Friedel−Crafts Peralkylation of Benzene with ω-Chloroalkyltrichlorosilanes: One-Pot Synthesis of Polyfunctionalized Hexakis[ω-(trichlorosilyl)alkyl]benzenes

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Hexakis[ω-(trichlorosilyl)alkyl]benzenes **2** [alkyl = ethyl (**a**), propyl (**b**)] containing 18 peripheral chlorine substituents on the six silicon atoms as functionalities were prepared in 72% and 53% yields by the one-pot reaction of benzene with a 6-fold excess of ω-chloroalkyltrichlorosilanes such as 2-chloroethyltrichlorosilane (**1a**) and 3-chloropropyltrichlorosilane (**1b**) in the presence of aluminum chloride, respectively. Single-crystal X-ray analysis of compound **2b** reveals that the 18 chlorine substituents on the six silicons are symmetrically located on the outside. Compounds **2a**,**b** reacted easily with methylmagnesium bromide in diethyl ether at room temperature to give hexakis[ω-(trimethylsilyl)alkyl] in high isolated yields of 93 and 94%.

Introduction

Compounds bearing many peripheral functional groups such as dendritic molecules have been received widespread attention.[1−3] These compounds are prepared in an iterative sequence of reaction steps. Although the reaction generally proceeds in good yield in each step, the overall yields are low.[1a,2b,4] Furthermore, it is difficult to isolate such compounds from their reaction mixtures. As one synthetic approach, simple organosilicon compounds containing many chlorine substitutents on a silicon are used as starting materials for the preparation of advanced and polyfunctionalized molecules through the repeated reactions of both alkenylation with alkenylmetal reagents and hydrosilylation with hydrosilanes in sequence.[1a,2a,b,3] For the preparation of organosilicon compounds with Si−Cl functionalities, we have studied the alkylation of aromatic compounds with organosilicon compounds[5] such as alkenylchlorosilanes[6] and (chloroalkyl)chlorosilanes,[7] which were catalyzed by Lewis acid. In a series, the peralkylation of benzene with excess vinylchlorosilanes in the presence of aluminum chloride has been conducted in order to prepare symmetric and polyfunctionalized compounds. Among these reactions, the reaction of benzene with 6 equiv of methyl(vinyl)dichlorosilane at room temperature for 4 h gave hexakis[2-(methyldichlorosilyl)ethyl]benzene containing 12 chlorine substituents on the six silicons as the peralkylated product in 56% yield.[6b] An attempt to obtain a higher functionalized peralkylated product with 18 chlorine substituents on the silicons using vinyltrichlorosilane in place of methylvinyldichlorosilane under the same reaction conditions

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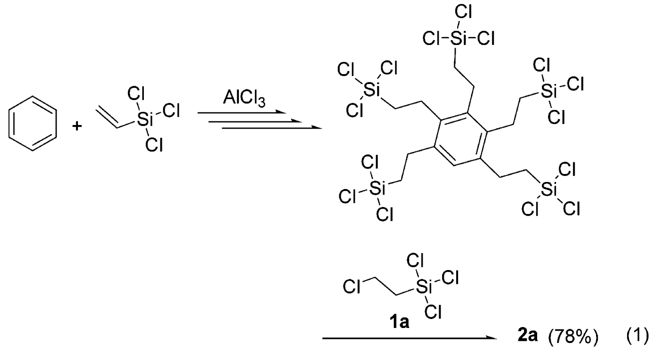
was unsuccessful. Even though this reaction was carried out under much more vigorous conditions (70 °C, 24 h), only a trace of hexakis[*ω*-(trichlorosilyl)ethyl]benzene (**2a**) was observed by GLC. This reaction gave pentaalkylated product as a major product. Alternatively, the peralkylation products, [*ω*-(trichlorosilyl)alkyl]benzenes containing 18 peripheral chlorine substituents on the six silicons, were successfully obtained as a major product when *ω*-chloroalkyltrichlorosilanes were used as alkylating agent for the peralkylation of benzene. In this paper, we wish to report a facile, efficient synthesis and isolations of polyfunctionalized hexakis[*ω*-(trichlorosilyl)alkyl]benzenes containing 18 peripheral chlorine substituents on the silicons [alkyl = ethyl (**2a**), propyl (**2b**)] by one-pot peralkylation of benzene with excess *ω*-chloroalkyltrichlorosilanes such as 2-chloroethyltrichlorosilane (**1a**) and 3-chloropropyltrichlorosilane (**1b**) in the presence of aluminum chloride.

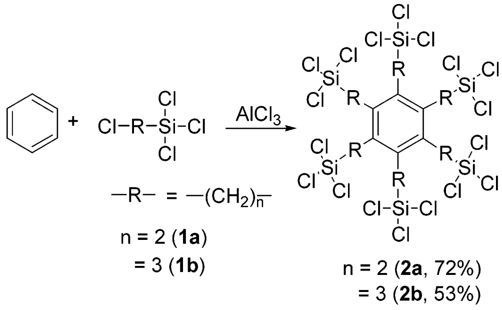
Results and Discussion

Polyalkylation of Benzene with Vinyltrichlorosilane. In the peralkylation of benzene with vinylchlorosilane, vinyl(methyl)dichlorosilane in the presence of 7 mol % aluminum chloride (based on benzene used) gave hexaalkylated benzene at room temperature,[6b] while vinyltrichlorosilane did not afford hexaalkylated benzene under the same reaction conditions. When the reaction was carried out in the presence of 60 mol % aluminum chloride at 70 °C for 24 h, only a trace of hexakis[*ω*-(trichlorosilyl)ethyl]benzene (**2a**) was observed by GLC. This reaction gave pentaalkylated product as a major product. In the study on the peralkylation of benzene with excess vinylsilanes, it was found that vinyltrichlorosilane required higher temperature and longer time than vinyl(methyl)dichlorosilane, but did not give hexaalkylated product in appreciable amount. It seems likely that a reactivity difference between both vinylsilanes is consistent with protonation of the vinyl group on the silicon by hydrogen chloride,[8] resulting from a reaction of aluminum chloride with water inevitably present in the reactants, leading to *β*-carbenium ions on the silicon. Generally the *β*-carbenium ion on the silicon is stabilized with increasing alkyl substituent(s) as electron-donating groups on the silicon.[9] In a test, methyl(vinyl)dichlorosilane reacted immediately with gaseous hydrogen chloride in the presence of 10 mol % of $AlCl_3$ at room temperature to give (2-chloroethyl)methyldichlorosilane (**1c**) as a minor product and the decomposed product, methyltrichlorosilane, as the major product, while vinyltrichlorosilane at a higher temperature of 70 °C smoothly gave only **1a**.[8] In the case of methyl(vinyl)dichlorosilane, methyltrichlorosilane was formed by the decomposition reaction of (2-chloroethyl)methyldichlorosilane in the presence of $AlCl_3$.

On the basis of these results, when benzene reacted with excess vinyltrichlorosilane under bubbling of HCl gas at the same reaction temperature, the peak of hexaalkylated **2a** was slowly increased. Thus, alternatively, when benzene reacted with excess vinyltrichlorosilane under the same conditions and in sequence with 1 equiv of **1a**, hexaalkylated product **2a** was obtained in 78% yield as the major product (eq 1). The results indicated that 2-chloroethylsilane **1a** formed by the reaction of vinylsilane with a trace of HCl was an important alkylating agent in the aluminum chloride-catalyzed peralkylation of benzene with vinylchlorosilanes.



Peralkylation of Benzene with *ω*-Chloroalkyltrichlorosilanes. (*ω*-Chloroalkyl)trichlorosilanes **1a** and **1b** as alkylating agents in place of vinylsilanes were employed in this reaction. When a mixture of benzene and 6 equiv of **1a** was stirred in the presence of aluminum chloride catalyst at 70 °C for 3 h, a hexaalkylated product containing 18 chlorine substituents on the silicons of **2a** was successfully obtained in 72% isolated yield (eq 2). This reaction works effectively with 2-chloroethylsilane **1a** under relatively mild conditions and can further be extended to employ 3-chloropropylsilane **1b** in this reaction. The reaction with **1b** at a lower reaction temperature of 40 °C gave hexaalkylated product **2b** (53%, eq 2), which links with a longer propylene spacer between the benzene ring and silicon atoms than the ethylene spacer at **2a**. A peralkylation of benzene with 2-chloroethylsilane **1c** substituted with a methyl substituent instead of one of three chlorines on a silicon atom was completed at room temperature within 20 min to give hexaalkylated product **2c** in 70% yield. These results showed that the reaction with **1a** required much more vigorous conditions than that[6b] with **1c**. The reactivity difference of both 2-chloroethylsilanes **1a** and **1c** can be rationalized in terms of the stability of their carbenium ion *β* to the silicon generated by the complexation of the carbon−carbon double bond of compound **1** with aluminum chloride.[9]



(2)

Such compounds bearing many Si−Cl groups could be easily isolated as crystals by cooling THF and hexane

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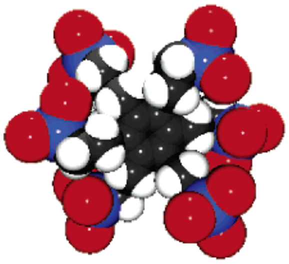
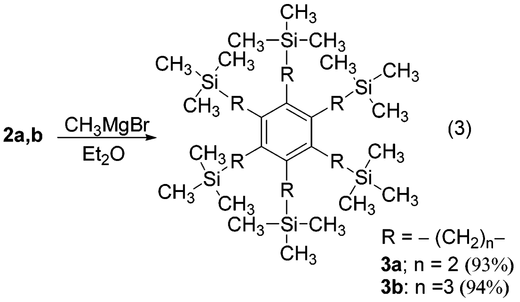


Figure 1. Space-filling view of the X-ray single-crystal structure of **2b**. Red, blue, black, and white correspond to Cl, Si, C, and H atoms, respectively.

solutions, respectively. The structures of the products were determined by analyses of the NMR spectra. Spectroscopic data of hexaalkylated benzenes **2a** and **2b** showed their high symmetries. In the ^{1}H NMR spectra of both compounds **2a** and **2b**, two (δ = 1.58 and 2.80) and three (δ = 1.61, 1.81, and 2.66) signals of alkylene units in the aliphatic region and no signals in the aromatic region indicated the hexaalkylation. The ^{13}C NMR spectra showing only two (δ = 22.09 and 26.76) and three (δ = 24.37, 25.03, and 32.09) signals in the aliphatic region and one signal at δ = 137.09 and 135.33 in the aromatic region, respectively, also corresponded well with their structures characterized by ^{1}H NMR spectra. More significant is the structure of **2b**, containing 18 Si−Cl groups, disclosed by the analysis of X-ray single-crystal diffraction data obtained at the low temperature of −100 °C (Figure 1). It is important that the 18 chlorine substituents at the silicons of **2b** are symmetrically located on the outside in its topology and can react with the organometal reagent to be modified.

Most significant are the easy preparation and isolation of compounds **2** containing many chlorine substituents on the silicons as functionalities, starting from commercially available ω-chloroalkyltrichlorosilanes.

Methylation of Hexakis[ω-(trichlorosilyl)alkyl]-benzenes. Compounds **2**, containing many chlorine substituents on the silicons as functionalities, are expected to be very useful precursors for a wide range of advanced and polyfunctional materials, due to the good reactivities of chlorine substituents at the silicon atoms with organometal reagents, water, alcohol, amine, etc.[11] As a test for the reactivity of 18 peripheral chlorine substituents of the six silicon atoms of compounds **2a**,**b**, compounds **2a** and **2b** were reacted with methylmagnesium bromide in ethyl ether at room temperature for 3 h, respectively. Hexakis[2-(trimethylsilyl)-alkyl]benzenes [alkyl = ethyl (**3a**) and propyl (**3b**)] were obtained in excellent, 93% and 94% isolated yields, respectively (eq 3), indicating that all chlorine substituents on the silicon atoms of compounds **2a** and **2b** can be easily substituted with organic substituents using organometal reagent. Products **3** were also characterized by analysis of NMR data. The data of compound **3a** were identical to the data reported previously.[6b] New signals of methyl substituents at silicon atoms of **3b** appeared at δ = 0.01 as a singlet and three methylene signals (δ = 0.65, 1.55, and 2.52) at the propylene unit were shifted upfield when compared with those of compound **2b** in the ^{1}H NMR spectrum.



(3)

R = – $(CH_2)_n$–
3a; n = 2 (93%)
3b: n =3 (94%)

As a whole, this chemistry will now enable the facile, efficient synthesis of the high-symmetric and polyfunctionalized aromatic compounds **2a**,**b** bearing 18 chlorine substituents of the six silicon atoms, starting from commercially available ω-chloroalkyltrichlorosilanes, which may be applicable to the synthesis of advanced materials such as dendrimers. The application of compounds **2a**−**c** to much higher polyfunctionalized dendritic molecules through repeated reactions[2a,b,3] of both reactions with alkenyl metal reagents such as vinyl- or allylmagnesium halides and hydrosilylation with Si−H containing chlorosilanes in sequence may be possible. In the reaction of these compounds containing Si−Cl bonds with organometal reagents, it was shown clearly that these compounds with 18 Si−Cl groups undergo easily substitution reactions.

Experimental Section

General Comments. All reactions and manipulations were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame-dried before use. Dried solvents were employed in all reactions. Aluminum chloride (99%), methylmagnesium bromide (3.0 M in ethyl ether), and benzene were purchased from Aldrich Chemical Co., and aluminum chloride was purified by sublimation. Chlorosilanes, vinyltrichlorosilane, methyl(vinyl)dichlorosilane), and ω-chloroalkylchlorosilanes **1a**−**c** were purchased from Gelest, Inc. and used without purification. Anhydrous hydrogen chloride (99.999%) was purchased from Solkatronic Chemicals and used without further purification. Product yields were determined chromatographically with *n*-dodecane as an internal standard, if not stated otherwise. The reaction products were analyzed by GLC using a capillary column (SE-30, 20 or 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ^{1}H), Bruker AMX 500 (FT, 500 MHz, ^{1}H; 125 MHz, ^{13}C), or Varian Gem 300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometer in $CDCl_3$ solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the chemical analysis laboratory of the Korea Institute of Science and Technology.

Reaction of Benzene with Vinyltrichlorosilane. Using the procedure described in the reaction of benzene with **1a**, the reaction of benzene (1.0 g, 12.8 mmol) with vinyltrichlorosilane (13.4 g, 83.0 mmol) in the presence of aluminum chloride (1.0 g, 7.5 mmol) was carried out at 70 °C for 24 h. Hexane (70 mL) and NaCl (4.9 g, 83.8 mmol) were added to the reaction mixture. This hexane solution was refluxed for 2 h. NaCl−$AlCl_3$ salt and excess NaCl insoluble in hexane were filtered off. Volatiles were removed from the filtrate. The nonvolatile compounds were dissolved in 60 mL of hexane. Penta[2-(trichlorosilyl)ethyl]benzene (5.4 g, 48%) was isolated by repeated recrystallizations from the hexane solution. Because of the difficulty of isolation of other polyalkylation products, a mixture of polyalkylated benzenes that remained was dissolved in diethyl ether (70 mL), methylated with 3.0 M methylmagnesium bromide in diethyl ether (14.0 mL, 42.0 mmol), and generally worked up.[6b] The GLC analysis of the methylated products (2.5 g) showed a pentaalkylated (7%), an isomeric mixture of three tetraalkylated (43%), and trialkylated compounds (50%). The methylated products were characterized by comparing with the data reported previously.[6b] Data for penta[2-(trichlorosilyl)ethyl]benzene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52−1.58 (m, 6H), 1.68 (m, 4H) (SiCH_2), 2.78−2.84 (m, 10H, benzylic-CH_2), 6.94 (s, 1H, aryl-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.54, 21.95, 25.35, 26,25, 26.35, 26.65 (CH_2), 128.71, 136.06, 138.24, 138.75 (aryl-*carbons*); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 11.06, 11.98. Anal. Calcd for $C_{16}H_{21}Cl_{15}Si_5$: C, 21.70; H, 2.39. Found: C, 21.39; H, 2.47.

Reaction of Benzene with Vinyltrichlorosilane in the Presence of HCl Gas. After HCl gas was bubbled for 2 min into the reaction mixture obtained under the same conditions of the reaction of benzene with vinyltrichlorosilane above, this reaction was carried out at 80 °C for 2 h. The GLC analysis of the reaction mixture showed a mixture of hexaalkylated compound **2a** (10%), pentaalkylated compounds (54%), tetraalkylated compounds (20%), and trialkylated compounds (5%).

Reaction of Methyl(vinyl)dichlorosilane with HCl. Into a 50 mL round-bottomed flask equipped with a reflex condenser were added methyl(vinyl)trichlorosilane (1.07 g, 7.6 mmol), aluminum chloride (0.10 g, 0.76 mmol), and *n*-dodecane (0.2 g) under a dry nitrogen atmosphere. When HCl gas was introduced to the reaction mixture at room temperature, an exothermic reaction was observed. Within 2 min with bubbling (20 mL/min) of HCl, (2-chloroethyl)methyldichlorosilane (15%) and methyltrichlorosilane (74%) were obtained with 90% consumption of methyl(vinyl)dichlorosilane. In a 5 min reaction, only methyltrichlorosilane was observed by GLC.

Reaction of Vinytrichlorosilanes with HCl. Into a 50 mL round-bottomed flask equipped with a reflex condenser were added vinyltrichlorosilane (1.31 g, 8.11 mmol), aluminum chloride (0.11 g, 0.81 mmol), and *n*-dodecane (0.2 g) under a dry nitrogen atmosphere. After HCl gas was bubbled into the stirring reaction mixture at a rate of 20 mL/min for 3 min, the reaction was carried out at room temperature for 30 min. In this reaction, a trace amount of the hydrochlorination product **1a** was observed by GLC. Then the temperature was raised to 70 °C for 2 min and the reaction mixture was stirred for 10 min at a bubbling rate of 10 mL/min of HCl gas. **1a**[8] was formed in 99% GLC yield. Unreacted vinyltrichlorosilane (1%) remained.

Reaction of Benzene with 1a. To a stirring suspension of benzene (1.0 g, 12.8 mmol) and $AlCl_3$ (1.0 g, 7.5 mmol) was added **1a** (16.7 g, 84.4 mmol) at the pumping rate of 0.3 mL/min using a syringe pump at 70 °C. A moderately exothermic reaction was observed. The reaction mixture was stirred for another 3 h at 70 °C. Dried hexane (100 mL) and NaCl (1.9 g, 32.5 mmol) were added to the reaction mixture, and the mixture was then stirred at the reflux temperature of hexane for 2 h. Solid products and NaCl−$AlCl_3$ complex insoluble in hexane were filtered out, washed three times with hexane (20 mL × 3), and dissolved in dried THF. The NaCl−$AlCl_3$ complex insoluble in THF was filtered off. The filtrate was concentrated by evaporation and cooled to −30 °C to afford yellowish white crystals. These crystals were powdered and then kept under vacuum conditions of 150 °C/0.2 mmHg for 24 h to give 9.7 g of a mixture of compound **2a** and THF (about 10 mol %). Yield of **2a** was 72% (based on the ^{1}H NMR data). Data for **2a**: mp, decomposed slowly above 260 °C; ^{1}H NMR ($CDCl_3$, 7.25 ppm) δ 1.58 (m, 12H; SiCH_2), 2.80 (m, 12H; benzylic-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.09 (SiCH_2), 26.76 (benzylic-CH_2), 137.09 (aryl-carbons); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 4.9.

Reaction of Benzene with 1b. Using the procedure described in the reaction with **1a**, the reaction of benzene (1.0 g, 12.8 mmol) with **1b** (17.9 g, 84.4 mmol) in the presence of $AlCl_3$ (1.0 g, 7.5 mmol) was carried out at 40 °C for 3 h in the same molar scales of the reaction with **1a** above. After the deactivation of aluminum chloride by NaCl, the NaCl−$AlCl_3$ complex insoluble in hexane (80 mL) was filtered off. The filtrate was concentrated by the evaporation of solvent and cooled to −30 °C to afford **2b** (7.7 g, 53%) as colorless crystals. An X-ray quality crystal of **2b** was obtained from a hexane solution at −30 °C. The isolations of pure products from the reaction mixture of other polyalkylated benzenes such as tris-, tetrakis-, and pentakisalkylated products by preparative GLC or recrystallization were difficult. Data for **2b**: mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (t, $J = 8$ Hz, 12H, SiCH_2), 1.81 (m, 12H, CH_2), 2.66 (t, $J = 8$ Hz, 12H, benzylic-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.37 (SiCH_2), 25.03 ($SiCH_2CH_2$), 32.09 (benzylic-CH_2), 135.33 (aryl-carbons); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 6.4. Anal. Calcd for $C_{24}H_{36}Cl_{18}Si_6$: C, 25.48; H, 3.21. Found: C, 25.87; H, 3.25.

Reaction of Benzene with 1c. Using the procedure described in the reaction with **1a**, the reaction of benzene (1.0 g, 12.8 mmol) with **1c** (15.0 g, 84.5 mmol) in the presence of $AlCl_3$ (1.0 g, 7.5 mmol) was carried out at room temperature for 20 min. An exothermic reaction occurred. After the deactivation of aluminum chloride by NaCl (1.8 g, 30.8 mmol), the NaCl−$AlCl_3$ complex insoluble in THF was filtered off. Recryatallization from the filtrate yielded **2c** (8.3 g, 70%). Other polyalkylbenzenes[6b] such as tris- (3%), tetrakis- (7%), and pentakisalkylated benzenes (12%) were observed by GLC.

Methylation of 2a with Methylmagnesium Bromide. To stirring solution of **2a** (1.50 g, 1.43 mmol) in ethyl ether (100 mL) was added dropwise 9.5 mL (28.5 mmol) of 3.0 M methylmagnesium bromide in ether for 30 min, and the reaction mixture was stirred for another 3 h at room temperature and treated with a saturated NH_4Cl aqueous solution (20 mL), respectively. General workup gave **3a** (0.90 g, 93%). The structure of **3a** was identified by comparing with the literature data.[6b]

Methylation of 2b with Methylmagnesium Bromide. Using the same reaction scale and procedure described in the reaction with **2a**, the methylation reaction of **2b** (1.62 g, 1.43 mmol) gave **3b** (1.03 g, 94%). Data for **3b**: mp 83−84 °C; ^{1}H NMR ($CDCl_3$, 7.25 ppm) δ 0.01 (s, 54H, SiCH_3), 0.65 (t, $J = 8$ Hz, 12H, SiCH_2), 1.55 (m, 12H, $SiCH_2CH_2$), 2.52 (t, $J = 8$ Hz, 12H, benzylic-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.56 (SiCH_3), 18.43 (SiCH_2), 26.06 ($SiCH_2CH_2$), 34.37 (benzylic-CH_2), 136.88 (aryl-carbons); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −3.9; FAB-MS (*m/z*) calcd for $C_{42}H_{90}Si_6$ (M^+), 762.5658; found, 762.5661. Anal. Calcd for $C_{42}H_{90}Si_6$: C, 66.06; H, 11.88. Found: C, 65.99; H, 11.90.

X-ray Crystallography. A colorless crystal of compound **2b** was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71069 Å) on a Siemens SMART CCD equipped with a graphite crystal, incident-beam monochromator. Data were collected at −100 °C. *Lp* and absorption corrections were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares calculations with SHELX97.[11] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were found on a difference Fourier map and refined with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. Crystal and intensity data of **2b** are as follows: empirical formula $C_{24}H_{36}Cl_{18}Si_6$, fw 1131.17, crystal size 0.3 × 0.35 × 0.17 mm^3; triclinic, space group $P\bar{1}$; a = 13.382(6) Å, b = 13.436(6) Å, c

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[10] (a) (b) Pawlenko, S. *Organosilicon Chemistry*; Walter de Gruyter: New York, 1986. (c) Noll, W. *Chemistry and Technology of Silicone*; John Wiley & Sons: New York, 1968.

[11] Sheldrick, G. M. *SHELX-97*, Program for Crystal Structure Analysis; University of Göttingen: Göttingen, Germany, 1997.

= 14.294(7) Å, α = 89.879(8)°, β = 79.459(8)°, γ = 74.784(7)°; V = 2435(2) Å^3, Z = 2, d_{calcd} = 1.543 Mg/m^3, μ = 1.179 mm^{-1}, R [$I > 2\sigma(I)$]: R1 = 0.1319, wR2 = 0.3460.

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Supporting Information Available: ^{1}H and ^{13}C spectra of new compounds **2a**, **2b**, **3b**, and penta[2-(trichlorosilyl)ethyl]benzene; X-ray data of compound **2b** are available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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