Synthetic Pathways to Hydrogen-Rich Polysilylated Arenes from Trialkoxysilanes and Other Precursors

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The use of tri(alkoxy)silanes $(RO)_3SiH$, which have recently become commercially available in greater than research scale quantities (R = Me, Et), has been probed for the preparation of hydrogen-rich arylsilanes $ArSiH_3$. It was found that the silylation of aryl-lithium or (in situ) aryl-Grignard reagents is followed by RO/H ligand redistribution and can lead to fully hydrogenated products in a one-pot reaction without employment of any additional metal hydride. After hydrolytic workup, the overall yields are between 20 and 30%. Silane gas and tetra(alkoxy)silanes are the main byproducts. At an early stage of the reactions, the whole set of mixed-ligand silanes $(RO)_{3-n}H_nSiAr$ can be detected by GLC/MS techniques. Induced by the organometallic base, the reaction also includes aryl scrambling to give silanes Ar_nSiH_{4-n}, $Ar_nSi(OR)_{4-n}$, and $Ar_nSi(H/OR)_{4-n}$. A reaction scheme is proposed that accounts for the product distribution. Examples are given for Ar = phenyl, 4-biphenylyl, 4,4′-biphenyldiyl, 1-naphthyl, and 2-anisyl. The reaction gives only very poor yields of di(silyl)arenes. Silanes of this type were therefore prepared from $(RO)_3SiH$ compounds and the corresponding di(halo)arenes by the in situ Grignard procedure followed by $LiAlH_4$ reduction. Representative cases are 1,2- and 1,4-di(silyl)benzene and 1,4-di(silyl)-2,5-dimethylbenzene. The primary reaction products 1,4-$(EtO)_3SiC_6H_4Si(OEt)_3$ and 1,4-$[(EtO)_3Si]_2$-2,5-$(CH_3)_2C_6H_2$ have been isolated, and the crystal structure of the latter was determined.

Introduction

Aromatic hydrocarbons with silyl substituents $-SiH_3$ are important precursors for the generation of di-, oligo-, and polysilanes with aryl substituents. 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.[1,2] Several efficient methods have been developed for dehydrogenative or desilanative coupling reactions of simple silyl-arenes to generate silyl or disilanyl bridges between the hydrocarbon units.[3−23] The structure of the resulting coupling products can be designed by choosing an appropriate substitution pattern of the silyl-arenes (aryl-silanes), but to date only a very limited selection of precursors is available.[4,10−14]

More often than not, the synthesis of hydrogen-rich arylsilanes Ar-SiH_3 is much more difficult than that of the corresponding alkyl/aryl-silanes Ar-SiR_3, for which many preparative pathways are known. The most convenient reactions are the stoichiometric Grignard reaction[24] or an in situ Grignard procedure[25] introduced by Tilley et al.—as a modified version of the Merker−Scott reaction[26]—which employs an aryl halide, elemental magnesium, and a tetra(alkoxy)silane. Subsequently the trialkoxysilyl-arene intermediates have to be converted into the silyl-arenes by reduction with metal hydrides, preferably $LiAlH_4$. Yields of *mono*silylation are acceptable, and the first step of the process is simple and uses cheap starting materials. However, *poly*silylation of arenes by in situ Grignard reaction is

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difficult because of limitations set by steric hindrance of the bulky $-Si(OR)_3$ groups.[27−31]

Higher yields can be achieved in the direct nucleophilic substitution reaction of an aryl halide with a metal silyl reagent M-SiH_3 (M = Na, K),[28−30,32−35] but this method is difficult to control, and the metal silyls are not readily accessible. On the other hand, *poly*-silylation is more readily achieved with $MSiH_3$ reagents since steric hindrance is not a problem.[33,34]

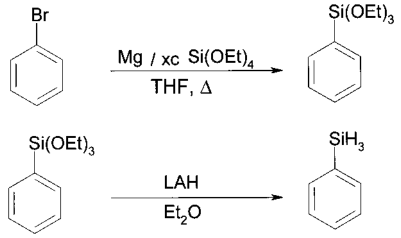
Arylsilanes with bulky aryl groups have been synthesized from the corresponding aryl-lithium reagents and silicon halides (including trichlorosilane) followed by hydride reduction.[36−38] Selectivity is only satisfactory with few and large aryl groups. Ortho-disubstitution can be assisted by employing difunctional amines as auxiliary reagents which direct the metalation to positions adjacent to the first silyl group.[39]

Aryl-silanes are subject to ligand redistribution reactions, mainly using base catalysis,[40] and this process can be used for the synthesis of compounds with a stoichiometry not directly accessible by other methods.[41] However, this ligand scrambling can also be a disadvantage in reaction mixtures where an excess of basic reagents (including, e.g., $LiAlH_4$) is used in the primary synthesis. The redistribution is not limited to base catalysis and may also be induced by late transition metal compounds.[42]

Aryl groups can be cleaved from their silyl substituents in dehydroarylation reactions with strong acid.[43] If different aryl groups are present, this cleavage is regioselective and allows the design of certain structural patterns from mixed aryl-substituted precursors.[44,45] Aryl groups with good leaving group properties can therefore be considered as protecting groups in multistep syntheses.[45]

In the present study we tried to open new or modified synthetic pathways to hydrogen-rich aryl-silanes using inter alia tri(alkoxy)silanes as starting materials. These mixed alkoxide hydrides of silicon have recently become commercially available.[46] They appeared to be very convenient reagents since they combine the experimental advantages of the tetra(alkoxy)silanes and the hydride functionality.

Scheme 1



This could open up a one-step route to silanes *without using metal hydride reagents* in a second step. To the best of our knowledge $HSi(OR)_3$ reagents have previously been probed for usage in the preparation of arylsilanes only for transition-metal-mediated reactions of iodo-silanes.[47] The method was not applicable to the cheaper aryl chlorides or bromides. In our own studies, for certain specific substitution patterns of poly(silyl)-arenes the conventional methods have also been employed where appropriate.

The work described herein is a continuation of our previous studies which led to the isolation of several poly(silyl)arenes including the fully silyl-substituted benzene[48] $C_6(SiH_3)_6$ and several naphthalene and anthracene derivatives.[30] However, several substitution patterns were not accessible by conventional procedures.

Preparative Results

Tetra(alkoxy)silanes $Si(OR)_4$ with R = Me, Et are known to give aryl-trialkoxysilanes in almost quantitative yield on treatment with an aryl-lithium reagent.[50] This was confirmed in the present study. The intermediates Ar-$Si(OR)_3$ must then be converted into the silanes Ar-SiH_3 by reduction with $LiAlH_4$ (Scheme 1). This second step is not a high-yield process owing to significant ligand redistribution.

When tri(alkoxy)silanes $HSi(OR)_3$ are reacted with aryl-lithium reagents under similar conditions, a complex mixture of products is observed. Thus equimolar quantities of $HSi(OEt)_3$ and PhLi (4 h in pentane/cyclohexane/Et_2O at 20 °C) afford the set of phenyl/ethoxysilanes $Si(OEt)_4$, $PhSi(OEt)_3$, $Ph_2Si(OEt)_2$, Ph_3SiOEt, and Ph_4Si, along with the set of phenyl/hydridosilanes $PhSiH_3$, Ph_2SiH_2, and Ph_3SiH, as shown by GC/MS analysis, with Ph_3SiH and $Si(OEt)_4$ as the predominant components. In addition, even mixed alkoxy-/hydrido-/phenylsilanes such as $Ph(H)Si(OEt)_2$ are detected in small quantities. This result shows that arylation of the trialkoxysilane is not only followed by Ph/OEt scrambling but also associated with hydride transfer between the products. As expected, a careful analysis of the product mixture and the headspace of

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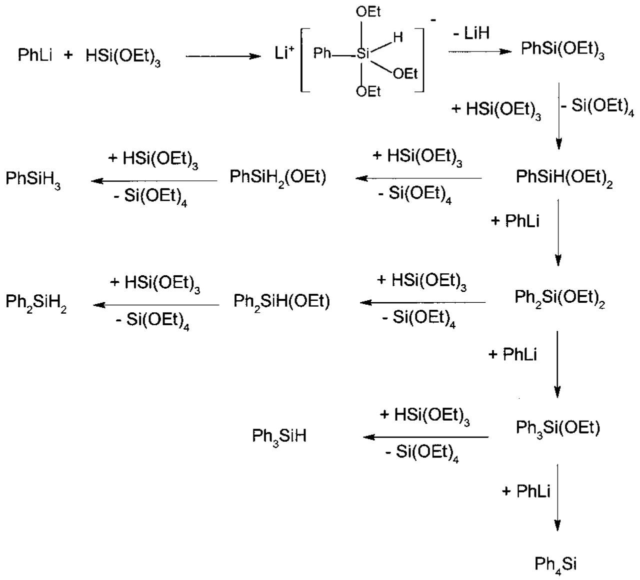
Scheme 2



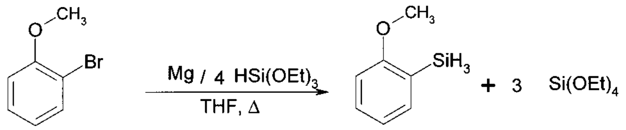
the reaction vessel gave proof also for the presence of silane SiH_4. The $(RO)_3SiH$ component thus acts as a hydride transfer reagent. The transfer reactions may be interpreted through a mechanism involving also the transitory existence of LiH, which can also play a role in the dehalogenation of the aryl halides. The reactions may be summarized as shown in Scheme 2.

Similar observations were made in related in situ Grignard reactions using bromobenzene, elemental magnesium, and $HSi(OEt)_3$ (in tetrahydrofuran at reflux temperature). The reaction is much slower than the PhLi reaction and affords predominantly $PhSi(OEt)_3$ as the primary product. However, this is accompanied by significant amounts of $Si(OEt)_4$, suggesting again a dismutation of $HSi(OEt)_3$ to give other hydrides. A careful study of the reactions in a closed system collecting also the gaseous products has shown that all five products $H_nSi(OEt)_{4-n}$ with $n = 0-4$ are present. Because these products are all converted into the corresponding aryl-/hydridosilanes, this reaction can be used to produce hydrogen-rich arylsilanes from trialkoxysilanes in one step and without an additional metal hydride reagent.

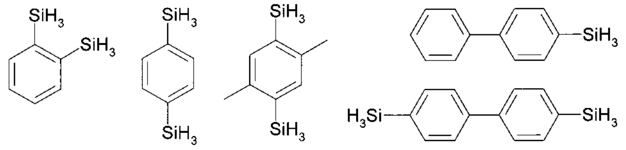
Monitoring the reaction of 1-bromonaphthalene with triethoxysilane and magnesium in tetrahydrofuran at 70 °C (reflux) by GC/MS has shown that $HSi(OEt)_3$ and $1\text{-}C_{10}H_7Br$ are rapidly consumed (within 30 min) to give mainly tetraethoxysilane, together with several byproducts, the relative concentrations of which become nearly constant after about 3 h. The dominant products after equilibration are 1-silylnaphthalene and 1-(triethoxysilyl)naphthalene. Workup of the reaction mixture for the fully hydrogenated silyl compound $1\text{-}(H_3Si)C_{10}H_7$ is convenient, because acid hydrolysis will degradate all alkoxysilanes to high molecular weight siloxanes, which can be easily separated.

In another specific example, the reaction of 2-bromoanisole with 4 equiv of $HSi(OEt)_3$ and magnesium in tetrahydrofuran gives, after 3 h and acid hydrolysis followed by extraction, 2-silylanisole in 28% isolated yield (Scheme 3). An analysis of the reaction mixture before hydrolysis shows small residual amounts of $HSi(OEt)_3$, together with minute amounts of anisole (from reductive debromination), 2-(ethoxysilyl)anisole, 2-(diethoxysilyl)anisole, and 2-(triethoxysilyl)anisole. The main component, $Si(OEt)_4$, is accompanied by traces of hexa(ethoxy)disiloxane, $(EtO)_3SiOSi(OEt)_3$, as its hydrolysis product. After hydrolysis and extraction the 2-silylanisole contains only small amounts of anisole.

Scheme 3



Scheme 4



The reaction sequence is also applicable for other aryls (Scheme 4): The diaryls 4-bromo- and 4,4′-dibromobiphenyl are the starting materials for the synthesis of the corresponding silylated biphenyls, $H_3Si\text{-}C_6H_4\text{-}C_6H_5$ and $H_3Si\text{-}C_6H_4\text{-}C_6H_4\text{-}SiH_3$, which are isolated in 65 and 60% yield, respectively.

Bis(silyl)benzenes $[C_6H_4(SiH_3)_2]$ can be observed as products in the reactions of the corresponding dibromobenzene precursors and triethoxysilane/magnesium in tetrahydrofuran at reflux temperature, but the complete hydrogenation is too slow and incomplete even after long reaction times. Therefore lithium aluminum hydride reduction of the product mixture, which contains the bis(triethoxysilyl)benzenes as the primary products already after about 30 min, gives better yields after acceptable reaction times. $1,4\text{-}C_6H_4(SiH_3)_2$ has thus been obtained from $1,4\text{-}C_6H_4Br_2/HSi(OEt)_3/Mg$, followed by $LiAlH_4$, in 68% yield.

The dimethylated homologue 1,4-dibromo-2,5-dimethylbenzene can be converted similarly into 1,4-di(silyl)-2,5-dimethylbenzene in 65% yield, with 1,4-bis(triethoxysilyl)-2,5-dimethylbenzene as the primary product. This intermediate could be crystallized and its structure determined (below).

By contrast, the same in situ Grignard reaction with the ortho-isomer, $1,2\text{-}C_6H_4Br_2$, gives only small yields (<30%), because the intermediate species, 2-(triethoxysilyl)bromobenzene, is subject to debromination, affording mainly phenylsilane $PhSiH_3$ before undergoing rearrangement to the sterically less hindered hydridoalkoxy-substituted compound which allows ortho-disilylation.

All compounds have been identified by standard analytical and spectroscopic methods, including mainly GLC/MS and NMR techniques.

Structural Studies

The crystal structures of 1,2-, 1,3-, and 1,4-di(silyl)benzene have recently been published from this laboratory. Preparation of the samples was in part based on the syntheses described in the present report. All three compounds are low-melting solids, and structural work requires sophisticated techniques which justified the presentation of this part of the studies in a separate account.[49]

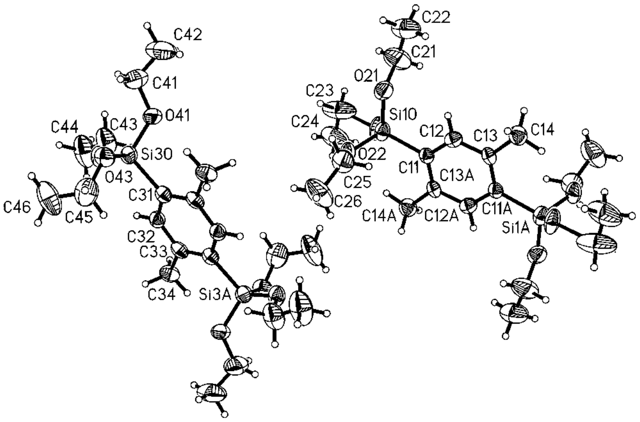


Figure 1. The two independent molecules of 1,4-[$(EtO)_3Si]_2$-2,5-$(CH_3)_2C_6H_2$ (ORTEP, 50% probability ellipsoids for the non-hydrogen atoms) with atomic numbering. In each molecule the ring atoms and their substituents are related by a center of inversion in the ring centroids. Selected bond lengths (Å) and angles (deg): Si10−O21 1.616(6), Si10−O22 1.598(6), Si10−O23 1.609(5); Si30−O41 1.603(6), Si30−SiO42 1.611(6), Si30−O43 1.624(5); Si10−C11 1.865(7), Si30−C31 1.858(8). C11−Si10−O21 109.9(3), C11−Si10−O22 107.8(3), C11−Si10−O23 111.7(3); C31−Si30−O41 108.1(3), C31−Si30−O42 110.8(3), C31−Si30−O43 110.0(3).

1,4-Bis(triethoxysilyl)-2,5-dimethylbenzene crystallizes on slow cooling of the liquid compound to −40 °C in a capillary on the diffractometer. The crystals thus obtained are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. The asymmetric unit contains one-half of each of two independent molecules, which have a center of inversion at the centroid of the benzene ring. The two molecules and the atomic numbering are shown in Figure 1. The triethoxysilyl groups are found in rotamer positions where the neighboring methyl groups have the least steric hindrance. Owing to the high flexibility of silicon-bound alkoxy groups, the structure is not very accurate. Therefore the structural details are not discussed here any further. The result serves as a proof that the silylation of the dibromoxylene occurred without any rearrangments or shift of substituents. It should be noted that substituent scrambling has been observed in several polysubstituted benzene molecules upon treatment with strong base or powerful nucleophiles which induce neighboring group effects.

Experimental Section

General Procedures. All bromoarenes were commercially available and used as received. Alkoxysilanes were purchased from ABCR and, when necessary, purified by distillation over a short column.

Reactions were carried out under an atmosphere of purified nitrogen. All solvents were distilled from an appropriate drying agent and stored above 4 Å molecular sieve and under nitrogen. Mass spectra were recorded on a Hewlett-Packard MS 5971 A spectrometer using EI at 70 eV as an ionization method. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonance of C_6D_6 (^1H,^{13}C) or relative to the external standard TMS (^{29}Si). GC/MS analyses of the reaction mixtures were carried out on a HP-5890 Series II (Hewlett-Packard) gas chromatograph with a HP-MS 5971 A mass-selective detector. The single-crystal X-ray diffraction measurements were performed at −130 °C on a Nonius DIP 2020 diffractometer using graphite-monochromated Mo Kα radiation.

Reaction of Triethoxysilane with Phenyllithium. To a solution of 1.05 g of triethoxysilane (6.4 mmol) in 10 mL of pentane was added dropwise 4.00 mL of a 1.6 M solution of phenyllithium in cyclohexane/Et_2O (7:3) via a rubber septum at room temperature. Spontaneous formation of a gray precipitate occurred. The resulting mixture was stirred at room temperature for another 4 h. Precipitated salts were filtered off, and the reaction mixture was investigated by GC/MS, showing a mixture of the different phenylsilanes H_nSiPh_{4-n} ($n = 0-3$) and alkoxysilanes $H_nSi(OEt)_{4-n}$ ($n = 0-3$). $PhSiH_3$: MS (m/z) 108 (100, M^+),107, 106, 105, 81. Ph_2SiH_2: MS (m/z) 184 (100, M^+), 183, 182, 107, 106, 105. Ph_3SiH: MS (m/z) 260 (M^+), 259, 183, 182 (100), 181, 180, 105. Ph_4Si: MS (m/z) 336 (M^+), 260, 259 (100), 258, 257, 183, 182, 181, 180, 105. $Si(OEt)_4$: MS (m/z) 208 (M^+), 207, 193, 163, 149 (100), 121, 119. $HSi(OEt)_3$: MS (m/z) 164 (M^+), 163 (100), 149, 119, 105. $H_2Si(OEt)_2$: MS (m/z) 121,120 (M^+, 100), 75.

Preparation of 2-Silylanisole. 2-Bromoanisole (2.0 g, 11 mmol), 7.2 g of triethoxysilane (44 mmol, 4.0 equiv), 0.60 g of magnesium turnings (14 mmol, 1.3 equiv), and 20 mL of THF were placed in a round-bottom flask. A tiny crystal of iodine was added, and the flask was closed by a rubber septum which was connected to a rubber balloon via a syringe needle. The reaction mixture was heated to 70 °C for 5 h. After cooling to 0 °C all volatile components were removed in vacuo, and the mixture was poured on cold 5% H_2SO_4. After 30 min of stirring hydrolysis of all alkoxy-substituted silanes was complete and the solution was decanted from the precipitated polysiloxanes. The aqueous phase was extracted two times with 40 mL of pentane, and the collected organic fractions were dried over $MgSO_4$. After evaporation of the solvent, the oily residue was distilled to give 0.42 g of 2-silylanisole (28%): bp 41 °C/8 Torr; MS m/z 138(M^+),107($M^+ - SiH_3$),77($M^+ - SiH_3 - OCH_3$); ^1H NMR δ (C_6D_6) 3.36 (s, 3H, OCH_3), 4.14 (d, 3H, H_3Si, $J = 201$ Hz), 7.10−7.20 (m, 4H, phenyl ring protons); ^{13}C NMR δ (C_6D_6) 54.2 (OCH_3), 115.1, 125.8, 131.6, 132.0, 136.6, 160.9 (C_6H_4); ^{29}Si NMR δ (C_6D_6) −60.9 (qd, $J = 201$ Hz, $J = 7$ Hz).

Preparation of 1,2-Disilylbenzene. In a 100 mL round-bottom flask equipped with a magnetic stirrer were placed 0.62 g of magnesium turnings (26 mmol, 1.3 bromo equiv), 3.1 g of 1,2-dibromobenzene (13 mmol), and 17 g of triethoxysilane (0.32 mol, 4 bromo equiv) in 30 mL of THF. A small crystal of iodine was added, and the flask was closed with a rubber septum that had a rubber ballon attached via a syringe needle. The mixture was heated to 60 °C for 5 h and then cooled to room temperature. THF and any volatile silanes (including tetraethoxysilane) were removed in vacuo. The residue was taken up in hexane and filtered from precipitated magnesium salts and unconsumed magnesium. Hexane was removed in vacuo and the remaining oil taken up in 80 mL of Et_2O. This solution was added dropwise to a suspension of $LiAlH_4$ (1.0 g, 26 mmol) in 100 mL of Et_2O at −20 °C. After addition was completed the mixture was stirred at room temperature for another 24 h. The reaction mixture was poured very slowly on cold 5% aqueous H_2SO_4 and the water layer extracted three times with 50 mL of hexane. The collected organic extracts were dried over $MgSO_4$ and the solvent evaporated. The remaining oil was distilled under reduced pressure to give 0.52 g (29%) of 1,2-disilylbenzene: bp 61 °C/10 Torr; MS m/z 138 (M^+), 107 ($M^+ - SiH_3$); ^1H NMR δ (C_6D_6) 4.29 (d, 6H, H_3Si, $J = 201$ Hz), 7.06 (d, 2H, $J = 7.0$ Hz, $HC_{3,6}$), 7.35 (d, 2H, $J = 7.0$ Hz, $HC_{4,5}$); ^{13}C NMR δ (C_6D_6) 129.8 ($C_{1,2}$), 136.6 ($C_{3,6}$), 137.6 ($C_{4,5}$); ^{29}Si NMR δ (C_6D_6) −61.5 (qd, $J = 201$ Hz, $J = 7$ Hz).

Preparation of 1,4-Disilylbenzene. In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed 82 g of triethoxysilane (0.50 mol, 5 bromo equiv), 3.6 g of magnesium turnings (150 mmol, 1.5 bromo equiv), and 1.2 g of 1,4-dibromobenzene (5.1 mmol) in 80 mL of THF. A small crystal of iodine was added, and the mixture was heated to 50 °C. A solution of a further 10.6 g of 1,4-dibromobenzene (44.9 mmol) in 80 mL of THF was then added in such a way that the reaction mixture was always kept at reflux. Monosilane evolving from the condenser was converted into silica by combustion as it left the mercury gauge. After addition was complete, the mixture was held at reflux for another 3 h. Then THF was removed at 0 °C under reduced pressure. The resulting oil was taken up in 200 mL of hexane and filtered from all solids. After evaporation of the solvent and the tetraethoxysilane in vacuo, the remaining oil was taken up in 150 mL of Et_2O and added to a suspension of 4.75 g of $LiAlH_4$ (125 mmol) in 200 mL of Et_2O at −20 °C. After addition was complete, the mixture was stirred for another 70 min at room temperature. The reaction mixture was poured very slowly on cold, aqueous 5% H_2SO_4 and the water phase extracted three times with 50 mL of hexane. The collected organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The remaining oil was distilled under reduced pressure to give 4.70 g (68%) of 1,4-disilylbenzene: bp 140 °C; MS *m/z* 138(M^+), 107 ($M^+ - SiH_3$); ^1H NMR δ (C_6D_6) 4.17 (d, 6H, $J = 201$ Hz, SiH_3), 7.29 (s, 4H, C_6H_4); ^{13}C NMR δ (C_6D_6) 130.2 (2C, *C*-Si), 135.6 (4C,*C*-H); ^{29}Si NMR δ (C_6D_6) −59.4 (q, $J = 201$ Hz).

Preparation of 1,4-Bis(triethoxysilyl)-2,5-dimethylbenzene. In a three-necked flask equipped with a reflux condenser and a dropping funnel were placed 54 g of triethoxysilane (0.33 mol, 5 bromo equiv), 2.5 g of magnesium turnings (0.10 mol, 1.5 bromo equiv), and 0.9 g of 1,4-dibromo-2,5-dimethylbenzene (3.4 mmol) in 100 mL of THF. After addition of a small iodine crystal the mixture was heated to 50 °C. A solution of 8.1 g of 1,4-dibromo-2,5-dimethylbenzene (44.9 mmol) in 80 mL of THF was added in such a way that the reaction mixture was always kept at reflux. Just like with the synthesis of 1,4-disilylbenzene, evolving monosilane from the condenser was oxidized to silica. After addition was complete, the mixture was held at reflux for another 3.5 h. It was then cooled to 0 °C and the solvent removed under reduced pressure. The resulting oil was taken up in 200 mL of hexane and filtered from all solids. After evaporation of the solvent and tetraethoxysilane in vacuo, the crude product was separated by kugelrohr distillation to give 8.5 g of 1,4-bis(triethoxysilyl)-2,5-dimethylbenzene (58%). Anal. Found: C 55.20, H 8.83. $C_{20}H_{38}Si_2O_6$ requires: C 55.80, H 8.91; bp 120 °C/5 Torr; MS *m/z* 430 (M^+), 415 ($M^+ - CH_3$), 385 ($M^+ - OEt$), 370 ($M^+ - OEt - CH_3$), 357 ($M^+ - Si - OEt$), 340 ($M^+ - 2\ OEt$), 313 ($M^+ - 2OEt - Si$); ^1H NMR δ (C_6D_6) 1.15 (t, 18H, $J = 7.0$ Hz, CH_3), 2.64 (s, 6H, CH_3), 3.86 (q, 12H, $J = 7.0$ Hz, OCH_2), 7.93 (s, 2H, $C_6\mathit{H}_2$); ^{13}C NMR δ (C_6D_6) 18.4 (CH_3), 22.3 (aryl-CH_3), 58.7 (CH_2), 133.3, 138.0, 140.6 (C_6H_2); ^{29}Si NMR δ (C_6D_6) −56.9 (s)

Preparation of 1,4-Disilyl-2,5-dimethylbenzene. 1,4-Bis(triethoxysilyl)-2,5-dimethylbenzene (8.4 g, 20 mmol) was dissolved in 100 mL of diethyl ether and added via a dropping funnel to a suspension of 2.3 g of $LiAlH_4$ (60 mmol) in 100 mL of Et_2O at 0 °C. After addition was complete, the resulting mixture was stirred for another 3 h before being poured slowly on cold 5% aqueous H_2SO_4. The water phase was extracted three times with 50 mL of Et_2O, and the organic fractions were collected and dried over $MgSO_4$. Removal of the solvent left a viscous oil, from which 3.18 g (96%) of 1,4-disilyl-2,5-dimethylbenzene was distilled under reduced pressure. Anal. Found: C 57.67, H 8.90. $C_8H_{14}Si_2$ requires: C 57.83, H 8.43; bp 155 °C; MS *m/z* 166 (M^+), 135 ($M^+ - SiH_3$), 120 ($M^+ - SiH_3 - CH_3$), 105 ($M^+ - SiH_3 - 2\ CH_3$); ^1H NMR δ (C_6D_6) 2.15 (s, 6H, CH_3), 4.22 (d, 6H, $J = 201$ Hz, SiH_3), 7.22 (s, 2H, $C_6\mathit{H}_2$); ^{13}C NMR δ (C_6D_6) 21.8 (CH_3), 130.8, 138.0, 141.1 (C_6H_2); ^{29}Si NMR δ (C_6D_6) −63.5 (q, $J = 201$ Hz).

Preparation of 4-Silylbiphenyl. A flask equipped with a reflux condenser was charged with 28 g of triethoxysilane (0.17 mol, 4.0 equiv), 1.4 g of magnesium turnings (56 mmol, 1.3 equiv), and 10.0 g of 4-bromobiphenyl (42.9 mmol) in 300 mL of THF. A small crystal of iodine was added, and the mixture was kept at reflux for 3 days. Monosilane evolving from the condenser was oxidized to silica. The mixture was cooled to 0 °C, and THF was removed under reduced pressure. The resulting oil was taken up in 200 mL of hexane and filtered from all solids. After evaporation of the solvent and tetraethoxysilane in vacuo, the remaining oil was taken up in 200 mL of Et_2O and added to a suspension of $LiAlH_4$ (64 mmol, 2.4 g) in 150 mL of Et_2O at −20 °C. After addition was complete, the mixture was stirred another 120 min at room temperature. The reaction mixture was poured very slowly on cold 5% aqueous H_2SO_4 and the water phase extracted three times with 100 mL of hexane. The collected organic extracts were dried over $MgSO_4$, and the solvent was evaporated to give 5.13 g (65%) of 4-silylbiphenyl as a white solid. Anal. Found: C 71.34, H 6.77. $C_{12}H_{12}Si$ requires: C 72.54, H 6.53; MS *m/z* 184 (M^+), 153 ($M^+ - SiH_3$), 106 ($M^+ - PhH$); ^1H NMR δ (C_6D_6) 4.30 (d, 3H, $J = 202$ Hz, SiH_3), 7.20 (t, 1H, $J = 6$ Hz, 4′-H), 7.38 (dd, 2H, $J = 8$ Hz, $J = 8$ Hz, 3′-H), 7.43 (m,2H, 2′-H), 7.57 (d, 2H, $J = 8.1$ Hz, 2-H), 7.95 (d, 2H, $J = 8.1$ Hz, 3-H); ^{13}C NMR δ (C_6D_6) 126.7, 127.2, 127.4, 129.0, 136.6, 141.1, 143.1, 143.5; ^{29}Si NMR δ (C_6D_6) −59.9 (qm, $J = 202$ Hz).

Preparation of 4,4′-Disilylbiphenyl. A flask equipped with a reflux condenser was charged with 43 g of triethoxysilane (0.26 mol, 4.0 bromo equiv), 2.0 g of magnesium turnings (84 mmol, 2.6 equiv), and 10.0 g of 4,4′-dibromobiphenyl (32.1 mmol) in 200 mL of THF. A small crystal of iodine was added, and the mixture was kept at reflux for 5 days. Monosilane evolving from the condenser was oxidized to silica. The mixture was cooled to 0 °C, and THF was removed under reduced pressure. The resulting oil was taken up in 200 mL of hexane and filtered from all solids. After evaporation of the solvent and the generated tetraethoxysilane in vacuo, the remaining oil was taken up in 300 mL of Et_2O and added to a suspension of $LiAlH_4$ (96 mmol, 3.7 g) in 200 mL of Et_2O at −20 °C. After addition was complete, the mixture was stirred another 120 min at room temperature. The reaction mixture was poured very slowly on cold aqueous 5% H_2SO_4 and the water phase extracted three times with 100 mL of hexane. The collected organic extracts were dried over $MgSO_4$, and the solvent was evaporated to give 4.1 g (60%) 4,4′-disilylbiphenyl as a white solid. Anal. Found: C 65.32, H 6.31. $C_{12}H_{14}Si_2$ requires: C 67.29, H 6.54; MS *m/z* 214 (M^+), 183 ($M^+ - SiH_3$), 105 ($M^+ - PhH - SiH_3$); ^1H NMR δ (C_6D_6) 4.29 (d, 6H, $J = 202$ Hz, SiH_3), 7.36 (d, 4H, $J = 8$ Hz, 2-H), 7.43 (d, 4H, $J = 8$ Hz, 3-H); ^{13}C NMR δ (C_6D_6) 127.1, 127.3, 127.8, 136.7; ^{29}Si NMR δ (C_6D_6) −59.9 (qm, $J = 202$ Hz).

Crystal Structure Determination. Crystals (0.30 × 0.30 × 0.20 mm) of 1,4-$[(EtO)_3Si]_2$-2,5-$(CH_3)_2C_6H_2$ ($C_{20}H_{18}O_6Si_2$, molecular mass 430.68) are triclinic [$a = 9.5928(9)$ Å, $b = 11.2948(9)$ Å, $c = 12.347(1)$ Å, $\alpha = 92.709(3)°$, $\beta = 102.533(3)°$, $\gamma = 107.942(9)°$], space group $P\bar{1}$, $Z = 2$, at 143(2) K ($V = 1232.9(2)$ Å^3, calcd density 1.160 g cm^{-3}, $F(000)$ 468, absorption coeff 0.173 mm^{-1}).

On a DIP 2020 diffractometer (λ 0.71073 Å) 41 756 reflections were collected for a θ range 3.44−25.33° and limiting indices $0 = h = 10$, $-13 = k = 12$, $-14 = l = 14$, of which 4055 were unique [$R(\mathrm{int}) = 0.0800$]. Full-matrix least-squares refinement on F^2 and with 4055 data, no restraints and 253 parameters gave final indices R1 = 0.1295, wR2 = 0.2971 [$I \geq 2\sigma(I)$] and R1 = 0.1764, $wR'' = 0.3278$ (all data). Largest difference peak and hole: 0.412/−0.308 e Å^{-3}. Further details of the structure determination have been deposited.

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Supporting Information Available: This material (six pages of atomic coordinates and a full list of interatomic distances and angles) is available free of charge via the Internet at http://pubs.acs.org.

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