Triethoxysilane, Tetraethoxysilane and Hexaethoxydisiloxane – Three Complementary Reagents for the Synthesis of Hydrogen-Rich Silylarenes

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

Triethoxysilane HSi(OEt)₃, tetraethoxysilane Si(OEt)₄ and hexaethoxydisiloxane Si₂O(OEt)₆ have been probed as reagents for the synthesis of hydrogen-rich silyl-arenes $Ar(SiH_3)_n$. A large set of new silyl-arenes, varying in their substitution patterns and grades, have been prepared. The results establish the two new silylating agents HSi(OEt)₃ and Si₂O(OEt)₆ as particularly useful alternatives to Si(OEt)₄. The products, which include trihydrosilyl-substituted methylbenzenes, naphthalenes and ferrocenes, have been characterized by NMR and IR spectroscopy, mass spectrometry and single crystal X-ray diffraction.

Key words: Arylsilanes, Silylarenes, Trialkoxysilane, Tetraethoxysilane, Hexaethoxydisiloxane

Introduction

The importance of hydrogen-rich silyl-arenes, i.e. aromatic hydrocarbons which bear one or more silyl substituents SiH₃, has been growing steadily over the last two decades and a selection of prototypes has become accessible. While being of interest initially only from a theoretical point of view as the higher analogues of methyl-substituted arenes, this class of compounds has now been recognized as important substrates for many potential applications, which include the use as single-source-precursors in CVD-processes for the generation of SiC thin films [1], as monomeric substrates for σ -bond metathesis and hydrosilylation [2] and as ligands for transition-metal catalysts [3]. Also, they are important precursors for the generation of di-, oligo- and polysilanes with aryl substituents via dehydrogenative [4] and desilanative [5] coupling. These arylpolysilanes have great potential for applications in a series of optoelectronic devices owing to their unique electronic structure with conjugated arene and polysilane systems [6].

Due to the reactivity of the Si-H-bond, more often than not the synthesis of hydrogen-rich arylsilanes Ar-SiH₃ is much more difficult than that of the corresponding alkyl/aryl-silanes Ar-SiR₃ for which many preparative pathways are known. A number of synthetic procedures using a wide range of different silylating agents has been reported in the past [7-11], but most of these are lacking either preparative versatility or require sophisticated preparative techniques. The most common standard agent for the synthesis of the hydrosilyl-arenes Ar-SiH₃ is *tetraethoxysilane* (TEOS), which is often used in a modified version [7] of the well known *Mercker-Scott*-reaction [12] which was developed initially for reactions with the silicon halides.

Results and Discussion

We have shown earlier [13] that triethoxysilane can readily be employed as a convenient silylating agent, when being reacted with organolithium and Grignard agents: The *in-situ* one-pot-reaction with the metalarenes is a straight pathway from bromoarenes to trihydrosilylarenes. However, yields are moderate and the presence of several substituted hydrido/alkoxy-silanes makes workup usually more difficult and time consuming. In the reactions of triethoxysilane with a series of polymethyl-bromobenzenes this drawback becomes even more obvious (Fig. 1a) and the use of the established silane TEOS has distinct advantages (Fig. 1b). Monosilylation of arenes therefore is achieved best using tetraethoxysilane (Scheme 1).

Table 1 gives a selection of ¹H and ²⁹Si NMR and IR data pertinent to the SiH₃-groups for the polymethyl-

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Fig. 1a. The reaction of aryl halides with triethoxysilane leads to a complicated equilibrium mixture of silylarenes, which can be converted into a single product upon treatment with excess LiAlH₄.



Fig. 1b. The reaction of aryl halides with tetraethoxysilane generally leads to a single product.



Scheme 1.

silylbenzenes synthesized in the present work. The extreme highfield shift of the silicon-29 resonance (²⁹Si-DEPT) in cases where two methyl groups are attached in the 2- and 6-positions is noteworthy. This effect is probably due to a bending of the Si-C-bond out of the plane of the arene resulting in a change of the influence of the local ring current. Similar observations were made in ¹³C-studies by Hayes and Pugmire [14] and in ²⁹Si-studies by Weber and Marsmann [15]. The frequencies of the stretching vibration of the Si-H-bond are basically the same for all silyl-arenes investigated and appear in the region of about 2150 cm⁻¹.

As an extension of the monosilylation studies, reactions of triethoxysilane with a variety of *dimetallated* species have also been carried out. Slow addition of triethoxysilane to a suspension of dilithiated arenes

Table 1. ¹*J* coupling constants [Hz], ²⁹Si and ¹H chemical shifts [ppm] and IR stretching frequencies $[cm^{-1}]$ for the silyl group SiH₃ in poly(methyl/silyl)benzenes.

2 6 1	5 1 5			
Substituents	δ^{29} Si	$\delta^1 \mathrm{H}_{\mathrm{Si}}$	$^{1}J_{\mathrm{Si-H}}$	$v_{\rm SiH}$
	-59.00	4.38	200.4	_
2-CH3	-62.60	4.24	199.6	_
3-CH3	-59.88	4.22	199.4	_
4-CH ₃	-59.52	4.28	199.6	_
2,3-CH ₃	-62.29	4.28	198.6	2147
2,4-CH3	-63.93	4.27	197.8	2150
2,5-CH3	-62.13	4.27	198.8	2149
2,6-CH ₃	-77.57	4.27	199.4	2146
3,4-CH3	-60.16	4.27	198.3	2146
2,4,5-CH ₃	-64.30	4.30	196.0	2149
2,4,6-CH ₃	-77.63	4.24	198.1	2146
2,3,5,6-CH ₃	-76.55	4.39	196.3	-
2,3,4,5,6-CH ₃	-75.98	4.46	198.5	-



Fig. 2a. Regioselective silylation of ferrocene with triethoxysilane.



Fig. 2b. Product mixture obtained from the silylation of ferrocene with tetraethoxysilane.

was found to lead solely to species in which the silicon atoms are monoarylated, whilst reactions with tetraethoxysilane usually lead to a mixture of products including polyarylated silanes. For example, the reaction of 1,1'-dilithio-ferrocene with two equivalents of triethoxysilane leads exclusively to 1,1'-*bis*(triethoxysilyl)-ferrocene with no silicon-bridged diferrocenes as byproducts as probed by GC-MS and ²⁹Si-NMR spectroscopy. The alkoxy-substituted product is readily converted into 1,1'-disilylferrocene (Fig. 2a).





It appears that the nucleophilic substitution of the Si-H bond is several orders of magnitude faster than that of the Si-OEt bond. With TEOS, the same reaction requires elevated temperatures, and a mixture of di- and polynuclear silylferrocenes is obtained (see Fig. 2b).

1,1'-Disilyl-ferrocene and its precursor 1,1'-*bis*(triethoxysilyl)-ferrocene show ²⁹Si NMR resonances at -62.12 and -50.48 ppm, respectively. The alkoxylated product thus is showing an unusual downfield shift of about 5.5 ppm compared to the shifts found for other alkoxysilylarenes (which, to a first approximation, are not dependent on the nature of the aryl group) and of about 12 ppm compared to the hydrogenated product. Dilithiated dibenzenechromium reacts with HSi(OEt)₃ in a similar way regarding the first step, but subsequent reduction of the alkoxysilylated species leads to decomposition.

Triethoxysilane can also be employed as a reagent in one-pot-reactions with dibrominated arenes to accomplish double silvlation. This process shows again advantages over reactions with tetraethoxysilane: Although the primary reaction mixture is a much more complicated set of differently alkoxy/hydridosubstituted disilylarenes, the reduction with LiAlH₄ affords the bis-trihydrosilyl-arene as the sole product. Also, the yield of disilylated product is much higher as compared to the analogous reaction with tetraethoxysilane where diarylated silanes are prominent byproducts. For example, reaction of 1,4-dibromo-2,5-dimethyl-benzene with triethoxysilane in an in-situ-Grignard manner affords a set of different 1,4-bis(alkoxy/hydrido)-substituted 2,5dixylenes (Fig. 3a), whereas the same reaction us-



Fig. 4. Molecular structure of 1,4-dimethyl-2,5-disilylbenzene. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å] and angles [°]: Si(1)-C(2)1.8699(15), C(1)-C(2) 1.398(2), C(2)-C(3) 1.409(2), C(3)-C(4) 1.5086(19), C(3)-C(1_2) 1.392(2); C(1)-C(2)-Si(1) 119.53(11), C(3)-C(2)-Si(1) 121.69(11), C(1)-C(2)-C(3) 118.77(13), C(2)-C(3)-C(1_2) 118.63(13), C(2)-C(1)-C(3_2) 122.60(13).

ing tetraethoxysilane also affords di-xylyl-substituted silanes as undesired byproducts (Fig. 3b).

The final product, 1,4-dimethyl-2,5-disilyl-benzene (10), is the only example, where the crystal structure could be determined (Fig. 4). Colourless crystals were grown upon slow evaporation of a solution of the silane in hexane at temperatures below 20 °C (triclinic, space group $P\bar{1}$). A center of inversion is located at the midpoint of the almost perfectly regular hexagon.



Fig. 5. Silylation of 1,2-dibromobenzene with hexaethoxydisiloxane leading to 1,2-disilylbenzene *via* the bicyclic 1,1,3,3-tetraethoxy-1,3-dihydro-benzo[1,2,5]oxadisilole.



Fig. 6. Silylation of 1,8-dilithio-naphthalene with hexaethoxydisiloxane leading to 1,8-disilyl-naphthalene after the reduction of the tricyclic intermediate with LAH.

Steric crowding associated with ortho-disubstitution of arenes as in 1,2-disilylbenzene or the 1,8disilylnaphthalene make compounds of this type a preparative challenge. These substitution patterns are not accessible via the classical tetraethoxysilane route, due to the bulkiness of a triethoxysilyl group which makes further silvlation in adjacent positions virtually impossible. Our studies have shown now that hexaethoxydisiloxane is a reagent which opens up a preparative pathway to these disilylarenes. This disiloxane is readily accessible in good yields via controlled hydrolysis of tetraethoxysilane followed by fractional distillation. The compound is a colourless liquid, stable at room temperature in a dry atmosphere. With a pair of silicon centers incorporated in one molecule, it can act as a double silylating agent. Thus, when reacted with 1,2-dibromobenzene in an in-situ Grignard manner it affords a sila-oxa-cycle. The Si-O-Si link is cleaved upon reduction with LiAlH₄ and after complete hydrogenation the procedure yields 1,2disilyl-benzene (Fig. 5). The primary product is a complex reaction mixture which has not been worked up, but GC-MS investigations confirmed the formation of the cyclic siloxane with m/z = 328.

In a similar manner, addition of hexaethoxydisiloxane to a vigorously stirred solution of 1,8-dilithionapthalene gives a 1,8-disilylated napthalene with an Si-O-Si bridging unit. When treated with LiAlH₄ this intermediate is reduced under ring-opening to give the hydrogenated product 1,8-disilyl-naphthalene (Fig. 6). It should be noted, that in the reaction of the aryllithium or aryl-Grignard reagents the Si-O-Si unit of hexaethoxydisiloxane remains unaffected. This extreme stability of siloxane functions is well documented [16, 17]. All attempts to synthesize 1,2,4,5-tetrasilyl-benzene from the corresponding tetrahalogenated benzenes using hexaethoxydisiloxane proved unsuccessful. GC-MS investigations of the product mixtures indicated formation of the *para*-disilylated dihalides. Due to its unique electronic structure this species is inert towards further metalation as pointed out in an earlier work [18].

Conclusion

Whilst tetraethoxysilane still is the most convenient reagent for the synthesis of monosilylated arenes *via* metallated aromatic hydrocarbons, both triethoxysilane and hexaethoxydisiloxane offer significant advantages over TEOS as complementary agents for the silylation of arenes with higher substitution grades and special substitution patterns. With this arsenal of alkoxysilanes a large variety of arylsilanes has now become readily accessible *via* convenient low-cost routes.

Experimental Section

General

All manipulations were performed in an atmosphere of dry nitrogen using standard equipment throughout. Solvents werde made anhydrous by standard procedures (Na/K-alloy, CaH₂), distilled, saturated with nitrogen and stored over molecular sieve 4 Å. Distillations were carried out in high vacuum (0.5–1 Torr). GC-MS measurements were performed on a Hewlett-Packard Model 5890 Series II with mass selective detector HP MS 5957A using EI at 70 eV. All arenes and bromo-arenes were commercially available and used without further purification. 1,1'-Dilithioferrocene, 1,1'-dilithio-dibenzenechromium and 1,8-dilithionaphthalene were prepared according to literature procedures [19–21]. Triethoxysilane and tetraethoxysilane were purchased from ABCR, checked for impurities by GC-MS and purified by fractional distillation, if neccessary.

¹H, ¹³C and ²⁹Si NMR spectra were recorded on a JEOL-Delta 400 GX instrument in C_6D_6 as a solvent using the residual solvent peak as an internal standard (¹H, ¹³C) and TMS as an external standard (²⁹Si). In the ¹³C-NMR spectra

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Table 2. Crystal data and structure refinement of 1,4-dimethvl-2.5-disilvl-benzene.

,			
Empirical formula	$C_8H_{14}Si_2$		
Formula weight	166.37		
Temperature	143(2) K		
Wavelength	0.71073 Å		
Crystal system, space group	triclinic, P1		
Unit cell dimensions	a = 4.9060(4) Å		
	b = 6.9990(5) Å		
	c = 7.8198(6) Å		
	$\alpha = 90.289(4)^{\circ}$		
	$\beta = 107.446(5)^{\circ}$		
	$\gamma = 99.339(5)^{\circ}$		
Volume	252.35(3) Å ³		
Z, calculated density	1, 1.095 g/cm ³		
Absorption coefficient	0.286 mm^{-1}		
F(000)	90		
Crystal size	$0.60 \times 0.30 \times 0.30 \text{ mm}^3$		
Theta range for data collection	2.73 to 27.58°		
Limiting indices	$0 \le h \le 6$,		
	$-9 \le k \le 8$,		
	$-10 \le l \le 9$		
Reflections collected / unique	14336/1063 [R(int) = 0.027]		
Completeness to $\theta = 27.58^{\circ}$	90.7%		
Absorption correction	None		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	1063/0/74		
Goodness-of-fit on F^2	1.099		
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0366, wR2 = 0.0930		
R Indices (all data)	R1 = 0.0374, wR2 = 0.0936		
Largest diff. peak and hole	0.333 and -0.262 e.A ⁻³		

of several silanes not all arene carbon resonances were observed owing to their low intensity. IR spectra were recorded of liquid samples between KBr plates on a Perkin-Elmer 1600 FTIR spectrometer.

For crystallographic measurements a specimen of suitable quality and size of 1,4-dimethyl-2,5-disilyl-benzene was mounted on the end of a quartz fiber in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP 2020 diffractometer, employing graphitemonochromated Mo-K α -radiation. The structure was solved by direct methods and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [22]. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located and refined with isotropic displacement parameters. Further informations on crystal data, data collection and structure refinement are summarized in Table 2 [23].

Hexaethoxydisiloxane

2 ml of distilled water is added at room temperature to commercially available tetraethoxysilane (2.40 mol, 500 ml). The resulting solution is stirred vigorously for 20 h and filtered from solids precipitated in the hydrolysis. Ethanol is removed under reduced pressure and the residual colourless liquid subjected to fractional distillation. Four fractions are collected which contain mainly tetraethoxysilane, hexaethoxydisiloxane, octaethoxytetrasiloxane, and decaethoxytetrasiloxane, respectively. Yield: 148 g (EtO)₆Si₂O (36%). B.p. 98 °C (1 Torr). MS (EI, 70 eV): 342 (M⁺), 313 (M⁺-Et), 297 (M⁺-OEt), 252 (M⁺-2OEt), 163 (M⁺-Si(OEt)₄).

Silylation of organolithium compounds with triethoxysilane (illustrated for 1,1-disilylferrocene)

A solution of triethoxysilane (12 g, 74 mmol) in hexane (20 ml) is added to a solution of the tmeda adduct of dilithioferrocene (37 mmol) in 160 ml of a diethylether/hexane mixture (2/1) while stirring at 0 °C. Subsequently the mixture is stirred at r. t. for 30 min. The solvent is evaporated under reduced pressure and other volatile components are removed under high vacuum. The residue is taken up in hexane again and undissolved lithium salts are removed by filtration. Evaporation of the solvent from the filtrate yields the 1,1'-bis(triethoxysilylated) ferrocene as a dark red, viscous oil (17.4 g, 92%).

The triethoxysilyl-substituted product is redissolved in diethylether and slowly added to a suspension of lithiumaluminiumhydride (LAH, 100 mmol, 3 eq.) in 20 ml of diethylether *via* a dropping funnel at 0 °C. After addition is complete the resulting suspension is stirred at r.t. overnight. The solvent is evaporated and the product isolated by Soxhlet-extraction of the residue using hexane as a solvent, resulting in orange crystals (8.3 g, 92%).

1,1'-Bis(triethoxysilyl)-ferrocene: ¹H NMR (270 MHz, C₆D₆): $\delta = 1.22$ (t, 18H, ³J = 6.7 Hz, CH₃), 3.92 (q, 12H, ³J = 6.7 Hz, CH₂), 4.46 (s, 4 H), 4.60 (s, 4 H); ¹³C NMR (100 MHz, C₆D₆): $\delta = 18.62$ (CH₃), 58.77 (CH₂), 72.95, 74.67 (cp); ²⁹Si NMR (79.4 MHz, C₆D₆): $\delta = -50.48$ (s); IR (KBr): v = 956.7, δ (O-Si-C); MS (EI, 70 eV): m/z = 481 (M⁺-Et), 465 (M⁺-OEt), 436 (M⁺-OEt-Et), 347 (M⁺-Si(OEt)₃), 306 (M⁺-Si(OEt)₃-C₃H₆); C₂₂H₃₈Si₂O₆Fe (510.56): calcd. C 51.76, H 7.50; found C 50.19, H 7.45.

1,1'-Disilyl-ferrocene: M.p.: 94 °C; ¹H NMR (270 MHz, C₆D₆): δ = 3.99 (s, 4H, cp), 4.10 (s, 4H, cp), 4.31 (d, 6H, ¹J = 199.8 Hz, SiH₃); ¹³C NMR (100 MHz, C₆D₆): δ = 72.91, 76.17 (cp); ²⁹Si NMR (53.6 MHz, DEPT, C₆D₆): δ = -62.12 (q, ¹J = 199.8); IR (KBr): v = 2149, v(Si-H); MS (EI, 70 eV): m/z = 246 (M⁺), 215 (M⁺-SiH₃), 186 (M⁺-2 SiH₃); C₁₀H₁₄FeSi₂ (246.24): calcd. C 48.78, H 5.73; found C 48.13, H 5.57.

1,1'-Bis(triethoxysilyl)dibenzenechromium: ¹H NMR (400 MHz, C₆D₆): δ = 1.20 (t, 18H, ³J = 7.3, CH₃), 3.82 (q, 12H, ³J = 7.3, CH₂), 6.83 – 6.93 (m, 6H, Ar), 7.53 – 7.57 (m, 4H, Ar); ¹³C NMR (100 MHz, C₆D₆): δ = 19.12 (CH₃), 58.99 (CH₂), 111.5, 121.4, 133.3, 134.5 (Ph); ²⁹Si NMR (79.4 MHz, coupled DEPT, C₆D₆): δ = -56.4 (s). Silylation of organolithium compounds with hexaethoxydisiloxane (illustrated for 1,8-dilithionaphthalene)

A solution of 0.73 g of the *bis*-tmeda adduct of 1,8dilithionaphthalene (1.96 mmol) in 10 ml of diethylether is added rapidly to 1.0 g of hexaethoxydisiloxane (2.9 mmol, 1.5 eq.) at 0 °C.

After stirring for 2 h at r. t. the solvent is removed under reduced pressure. The residue is taken up in 20 ml of hexane, the solution filtered several times to remove precipitated lithium salts, and the solvent evaporated. The residue is redissolved in diethylether (10 ml) and the solution added dropwise at 0 °C to a suspension of 0.12 g of LAH (3 mmol) in 10 ml of diethylether. The slurry is stirred at r. t. for another 10 h. The solvent is removed *in vacuo*, the residue taken up in hexane (2 × 20 ml) and the solution filtered from insoluble salts. Upon evaporation of the solvent, 1,8-disilylnaphthalene remains as a colourless solid. Its physical constants and spectroscopic data are in agreement with published data [11a].

Silylation of polymethylbromobenzenes with tetraethoxysilane (exemplified for the bromo-xylenes 1-5in Scheme 1)

10 g of the corresponding bromo-dimethylbenzene (54 mmol) is dissolved in 40 ml of THF, and about 10% of this solution is added to a slurry of magnesium turnings (1.7 g, 70 mmol, 1.3 eq.) and tetraethoxysilane (0.16 mol, 34 g, 3 eq.) in 50 ml of THF containing a small crystal of iodine. The suspension is heated to reflux and the remainder of the bromo-xylene solution is added *via* a dropping funnel at such a rate, that the reaction mixture continues to reflux. Subsequently the mixture is kept at reflux for another 2 h. THF is then removed *in vacuo* at r. t. and the remaining white solid taken up in pentane (2×50 ml) and filtered. Pentane is evaporated to leave an oily, yellow liquid. Fractional distillation yields the triethoxysilylated compound as a clear colourless oil.

This product is then dissolved in 30 ml of diethylether and added to a slurry of LAH (1.5 eq.) in 50 ml of diethylether with cooling to 0 °C. After stirring for about 10 h at r. t. the solvent is removed in a vacuum at 0 °C and the residue is taken up in 100 ml of pentane and filtered from any precipitated salts. The solvent of the usually cloudy solution is evaporated and the residue purified by short-path distillation. Yield: 60 to 85%.

2,5-Dimethyl-1-silyl-benzene (1): B.p.: 32 °C (1 Torr); ¹H NMR (400 MHz, C₆D₆): $\delta = 1.55$ (s, 3H, CH₃), 2.17 (s, 3H, CH₃), 4.23 (d, 3H, ¹J = 199.6 Hz, SiH₃), 6.94 (d, 1H, Ar-3, ³J = 6.8 Hz), 7.07 (d, 1H, Ar-4, ³J = 6.8 Hz), 7.20 (s, 1H, Ar-6); ¹³C NMR (67.8 MHz, C₆D₆): $\delta =$ 20.34, 21.81 (2 CH₃), 130.8, 138.0, 141.1 (*C*-H); ²⁹Si NMR (coupled DEPT, 53.6 MHz, C₆D₆): $\delta = -63.32$ (qd, ¹J = 196.9 Hz, ${}^{3}J = 7.8$ Hz); MS (EI, 70 eV): m/z = 150 (M⁺), 135 (M⁺-CH₃), 120 (M⁺-SiH₃), 105 (M⁺-SiH₃-CH₃); C₈H₁₂Si (136.27):: calcd. C 70.51, H 8.88; found C 70.00, H 8.98.

3,4-Dimethyl-1-silyl-benzene (**2**): B. p.: 34 °C (1 Torr); ¹H NMR (270 MHz, C₆D₆): $\delta = 1.43$ (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 4.27 (d, 3H, ¹J = 198.3 Hz, SiH₃), 6.93 (d, 1H, ³J = 7.7 Hz, Ar), 7.21 (d, 1H, ³J = 7.7 Hz, Ar), 7.99 (s, 1H, Ar-2); ¹³C NMR (67.8 MHz, C₆D₆): $\delta = 14.40$ (CH₃), 32.14 (CH₃), 124.8, 129.8, 133.9, 137.4, 142.7 (Ar); ²⁹Si NMR (coupled DEPT, 53.7 MHz, C₆D₆): $\delta = -60.16$ (qdd (qt)), ¹J = 198.3 Hz, ³J = 6.7 Hz); IR (KBr): v = 2146, v(Si-H), 726, v(Si-C); MS (EI, 70 eV): m/z = 136 (M⁺), 121 (M⁺-CH₃), 106 (M⁺-2 CH₃), 91 (M⁺-SiH₃-CH₃); C₈H₁₂Si (136.27): calcd. C 70.51, H 8.88; found C 71.50, H 9.78.

2,3-Dimethyl-1-silyl-benzene (**3**): B.p.: 30 °C (1 Torr); ¹H NMR (270 MHz, C₆D₆): $\delta = 1.43$ (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 4.28 (d, 3H, ¹J = 198.6 Hz, SiH₃), 6.98 (d, 1H, ³J = 7.0 Hz, Ar), 7.21 (d, 1H, ³J = 5.5 Hz, Ar), 8.58 (m, 1H, Ar); ¹³C NMR (67.8 MHz, C₆D₆): $\delta = 23.18$ (CH₃), 27.38 (CH₃), 128.2, 132.6, 135.4, 136.2, 138.5 (Ar-C); ²⁹Si NMR (coupled DEPT, 53.7 MHz, C₆D₆): $\delta = -62.28$ (qd, ¹J = 198.6 Hz, ³J = 6.7 Hz); IR (KBr): v = 2147, v(Si-H), 726, v(Si-C); MS (EI, 70 eV): m/z = 136 (M⁺), 121 (M⁺-CH₃), 106 (M⁺-2 CH₃), 91 (M⁺-SiH₃-CH₃); C₈H₁₂Si (136.27): calcd. C 70.51, H 8.88; found C 70.50, H 9.23.

2,4-Dimethyl-1-silyl-benzene (4): B. p.: 38 °C (1 Torr); ¹H NMR (400 MHz, C₆D₆): $\delta = 2.09$ (s, 3H, CH₃), 2.23 (s, 3H, CH₃), 4.27 (d, 3H, ¹J = 197.8 Hz, SiH₃), 6.78 (s, 1H, Ar-3), 6.81 (d, 1H, ³J = 7.5 Hz, Ar), 7.39 (d, 1H, ³J = 7.5 Hz, Ar); ¹³C NMR (100 MHz, C₆D₆): $\delta = 14.30$ (CH₃), 23.06 (CH₃), 126.5, 130.6, 137.5, 140.6, 144.4 (Ar-C); ²⁹Si NMR (coupled DEPT, 79.4 MHz, C₆D₆): $\delta = -63.93$ (qd, ¹J = 197.8 Hz, ³J = 6.8 Hz); IR (KBr): v = 2150, v(Si-H), 727, v(Si-C); MS (EI, 70 eV): m/z = 136 (M⁺), 121 (M⁺-CH₃), 106 (M⁺-2CH₃), 91 (M⁺-SiH₃-CH₃); C₈H₁₂Si (136.27): calcd. C 70.51, H 8.88; found C 69.30, H 9.10.

2,6-Dimethyl-1-silyl-benzene (**5**): B.p.: 37 °C (1 Torr); ¹H NMR (400 MHz, C₆D₆): δ = 2.27 (s, 6H, 2 CH₃), 4.20 (d, 3H, ¹J = 199.4 Hz, SiH₃), 6.85 (d, 2H, ³J = 7.7 Hz, Ar-3/5), 7.04 (t, 1H, ³J = 7.7 Hz, Ar-4); ¹³C NMR (100 MHz, C₆D₆): δ = 21.32 (2 CH₃), 124.3, 127.5, 130.1, 145.0 (Ar); ²⁹Si NMR (coupled DEPT, 79.4 MHz, C₆D₆): δ = -77.47 (q, ¹J = 199.4 Hz); IR (KBr): v = 2146, v(Si-H), 724, v(Si-C); MS (EI, 70 eV): m/z = 136 (M⁺), 121 (M⁺-CH₃), 106 (M⁺-2 CH₃), 91 (M⁺-SiH₃-CH₃); C₈H₁₂Si (136.27): calcd. C 70.51, H 8.88; found C 69.44, H 9.00.

1-Silyl-2,4,5-trimethyl-benzene (**6**): B.p.: 44 °C (1 Torr); ¹H NMR (270 MHz, C₆D₆): $\delta = 1.41$ (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 4.30 (d, 3H, ¹*J* = 196.0 Hz, SiH₃), 6.78 (s, 1H, Ar), 7.28 (s, 1H, Ar); ¹³C NMR (67.8 MHz, C₆D₆): δ = 14.28, 23.05, 32.00 (CH₃), 124.6, 131.1, 133.4, 138.8, 139.2, 142.0 (Ar); ²⁹Si NMR (coupled DEPT, 53.7 MHz, C₆D₆): δ = -64.30 (qd, ¹*J* = 196.0 Hz, ³*J* = 7.5 Hz); IR (KBr): *v* = 2149, *v*(Si-H), 726, *v*(Si-C); MS (EI, 70 eV): *m*/*z* = 150 (M⁺), 135 (M⁺-CH₃), 119 (M⁺-SiH₃), 105 (M⁺-SiH₃-CH₃), 91 (M⁺-SiH₃-2 CH₃); C₈H₁₂Si (150.30): calcd. C 71.92, H 9.39; found C 71.38, H 9.33.

1-Silyl-2,4,6-trimethyl-benzene (7): B.p.: 50 °C (1 Torr), ¹H NMR (400 MHz, C₆D₆): δ = 2.08 (s, 3H, 4-CH₃), 2.29 (s, 6H, 2-CH₃ + 6-CH₃), 4.25 (d, 3H, ¹J = 198.1 Hz, SiH₃), 6.88 (s, 2H, 2 Ar-H); ¹³C NMR (100 MHz, C₆D₆): δ = 21.2 (4-CH₃), 23.6 (2-/6-CH₃), 127.3, 128.5, 139.8, 145.0 (Ar-C); ²⁹Si NMR (coupled DEPT, 79.4 MHz, C₆D₆): δ = -77.63 (qd, ¹J = 198.1 Hz); IR (KBr): v = 2164, v(Si-H), 734, v(Si-C); MS (EI, 70 eV): m/z = 150 (M⁺), 135 (M⁺-CH₃), 119 (M⁺-SiH₃), 105 (M⁺-SiH₃-CH₃), 91 (M⁺-SiH₃-2 CH₃); C₈H₁₂Si (150.30): calcd. C 71.92, H 9.39; found C 69.44, H 9.00.

1-Silyl-2,3,5,6-tetramethyl-benzene (*silyldurene*) (**8**): M. p.: 142 °C; ¹H NMR (270 MHz, C₆D₆): δ = 2.03 (s, 6H, 2 CH₃), 2.23 (s, 6H, 2 CH₃), 4.39 (d, 3H, ¹J = 196.3 Hz, SiH₃), 6.87 (s, 1H, Ar); ¹³C NMR (67.8 MHz, C₆D₆): δ = 19.9 (2 CH₃), 20.4 (2 CH₃), 127.8, 133.6, 134.1, 140.8 (Ar); ²⁹Si NMR (coupled DEPT, 53.6 MHz, C₆D₆): δ = -76.55 (q, ¹J = 196.3 Hz); MS (EI, 70 eV): m/z = 164 (M⁺), 149 (M⁺-CH₃), 133 (M⁺-SiH₃), 119 (M⁺-SiH₃-CH₃), 105 (M⁺-SiH₃-2 CH₃), 91 (M⁺-SiH₃-3 CH₃); C₉H₁₄Si (164.32): calcd. C 73.09, H 9.81, found C 72.84, H 9.81.

1-Silyl-2,3,4,5,6-pentamethyl-benzene (permethylsilylbenzene), (**9**): M.p.: 156 °C; ¹H NMR (400 MHz, C₆D₆): δ = 1.98 (s, 6H, 2 CH₃), 2.02 (s, 3H, 4-CH₃), 2.31 (s, 6H, 2 CH₃), 4.46 (d, 3H, ¹J = 198.5 Hz, SiH₃); ¹³C NMR (100 MHz, C₆D₆): δ = 16.5 (2 CH₃), 16.9 (CH₃), 21.5 (2 CH₃), 129.5, 132.4, 137.1, 140.2 (Ar); ²⁹Si NMR (coupled DEPT, 79.4 MHz, C₆D₆): δ = -75.98 (q, ¹J = 198.5 Hz); MS (EI, 70 eV): m/z = 178 (M⁺), 163 (M⁺-CH₃), 147 (M⁺-SiH₃), 132 (M⁺-SiH₃-CH₃), 117 (M⁺-SiH₃-2 CH₃), 103 (M⁺-SiH₃-3 CH₃); C₁₁H₁₈Si (178.35): calcd. C 74.08, H 10.17, found C 73.73, H 10.21.

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Reaction of dibromobenzenes with triethoxysilane (10, 11 in Scheme 1)

45 mmol of a dibrominated xylene or mesitylene is added *via* a dropping funnel to a slurry of magnesium turnings (2.7 g, 117 mmol, 2.6 eq.) in a mixture of triethoxysilane (30.0 g, 180 mmol, 4 eq.) and THF (100 ml) heated to reflux temperatures. After addition is complete, the mixture is heated for another 5 h. Volatile silanes formed during the reaction are allowed to leave the reaction vessel into an aqueous solution of KOH.

Subsequently, all volatile components are removed at 50 °C in a vacuum. The residue is taken up in hexane $(2 \times 200 \text{ ml})$ and the extract is filtered. Hexane is removed under reduced pressure and the product is then reacted with LAH (3 eq.) as described for the polymethylsilylbenzenes above.

1,4-Dimethyl-2,5-disilyl-benzene (**10**): M.p.: 20 °C; ¹H NMR (400 MHz, C₆D₆): δ = 2.15 (s, 6H, 2 CH₃), 4.22 (d, 6H, ¹J = 199.6 Hz, 2 SiH₃), 7.22 (s, 2H, Ar); ¹³C NMR (67.8 MHz, C₆D₆): δ = 21.81 (2 CH₃), 130.8, 138.0, 141.1 (Ar); ²⁹Si NMR (coupled DEPT, 53.6 MHz, C₆D₆): δ = -63.51 (qd, ¹J = 199.6 Hz, ³J = 8.0 Hz); IR (KBr): v = 2152.9, v(Si-H); MS (EI, 70 eV): m/z = 166 (M⁺), 151 (M⁺-CH₃), 135 (M⁺-SiH₃), 120 (M⁺-SiH₃-CH₃), 105 (M⁺-2 SiH₃); C₈H₁₄Si₂ (166.37): calcd. C 57.76, H 8.48, found C 57.67, H 6.90.

1,3-Disilyl-2,4,6-trimethyl-benzene (**11**): M.p.: 25 °C; ¹H NMR (400 MHz, C₆D₆): $\delta = 2.24$ (s, 6H, 4/6-CH₃), 2.30 (s, 3H, 2-CH₃), 4.25 (d, 6H, ¹J = 197.8 Hz, SiH₃), 7.15 (s, 1H, 5-Ar); ¹³C NMR (100 MHz, C₆D₆): $\delta = 23.59$ (2-CH₃), 24.00 (4/6-CH₃), 124.5, 129.6, 145.0, 147.0 (Ar); ²⁹Si NMR (79.4 MHz, coupled DEPT, C₆D₆): $\delta = -76.95$ (q, ¹J = 197.8 Hz); MS (EI, 70 eV): m/z = 180 (M⁺), 165 (M⁺-CH₃), 149 (M⁺-SiH₃), 134 (M⁺-SiH₃-CH₃), 117 (M⁺-2 SiH₃), 107 (M⁺-SiH₃-2 CH₃); C₉H₁₆Si₂ (180.40): calcd. C 59.92, H 8.94, found C 59.46, H 9.00.

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