Syntheses and Structures of Silyl-Group-Containing Hexaalkylated Benzenes

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Friedel−Crafts alkylation of vinyldichloromethylsilane to benzene in the presence of aluminum chloride catalyst at room temperature gave hexakis((dichloromethylsilyl)ethyl)benzene (**1**) in 56% yield, along with small amounts of less alkylated products. **1** was easily converted to the corresponding compounds, $C_6(CH_2CH_2SiMeR_2)_6$; (**5** (R = OCH_3), **6** (R = H), **7** (R = CH_3), **8** (R = vinyl), **9** (R = allyl), **10** (R = ethynyl), and **11** (R = benzyl)) by reaction with the appropriate nucleophilic reagents. The molecular structures of hexakis((methylsilylethyl)benzene (**6**) and the solvent adducts of hexakis((trimethylsilyl)ethyl)benzene (**7**·$2CH_2Cl_2$) and hexakis((dibenzylmethylsilyl)ethyl)benzene (**11**·$2CHCl_3$) have been determined by X-ray diffraction studies. Each dichloromethane and chloroform molecule formed C−H···aryl hydrogen bonds, one above and one below, to the ring centroid. The distances between the carbon and the ring centroid were 3.469 and 3.466 Å for CH_2Cl_2 and $CHCl_3$, respectively.

Introduction

Alkylations of aromatic compounds with alkyl halides or olefins in the presence of Lewis acid catalysts have been reported in many articles since the reaction of benzene with amyl chloride to produce amylbenzene was reported by Friedel and Crafts in 1877.[1] The Friedel−Crafts type alkylation of benzene with small alkylating agents does not stop with the introduction of one alkyl group onto the ring but gives polyalkylated products. Thus, hexamethylbenzene and hexaethylbenzene were prepared by alkylating benzene with methyl chloride and ethyl chloride or ethylene a century ago.[2] Propylation of benzene and propylbenzene with *n*-propyl chloride in the presence of aluminum chloride was reported to give a mixture of hexapropylbenzenes having *n*-propyl- and isopropyl groups in low yield, while the trimerization of dipropylacetylene using a transition-metal catalyst gave hexapropylbenzene in 70% yield.[3] However, the same trimerization of diisopropylacetylene to hexaisopropylbenzene gave only 3.1% yield due to the steric interaction of bulky isopropyl groups. Although hexaalkylbenzenes have received much attention[4−7] because of the synthetic challenges for the sterically crowded molecular structures and their unique properties, the alkylation of benzene with alkyl halides or olefins containing silyl groups to peralkylated products has never been reported. Hexaalkylbenzenes containing functional groups such as ethynyl and ferrocenyl have been only prepared in multistep syntheses and in poor yields.[6,7]

The alkylation of substituted benzenes with alkenylsilanes has attracted little attention because of the low reactivity of vinylsilanes[8] and the difficulties of allylsilane syntheses.[9] Nametkin *et al.* first reported that the reaction of substituted benzenes with alkenylsilanes such as allylsilanes and vinylsilanes afforded mono- and bis(silylethyl)benzene derivatives.[10] We also reported detailed information on the Friedel−Crafts type alkylation of substituted benzenes with allyldichlorosilane, including relative reaction rates and product isomer distribution.[11] In an extension of this study, the polyalkylation of benzene with allylchlorosilanes was attempted but trialkylated products were the most highly alkylated compounds obtained, perhaps because of steric hindrance due to the bulky silyl-containing isopropyl groups.[12] Thus, it seemed worthwhile to investigate benzene alkylation with the less bulky vinylchlorosilanes.

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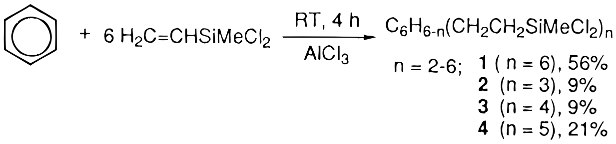
Scheme 1



In the present paper, we wish to report a convenient one-step synthesis of hexaalkylated benzene **1** by the Friedel−Crafts alkylation of benzene with dichloromethylvinylsilane and the derivatization of **1** with nucleophilic reagents such as MeOH, $LiAlH_4$, and Grignard reagents. The X-ray structures of three derivatives, hexakis(methylsilylethyl)benzene (**6**) and the solvent adducts of hexakis(trimethylsilylethyl)benzene (**7**·$2CH_2Cl_2$) and hexakis(dibenzylmethylsilylethyl)benzene (**11**·$2CHCl_3$), are also reported.

Results and Discussion

Polyalkylation of Benzene with Dichloromethylvinylsilane. When benzene was reacted with 6 equiv of dichloromethylvinylsilane in the presence of aluminum chloride at room temperature for 4 h, hexakis((dichloromethylsilyl)ethyl)benzene (**1**) precipitated from the reaction solution as the major product in 56% yield. The remaining solution contained less alkylated products: bis((dichloromethylsilyl)ethyl)benzene[8b] (4%), tris((dichloromethylsilyl)ethyl)benzene (**2**; 9%), tetrakis((dichloromethylsilyl)ethyl)benzene (**3**; 9%), and pentakis((dichloromethylsilyl)ethyl)benzene (**4**; 21%) (yields based on GLC area percentage). The results are shown in Scheme 1.

The hexaalkylation product **1** was further recrystallized from THF solution as colorless needlelike crystals, and spectroscopic analysis showed its high symmetry. In ^1H NMR spectroscopy, only three signals were observed at 0.87, and 1.30−1.36, and 2.71−2.77 ppm due to the SiMe and two CH_2 protons next to the silyl group and no signals in the benzene region appeared, indicating the hexaalkylation. The ^{13}C NMR spectrum, showing only four signals at 5.17, 22.08, 24.29, and 137.48 ppm in the benzene region, also corresponded well with the ^1H NMR spectrum.

Less alkylated compounds were purified by preparative GLC, and subsequent NMR spectral analysis allowed the assignments of their structures on the basis of the chemical shift and the integration ratio of peaks of two CH_2 protons and benzene protons in their ^1H NMR spectra. **2** and **3** were obtained as mixtures of three isomers, while **4** was only one product, as expected. The structures of isomeric products were deduced from the identification of the corresponding methylated compounds obtained from the methyl Grignard reaction. The methylated compounds are stable toward the atmosphere and allowed better separation of isomers by preparative GLC. All isomers were identified using ^1H NMR spectra, because the chemical shifts of the benzene hydrogens were very characteristic. GC/MS spectra of isomeric products showed the same fragmentation patterns with the same relative peak intensities.

Table 1. Reactant Mole Ratios and Product Distributions

mole ratio C_6H_6/silane[b]	products (%)[a] mono	bis	tris (**2**)	tetrakis (**3**)	pentakis (**4**)	hexakis (**1**)
2/1	55	29	10	6	0	0
1/1	48	28	16	4	4	0
1/2	27	29	13	14	12	5
1/3	16	7	8	11	26	32
1/6	0	4	10	9	21	56
1/9	0	4	11	9	18	58

[a] GLC yield. [a] Dichloromethylvinylsilane.

One of the two isomers of **2′** gave only a singlet in the benzene region, at high field. This was therefore assigned to the symmetric 1,3,5-isomer **2a′**. The other isomer, **2b′**, showed a multiplet, consistent with the assigned 1,2,4-structure. The isomers of **3′**, 1,2,4,5- and 1,3,4,5-tetrakis(trimethylsilylethyl)benzene (**3a** and **3b′**, respectively) were assigned by comparing their signals in the benzene region with those of tetramethylbenzene isomers.[13] The ratios **2a′**/**2b′** and **3a′**/**3b′** were 3/1 and 1/1, respectively, based on area percentage of GC/MS and ^1H NMR data. 1,2,3-Tris((trimethylsilyl)ethyl)benzene (**2c′**) and 1,2,3,4-tetrakis((trimethylsilyl)ethyl)benzene (**3c′**) were obtained in trace amounts, which could not be separated by preparative GLC, but structures were assigned by comparing the GC/MS spectra with those of isomers already identified. This alkylation is a convenient synthetic route to polyalkylated benzenes containing dichloromethylsilyl groups.

Reactant Ratio and Product Distribution. The alkylation was carried out using mole ratios ranging from 2/1 to 1/9 of benzene to dichloromethylvinylsilane for 4 h. Products from each run were methylated with methyl Grignard reagent, and the product distribution was then determined on the basis of GLC area percentages of the methylated products. The results are summarized in Table 1.

Product distributions varied, depending upon the mole ratio of benzene to dichloromethylvinylsilane. When an equivalent amount or a 2-fold excess of benzene with respect to dichloromethylvinylsilane was used, the yields of the major products, the mono- and dialkylated benzenes, remained about the same, around 50% and 30%, respectively. As the proportion of dichloromethylvinylsilane to benzene increased, mono- and dialkylated products decreased and disappeared or were formed in less than 5% yield, while **1** increased rapidly, becoming the major products (56−58%) at chlorosilane/benzene ratios of 6 or more. **4** increased to 26% yield at maximum and then decreased smoothly to 18%. **2** and **3**, however, were produced in yields near 10% at all chlorosilane/benzene ratios, suggesting that an equilibrium may exist.

To optimize the reaction time for the synthesis of **1**, the alkylation was carried out using a 1/6 mole ratio of benzene to dichloromethylvinylsilane at room temperature. Product distributions were determined at various time intervals. The results are summarized in Table 2. As shown in Table 2, the monoalkylated compound was a major product at the initial stage of alkylation, but it decreased drastically and almost disappeared after 4 h. However, **1** increased gradually and became the major product after 2 h. Similarly, as observed in Table 1, **2** and **3** maintained about 10% yields most of the time, indicating that they were being produced from

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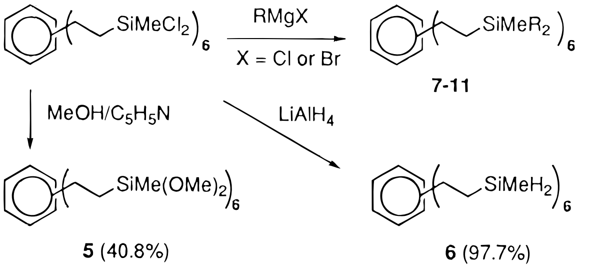
Table 2. Reactant Mole Ratios at Various Reaction Times

	products (%)[a]					
reacn time (min)	mono	bis	tris (**2**)	tetrakis (**3**)	pentakis (**4**)	hexakis (**1**)
2	98	2	0	0	0	0
10	39	23	14	9	10	5
20	34	31	8	10	11	6
40	27	21	14	9	15	14
60	19	17	15	11	17	21
120	4	9	13	12	20	42
240	0	4	9	9	22	58

[a] GLC yield.

Scheme 2



7 (R = CH_3), 66.7%
8 (R = Vinyl), 65.5%
9 (R = Allyl), 64.7%
10 (R = Ethynyl), 96.1%
11 (R = Benzyl), 98.8%

mono- and dialkylated products at almost the same rate at which they were being consumed to give higher alkylation products. These results show that **1** can be produced efficiently by using a 6-fold excess of chlorosilane and a reaction time of 2 h.

Derivatization of Hexakis((dichloromethylsilyl)ethyl)benzene. Chlorosilyl-containing organosilanes can easily react with organometallic reagents, alcohols, and amines to afford useful new organosilicon compounds in which Si−C, Si−O, and Si−N bonds are present.[14] The polyalkylated benzenes having chlorosilyl groups could serve as possible precursors for new silicon-containing materials.[15] To synthesize new silyl-group-containing hexaalkylated benzenes, **1** was treated with a variety of reagents such as methyl, vinyl, allyl, ethynyl, and benzyl Grignard reagents, methanol, and $LiAlH_4$ to give the corresponding derivatives (Scheme 2). These were obtained in good to excellent yield after purification by column chromatography or recrystallization. All new derivatives were satisfactorily characterized by elemental analysis and by NMR spectroscopy. Exact equivalence of the six silylethyl branches was observed by ^1H and ^{13}C NMR spectroscopy, consistent with the expected highly symmetrical structure of the hexasubstituted benzenes.

X-ray Crystallographic Analyses of 6, 11·2CHCl$_3$, and 7·2CH$_2$Cl$_2$. To further substantiate the molecular properties of the derivatives prepared above, the structures of compounds **6**, **11**, and **7** were determined by X-ray crystallography. Thermal ellipsoid diagrams for the three compounds are shown in Figures 1−3, wherein the atomic numbering schemes for each compounds are defined. As shown in Figures 2 and 3, **11** and **7** were crystallized as **11**·$2CHCl_3$ and **7**·$2CH_2Cl_2$ containing 2 mol of solvent.

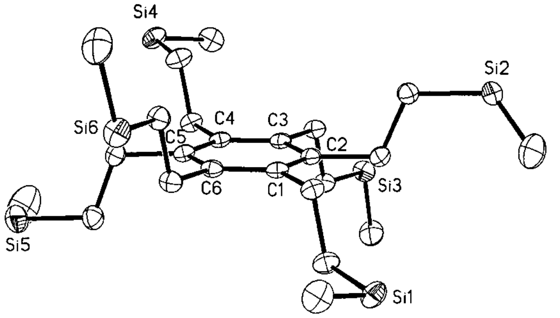


Figure 1. Molecular structure of **6** in the crystal state.

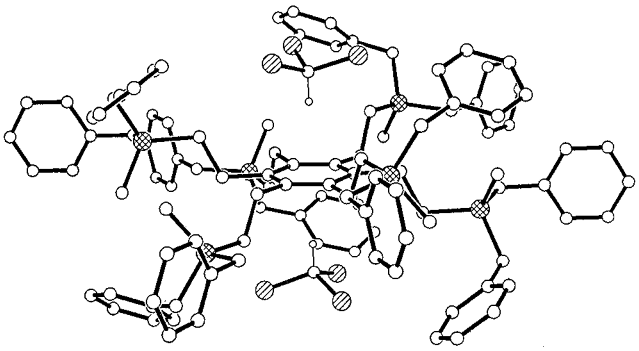


Figure 2. Molecular structure of **11**·$2CHCl_3$ in the crystal state.

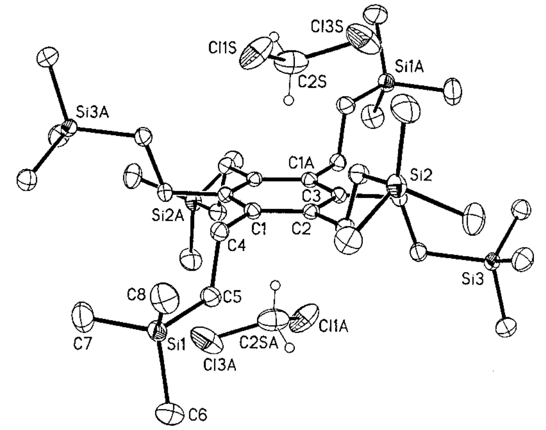


Figure 3. Molecular structure of **7**·$2CH_2Cl_2$ in the crystal state.

In **6**, the up and down alternation of silylethyl groups around the ring perimeter (Figure 1) closely resembled that in hexaalkylbenzenes[16] such as hexaethylbenzene[17] and hexakis((trimethylsilyl)methyl)benzene.[18] The average value of the ring-carbon bond distances ($C_{ar}-C_{ar}$), 1.409 Å, is slightly longer than in benzene (1.39 Å), but the six benzene carbons are nearly coplanar. The average $C_{ar}-C_{ar}-C_{ar}$ bond angles and $C_{ar}-CH_2CH_2-Si$ bond angles are 120.0 and 112.4°, respectively. The average bond lengths between silicon and carbon atoms for $Si-CH_3$ (1.859 Å) and $Si-CH_2CH_2$ (1.845 Å) are

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similar to the values of 1.89 and 1.87 Å reported for Si$-$(CH$_3$)$_4$[19] and PhSi$-$(CH$_3$)$_3$.[20] The average dihedral angle between the C$_{ar}-$CH$_2$CH$_2-$Si planes and the least-squares plane of the ring is 88.7°, and therefore the C$_{ar}-$CH$_2$CH$_2$ planes are essentially perpendicular to the benzene ring.

X-ray-quality crystals of the 1/2 chloroform solvate **11**·2CHCl$_3$ were grown by the slow evaporation of a saturated hexane solution including chloroform-*d*. The structure, shown in Figure 2, exhibits several features similar to those of **6**. (1) The six silyl-containing substituents are arranged alternatively above and below the plane of the central benzene ring, minimizing the steric interactions between the bulky substituents. (2) The six benzene carbons are nearly coplanar. The average value of the ring-carbon bond distances (C$_{ar}-$C$_{ar}$), 1.414 Å, is significantly longer than in benzene (1.39 Å) and in crystalline **6** (1.409 Å). The average C$_{ar}-$C$_{ar}-$C$_{ar}$ bond angles and C$_{ar}-$CH$_2$CH$_2-$Si bond angles are 120.0 and 115.2°, respectively. The average bond lengths between silicon and carbon atom for Si$-$CH$_3$ (1.866 Å), Si$-$CH$_2$Ph (1.886 Å), and Si$-$CH$_2$CH$_2$ (1.889 Å) are slightly longer than in crystalline **6** (Si$-$CH$_3$ = 1.859 Å and Si$-$CH$_2$CH$_2$ = 1.845 Å) due to the sterically bulky benzyl groups. The average dihedral angle between the C$_{ar}-$CH$_2$CH$_2-$Si planes and the least-squares plane of the ring is 88.1°, and thus the C$_{ar}-$CH$_2$CH$_2$ planes are essentially perpendicular to the benzene ring.

The two chloroform molecules are located above and below the central benzene ring, embedded in a cavity formed by three of the substituent groups. This is in contrast with previous reports on the structures of benzene$-$chloroform complexes.[21] The study of the C$_6$H$_6$·2CHCl$_3$ cluster using a combination of laser-induced fluoresence and resonant two-proton ionization techniques suggested a structure placing both CHCl$_3$ molecules on the same side of the benzene ring.

The angle CH$-$ring centroid$-$HC is 180°; therefore, the solvent molecules lie on the symmetry axis. The distance between the CHCl$_3$ carbon atom and the ring centroid, 3.466 Å, is determined by the hydrogen$-\pi$ interaction with the benzene ring.[22] The ideal distance between the CHCl$_3$ carbon atom and the arene centroid in the chloroform/benzene 1/1 complex has been calculated to be 3.36 Å.[23] For comparison, the distance has been reported to be 3.23 Å (2.27 Å for the chloroform hydrogen atom)[24] in the 1/1 adduct of spheriphane and chloroform. The longer distance shown in **11**·2CHCl$_3$ may arise because the two chloroform molecules are hydrogen-bonded to opposite sides of the central benzene ring, reducing basicity toward the protons.

It is of interest that the hydrogen bonding between **11** and chloroform takes place in a 1/2 ratio rather than the 1/1 proportions indicated by earlier calorimetric and spectroscopic studies.[25] The fact that hydrogen bonding takes place twice to the central benzene ring, but not to any of the 12 benzene rings in the benzyl substituents, is consistent with significantly greater basicity in the hexasubstituted ring.

Colorless cubic crystals of **7**·2CH$_2$Cl$_2$ were obtained from slow evaporation of a 1/1 dichloromethane/hexane solution of **7** as a solvent adduct in the monoclinic space group $P2_1/c$. The molecular structure closely resembled that of **11**·2CHCl$_3$, with the six silyl substituents arranged alternatively above and below the plane of the central benzene ring and solvent molecules located above and below the central benzene ring, embedded in a cavity formed by three of the substituent groups, and the six benzene carbons are nearly coplanar.

The average value of the ring-carbon bond distances (C$_{ar}-$C$_{ar}$), 1.414 Å, is significantly longer than in benzene (1.39 Å) and in crystalline **6** (1.409 Å) but is the same as in crystalline **11**·2CHCl$_3$ (1.414 Å). The average C$_{ar}-$C$_{ar}-$C$_{ar}$ bond angles and C$_{ar}-$CH$_2$CH$_2-$Si bond angles are 120.0 and 111.9, respectively. The average bond lengths between silicon and carbon atoms for Si$-$CH$_3$ (1.870 Å) and Si$-$CH$_2$CH$_2$ (1.880 Å) conformed with the values of 1.866 and 1.889 Å shown in crystalline **11**·2CHCl$_3$ but were longer than in crystalline **6** (Si$-$CH$_3$ = 1.859 Å and Si$-$CH$_2$CH$_2$ = 1.845 Å) due to the sterically bulky methyl groups. The average dihedral angle between the C$_{ar}-$CH$_2$CH$_2-$Si planes and the least-squares plane of the ring is 88.5°, and the C$_{ar}-$CH$_2$CH$_2$ planes are therefore essentially perpendicular to the benzene ring.

Considering the bond angle for CH$-$ring centroid$-$HC, 180°, and the bond distance between the CH$_2$Cl$_2$ carbon atom and the ring centroid, 3.469 Å, the solvent molecules hydrogen-bonded to the benzene ring centroid lie on the symmetry axis, as in crystalline **11**·2CHCl$_3$. The bond distances for C$-$H (0.98 Å) and C$-$Cl (1.775 Å) conform with the reported values of 1.10 Å (H$_3$C$-$H) and 1.78 Å (H$_3$C$-$Cl).[26]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. All glassware was flame-dried or oven-dried prior to use. Solvents were purified by standard procedures. Dichloromethylvinylsilane was distilled immediately before use. Anhydrous aluminum chloride was purchased from Aldrich Chemical Co. and used without further purification. Benzene (extra pure) was purchased from Oriental Chemical Ind. and used without further purification. All air-sensitive liquids and dried solvents were transferred by standard syringe or double-tipped-needle techniques. Reaction products were analyzed by GLC using a capillary column (SE-30, 30 m) or a packed column (10% OV-101 on 80$-$100 mesh Chromosorb W/AW, $^1/_8$ in. × 1.5 in.) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The samples for characterization were purified by preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2 m by $^1/_8$ in. stainless steel column packed with 20% OV-101 on 80$-$100 mesh Chromosorb P/AW. Mass spectra were obtained using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5972 mass selective detector. High-resolution mass spectra (70 eV, EI)

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were obtained by the Chemistry Instrumentation Center of the University of Wisconsin, Madison, WI.

NMR spectra were recorded on a Varian spectrometer using samples in $CDCl_3$ solution: ^{1}H NMR spectra at 300 MHz and ^{13}C NMR at 75.4 MHz. Melting points were obtained with a Mel-Temp II. Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea.

Polyalkylation of Benzene with Dichloromethylvinylsilane. To a solution of 0.10 g (0.75 mmol) of aluminum chloride and 0.87 g (11.1 mmol) of benzene was added 9.31 g (66.1 mmol) of dichloromethylvinylsilane at the rate of 0.2 cm^3/min using a syringe pump, at room temperature with stirring. A moderately exothermic reaction was observed. After the mixture was stireed for 4 h, a large amount of solid was formed, which made stirring impossible. Freshly distilled hexane (20 mL) and 0.3 g (5.13 mmol) of NaCl powder were added to the reaction mixture, and the mixture was then warmed to 70 °C to deactivate the aluminum chloride. Solids and $AlCl_3-NaCl$ complex insoluble in hexane were filtered from the mother liquid. Solids were washed twice with hexane and dissolved in dried THF, and the solid $AlCl_3-NaCl$ complex was filtered off. Evaporation of THF from the solution yielded 5.75 g (56%) of the yellowish white crystalline hexakis((dichloromethylsilyl)ethyl)benzene (**1**), and recrystallization from THF gave 4.03 g (39.3%) of **1** as colorless needles (mp 218−220 °C). Then the mixtures of bis((dichloromethylsilyl(ethyl)-benzenes^{8b} (0.15 g) and tris((dichloromethylsilyl)ethyl)benzenes (0.50 g; bp 185−186 °C) were distilled from the remaining residue, respectively. Tetrakis((dichloromethylsilyl)ethyl)benzenes and pentakis((dichloromethylsilyl)ethyl)benzene for characterization were then purified by GLC. They were also methylated with methyl Grignard reagent and then separated by vacuum distillation. For **1**: ^{1}H NMR δ 0.87 (s, 18H, CH_3), 1.30−1.36 (m, 12H, CH_2), 2.71−2.77 (m, 12H, CH_2); ^{13}C NMR δ 5.17 (CH_3), 22.08 (CH_2), 24.29 (CH_2), 137.48 (phenyl *C*). Because of the hygroscopic nature of **1**, C and H analysis was performed after reducing with $LiAlH_4$ (see compound **6**). For a mixture of two isomeric tris((dichloromethylsilyl)ethyl)benzenes: HRMS (*m*/*e*): calcd for $C_{15}H_{24}Si_3Cl_6$ (M^+) 497.9317, found 497.9317. For 1,3,5-tris((dichloromethylsilyl)ethyl)benzene (**2a**): ^{1}H NMR δ 0.88 (s, 9H, CH_3), 1.62−1.67 (m, 6H, CH_2), 2.94−2.99 (m, 6H, CH_2), 7.09 (s, 3H, phenyl *H*); ^{13}C NMR δ 5.56 (CH_3), 23.84 (CH_2), 28.68 (CH_2), 125.74, 143.27 (phenyl *C*). For 1,2,4-tris((dichloromethylsilyl)ethyl)benzene (**2b**): ^{1}H NMR δ 0.93 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.62−1.67 (m, 6H, CH_2), 2.94−2.99 (m, 6H, CH_2), 7.16−7.29 (m, 3H, phenyl *H*); ^{13}C NMR δ 5.56 (CH_3), 22.56, 22.78 (CH_2), 28.68 (CH_2), 123.31, 124.45, 124.88, 139.12, 140.24, 140.62 (phenyl *C*). For 1,2,4,5-tetrakis((dichloromethylsilyl)ethyl)-benzene (**3a**): ^{1}H NMR δ 0.80 (s, 12H, CH_3), 1.41−1.48 (m, 8H, CH_2), 2.76−2.82 (m, 8H, CH_2), 7.00 (s, 2H, phenyl *H*); ^{13}C NMR δ 5.19 (CH_3), 23.60 (CH_2), 24.84 (CH_2), 129.49, 138.47 (phenyl *C*). For 1,3,4,5-tetrakis((dichloromethylsilyl)ethyl)benzene (**3b**): ^{1}H NMR δ 0.81 (s, 12H, CH_3), 1.41−1.48 (m, 8H, CH_2), 2.76−2.82 (m, 8H, CH_2), 6.92 (s, 2H, phenyl *H*); ^{13}C NMR δ 5.19 (CH_3), 23.70, 23.95 (CH_2), 24.94 (CH_2), 129.49, 138.47 (phenyl *C*). For pentakis((dichloromethylsilyl)ethyl)benzene (**4**): HRMS (*m*/*e*): calcd for $C_{21}H_{36}Si_5Cl_{10}$ (M^+) 777.8549; found 777.8549; ^{1}H NMR δ 0.81 (s, 6H, CH_3), 0.86 (s, 9H, CH_3), 1.27−1.30 (m, 4H, CH_2), 1.31−1.39 (m, 6H, CH_2), 2.73−2.79 (m, 10H, CH_2), 7.27 (s, 1H, phenyl *H*); ^{13}C NMR δ 5.08 (CH_3), 21.51, 21.91 (CH_2), 23.86, 24.30, 25.46 (CH_2), 128.06, 136.65, 138.96, 139.17 (phenyl *C*). For tris((trimethylsilyl)ethyl)benzene (**2′**): Anal. Calcd for $C_{21}H_{42}Si_3$: C, 66.58; H, 11.18. Found: C, 66.6; H, 11.3. For 1,3,5-tris((trimethylsilyl)ethyl)benzene (**2a′**): ^{1}H NMR δ 0.05 (s, 27H, CH_3), 0.86−0.92 (m, 6H, CH_2), 2.56−2.62 (m, 6H, CH_2), 6.87 (s, 3H, phenyl *H*). For 1,2,4-tris((trimethylsilyl)ethyl)benzene (**2b′**): ^{1}H NMR δ 0.06 (s, 9H, CH_3), 0.07 (s, 9H, CH_3), 0.08 (s, 9H, CH_3), 0.86−0.92 (m, 6H, CH_2), 2.56−2.62 (m, 6H, CH_2), 6.96−7.13 (m, 3H, phenyl *H*). For tetrakis((trimethylsilyl)ethyl)benzene (**3′**): Anal. Calcd for $C_{26}H_{54}Si_4$: C, 65.19; H, 11.36. Found: C, 65.2; H, 11.5. For 1,2,4,5-tetrakis((trimethylsilylethyl)benzene (**3a′**): ^{1}H NMR δ 0.06 (s, 36H, CH_3), 0.78−0.86 (m, 8H, CH_2), 2.51−2.58 (m, 8H, CH_2), 6.93 (s, 2H, phenyl *H*). For 1,3,4,5-tetrakis((trimethylsilyl)ethyl)benzene (**3b′**): ^{1}H NMR δ 0.02 (s, 9H, CH_3), 0.06 (s, 18H, CH_3), 0.08 (s, 9H, CH_3), 0.78−0.86 (m, 8H, CH_2), 2.51−2.58 (m, 8H, CH_2), 6.85 (s, 2H, phenyl *H*). For pentakis((trimethylsilyl)ethyl)benzene (**4′**): ^{1}H NMR δ 0.07 (s, 18H, CH_3), 0.09 (s, 18H, CH_3), 0.10 (s, 9H, CH_3), 0.73−0.78 (m, 4H, CH_2), 0.83−0.87 (m, 6H, CH_2), 2.52−2.57 (m, 10H, CH_2), 6.88 (s, 1H, phenyl *H*); ^{13}C NMR δ −1.48 (CH_3), 18.95, 19.52, 20.12 (CH_2), 22.64, 23.00, 26.81 (CH_2), 126.34, 137.78, 139.96, 140.21 (phenyl *C*). Anal. Calcd for $C_{31}H_{66}Si_5$: C, 64.28; H, 11.48. Found: C, 64.1; H, 11.6.

General Procedure for Study on the Molar Ratio Effect of Reactants. Various amounts of dichloromethylvinylsilane, from 0.5 to 9 equiv based on benzene, were added to the mixture of 0.44 g (5.60 mmol) of benzene and 0.075 g (0.56 mmol) of $AlCl_3$, and the reaction mixture was stirred for 4 h. Freshly dried THF (5 mL) was added, and the reaction mixture was methylated by methyl Grignard reagent.

General Procedure for Study on the Reaction Time Dependence. Dichloromethylvinylsilane (4.74 g, 33.6 mmol) was added to the mixture of benzene (0.44 g, 5.63 mmol) and $AlCl_3$ (0.067 g, 0.50 mmol). The reaction mixture was stirred and checked by GLC every 10 or 20 min for 4 h. Determination of the product distribution was monitored by GLC.

Hexakis((dimethoxymethyl)silylethyl)benzene (5). To a solution of 0.58 g (18.0 mmol) of dried MeOH and 0.71 g (8.96 mmol) of dried pyridine surrounded with a ice bath was added 0.69 g (0.75 mmol) of **1** in 10 mL of THF solution dropwise with stirring. The resulting mixture was stirred for 30 min, dried hexane was added, and the mixture was transferred to a separating funnel. The upper layer was separated, and solvent was removed under vacuum. Recrystallization from hexane yielded 0.26 g of colorless cubes: mp <25 °C, yield 40.8%. ^{1}H NMR: δ 0.21 (s, 18H, CH_3), 0.84−0.90 (m, 12H, CH_2), 2.57−2.63 (m, 12H, CH_2), 3.54 (s, 36H, OCH_3). ^{13}C NMR: δ 6.07 (CH_3), 16.22 (CH_2), 22.06 (CH_2), 50.21 (OCH_3), 138.14 (phenyl *C*).

Hexakis((methylsilyl)ethyl)benzene (6). To a solution of 0.34 g (9.00 mmol) of lithium aluminum hydride and 30 mL of dried THF was added 1.33 g (1.44 mmol) of **1** in 10 mL of THF solution dropwise with stirring. The resulting mixture was stirred for 30 min and hydrolyzed. The organic layer was extracted with diethyl ether, and the extracts were washed with water and dried over anhydrous $MgSO_4$. Recrystallization from hexane yielded 0.72 g of colorless needles in 97.7% yield: mp 98−100 °C. Anal. Calcd for $C_{24}H_{54}Si_6$: C, 56.39; H, 10.65. Found: C, 56.6; H, 10.7. HRMS (*m*/*e*): calcd for $C_{24}H_{54}Si_6$ (M^+) 510.2841, found, 510.2841. ^{1}H NMR: δ 0.24 (t, $J = 4.1$ Hz, 18H, CH_3), 0.93−0.98 (m, 12H, CH_2), 2.56−2.61 (m, 12H, CH_2), 3.84 (hex, $J = 4.1$ Hz, 12H, CH_2). ^{13}C NMR: δ −8.67 (CH_3), 13.24 (CH_2), 24.79 (CH_2), 138.12 (phenyl *C*).

Hexakis((trimethylsilyl)ethyl)benzene (7). To a solution of 0.53 g (0.57 mmol) of **1** and 30 mL of THF was added 2.8 mL of 3 M methylmagnesium chloride in THF (8.40 mmol) dropwise with stirring. A slightly exothermic reaction was observed. After the addition was complete, the mixture was stirred at room temperature for 2 h. Subsequently, it was poured into a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed twice with 50 mL of water and 20 mL of saturated NaCl and were dried over anhydrous $MgSO_4$. Rotary evaporation of the volatiles left 0.34 g of a yellow semisolid, which was dissolved in 1 mL of hexane and subjected to column chromatography (silica gel, hexane) to give a white powder (0.26 g, 66.7%). Recrystallization from hexane yielded colorless needles: mp 222−225 °C. Anal. Calcd for $C_{36}H_{78}Si_6$: C, 63.63; H, 11.57. Found: C, 63.64; H, 11.7. ^{1}H NMR: δ 0.11 (s, 54H, CH_3), 0.77−0.83 (m, 12H, CH_2),

Table 3. Crystallographic Details for 6, $7\cdot 2CH_2Cl_2$, and $11\cdot 2CHCl_3$

	6	**7**·$2CH_2Cl_2$	**11**·$2CHCl_3$
formula	$C_{24}H_{54}Si_6$	$C_{38}H_{78}Si_6\cdot 2CH_2Cl_2$	$C_{108}H_{126}Si_6\cdot 2CHCl_3$
M_r	511.20	849.38	1831.36
cryst size, mm	0.50 × 0.50 × 0.02	0.48 × 0.42 × 0.34	0.40 × 0.40 × 0.20
cryst syst	monoclinic	orthorhombic	trigonal
space group	$P2_1/c$	$Pbca$	$R\bar{3}c$
a, Å	0.6727(2)	19.9281(6)	19.3692(2)
b, Å	15.254(4)	12.1691(4)	19.3692(2)
c, Å	22.778(6)	22.0971(6)	47.3160(2)
α, deg	90	90	90
β, deg	94.15(2)	90	90
γ, deg	90	90	120
Z	4	4	6
d_{calcd}, Mg m^{-3}	1.013	1.053	1.187
μ(Mo Kα), cm^{-1}	0.259	0.378	0.284
scan type	ϕ	ϕ	ϕ
θ, deg	3.22−51.9	3.68−56.4	2.98−52.0
scan width, deg	0.3 in ϕ	0.3 in ϕ	0.3 in ϕ
no. of indep rflns	5866	5915	3159
no. of obsd data ($I > 2\sigma(I)$)	5377	4490	2800
no. of params	272	243	184
R1(F)[a]	0.0470	0.0427	0.0644
wR2(F)[a]	0.1166	0.0974	0.1612
GOF	1.16	1.056	1.53
largest diff peak, hole, e Å^{-3}	+0.753, −0.524	+0.601, −0.596	+0.430, −1.051

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_c^2) + (0.0373P)^2 + 4.8820P]$, where $P = [F_o^2 + 2F_c^2]/3$ for **6**. $w = 1/[\sigma^2(F_c^2) + (0.0435P)^2 + 2.5882P]$, where $P = [F_o^2 + 2F_c^2]/3$ for **7**. $w = 1/[\sigma^2(F_c^2) + (0.034P)^2 + 70.1376P]$, where $P = [F_o^2 + 2F_c^2]/3$ for **11**.

2.48−2.54 (m, 12H, C*H*$_2$). ^{13}C NMR: δ −1.41 (*C*H$_3$), 20.21 (*C*H$_2$), 23.14 (*C*H$_2$), 138.15 (phenyl *C*).

Hexakis((divinylmethylsilyl)ethyl)benzene (8). Reaction of 0.30 g (0.32 mmol) of **1** with 4 mL of 1 M vinylmagnesium bromide in THF (4.00 mmol) using the procedure described for **7** gave 0.19 g of a yellow semisolid. Chromatography (silica gel, 20/1 v/v hexane/EtOAc) gave a white powder. Recrystallization from hexane yielded 0.18 g (65.5%) of colorless cubes: mp 160−166 °C. Anal. Calcd for $C_{48}H_{78}Si_6$: C, 70.0; H, 9.55. Found: C, 70.3; H, 9.75. HRMS (*m/e*): calcd for $C_{48}H_{78}Si_6$ (M$^+$) 822.4719, found 822.4719. ^{1}H NMR: δ 0.24 (s, 18H, C*H*$_3$), 0.84−0.90 (m, 12H, C*H*$_2$), 2.46−2.50 (m, 12H, C*H*$_2$), 5.75−5.83 (m, 12H, ═C*H*), 6.05−6.29 (m, 24H, ═C*H*$_2$). ^{13}C NMR: δ −5.26 (*C*H$_3$), 17.63 (*C*H$_2$), 23.05 (*C*H$_2$), 133.31 (═*C*H), 136.78 (═*C*H$_2$), 138.26 (phenyl *C*).

Hexakis((diallylmethylsilyl)ethyl)benzene (9). Reaction of 9.83 g (10.6 mmol) of **1** with 65 mL of 2 M allylmagnesium chloride in THF (0.13 mol) using the procedure described for **7** gave 10.5 g of a yellow oil. Chromatography (silica gel, 10/1 v/v hexane/EtOAc) gave 6.80 g (64.7%) of a colorless viscous liquid. Anal. Calcd for $C_{60}H_{102}Si_6$: C, 72.65; H, 10.36. Found: C, 73.1; H, 10.4. ^{1}H NMR: δ 0.17 (s, 18H, C*H*$_3$), 0.85−0.91 (m, 12H, C*H*$_2$), 0.69 (d, *J* = 7.9 Hz, 24H, SiC*H*$_2$CH═), 2.51−52.57 (m, 12H, C*H*$_2$), 4.91−4.97 (m, 24H, ═C*H*$_2$), 5.78−5.92 (m, 12H, ═C*H*). ^{13}C NMR: δ −5.63 (*C*H$_3$), 16.51 (Si*C*H$_2$CH═), 21.52 (*C*H$_2$), 23.19 (*C*H$_2$), 113.66 (═*C*H$_2$), 134.41 (*C*H═), 138.25 (phenyl *C*).

Hexakis((diethynylmethylsilyl)ethyl)benzene (10). Reaction of 0.53 g (0.57 mmol) of **1** with 16.5 mL of 0.5 M ethynylmagnesium bromide in THF (8.30 mmol) using the procedure described for **7** gave 0.61 g of a dark red crude product. Chromatography (silica gel, 5/2 v/v hexane/EtOAc) gave 0.44 g (96.1%) of a white powder. Recrystallization (hexane/EtOAc 1/1) yielded colorless diamonds: mp 180−183 °C. Anal. Calcd for $C_{48}H_{54}Si_6$: C, 72.11; H, 6.81. Found, C, 72.2; H, 6.91. HRMS (*m/e*): calcd for $C_{48}H_{54}Si_6$ (M$^+$) 798.2841; found, 798.2841. ^{1}H NMR: δ 0.41 (s, 18H, C*H*$_3$), 0.97−1.04 (m, 12H, C*H*$_2$), 2.53 (s, 12H, C*H*), 2.65−2.71 (m, 12H, C*H*$_2$). ^{13}C NMR: δ 1.46 (*C*H$_3$), 18.44 (*C*H$_2$), 22.82 (*C*H$_2$), 85.38 (≡*C*), 95.75 (≡*C*H), 137.96 (phenyl *C*).

Hexakis((dibenzylmethylsilyl)ethyl)benzene (11). Reaction of 1.17 g (1.27 mmol) of **1** with 11 mL of 2 M benzylmagnesium chloride in THF (22.8 mmol) using the procedure described for **7** followed by refluxing for 4 h gave 4.36 g of a yellow slurry. Chromatography (silica gel, 5/2 v/v hexane/EtOAc) gave 2.00 g (98.8%) of a white powder: mp 100-101 °C. FAB MS (*m/e*): calcd for $C_{108}H_{126}Si_6Na$ (M$^+$Na$^+$) 1614.840, found 1614.6. Anal. Calcd for $C_{108}H_{126}Si_6$: C, 81.45; H, 7.97. Found: C, 81.4; H, 8.27. ^{1}H NMR: δ −0.06 (s, 18H, C*H*$_3$), 0.81−0.86 (m, 12H, C*H*$_2$), 2.08 (s, 24H, C*H*$_2$), 2.37−2.40 (m, 12H, C*H*$_2$), 6.91−7.24 (m, 60H, phenyl *H*). ^{13}C NMR: δ −4.97 (*C*H$_3$), 16.43 (*C*H$_2$), 23.47 (*C*H$_2$), 24.01 (*C*H$_2$), 128.58, 126.66, 138.60, 139.54 (phenyl *C*), 139.68 (central phenyl *C*).

X-ray Crystallographic Studies. The X-ray crystallographic analysis was carried out with a Siemens P4/DCC instrument using Mo Kα radiation (λ = 0.710 73 Å) with a graphite monochromator. The structures were solved using direct methods and refined by full-matrix least squares on F^2 using the SHELXTL PLUS 5.0 (PC) software package.[27] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of methyl groups were placed in idealized positions and refined using the riding model with general isotopic temperature factors. Details of the crystal data and a summary of intensity data collection parameters are given in Table 3.

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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, bond distances and angles, and torsion angles and figures giving additional views of **6**, **11**, and **7** (36 pages). Ordering information is given on any current masthead page.

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[27] Sheldrick, G. M. SHELXTL PC version 5.0; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.