

Synthesis of oligosilyldi- and trianions

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Abstract

1,3- and 1,4-Bis[tris(trimethylsilyl)silylethynyl]benzenes as well as 1,3,5-tris[tris(trimethylsilyl)silylethynyl]benzene were synthesized employing Sonogashira cross-coupling conditions. All three molecules underwent facile di- or trimetalation with potassium *tert*-butoxide to afford the respective oligosilyldi- and trianions.

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1. Introduction

In our studies toward the chemistry of silylanions [1], we recently reported on the synthesis of a number of dianions [2]. These compounds are useful building blocks for the synthesis of homo- and heterocyclic oligosilanes or polymeric chains. The key-reaction in our studies is the conversion of oligosilanes with potassium alkoxides, typically *tert*-butoxide. The main advantage of this method over the generation of oligosilylanions using methylolithium is the high selectivity for cleaving terminal silicon–silicon bonds. This feature enables the selective formation of dianions by the reaction of a precursor with two equivalents of potassium alkoxides. It should also provide access to oligosilyltrianions from suitable precursor molecules. Such trianions may be used for the generation of polycyclic silanes or polysilane networks.

One important aspect of the chemistry of silylanions is to study the different substituent environments around silicon. Among the substituents found compatible with the formation of silylpotassium compounds the alkynyl group is especially interesting. The carbon-carbon triple bond allows for further derivatisation by means of hydro-

metalation or related reactions. In addition the group is also exhibiting a strongly activating influence on the oligosilane which facilitates the formation of the silylanions [3].

2. Results and discussion

Our first attempt to generate an example of an oligosilyltrianion was inspired by our previous strategy to obtain dianions. The concept which was successful for the dianion case was to link tris(trimethylsilyl)silyl groups with spacers such as alkyl [2a] or silyl [2b,2c,2d] chains.

A suitable starting material for the synthesis of a trianion, thus, would be a dendrimeric structure (Scheme 1) [4,5]. Dendrimer 1 [5a] (see Scheme 3) which can be obtained by conversion of tris(chlorodimethylsilyl)methylsilane with three equivalents of tris(trimethylsilyl)silylpotassium or -lithium was thought to be the right compound. Its reaction with three equivalents of potassium *tert*-butoxide, however, indicated formation of tris(trimethylsilyl)silylpotassium (2) as the only anionic oligosilane. This seemingly strange result hints at a back-biting mechanism. Previously, Gilman has pointed out that tris(trimethylsilyl)silyllithium can be used to obtain pentakis(trimethylsilyl)disilanylolithium from hexakis(trimethylsilyl)disilane. Recently, we have shown a similar reaction where bis(trimethylsilyl)methylsilylpotassium undergoes silyl exchange with tris(dimethylphenylsilyl)methylsilane

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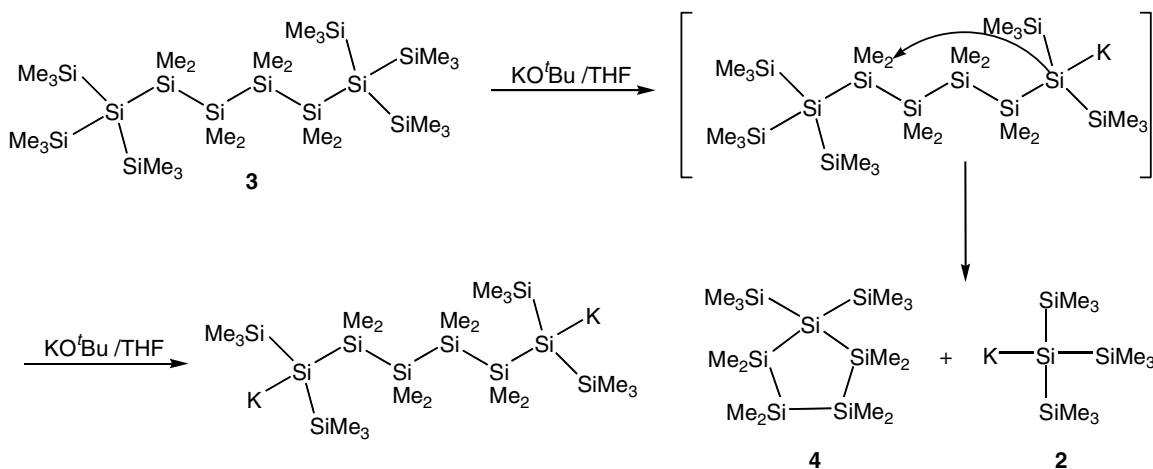
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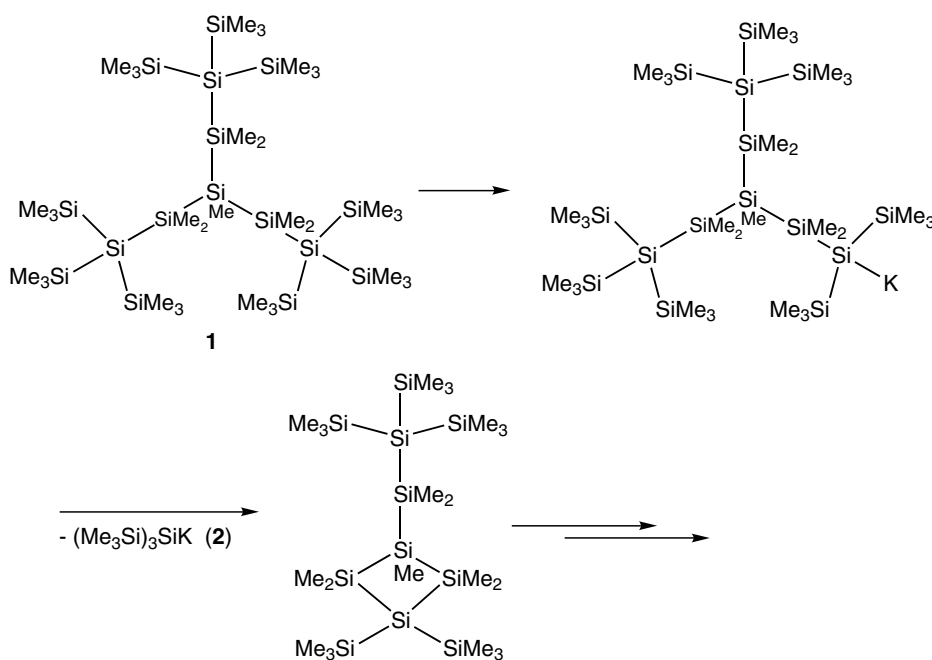
Scheme 1. Retrosynthetic analysis of a silyltrianion.

[1b]. Thus, silyl–metal exchange seems to be a thermo-neutral reaction which can be kinetically favored. A typical case was encountered during attempts to obtain a 1,6-dianion from the reaction of compound **3** with two equivalents of potassium *tert*-butoxide (Scheme 2). Initial formation of the mono-anion

was followed by intramolecular attack on the dimethylsilylene group in α -position to the tris(trimethylsilyl)silyl group. The generation of tris(trimethylsilyl)silylpotassium (**2**) and 1,1-bis(trimethylsilyl)octamethylcyclopentasilane [**6**] (**4**) was achieved this way.



Scheme 2. Intramolecular silyl metal exchange reaction.



Scheme 3. Intramolecular metalation process.

In a similar scenario the monoanion derived from **1** would be able to react in an intramolecular attack to give **2** and a cyclotetrasilane derivative (Scheme 3). Excess potassium *tert*-butoxide and **2** can ring-open the four-membered ring. The likely product again is a silylanion and can participate in similar chemistry (Scheme 3). The plethora of silylanions which can be formed and participate in follow-up reactions leads to a fairly complicated situation as indicated also by the ^{29}Si NMR spectrum of the reaction.

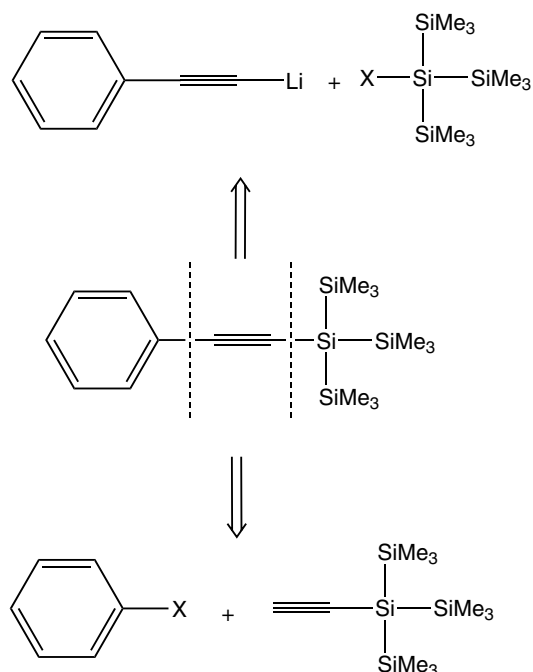
2.1. Synthesis of oligosilylalkynyl benzenes

To avoid a back-biting mechanism we decided to introduce a rigid spacer instead of the isotetrasilanyl unit. A benzene substituted in 1-, 3- and 5-position was thought to be a good core unit. As 1,3,5-tris[tris(trimethylsilyl)silyl]benzene and even 1,3-bis[tris(trimethylsilyl)silyl]benzene are not known we decided to employ a 1,3,5-triethynylbenzene core instead. As it was shown that alkynyloligosilanes undergo metalation with potassium *tert*-butoxide easily this would further facilitate formation of a trianion [3].

For the synthesis of oligosilylalkynylbenzenes we considered two different strategies (Scheme 4). Depending on what bonds would be closed in the product forming step the possible options are either reaction of lithiated arylalkynes with halosilanes or cross-coupling reaction of aryl halides with silyl alkynes.

Both synthetic routes consist of a Sonogahira–Hagihara-coupling and a salt elimination step. To test the first option we prepared 1,4-diethynylbenzene by cross-coupling of the respective iodobenzene with trimethylsilylacetylene and subsequent deprotection. The diethynylbenzene could be dilithiated with methyl lithium and then was treated with tris(trimethylsilyl)silylchloride (Scheme 5). While the cross-coupling reaction and also the subsequent deprotection could be carried out in an almost quantitative manner the final salt elimination gave a disappointingly low (by no means optimized) yield of 12% (Scheme 5).

The second approach attempted direct cross-coupling of tris(trimethylsilyl)silylacetylene with the respective iodobenzenes. After some initial difficulties it was found that the purity of the iodobenzenes [7,8] was crucial for the success of the reactions [9]. The coupling of iodobenzene with the alkynyl silanes was done employing a modified Sonogahira–Hagihara-coupling protocol [7,10]. In all three



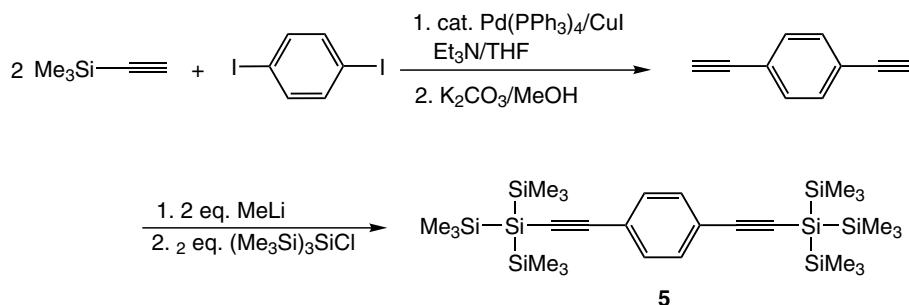
Scheme 4. Synthetic strategies for oligosilylethynylbenzene formation.

cases an excess of tris(trimethylsilyl)silylacetylene was used in order to reduce the reaction times. Unchanged material was recovered afterwards (Scheme 6). Isolated yields in all three cases were excellent.

2.2. Preparation of alkynylsilylanions

With compounds **5**, **6**, and **7** in hand the formation of dianions and the trianion could be attempted. The conversion to the respective di- or trianions with potassium *tert*-butanolate in THF proceeded smoothly at room temperature within minutes and even at $-20\text{ }^\circ\text{C}$ within less than 1 h (Scheme 7). Attempts to obtain monoanion, employing only one equivalent of potassium alkoxides led to the formation of mixtures of starting material, mono-metalated and dimetalated compound. Clearly, the influence of a negative charge on the molecule on the next metalation step seems to be very small.

All anions could be further alkylated toward the methyl compounds **5b**, **6b**, and **7b** employing dimethyl sulfate (Scheme 8).



Scheme 5. Synthesis of 1,4-bis[tris(trimethylsilyl)silylethynyl]benzene (**5**).

us were either oils or solids with melting points close to room temperature. Nevertheless, we were able to determine crystal structures of compounds **5** and **6** (Table 1, Figs. 1 and 3). The structural features of both compounds are within the ranges of what could be predicted. The unit cell of **5** contains two independent molecules, one with strongly disordered trimethylsilyl groups, the other one is shown in Fig. 1. The crystal packing in the unit cell of **5** and **6** is interesting and shown in Figs. 2 and 4. CH/ π interactions [13] seem to play a role. The intermolecular close contacts

Table 1
Crystallographic data for compounds **5** and **6**

Compound	5	6
Empirical formula	C ₂₈ H ₅₈ Si ₈	C ₂₈ H ₅₈ Si ₈
Molecular weight	619.46	619.46
<i>T</i> (K)	213(2)	213(2)
Size (mm)	0.56 × 0.30 × 0.28	0.48 × 0.42 × 0.38
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.5262(19)	9.1046(18)
<i>b</i> (Å)	23.493(5)	16.475(3)
<i>c</i> (Å)	19.603(4)	29.780(6)
α (°)	90	90
β (°)	96.90(3)	90.91(3)
γ (°)	90	90
<i>V</i> (Å ³)	4355.5(15)	4466.4(15)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	0.945	0.921
Absorption coefficient (mm ⁻¹)	0.261	0.254
<i>F</i> (000)	1352	1352
θ Range (°)	1.73 < θ < 21.96	1.37 < θ < 20.81
Reflections collected/unique	23 170/5297	20 921/4662
Completeness to θ (%)	99.8	99.8
Data/restraints/parameters	5297/36/443	4664/0/343
Goodness-of-fit on <i>F</i> ²	1.071	1.537
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1727	<i>R</i> ₁ = 0.0935, <i>wR</i> ₂ = 0.3127
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0685, <i>wR</i> ₂ = 0.1818	<i>R</i> ₁ = 0.0989, <i>wR</i> ₂ = 0.3263
Largest difference in peak and hole (e Å ⁻³)	0.532 and -0.201	1.272 and -0.336

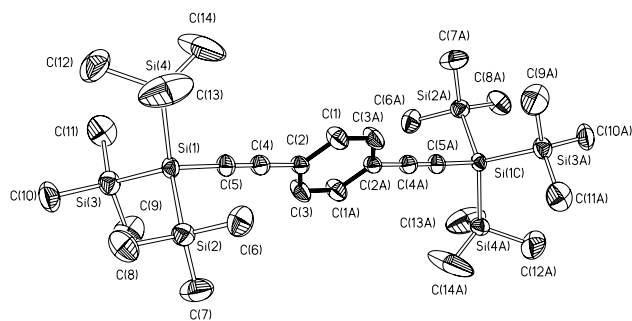


Fig. 1. The molecular structure and numbering of **5** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°) with standard uncertainties: Si(1)–C(5) 1.833(4), Si(1)–Si(2) 2.3304(15), Si(1)–Si(3) 2.3380(15), Si(1)–Si(4) 2.3529(15), C(4)–C(5) 1.193(5), C(5)–C(4)–C(2) 179.5(4), C(4)–C(5)–Si(1) 178.7(3), Si(2)–Si(1)–C(5)–C(4) 61(16), Si(3)–Si(1)–C(5)–C(4) –58(16), Si(4)–Si(1)–C(5)–C(4) –178(100).

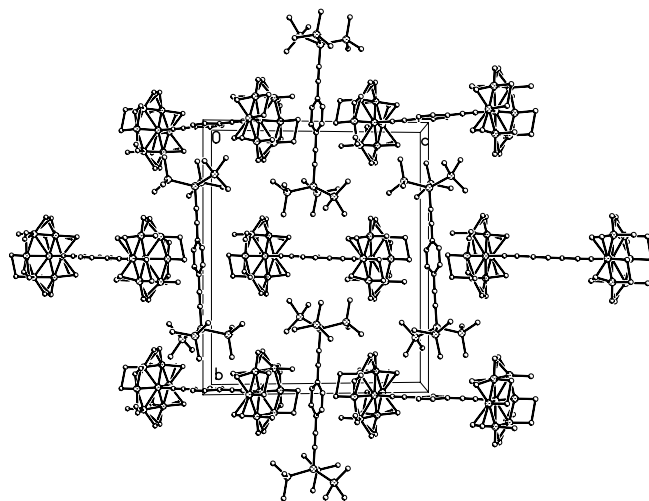


Fig. 2. Perspective view of crystal packing in compound **5**. Hydrogen atoms omitted for clarity.

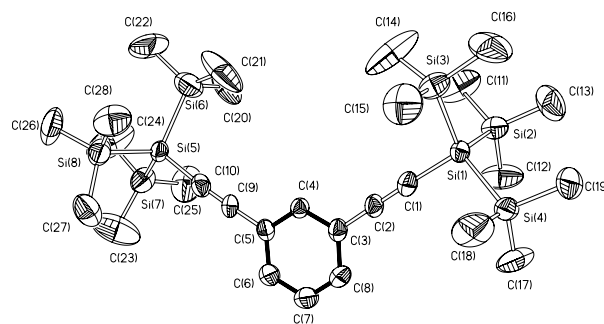


Fig. 3. The molecular structure and numbering of **6** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°) with standard uncertainties: Si(1)–C(1) 1.851(6), Si(1)–Si(3) 2.338(2), Si(1)–Si(4) 2.339(2), Si(1)–Si(2) 2.349(2), Si(5)–C(10) 1.848(7), C(1)–C(2) 1.218(7), C(9)–C(10) 1.197(7), C(1)–Si(1)–Si(3) 107.25(18), C(1)–Si(1)–Si(4) 103.93(17), Si(3)–Si(1)–Si(4) 114.90(9), Si(3)–Si(1)–Si(2) 111.18(8), C(10)–Si(5)–Si(8) 104.86(19), C(2)–C(1)–Si(1) 178.0(5), C(1)–C(2)–C(3) 176.4(5), C(10)–C(9)–C(5) 177.8(6), C(9)–C(10)–Si(5) 176.2(5), Si(2)–Si(1)–C(1)–C(2) 125(14), Si(1)–C(1)–C(2)–C(3) –117(14).

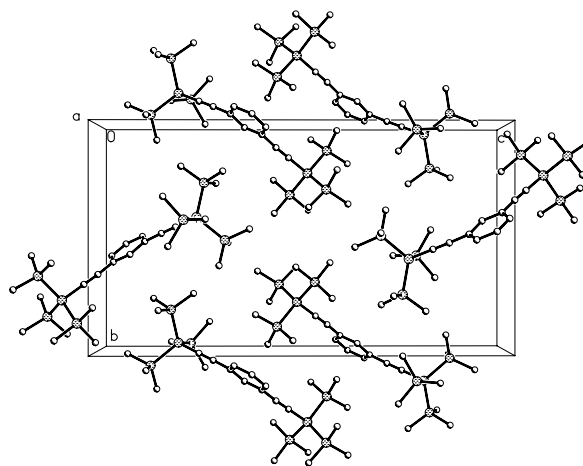


Fig. 4. Perspective view of crystal packing in compound **6**. Hydrogen atoms omitted for clarity.

of C–H distances between the carbons of the aromatic ring and the hydrogen atoms of a methyl group ranged from 3.02 up to 3.39 Å in **5** and from 3.18 to 3.28 Å in **6**.

Examples for the acetylenic triple bond length of alkylnylsilanes range from 1.16 to 1.22 Å [14]. Compounds **5** (1.193(5) and 1.204(4) Å) and **6** (1.197(7), 1.218(7) Å) fit into this. Deviations from the expected 180° for the CCSi angle are comparatively small for **5** (178.4(3)° and 178.7(3)°) and **6** (178.0(5)° and 176.2(5)°).

3. Conclusion

In an attempt to obtain dendrimeric oligosilanes which contain three silylanionic units it was found that back-biting of an anionic part into one of the chains is a serious problem. In order to avoid such behavior di- and trialkynylphenyl units were employed as cores of the starting materials. The use of the alkynyl substituents facilitates the formation of silylanions via reaction with potassium alkoxides. It also prevents the back-biting process and thus allowed for the formation of the first example of an oligosilyltrianion.

With respect to the use of silyltrianions for the synthesis of polycyclic compounds or tripodal ligands the change from the originally perceived isotetrasilanyl core to a trialkynylphenyl unit has to be considered as a drawback. The flat geometry of the spacer unit prevents the formation of small rings. However, the use of a trianion for the generation of polysilane networks is greatly facilitated by this geometry. The formation of the oligosilylmagnesium polymers can already be seen as a first example. With respect to the electronic properties of polysilanes which are altered by the incorporation of the phenylalkynyl groups further investigations in this direction are on the way.

4. Experimental

4.1. General remarks

All reactions involving air-sensitive compounds were carried out under an atmosphere of nitrogen or argon using either Schlenk techniques or a glovebox. All solvents besides CDCl₃ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butanolate was purchased exclusively from Merck. 1,3-Diiodobenzene was purchased from Aldrich but had to be further purified by Kugelrohr-distillation and additional recrystallization from ethanol to obtain colorless crystals without any yellow color.

Aqueous work-up was performed by pouring the reaction mixture on 1 M HCl/50 mL Et₂O and separation of the layers. Subsequently, the aqueous layer was extracted twice with Et₂O. The combined organic layers were washed with a saturated aqueous sodium hydrogen carbonate solution and then dried over sodium sulfate.

¹H (300 MHz), ¹³C (75.4 MHz), and ²⁹Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300

spectrometer. Samples for ²⁹Si spectra were either dissolved in deuterated benzene or chloroform, or in case of reaction samples measured with a D₂O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ²⁹Si the INEPT pulse sequence was used for the amplification of the signal [15].

GC analyses were carried out on a HP 5890 series II equipped with capillary column HP-1 ms (25 m × 0.251 mm; 0.33 μm) and a HP 5971 mass spectrometer. The MS fragmentation pattern is given for every substance, relative intensities are given in brackets.

GC/MS samples of the derivatized silylanions were obtained by adding a solution of the nucleophile to a mixture of 10% ethyl bromide in diethyl ether or to the organic layer of a mixture of diethyl ether/2 M H₂SO₄ to give the corresponding ethyl-, respectively, hydro-silane species in a very rapid, clean and quantitative reaction.

Elementary analysis was carried out using a Heraeus VARIO ELEMENTAR. As found on numerous other occasions for silylpotassium compounds no satisfactory elementary analysis data could be obtained.

For X-ray structure analysis the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer. The data were reduced to F_o^2 and corrected for absorption effects with SAINT [16] and SADABS [17], respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL-97) [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles.

Tris(trimethylsilyl)silylacetylene [1c], and 1,4-diethynylbenzene [19] were prepared according to literature procedures.

4.2. 1,4-Bis[2-(tris(trimethylsilyl)silyl)ethynyl]benzene (5): (Salt elimination procedure)

To a solution of 1,4-diethynylbenzene (412 mg, 3.27 mmol) in diethyl ether (30 mL) at –70 °C methyllithium (1.6 molar solution in ether, 4.08 mL, 6.53 mmol) was added dropwise. After 30 min the reaction was allowed to reach ambient temperature. This solution was added dropwise to a solution of chlorotris(trimethylsilyl)silane (1.85 g, 6.53 mmol) in ether (50 mL) which was cooled to –70 °C. After 2 h the solution was allowed to warm up and a white salt precipitated. After 2 h the reaction was poured on a mixture of ice sulfuric acid (2 molar, 50 mL) and ether (50 mL). The aqueous layer was saturated with rock salt and twice washed with portions of ether (50 mL each). The combined organic layers were dried over sodium sulfate and the solvent evaporated. The slightly yellow waxy residue contained substantial amounts of methyltris(trimethylsilyl)silane which was removed using Kugelrohr distillation. The remaining solid gave identical spectroscopic data as

the product obtained via the alternative Sonogashira coupling route.

4.3. 1,4-Bis[2-(tris(trimethylsilyl)silyl)ethynyl]benzene (5): (Sonogashira coupling)

Preparation of the catalyst: To Pd(dba)₂ (174 mg, 0.303 mmol) and PPh₃ (318 mg, 1.21 mmol) THF (5 mL) was added. The solution became bright yellow-orange after a few minutes.

To a suspension of 1,4-diiodobenzene (1.00 g, 3.03 mmol), CuI (115 mg, 0.606 mmol), and tris(trimethylsilyl)silylacetylene (4.92 g, 18.0 mmol) in THF (20 mL) the solution of catalyst and Et₃N (5.0 mL, 36 mmol) were added. The mixture was stirred for 4 days at room temperature before aqueous work-up, flash chromatography with n-heptane and Kugelrohr distillation yielded **5** (1.75 g, 93%) as colorless crystals. mp 118–121 °C. Tris(trimethylsilyl)silylacetylene (1.8 g) could be recovered unchanged. ¹H NMR (C₆D₆) δ = 7.20 (s, 4H), 0.31 (s, 54H) ppm. ¹³C NMR (C₆D₆) δ 131.9, 124.0, 109.1, 90.3, 0.4 ppm. ²⁹Si NMR (C₆D₆) δ = -11.7, -100.7 ppm. MS: *m/z* 618(80) M⁺; 603(15) M⁺ - Me, 545(20) M⁺ - SiMe₃, 174(100) Si(SiMe₃)₂, 73(98) SiMe₃. Anal. Calc. for C₂₈H₅₈Si₈: C 54.29, H 9.44. Found: C 53.91, H 9.24%.

4.4. 1,3-Bis[2-(tris(trimethylsilyl)silyl)ethynyl]benzene (6)

Preparation of the catalyst according to the procedure for 5: Pd(dba)₂ (164 mg, 0.285 mmol), PPh₃ (299 mg, 1.14 mmol), and THF (5 mL). Similar procedure as for compound **5** using 1,3-diiodobenzene (940 mg, 2.85 mmol), tris(trimethylsilyl)silylacetylene (3.20 g, 11.7 mmol), THF (15 mL), CuI (108 mg, 0.570 mmol), and Et₃N (4.0 mL, 29 mmol). The mixture was stirred for 12 h at 55 °C and then for 3 days at room temperature. After purification **6** (1.63 g, 92%) was obtained as colorless crystals. mp 99–104 °C. Tris(trimethylsilyl)silylacetylene (1.0 g) could be recovered unchanged. ¹H NMR (C₆D₆) δ = 7.82 (dt, 1H, *J* = 0.6, 1.7 Hz), 7.23 (dd, 2H, *J* = 1.7, 7.7 Hz), 6.70 (dt, 1H, *J* = 0.6, 7.7 Hz), 0.28 (s, 54H) ppm. ¹³C NMR (C₆D₆) δ 135.1, 131.3, 128.5, 125.0, 108.5, 89.1, 0.4 ppm. ²⁹Si NMR (C₆D₆) δ = -11.7, -100.6 ppm. MS: *m/z* 618(80) M⁺; 603(15) M⁺ - Me, 545(20) M⁺ - SiMe₃, 174(100) Si(SiMe₃)₂, 73(98) SiMe₃. Anal. Calc. for C₂₈H₅₈Si₈: C 54.29, H 9.44. Found: C 53.87, H 9.37%.

4.5. 1,3,5-Tris[2-(tris(trimethylsilyl)silyl)ethynyl]benzene (7)

4.5.1. 1,3,5-Tris(trimethylsilyl)benzene

To 1,3,5-tribromobenzene (10.1 g, 32.0 mmol) in THF (60 mL) trimethylsilylchloride (25.0 mL, 197 mmol) was added drop-wise. The solution was cooled to -80 °C and *n*-BuLi (1.6 M/hexane, 90 mL, 144 mmol) was added drop-wise over a period of 90 min. After further 2 h at this temperature the reaction was allowed to reach room temperature

and poured on saturated NH₄Cl. The aqueous layer was extracted three times with CH₂Cl₂ and the combined organic layers dried over sodium sulfate. The solvent was removed in vacuo and the residue was subjected to a Kugelrohr distillation. 1,3,5-Tris(trimethylsilyl)benzene (8.9 g, 94%) was obtained as a colorless oil. ¹H NMR (CDCl₃) δ = 7.76 (s, 3H), 0.36 (s, 27H) ppm. ¹³C NMR (CDCl₃) δ 139.1, 138.6, -0.8 ppm. MS: *m/z* 294(13) M⁺; 279(100) M⁺ - Me; 73(54) SiMe₃.

4.5.2. 1,3,5-Triiodobenzene

1,3,5-Tris(trimethylsilyl)benzene (4.96 g, 16.8 mmol) was dissolved in CCl₄ (100 mL) and ICl (16.8 g, 103 mmol) was added at room temperature. After stirring for 24 h the excess of ICl was removed by adding 200 mL of a saturated Na₂S₂O₃ solution. The aqueous layer was extracted twice with CH₂Cl₂ and the combined organic layers were dried over sodium sulfate. The solvent was concentrated in vacuo until crystallization started. The remaining solution was slowly cooled to 0 °C and the precipitated solid was filtered off (mp 173–178 °C). After a further recrystallization step from ethanol (about 400 mL) 1,3,5-triiodobenzene (2.78 g, 36%) was obtained as colorless crystals (mp 178–180 °C). ¹H NMR (CDCl₃) δ = 8.03 (s, 3H) ppm. ¹³C NMR (CDCl₃) δ 144.7, 95.6 ppm. MS: *m/z* 456(100) M⁺; 329(40) M⁺ - I; 202(28) M⁺ - 2I; 75(80) M⁺ - 3I.

4.5.3. Synthesis of 7

Preparation of the catalyst according to the procedure for 5: Pd(dba)₂ (240 mg, 0.417 mmol), PPh₃ (437 mg, 1.67 mmol), and THF (5 mL). A similar procedure as for compound **5** using 1,3,5-triiodobenzene (1.00 g, 2.19 mmol), tris(trimethylsilyl)silylacetylene (5.40 g, 19.8 mmol), THF (10 mL), CuI (159 mg, 0.834 mmol), and Et₃N (5.0 mL, 36 mmol) was employed. After purification **7** (1.72 g, 88%) was obtained as colorless crystals. mp 133–141 °C. Tris(trimethylsilyl)silylacetylene (2.15 g) could be recovered unchanged. ¹H NMR (C₆D₆) δ = 7.68 (s, 3H), 0.28 (s, 81H) ppm. ¹³C NMR (C₆D₆) δ 134.5, 125.6, 107.7, 90.5, 0.5 ppm. ²⁹Si NMR (CDCl₃) δ = -11.4, -100.4 ppm. MS: *m/z* 888(2) M⁺; 618(17) M⁺ - Si(SiMe₃)₃ + H, 348(10) M⁺ - 2Si(SiMe₃)₃ + H, 174(30) Si(SiMe₃)₂, 73(100) SiMe₃. Anal. Calc. for C₃₉H₈₄Si₁₂: C 52.63, H 9.51. Found: C 52.13, H 9.52%.

4.6. General procedure for the synthesis of potassiumsilyls

In a nitrogen filled glove box the respective silane and potassium *tert*-butanolate (1.05 equiv for the mono-, 2.10 equiv for the di-, and 3.17 equiv for the tripotassium compounds) are dissolved in THF. The solution immediately turns to dark red. After 30 min complete conversion was monitored by ²⁹Si NMR spectroscopy of a small aliquot (0.1 mL (C₆D₆) was added for internal lock).

4.6.1. 1,4-Bis[bis(trimethylsilyl)silyl]ethynyl]benzene-dipotassium (5a)

¹H NMR (C₆D₆, THF, THF-*d*₈) δ = 7.18 (s, 4H), 0.58 (s, 36H) ppm. ¹³C NMR (C₆D₆, THF, THF-*d*₈) δ 129.9,

123.8, 116.5, 108.2, 3.8 ppm. ^{29}Si NMR (THF/ C_6D_6) $\delta = -7.3, -154.8$ ppm.

4.6.2. 1,3-Bis[*bis*(trimethylsilyl)silyl]ethynyl]benzene-dipotassium (**6a**)

^1H NMR (C_6D_6 , THF, THF- d_8) $\delta = 7.24$ (m, 1H), 7.03 (d, 2H, $J = 7.4$ Hz), 6.87 (t, 1H, $J = 7.4$ Hz), 0.58 (s, 36H) ppm. ^{13}C NMR (C_6D_6 , THF, THF- d_8) $\delta = 130.9, 130.3, 127.7, 126.3, 116.0, 107.9, 3.8$ ppm. ^{29}Si NMR (THF/ C_6D_6) $\delta = -7.3, -155.3$ ppm.

4.6.3. 1,3,5-Tris[*bis*(trimethylsilyl)silyl]ethynyl]benzene-tripotassium (**7a**)

^1H NMR (C_6D_6 , THF, THF- d_8) $\delta = 7.10$ (s, 3H), 0.56 (s, 54H), 0.24 (s, 36H) ppm. ^{13}C NMR (C_6D_6 , THF, THF- d_8) $\delta = 127.2, 125.3, 114.3, 107.4, 3.8$ ppm. ^{29}Si NMR (THF/ C_6D_6) $\delta = -7.7, -155.3$ ppm.

4.6.4. 1,4-Bis[*bis*(trimethylsilyl)methylsilyl]ethynyl]benzene (**5b**)

To dimethylsulfate (0.26 mmol) in diethylether (3 mL) the dipotassium compound **5a** (0.09 mmol) in THF (2 mL) was added at 0 °C. The dark red color disappeared immediately. The solution was stirred for 2 h at room temperature before it was subjected to an extractive work-up. A colorless oil of **7** (42 mg, 99%) was obtained. ^1H NMR (C_6D_6) $\delta = 7.22$ (s, 4H), 0.34 (s, 3H), 0.24 (s, 36H) ppm. ^{13}C NMR (C_6D_6) $\delta = 132.2, 131.9, 109.0, 93.5, -1.4, -7.9$ ppm. ^{29}Si NMR (C_6D_6) $\delta = -15.3, -64.3$ ppm.

4.6.5. 1,3-Bis[*bis*(trimethylsilyl)methylsilyl]ethynyl]benzene (**6b**)

Similar procedure as for compound **5b** using **6a** (0.09 mmol) and dimethylsulfate (0.26 mmol). Compound **6b** (43 mg, 100%) was obtained as a colorless oil. ^1H NMR (C_6D_6) $\delta = 7.75$ (t, 1H, $J = 1.6$ Hz), 7.25 (dd, 2H, $J = 1.6; 7.8$ Hz), 6.67 (t, 1H, $J = 7.8$ Hz), 0.32 (s, 9H), 0.23 (s, 18H), 0.22 (s, 18H) ppm. ^{13}C NMR (C_6D_6) $\delta = 135.5, 131.6, 128.6, 124.6, 108.4, 92.2, -1.5, -7.9$ ppm. ^{29}Si NMR (C_6D_6) $\delta = -15.3, -64.3$ ppm.

4.6.6. 1,3,5-Tris[2-(*bis*(trimethylsilyl)methylsilyl)ethynyl]benzene (**7b**)

Similar procedure as for compound **5b** using **7a** (0.06 mmol) and dimethylsulfate (0.26 mmol). Compound **7b** (44 mg, 100%) was obtained as a colorless oil. ^1H NMR (C_6D_6) $\delta = 7.67$ (s, 3H), 0.21 (s, 9H), 0.20 (s, 27H), 0.19 (s, 27H) ppm. ^{13}C NMR (C_6D_6) $\delta = 134.6, 125.0, 107.4, 93.4, -1.5, -8.0$ ppm. ^{29}Si NMR (C_6D_6) $\delta = -15.3, -64.2$ ppm.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures of compounds **5** and **6** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-

272831 for **5**, and 272832 for **6**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44 1223 336 033; e-mail: deposit@chemcrs.cam.ac.uk).

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