), 2032 ($C\equiv C$) cm^{-1} . Anal. Calc. for $C_{58}H_{64}N_2Si_6$ (956.7): C, 72.74; H, 6.74; N, 2.93. Found: C, 72.81; H, 6.65; N, 2.79.

3.5. Reaction of aminosilanes with triflic acid (conversion of silyl amino in silyl triflate groups, general procedure)

A solution of triflic acid (0.02 mol per each silyl amino group) in 50 ml of diethyl ether was added to a

solution of the aminosilane (0.01 mol) in 100 ml of diethyl ether at 0 °C over 30 min with stirring. The ammonium salt of triflic acid precipitated quantitatively as white solid and was filtered off. The solvent was removed under reduced (50 °C/1 mbar) and the silyl triflates were obtained as pale yellow oils.

Attention! Silyl triflates containing Si–H bonds should not be distilled. Attempts to distill these compounds often lead to explosion.

2a: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.37$ (d, MeSi), 3.88 (q, SiH), 7.09–7.86 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -1.5$ (MeSi), 118.4 (CF_3), 125.5, 126.3, 132.0, 138.3 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +16.5$ (SiOTf), -61.3 (SiH). IR (film): $\nu = 2153$ (SiH) cm^{-1} . Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2\text{Si}_3$ (706.8): C, 45.88; H, 3.42. Found: C, 46.17; H, 3.67.

2b: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.67$ (s, Me_2Si), 7.04–7.79 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -0.9$ (MeSi), 117.8(CF_3), 125.0, 125.9, 132.4, 138.3 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +17.8$ (SiOTf), -38.3 (SiMe). Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{F}_6\text{O}_6\text{S}_2\text{Si}_3$ (720.9): C, 46.65; H, 3.64. Found: C, 46.25; H, 3.55.

2c: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.73$ (s, MeSi), 5.59–6.38 (m, Vi), 7.04–7.77 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -1.7$ (MeSi), 118.2 (CF_3), 125.3, 127.0, 133.1, 140.2 (Ph), 132.0, 136.1 (Vi). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +16.0$ (SiOTf), -42.1 (SiVi). Anal. Calc. for $\text{C}_{29}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2\text{Si}_3$ (732.9): C, 47.53; H, 3.58. Found: C, 47.16; H, 3.34.

5a: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.55$ (d, MeSi), 3.73 (sept, SiH), 7.03–7.81 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -1.0$ (MeSi), 117.6 (CF_3), 124.8, 127.3, 135.1, 139.7 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +17.5$ (SiOTf), -36.8 (SiH). IR (film): $\nu = 2144$ (SiH) cm^{-1} . Anal. Calc. for $\text{C}_{15}\text{H}_{17}\text{F}_3\text{O}_3\text{SSi}_2$ (390.5): C, 46.13; H, 4.39. Found: C, 45.75; H, 4.20.

5b: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.68$ (s, MeSi), 5.70–6.55 (m, Vi), 6.99–7.62 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -1.3$ (MeSi), 119.5 (CF_3), 125.0, 127.4, 135.4, 140.6 (Ph), 132.8, 134.6 (Vi). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +16.9$ (SiOTf), -20.0 (SiVi). Anal. Calc. for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{O}_3\text{SSi}_2$ (416.6): C, 49.02; H, 4.60. Found: C, 48.71; H, 4.40.

5c: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.49$ (s, MeSi), 1.62 (d, SiCH_2), 4.97 (m, CH_2), 5.88 (m, CH), 7.05–7.61 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -2.6$ (MeSi), 118.0 (CF_3), 126.0, 127.5, 135.6, 139.7 (Ph), 14.1, 116.9, 137.0 (Allyl). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +17.7$ (SiOTf), -16.9 (SiAllyl). Anal. Calc. for $\text{C}_{18}\text{H}_{21}\text{F}_3\text{O}_3\text{SSi}_2$ (430.6): C, 50.21; H, 4.92. Found: C, 49.83; H, 5.20.

8: $^1\text{H-NMR}$ (C_6D_6): $\delta = 0.65$ (d, MeSi), 3.87 (sept, SiH), 7.08–7.89 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 1.4$ (MeSi), 119.5 (CF_3), 127.0, 127.9, 136.2, 141.3 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +1.8$ (SiOTf), -35.7 (SiH). Anal. Calc. for $\text{C}_{10}\text{H}_{12}\text{F}_6\text{O}_6\text{S}_2\text{Si}_2$ (462.5): C, 25.97; H, 2.62. Found: C, 26.44; H, 2.44.

13: $^1\text{H-NMR}$ (C_6D_6): $\delta = 4.16$ (s, SiH), 7.09–7.73 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 117.6$ (CF_3), 126.6, 128.1, 136.0, 140.8 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +15.3$ (SiOTf), -77.0 (SiH). IR (film): $\nu = 2147$ (SiH) cm^{-1} . Anal. Calc. for $\text{C}_{26}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2\text{Si}_4$ (722.9): C, 43.20; H, 3.35. Found: C, 42.98; H, 3.45.

14: $^1\text{H-NMR}$ (C_6D_6): $\delta = 4.13$ (s, SiH), 7.11–7.64 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 111.2$ ($\text{C}\equiv\text{C}$), 117.3 (CF_3), 126.5–140.5 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +18.6$ (SiOTf), -72.9 (SiH). IR (film): $\nu = 2153$ (SiH), 2031 ($\text{C}\equiv\text{C}$) cm^{-1} . Anal. Calc. For $\text{C}_{28}\text{H}_{24}\text{F}_6\text{O}_6\text{S}_2\text{Si}_4$ (746.9): C, 45.02; H, 3.24. Found: C, 45.46; H, 3.01.

15: $^1\text{H-NMR}$ (C_6D_6): $\delta = 4.28$ (s, SiH), 6.97–7.71 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 127.0$ – 142.5 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = +17.3$ (SiOTf), -61.6 (SiH). IR (film): $\nu = 2156$ (SiH) cm^{-1} . Anal. Calc. For $\text{C}_{32}\text{H}_{28}\text{F}_6\text{O}_6\text{S}_2\text{Si}_4$ (799.0): C, 48.10; H 3.53. Found: C, 47.77; H, 3.39.

3.6. Synthesis of the polymers 17, 19, 21, 23 (general procedure)

The silyl bis(triflates) **13** or **14**, respectively (0.02 mol) dissolved in 100 ml of diethyl ether were added to a slurry or solution of the corresponding organolithium compound (Li_2C_2 or $\text{LiC}_4\text{H}_2\text{SLi}$, 0.021 mol), in 200 ml of THF, at 0 °C within 10 min. The reaction mixture was stirred at room temperature for 2 h. Afterwards 2 ml of isopropanol were added to destroy remaining traces of the organometallic reagents. The solvent was removed under reduced pressure and replaced by 300 ml of toluene. Lithium triflate precipitated as a white solid and was filtered off. Toluene was removed under vacuum leaving the polymers as yellow–brown powders in high yields.

17: M.p.: > 200 °C (dec.). $^1\text{H-NMR}$ (C_6D_6): $\delta = 3.92$ (s, SiH), 7.25–7.66 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 111.6$ ($\text{C}\equiv\text{C}$), 126.5–140.0 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -38.2$ (SiPh), -82.0 (SiH). IR (film): $\nu = 2146$ (SiH), 2036 ($\text{C}\equiv\text{C}$) cm^{-1} . $M_w = 8300$; $M_w:M_n = 2.5$. Anal. Calc. for $\text{C}_{26}\text{H}_{24}\text{Si}_4$ (448.8): C, 69.58; H, 5.39. Found: C, 69.77; H, 5.49.

19: M.p.: > 200 °C (dec.). $^1\text{H-NMR}$ (C_6D_6): $\delta = 4.04$ (s, SiH), 7.18–7.64 (Ph, Th). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 127.0$ – 141.5 (Ph, Th). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -21.3$ (SiPh), -82.4 (SiH). IR (film): $\nu = 2153$ (SiH) cm^{-1} . $M_w = 12400$; $M_w:M_n = 2.8$. Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{SSi}_4$ (506.9): C, 66.34; H, 5.17. Found: C, 66.18; H, 5.31.

21: M.p.: > 200 °C (dec.). $^1\text{H-NMR}$ (C_6D_6): $\delta = 3.87$ (s, SiH), 7.14–7.71 (Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = 111.6$, 112.2 ($\text{C}\equiv\text{C}$), 128.0–141.5 (Ph). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (C_6D_6): $\delta = -36.5$ (SiPh), -79.7 (SiH). IR (film): $\nu = 2145$ (SiH), 2038 ($\text{C}\equiv\text{C}$) cm^{-1} . $M_w = 15600$; $M_w:M_n = 2.7$. Anal. Calc. for $\text{C}_{28}\text{H}_{24}\text{Si}_4$ (472.8): C, 71.12; H, 5.12. Found: C, 71.31; H, 5.21.

23: M.p.: > 200 °C (dec.). ¹H-NMR (C₆D₆): δ = 3.99 (s, SiH), 7.12–7.66 (Ph, Th). ¹³C{¹H}-NMR (C₆D₆): δ = 111.8 (C≡C), 125.5–139.5 (Ph, Th). ²⁹Si{¹H}-NMR (C₆D₆): δ = –20.8 (SiPh), –78.9 (SiH). IR (film): ν = 2138 (SiH), 2041 (C≡C) cm^{–1}. M_w = 13 900; M_w:M_n = 2.6. Anal. Calc. for C₃₀H₂₆SSi₄ (530.9): C, 67.87; H, 4.94. Found: C, 68.01; H, 5.12.

3.7. Synthesis of the polymers **18** and **22** by reduction of silyl triflates with potassium graphite

A solution of the silyl bis(triflates) **13** or **14**, respectively (0.01 mol) in 150 ml of diethyl ether was stirred at 0 °C. Potassium graphite C₈K was added in small portions over a period of 2 h. Afterwards the mixture is stirred for 3 h at room temperature. During this time the colour was changing from gold bronze to black. The resulting graphite was filtered off. The solvent was removed under reduced pressure and replaced by 200 ml of toluene. Potassium triflate precipitated as a white solid and was filtered off. Toluene was removed under reduced pressure leaving the polymers as yellow–brown powders in 85–90% yield.

18: M.p.: > 200 °C (dec.). ¹H-NMR (C₆D₆): δ = 3.92 (s, SiH), 7.20–7.75 (Ph). ¹³C{¹H}-NMR (C₆D₆): δ = 127.0–139.5 (Ph). ²⁹Si{¹H}-NMR (C₆D₆): δ = –36.0 (SiPh), –84.7 (SiH). IR (film): ν = 2151 (SiH) cm^{–1}. M_w = 11100; M_w:M_n = 3.1. Anal. Calc. for C₂₄H₂₄Si₄ (424.8): C, 67.86; H, 5.69. Found: C, 67.77; H, 5.55.

22: M.p.: > 200 °C (dec.). ¹H-NMR (C₆D₆): δ = 3.83 (s, SiH), 7.12–7.70 (Ph). ¹³C{¹H}-NMR (C₆D₆): δ = 110.9 (C≡C), 127.0–139.5 (Ph). ²⁹Si{¹H}-NMR (C₆D₆): δ = –37.1 (SiPh), –81.5 (SiH). IR (film): ν = 2138 (SiH), 2040 (C≡C) cm^{–1}. M_w = 10 400; M_w:M_n = 2.9. Anal. Calc. for C₂₆H₂₄Si₄ (448.8): C, 69.58; H, 5.39. Found: C, 69.81; H, 5.44.

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