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LETTER

Selective ring opening of 4*H*-1,3,2-benzodioxasiline twin monomers†

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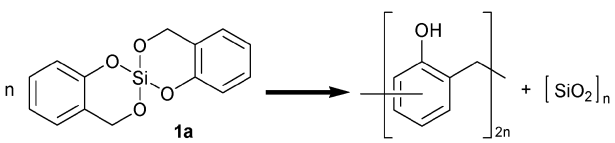
4*H*-1,3,2-Benzodioxasilines represent a class of monomers, which are suitable for the recently developed concept of twin polymerization. Relating to the prediction of quantum chemical calculations we are now able to confirm the results for the first step of the reaction: the selective ring opening of 4*H*-1,3,2-benzodioxasilines. An electrophilic attack of iodotrimethylsilane leads firstly to a bond cleavage at the oxymethylene group and not at the more stable Si–O–aryl bond, yielding ring-opened species.

In previous works the twin polymerization of different monomers, which were combinations of inorganic and organic moieties, was reported.[1–5] Especially the use of furfuryl and 2-hydroxybenzyl ethers of silicon, titanium or tungsten led to monomers, which were polymerized to inorganic–organic nanocomposites in a simple cationic catalysis process without any further requirements in reaction control (Scheme 1).[1–5]

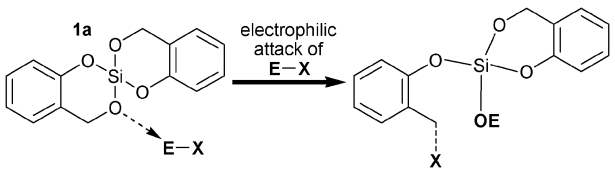
Quantum chemical calculations of the cationic polymerization process of 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] (**1a**) proposed a selective ring opening of the bidentate 2-hydroxybenzyl alcohol (salicyl alcohol) at the oxymethylene group by electrophilic attack of a proton as the first step in the cationic catalysis.[4] Here we report on our experimental results, which prove the predicted selective ring opening of **1a** and further 4*H*-1,3,2-benzodioxasilines (Scheme 2).

The search for electrophiles, which are suitable to perform a mechanistic investigation, included different difficulties. The use of Brønsted acids would lead to the formation of silanols and therefore to additional side reactions, such as condensation and hydrolysis. On the other hand, electrophilic CH_3I and $(CH_3)_3SiCl$ were not reactive enough to open the ring of 4*H*-1,3,2-benzodioxasilines. The use of $(CH_3)_2SO_4$ led to an immediate polymerization resulting in phenolic resins, because the anion was not able to form a stable bond with the reactive benzyl cation (see ESI†).

Fortunately, the use of iodotrimethylsilane was suitable to open the ring of the used 4*H*-1,3,2-benzodioxasilines yielding benzyl iodides,[6] which were stable long enough for the used analyzing procedures before a polymerization process



Scheme 1 Twin polymerization of **1a** to phenolic resin and silica.



Scheme 2 Selective ring opening reaction of **1a** by an electrophilic attack on the oxymethylene group.

consumed all ring-opened reactive benzyl iodide species. This reaction was investigated with three different 4*H*-1,3,2-benzodioxasilines: **1a**,[4] 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline (**2a**),[7] and the new compound 2,2'-spirobi[8-tert-butyl-6-methyl-4*H*-1,3,2-benzodioxasiline] (**3a**).

Spiro compounds **1a** and **3a** are chiral substances, each consisting of two enantiomers (racemic mixture). The ^{1}H NMR signals of the diastereotopic hydrogens of the methylene bridges of **1a** and **3a** have a quite small difference in their chemical shifts, and due to geminal coupling (^2J) two close doublets with a strong roofing effect occur (see ESI†).

Iodotrimethylsilane was used in nearly equimolar ratios relative to the present number of 4*H*-1,3,2-benzodioxasiline rings. At 25 °C the solid substances **1a** and **3a** were dissolved in d_2-dichloromethane (CD_2Cl_2) before iodotrimethylsilane was added. The reaction mixture was analyzed directly *via* NMR spectroscopy. The liquid substance **2a** was reacted without prior dissolving and only samples of the reaction mixture were diluted in CD_2Cl_2 for the NMR analyses. ^{1}H, ^{13}C and ^{29}Si NMR spectra were taken immediately after addition of iodotrimethylsilane and at further time intervals; an overview of the product spectra is given in Fig. 1.

After the ring-opening reaction with iodotrimethylsilane the ^{1}H NMR signals of the iodomethylene hydrogens of **1b**, **2b**, and **3b** are shifted to a higher field compared to the oxymethylene groups of **1a**, **2a**, and **3a**. In the ^{13}C NMR spectra a strong shift to high field of $\Delta\delta \approx 63$ ppm occurs, due to the strong heavy-atom effect of iodine. The ^{13}C NMR signals of the

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† Electronic supplementary information (ESI) available: Mass spectrograms, further reaction information, additional NMR analyses and information on derivatization reactions. See DOI: 10.1039/c1nj20654k

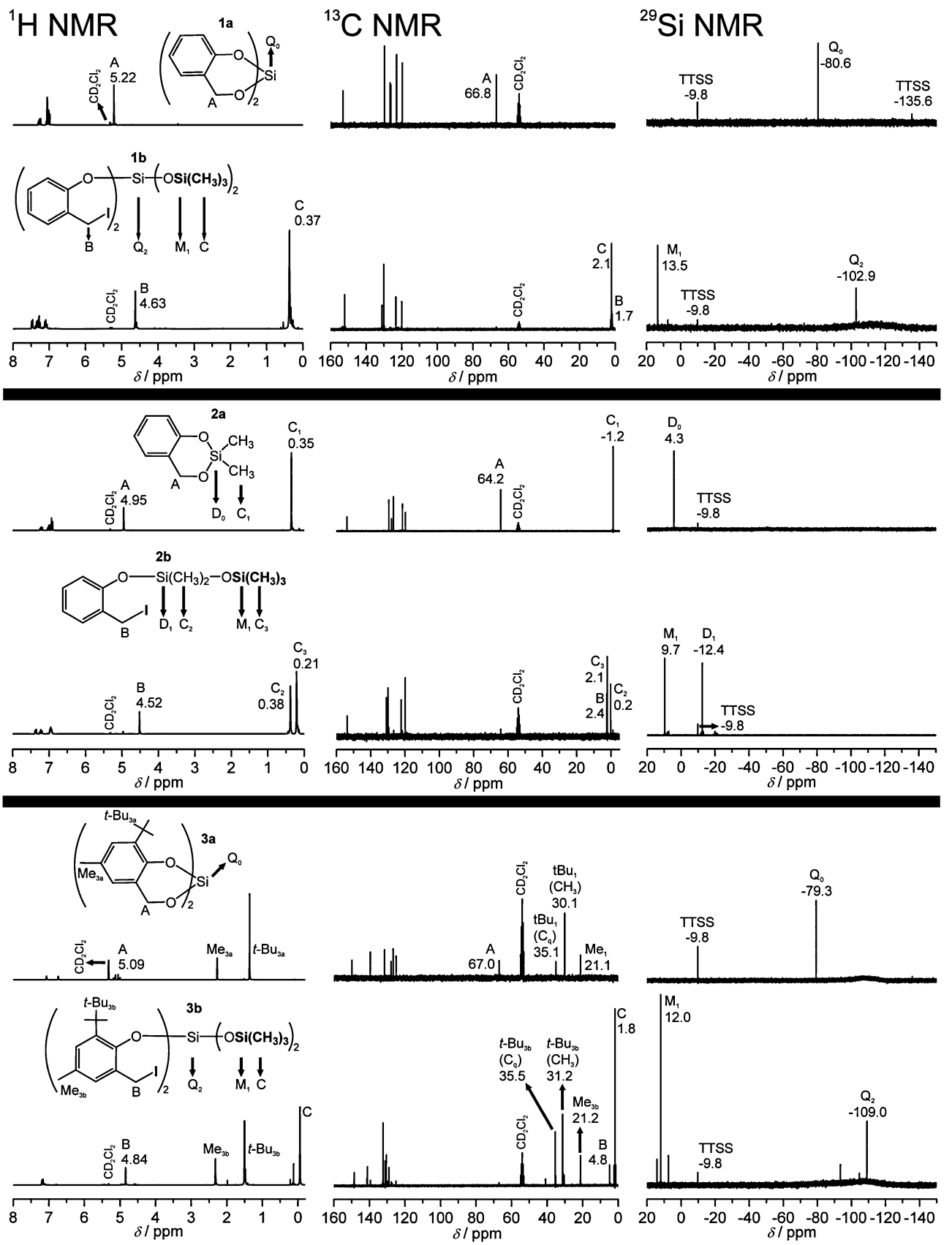

Fig. 1 NMR spectra of educts **1a**, **2a**, and **3a** in CD_2Cl_2 and their ring-opened products **1b**, **2b**, and **3b** in their reaction mixtures are depicted. ^{1}H, ^{13}C and ^{29}Si NMR spectra are arranged from the left to the right and are referenced to CD_2Cl_2 [$\delta(^{1}H/^{13}C)$ = 5.32/54.0 ppm] and tetrakis(trimethylsilyl)silane (TTSS, TMS_4Si) [$\delta(^{29}SiMe_3)$ = −9.8 ppm]. Magnifications of the spectra are depicted in the ESI† as well as NMR data of side products.

iodomethylene groups have chemical shifts of δ = 1–5 ppm and are very close to the signals of the trimethylsilyl groups, they were distinguished by means of $^{1}H/^{13}C$-HMQC NMR spectroscopy (for 2D NMR signal assignment see ESI†). ^{29}Si NMR proves conversion to ring-opened benzyl iodides, too (conventional labeling is used: M, D, T, Q).[8]

Besides the selective ring-opening reaction the occurrence of a small amount of side reactions cannot be excluded. Iodotrimethylsilane is also able to interact with the surface of the used glass flasks, small moieties of trimethylsilyl species such as trimethylsilanol (TMSOH), hexamethyldisiloxane (TMS_2O), and tetrakis(trimethylsiloxy)silane ($TMSO_4Si$) are able to form (see ESI†). Another side reaction represents the polymerization tendency of unstable benzyl iodide species, especially in higher concentrations and without cooling. The polymerization process leads to dimer and oligomer species and finally to the formation of phenolic resins and involves the condensation of reactive hydroiodic acid, which will lead to further side reactions and can act as a catalyst. Typically, the methylene group of phenolic resins has a chemical NMR shift of $\delta(^{1}H) \approx 3.9$ ppm in CD_2Cl_2. When mass spectrometry was applied for the characterization of the ring-opened benzyl iodides only very soft ionization conditions led to a product spectrogram equivalent to the NMR spectra, otherwise dimers were observed or even no more clear spectrograms were obtained (see ESI†). Redox processes probably lead to the formation of spurious iodine, which explains the increasing coloration intensity (red-brownish) of the reaction mixture. Side reactions of iodotrimethylsilane and its sub-equimolar use also explain remaining small amounts of educts (**1a**, **2a**, **3a**) and only single ring-opened intermediate species (in the case of **1a** and **3a**). That is why exact knowledge about the time-, solvent- and concentration-dependence of this reaction had to be explored in order to obtain the ring-opened benzyl iodide in nearly quantitative yields.

Under the used reaction conditions the nearly quantitative conversion of **1a** and **2a** into **1b** and **2b** occurred in about 5–20 min (see Fig. 1 and the experimental part). A nearly quantitative conversion of **3a** into **3b** is achieved after hours (^{1}H NMR of **3b** in Fig. 1 was taken after 11 h). Being sterically blocked and, due to its lower solubility, more dilute, **3a** showed a slower reaction rate and therefore undesired side reactions of iodotrimethylsilane increased slightly.

At 25 °C and at the used concentrations **1b** and **2b** were only stable for some hours and polymerized slowly to phenolic resins. Diluting and freezing down the reaction mixture decelerated this process. At 25 °C and at the used concentration **3b** was stable for several days and almost no polymerization species was observed after 5 days. This difference to **1b** and **2b** is due to the full substitution of all *ortho*- and *para*-positions of the phenolic ring. Electrophilic attack and substitution with benzylic species is therefore rather improbable.

In order to stabilize the ring-opened benzyl iodides they must be further derivatized. Among different possibilities, nucleophilic substitution of iodide yielded stable molecules that were isolated as shown in the ESI.† Of course only aprotic nucleophiles were tested, because the liberation of hydrogen iodide interferes and could cleave the siloxy groups. Ionic nucleophiles often require strong polar solvents, which are to

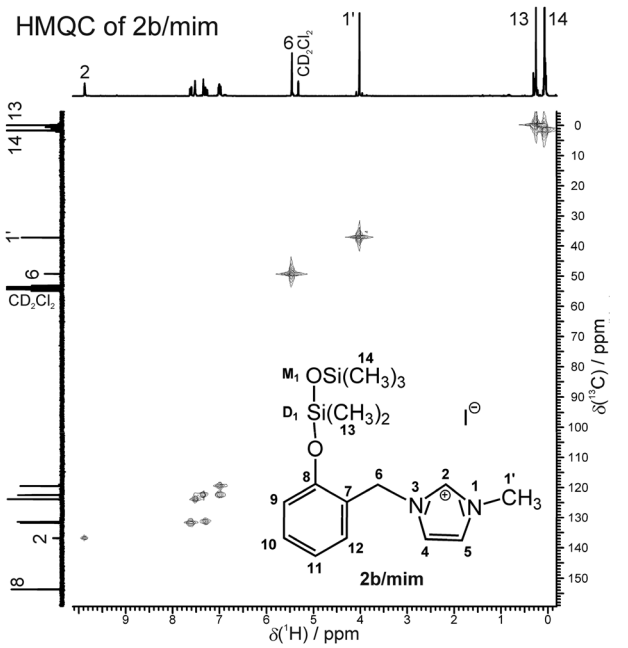

Fig. 2 HMQC NMR spectrum of **2b/mim**, the reaction product of **2b** and 1-methylimidazole. The 2D NMR spectrum and the additional ^{1}H and ^{13}C NMR spectra were taken from a CD_2Cl_2 solution ($\delta(^{1}H/^{13}C)$ = 5.32/54.0 ppm). Magnified ^{1}H, ^{13}C, and ^{29}Si NMR spectra and a mass spectrogram are depicted in the ESI.†

be avoided for the work with the benzyl iodides. Therefore, 1-methylimidazole is a convenient aprotic non-ionic nucleophile, which attacks the electrophilic iodomethylene group forming an imidazolium salt with an iodide anion. The obtained oil is comparable to an ionic liquid (**2b/mim**, see the HMQC spectrum in Fig. 2). In this way the polymerization tendency is vanished and the only molecular instability of the imidazolium cation is due to the possible hydrolysis of the siloxy-groups.

Substitution of iodide of **2b** with an ionic nucleophile like an acetate ion could be fulfilled using tetra-*n*-butylammonium acetate, which is advantageously soluble in less polar solvents. The obtained benzyl acetate can be purified, but it is still able to polymerize, as described in the ESI.†

A selective ring-opening reaction at the oxymethylene group of the three 4*H*-1,3,2-benzodioxasilines (**1a**, **2a**, and **3a**) was evidenced by the use of electrophilic iodotrimethylsilane and previous quantum chemical calculations were confirmed.[4] With this work, the initial step of the cationic twin polymerization is considered to be investigated sufficiently enough, the following process of polymerization is part of our future work. As shown in this article the Si–O–aryl bonds are stable in the initial phase of the twin polymerization, which is regarded as a reason why phase separation of both polymers (organic/inorganic) is suppressed and nanocomposites can be obtained at the end of the polymerization process.[4]

The not yet described ring-opened benzyl iodides **1b**, **2b**, and **3b** were clearly identified by ^{1}H, ^{13}C, ^{29}Si NMR, $^{1}H/^{13}C$-HMQC NMR, and mass spectrometry (see Fig. 1, for mass spectrograms and further NMR details see ESI†).

The obtained benzyl iodides offer the opportunity of further modification *via* substitution of iodide in order to stabilize the

benzylic group or to adjust the molecule to a desired application—as shown in the ESI†, three new derivative substances were obtained. Nucleophilic attack onto the silicon atom next to the phenoxy group should lead to *ortho* quinone methide intermediates that are of synthetic interest in cycloaddition reactions,[9] but polymerization must be avoided.

Experimental

Analytical methods

NMR spectroscopy. The depicted ^{1}H, ^{13}C, ^{29}Si and $^{1}H/^{13}C$-HMQC NMR spectra were recorded at 25 °C on a Bruker Avance 250, the residual peak of the used solvent CD_2Cl_2 was used as reference, $\delta(^{1}H/^{13}C)$ = 5.32/54.0 ppm; as ^{29}Si reference TTSS was added just before the measurement, $\delta(^{29}Si(CH_3)_3)$ = −9.8 ppm. Different experiments of ^{29}Si NMR were used according to the investigated molecular structure (**1a**, **2b**: DEPT45, d_1 = 5 s, CNST2 = 9 Hz; **1b**, **2a**, **3a**: ig30, d_1 = 30 s; **3b**: ig30, d_1 = 20 s). For the analyses of the diastereotopic hydrogens of **1a** spectra were recorded on a Varian Unity Inova 400 spectrometer at 25 °C, as reference the residual peak of the used solvent $CDCl_3$ (δ = 7.26 ppm) was used (Fig. S3, ESI†).

Mass spectrometry. Mass spectrograms (Fig. S1, ESI†) of **1b** have been recorded on a Bruker micrOTOF-Q II spectrometer using the electrospray ionization method (ESI-MS). ESI-MS was also applied for analyzing **2b**, **3b** and the imidazolium derivative of **2b** (**2b/mim**), a Bruker Esquire with an ion trap detector at TU Dresden was used.

Substances

Tetramethylorthosilicate was used as purchased from Fluka/Sigma Aldrich Chemie GmbH (>98%).

Tetra-*n*-butylammonium fluoride (1 M solution in THF) was used as purchased from ABCR GmbH & Co. KG.

Toluene and hexane were dried over sodium and freshly distilled prior use.

2-*tert*-Butyl-4-methylphenol was used as purchased from Acros Organics (99%).

Iodotrimethylsilane was used as purchased from ABCR & Co. KG (97%, stabilized with copper).

D2-Dichloromethane (CD_2Cl_2) was purchased from Deutero GmbH (99.6%) and dried with a molecular sieve of 3 Å prior use.

Tetrakis(trimethylsilyl)silane (TTSS) was used as purchased from ABCR & Co. KG (98%).

1-Methylimidazole (99%) was used as purchased from Carl Roth GmbH & Co. KG.

Syntheses

2-*tert*-Butyl-6-(hydroxymethyl)-4-methylphenol (used for the synthesis of 3a). 2-*tert*-Butyl-6-(hydroxymethyl)-4-methylphenol was synthesized by hydroxymethylation of 2-*tert*-butyl-4-methylphenol with formaldehyde.[10,11]

1a and **2a** were synthesized as described in the literature.[4,7]

2,2′-Spirobi[8-*tert*-butyl-6-methyl-4*H*-1,3,2-benzodioxasiline] (3a) (modified synthesis of **1a**)[4]. Under dry argon 16.71 g (0.086 mol) of 2-*tert*-butyl-6-(hydroxymethyl)-4-methylphenol was dissolved in 100 ml toluene. At 80 °C 6.55 g of tetramethylorthosilicate (0.043 mol) was dropped into the solution and 20 µl of tetra-*n*-butylammonium fluoride (1 M in THF) was added. The reaction mixture was kept at 80 °C for the next few hours while resulting methanol was removed slowly under reduced pressure. Colorless crystals were obtained after evaporation of toluene and recrystallization using hexane. Yield: 52% of theory (0.022 mol, 9.23 g). ^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm): 7.06 (2 × 1H, d, aryl), 6.74 (2 × 1H, d, aryl), 5.15/5.03 (4H, 2d, 2 × CH_2O, ^{2}J = 13.8 Hz), 2.27 (2 × 3H, s, 2 × aryl-CH_3), 1.36 (2 × 9H, s, 2 × *t*-Bu) ppm. ^{13}C NMR (CD_2Cl_2, δ = 54.0 ppm): 149.8 (C_{aryl}–O), 139.5, 131.5, 127.8, 126.6, 125.0, 67.0 (CH_2O), 35.1 *t*-Bu(C_q), 30.1 *t*-Bu(CH_3), 21.1 (aryl-CH_3) ppm. ^{29}Si NMR (CD_2Cl_2, TTSS δ = −9.8 ppm): −79.3 ppm (Q_0). Further characterization, such as X-ray crystallographic data will be published separately.[10]

Ring-opening reactions of 1a, 2a, and 3a with iodotrimethylsilane

Bis(2-iodomethylphenoxy)-bis(trimethylsiloxy)silane (**1b**). Under dry argon 0.884 g (3.246 mmol) of **1a** was dissolved in 1.945 g of CD_2Cl_2. At 25 °C 1.297 g (6.485 mmol) of iodotrimethylsilane was added at once to the stirred solution. After 15 min ^{1}H NMR proved a nearly quantitative formation of **1b**, as depicted in Fig. 1. At 25 °C and at the used concentration (c_{1b} = 2.27 mol l^{-1}) **1b** is only stable for some hours and polymerizes slowly to a phenolic resin. ^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm): 7.50–7.44 (2 × 1H, m, aryl), 7.39–7.24 (2 × 2H, m, aryl), 7.14–7.05 (2 × 1H, m, aryl), 4.63 (2 × 2H, s, 2 × CH_2I), 0.37 (2 × 9H, s, 2 × $Si(CH_3)_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ = 54.0 ppm): 152.00 (C_{aryl}–O), 131.09, 130.06, 130.04, 123.24, 119.94, 2.14 ($Si(CH_3)_3$), 1.72 (CH_2I) ppm. ^{29}Si NMR (CD_2Cl_2, TTSS δ = −9.8 ppm): +13.5 ($Si(CH_3)_3$, M_1), −102.9 ('SiO_4', Q_2) ppm. *m/z*: 673.06 $[M + H]^+$, 694.94 $[M + Na]^+$, 710.91 $[M + K]^+$.

2-Iodomethylphenoxy-trimethylsiloxy-dimethylsilane (**2b**). Under dry argon at 25 °C 1.519 g (7.591 mmol) of iodotrimethylsilane was added at once to the stirred 1.372 g (7.591 mmol) of **2a**. After 5 min ^{1}H NMR proved a nearly quantitative formation of **2b**, as depicted in Fig. 1. At 25 °C and at the used reaction conditions **2b** is only stable for some hours and polymerizes slowly to a phenolic resin. ^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm): 7.40–7.33 (1H, m, aryl), 7.27–7.18 (1H, m, aryl), 7.00–6.90 (2H, m, aryl), 4.52 (2H, s, CH_2I), 0.38 (6H, s, $Si(CH_3)_2$), 0.21 (9H, s, $Si(CH_3)_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ = 54.0 ppm): 153.6 (C_{aryl}–O), 130.8, 130.2, 129.9, 122.3, 119.8, 2.4 (CH_2I), 2.1 $Si(CH_3)_3$, 0.2 $Si(CH_3)_2$. ^{29}Si NMR (CD_2Cl_2, TTSS δ = −9.8 ppm): +9.7 ($Si(CH_3)_3$, M_1), −12.4 ($Si(CH_3)_2$, D_1) ppm. *m/z*: 398.0 $[M + NH_4]^+$.

Bis(2-tert-butyl-6-iodomethyl-4-methylphenoxy)-bis(trimethylsiloxy)silane (**3b**). Under dry argon 0.242 g (0.586 mmol) of **3a** was dissolved in 1.639 g of CD_2Cl_2. At 25 °C 0.234 g (1.171 mmol) of iodotrimethylsilane was added at once to the stirred solution. After 11 h ^{1}H NMR proved a nearly quantitative formation of **3b**, as depicted in Fig. 1. At 25 °C and at the used concentration (c_{3b} = 0.49 mol l^{-1}) **3b** was stable for several days.

^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm): 7.20 (2 × 1H, d, aryl), 7.16 (2 × 1H, d, aryl), 4.84 (2 × 2H, s, 2 × CH_2I), 2.32 (6H, s, 2 × aryl-C$\underline{H}_3$), 1.51 (2 × 9H, s, 2 × *t*-Bu), −0.06 (2 × 9H, s, 2 × $Si(CH_3)_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ = 54.0 ppm): 148.61, 141.14, 132.34, 131.10, 130.50, 128.98, 35.46 (*t*-Bu(C_q)), 31.24 (*t*-Bu(CH_3)), 21.18 (aryl-$\underline{C}H_3$), 4.84 (CH_2I), 1.84 ($Si(CH_3)_3$) ppm. ^{29}Si NMR (CD_2Cl_2, TTSS δ = −9.8 ppm): +12.0 ($Si(CH_3)_3$, M_1), −109.0 ('SiO_4', Q_2) ppm. *m*/*z*: 830.40 $[M + NH_4]^+$.

1-(2-((1,1,3,3,3-Pentamethyldisiloxanyl)oxy)benzyl)-3-methylimidazolium iodide (**2b/mim**). In a 50 ml flask at 25 °C 0.947 g (5.25 mmol) of **2a** are stirred and 1.020 g (5.10 mmol) of iodotrimethylsilane were added with a syringe at once. After 5 min 10 ml of CH_2Cl_2 were added and a small sample (2 drops) of the diluted mixture was analyzed *via* ^{1}H NMR spectroscopy. As the NMR data proved nearly quantitative consumption of **2a** to **2b** 0.412 g (5.02 mmol) of 1-methylimidazole was added to the solution and the reaction mixture was continued to stir at ϑ = 25 °C for 3 h. The solvent was removed under vacuum, and the residue was washed 5 times with 3 ml hexane. The obtained product is yellow oil. Yield: ~100% relative to the used 1-methylimidazole. ^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm): 9.87 (1H, s(br), N–CH–N), 7.65–6.95 (6H, m), 5.46 (2H, s, CH_2), 4.02 (3H, s, mimC$\underline{H}_3$), 0.26 (6H, s, $Si(CH_3)_2$), 0.07 (9H, s, $Si(CH_3)_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ = 54.0 ppm): 153.7 (C–O), 136.9 (N–CH–N), 131.8, 131.4, 123.9, 123.8, 122.5, 122.4, 119.5, 49.2 (CH_2), 37.3 (mim$\underline{C}H_3$), 1.7 ($Si(CH_3)_3$), 0.0 ($Si(CH_3)_2$) ppm. ^{29}Si NMR (CD_2Cl_2, δ(TTSS, $^{29}Si(CH_3)_3$) = −9.8 ppm): +10.6 (M_1), −11.0 (D_1) ppm. *m*/*z*: 335.2 $[M - I]^+$.

Acknowledgements

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