

Friedel-Crafts Type Alkylation of 1,2,3,4,5,6,7,8-Octahydroanthracene with Vinylchlorosilanes: Synthesis of Mono, Bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes[†]

Seong Deok Kong,^{1,2} Chang Yeob Lee,¹ Bok Ryul Yoo,¹ Myong Euy Lee,² and Il Nam Jung^{1,*}

¹Organosilicon Chemistry Laboratory, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

²Department of Chemistry, Graduate School, Yonsei University, Seoul 120-749, Korea

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Friedel-Crafts alkylation reaction of an isomeric mixture of 1,2,3,4,5,6,7,8- (2) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (2') with excess vinylchlorosilanes such as vinyl(methyl)dichlorosilane (1a) and vinyltrichlorosilane (1b) in the presence of aluminum chloride catalyst at 80 °C gives only one dialkylated products, 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes [(Cl₂XSiCH₂CH₂)₂C₁₄H₁₆; X = Me (4a), Cl (4b)] in good yields, but 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydrophenanthrenes are not obtained. However, monoalkylation of 2 with 1 affords a mixture of both isomeric compounds, 9-[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes 3 and -phenanthrenes 3'. The yield of product 3' is always higher than that of 3. When a mixture of 3 and 3' is alkylated again with 1, only product 4 without phenanthrene type compounds is obtained, indicating that the isomerizations between 2 and 2', or 3 and 3' occur under the alkylation condition. The alkylation with dimethylvinylchlorosilane or trimethylvinylsilane did not proceed. The structure of 4a is determined by X-ray single crystal diffraction analysis.

Key Words : Friedel-Crafts alkylation, Octahydroanthracene, Organosilicon, Vinylchlorosilanes

Introduction

Polymers with π -electron system such as anthracenes have recently attracted a great deal of interests because of their optical and electric properties due to the delocalization of π -electrons.¹⁻³ Generally, organosilicon compounds containing an anthracene group such as 9,10-bis(trialkylsilyl)anthracene or 9,10-bis(trialkylsilylmethyl)anthracene are prepared by the coupling reaction of chlorosilanes such as chlorotrialkylsilanes^{4,5} or (chloromethyl)trialkylsilanes⁶ with an anthracenyl anion generated by the dehalogenation of 9,10-dihaloanthracene with organometallic reagents. However, it is difficult to obtain anthracenylchlorosilanes having reactive chlorine atoms on the silicon by this method because of the strong reactivity of organometallic reagents toward the coupling reaction.⁷

We have previously reported the Friedel-Crafts alkylations of simple ring compounds such as benzene derivatives,⁸⁻¹¹ ferrocene,¹² and biphenyl⁷ with organosilicon compounds such as allylchlorosilanes, vinylchlorosilanes, and (*o*-chloroalkyl)chlorosilanes in the presence of Lewis acid catalysts to give (phenylalkyl)chlorosilanes with Si-Cl bonds.¹³ However, the reaction of poly-annulated anthracene with vinylchlorosilanes in the presence of Lewis acid catalyst was not successful because of the deactivation of catalyst by complexation with anthracene ring.¹⁴ Encouraged by the success on the syntheses of these simple benzene derivatives with organochlorosilane, we attempted the Friedel-Crafts

alkylation of 1,2,3,4,5,6,7,8-octahydroanthracene (2) as one of simple benzene derivatives with vinylchlorosilanes [CH₂=CHSiCl₂X, X = Me (1a), Cl (1b)]. The alkylation products might be aromatized by dehydrogenation¹⁵ to give anthracene-substituted chlorosilanes.

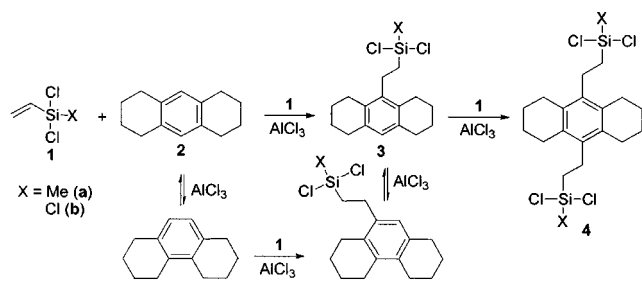
The alkylation reaction of 2 with 1 certainly gave 9-alkylated products or 9,10-dialkylated products depending upon the mole ratio of 2 and vinylsilanes 1a, b. Such a process without using expensive organometallic reagents should be attractive to both industry and academia. In this paper, we wish to report the alkylation of 2 with 1a, b to give 1,2,3,4,5,6,7,8-octahydroanthracene-substituted chlorosilanes and also the observations of the isomerizations between 2 and 1,2,3,4,5,6,7,8-octahydrophenanthrene (2'), and between both monoalkylated isomeric products, 9-[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracene (3a) and -phenanthrene (3a') etc.

Results and Discussion

Synthesis of 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes. 9,10-Bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes [(Cl₂XSiCH₂CH₂)₂C₁₄H₁₆; X = Me (4a), Cl (4b)] were synthesized by two step reactions: first, compounds of 2 and 2' were prepared, starting from 1,2,3,4-tetrahydronaphthalene and 1,4-dichlorobutane, second, the one potted Friedel-Crafts alkylations of 2 or 2' with excess vinylsilanes 1a, b gave the desired dialkylation products 4a and 4b (Scheme 1).

A 2 : 1 mixture of both isomers 2 and 2' was prepared in

[†]This paper is dedicated to Professor Sang Chul Shim for his outstanding achievements in organic photochemistry.



Scheme 1

43% yield by the Friedel-Crafts alkylation of 1,2,3,4-tetrahydronaphthalene with 1,4-dichlorobutane in the presence of AlCl_3 as a catalyst as described in literature.¹⁶ The compound 2 was isolated by recrystallization from *n*-pentane solution of a mixture of 2 and 2'.

When 2 was alkylated with 1a in the presence of AlCl_3 , monoalkylated compounds of 3a and 3a' were obtained along with dialkylated compound 4a. The isomeric compound 2' was detected during the reaction, indicating the isomerization between 2 and 2' under the reaction condition. Thus, the 2:1 isomeric mixture of 2 and 2' was used for dialkylation without purification. The reaction conditions for the dialkylation were optimized by varying the mole ratios of 1 and 2 and reaction time. The results are summarized in Table 1.

As shown in Table 1, the yield of dialkylation product 4 increases as the mole ratio of 1 to 2 increases from 1:1 to 1:3, but it did not increase higher than 85% even with the use of 2 in 4-fold excess. When a 1:1 reaction of 1 and 2 was carried out, mono-alkylation products of 3 and 3' were the major products and 3' was obtained 4 times more than 3. These results indicate that phenanthrene type compound 2' is more favorable than 2 for the alkylation due to the less steric hindrance in the nucleophilic attack of vinylchlorosilanes to 9-positioned carbon of benzene-ring. In the dialkylation reaction, anthracene type products 4a, b were only obtained from the alkylation of 3 or 3' with vinylchlorosilanes 1a, b, but no phenanthrene type products were

Table 1. Friedel-Crafts Alkylation of 2 with vinylchlorosilanes^a

vinylsilane (1)	mole ratio (1/2 ^b)	reaction time (h)	products (%)		
			3 ^c	3' ^c	4 ^d
a	1.0	2	8	36	20
a	2.0	3	2	8	69
a	3.0	4	0	0	85
a	4.0	4	0	0	84
b	1.0	3	7	39	19
b	2.0	4	2	12	63
b	3.0	4	0	0	81
b	4.0	5	0	0	79

^aThe reaction was carried out at 80 °C and using 20 mol % of AlCl_3 based on 2 used. ^bThe 2:1 mixture of 2 and 2' was used. ^cGLC yields based on 2 used. ^dIsolation yields.

observed. The results suggest that 3' isomerized to 3, followed by the second alkylation with 1 to give 4. The reactivity of 1a was slightly higher than 1b in the alkylation. But the alkylation of 2 with vinyltrimethylchlorosilane or vinyltrimethylsilane did not proceed, probably due to the presence of bulkier silyl group.

New compounds 3a, 3a', 3b, 3b', 4a and 4b were characterized by the analysis of NMR spectroscopy. ¹³C NMR spectra are helpful for the identification of such alkylation products. Both types of isomeric compounds 3a, b and 3a', b' showed 4 peaks and 6 peaks in aromatic region, respectively, due to their symmetries. For the dialkylated products 4a and 4b, two peaks in the aromatic region appeared due to their higher symmetries, respectively.

The structure of 4a was determined by X-ray single crystal diffraction. Details of the structure determinations of 4a are given in Tables 2 and 3. The molecular structures are shown in Figure 1. In Figure 1, 4a showed a good symmetric structure that two silyl-groups substituted at the C9 and C10 of 4a are symmetrically located in the opposite side.

Table 2. Crystal Data and Structure Refinement for 4a^a

Empirical formula	$\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{Si}_2$
Formula weight	468.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic P-1
Unit cell dimensions	$a = 6.6325(11)$ Å $\alpha = 69.88(2)$ deg. $b = 9.501(2)$ Å $\beta = 77.37(2)$ deg. $c = 9.948(4)$ Å $\gamma = 86.35(2)$ deg.
Volume	$574.3(3)$ Å ³
Z, Calculated density	1, 1.354 mg/m ³
Absorption coefficient	0.623 mm ⁻¹
$F(000)$	246
Crystal size	$0.10 \times 0.40 \times 0.50$ mm
Theta range for data collection	2.23 to 24.97 deg.
Limiting indices	$0 < h < 7$, $-11 < k < 11$, $-11 < l < 11$
Reflections collected / unique	1929 / 1767 [R(int) = 0.0246]
Completeness to theta = 24.97	87.4%
Final R indices [I > 2sigma(I)]	R1 = 0.0474, wR2 = 0.1411
R indices (all data)	R1 = 0.0479, wR2 = 0.1414

^aCompound 4a has inversion symmetry at the center of molecule.

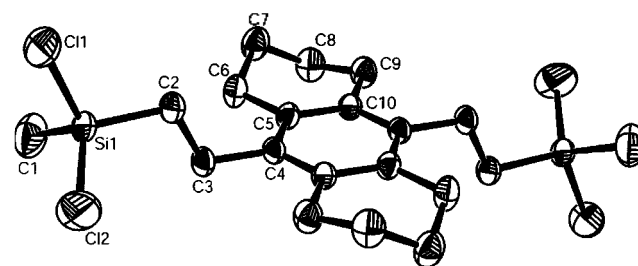


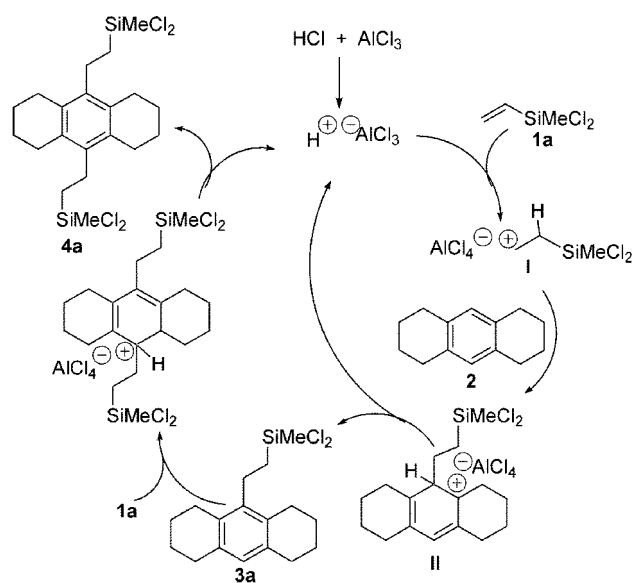
Figure 1. ORTEP diagram of 4a shown at the 50% probability level.

Table 3. Bond lengths [Å] and angles [deg.] for **4a**

Si(1)-C(1)	1.977(2)	C(1)-Si(1)-C(2)	110.23(13)
Si(1)-C(2)	1.840(3)	C(2)-Si(1)-Cl(1)	109.08(12)
Si(1)-Cl(1)	2.0454(15)	C(2)-Si(1)-Cl(2)	110.58(14)
Si(1)-Cl(2)	2.022(2)	C(3)-C(2)-Si(1)	112.0(2)
C(2)-C(3)	1.548(4)	C(4)-C(3)-C(2)	113.8(3)
C(3)-C(4)	1.517(4)	C(5)-C(4)-C(3)	119.6(3)
C(4)-C(5)	1.401(4)	C(4)-C(5)-C(6)	119.9(3)
C(4)-C(10)#1	1.396(4)	C(4)-C(5)-C(10)	119.6(3)
C(5)-C(6)	1.519(4)	C(10)#1-C(4)-C(3)	119.6(3)
C(6)-C(7)	1.509(5)	C(10)#1-C(4)-C(5)	120.9(3)
C(7)-C(8)	1.515(5)	C(10)-C(5)-C(6)	120.5(3)
C(8)-C(9)	1.520(5)	C(7)-C(6)-C(5)	114.3(3)
C(9)-C(10)	1.517(4)	C(6)-C(7)-C(8)	109.9(3)
C(10)-C(4)#1	1.396(4)	C(9)-C(8)-C(7)	109.8(3)
		C(4)#1-C(10)-C(5)	119.5(3)
C(1)-Si(1)-Cl(1)	107.08(8)	C(4)#1-C(10)-C(9)	119.8(3)
C(1)-Si(1)-Cl(2)	112.06(12)	C(5)-C(10)-C(9)	120.6(3)

Symmetry transformations used to generate equivalent atoms: #1-x-1, -y+1, -z-2.

Mechanism. On the basis of our results, a plausible mechanism for the alkylation of **2** with vinylsilane **1a** is outlined in Scheme 2. In the Friedel-Crafts alkylation of arenes with aluminum chloride as a catalyst, a small amount of hydrogen chloride resulting from the reaction of anhydrous aluminum chloride with moisture inevitably present in the reactants would initiate the reaction.¹⁷ The proton from hydrogen chloride interacts with the π -bond of **1a** to give the carbocation intermediate **I** on the carbon β to silicon atom

**Scheme 2.** Mechanism for the alkylation of **2** with **1a**.

which is stabilized by the electron-donating silyl group through σ - π conjugation known as β -stabilization.¹⁸⁻²⁰ Electrophilic attack of this carbocation intermediate **I** to the π -bond of the aromatic ring generates a cation on the aromatic

ring,²¹ which is followed by deprotonation to give silylalkylated aromatic compounds **3a** along with the regeneration of a proton. This proton initiates the catalytic cycle of the Friedel-Crafts alkylation with **1a**. Finally the intermediate **1** attacks **3a** to give dialkylated product **4a**.

In conclusion, Friedel-Crafts alkylation reaction of **2** with vinylchlorosilanes at 80 °C in the presence of AlCl_3 gave dialkylated products **4** in good yields. In these reactions, the reactivity of **1a** is higher than that of **1b**. However, no alkylation of **2** was observed in the case of vinylchlorosilanes having two or more methyl groups on the silicon atom. In monoalkylation reactions, the formation of phenanthrene type compounds **3'** is more favorable than anthracene type compounds **3**. In the dialkylation reaction, 9,10-dialkylated anthracene type compounds **4** were only produced, indicating the rearrangement of monoalkylated phenanthrene type product **3'** to anthracene type product **3** under the alkylation condition and followed by the second alkylation because of the less steric hindrance of **3**. The structure of **4a** was determined by X-ray single crystal diffraction.

Experimental Section

General Comments. All reaction and manipulations were carried out under prepurified dinitrogen atmosphere using Schlenk techniques. Glasswares were flame-dried before use. Dried solvents were employed in all the reactions. Aluminum chloride (99%) and 1,2,3,4-tetrahydronaphthalene were purchased from Aldrich Chemical Co. Vinylchlorosilanes **1a**, **b** were purchased from Gelest, Inc. and used without purification. The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80-100 mesh chromosorb W/AW, 1/8 in. \times 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and ds chrom 99 program connected to a computer. The progress of the reaction was monitored by GLC. NMR spectra were recorded on a Bruker Avance 300 (300 MHz, ^1H : 75 MHz, ^{13}C) spectrometer in CDCl_3 or benzene- d_6 solvent. Mass spectra were obtained using a Hewlett Packard 6890GC/5973MSD. High-resolution mass spectra (EI) were obtained at the Korea Basic Science Institute, Seoul, Korea on a JEOL JMS-700 mass spectrometer at an ionizing voltage of 70 eV. Elemental analyses of new compounds were performed at the chemical analysis laboratory of Korea Institute of Science and Technology.

Alkylation of 1,2,3,4-tetrahydronaphthalene with 1,4-dichlorobutane. To a mixture of 1,2,3,4-tetrahydronaphthalene (198.3 g, 1.5 mol) and aluminum chloride (6.7 g, 0.05 mol) under nitrogen atmosphere at 0 °C was added 1,4-dichlorobutane (63.5 g, 0.5 mol) for 20 min. After addition, the temperature was raised to room temperature. The reaction mixture was stirred for 1 h at room temperature and then quenched with water. Benzene (400 mL) was added the reaction mixture. The organic layer was separated and dried over anhydrous magnesium sulfate. The reaction mixture was vacuum-distilled to give the 2 : 1 mixture (20.0 g) of **2**

and **2'** in 43% yield (based on 1,4-dichlorobutane used) and dodecahydrotriphenylene (40.1 g). Compound **2** was purified as colorless crystals by the repeated recrystallization of *n*-pentane solution of a mixture of **2** and **2'**. Compound **2** was identified by comparing the spectral data with those of commercial compound from Aldrich Chemical Co.

Data for **2b**: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.01 (s, 8H, ring- CH_2), 2.79 (t, $J = 6.3$ Hz, 8H, benzylic- CH_2), 7.01 (s, 2H, aromatic- H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 23.45 (ring- CH_2), 26.20, 30.01 (benzylic- CH_2), 126.34, 134.10 (aromatic-carbons).

Reaction of the mixture of 2 and 2' with 1a. A stirred mixture of aluminum chloride (0.20 g, 1.5 mmol), a 2 : 1 mixture of **2** and **2'** (2.80 g, 15.0 mmol), and **1a** (2.12 g, 15.0 mmol) was heated at 80 °C for 2 h. Then, POCl_3 (0.91 g, 6.0 mmol) was added to the reaction mixture at room temperature and stirred for another 2 h. Toluene (10 mL) was then added to the reaction mixture. The insoluble complex was filtered off. The filtrate was bulb-to-bulb distilled to give a 1 : 4.5 mixture (2.16 g) of **3a** and **3a'**, and **4a** (1.41 g). Pure **4a** was isolated as single crystals by the recrystallization of toluene solution. The results obtained from the reactions using various mole ratio of **1a** and **2** are summarized in Table I, in details.

Data for **3a**: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.85 (s, 3H, SiCH_3), 1.27 (s, 2H, SiCH_2), 1.79 (s, 8H, ring- CH_2), 2.54 (s, 8H, benzylic ring- CH_2), 2.70-2.76 (m, 2H, SiCH_2CH_2), 6.74 (s, 1H, aryl- H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 5.12 (SiCH_3), 22.86 (SiCH_2), 22.90 (ring- CH_2), 25.92 (SiCH_2CH_2), 26.83 (benzylic ring- CH_2), 123.74, 135.83, 137.77, 140.17 (aryl-carbons); HRMS (m/z) calcd for $\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{Si}$ (M^+), 326.1024; found, 326.0988. Data for **3a'**: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.81 (s, 3H, SiCH_3), 1.40 (t, $J = 3.9$ Hz, 2H, SiCH_2), 1.79 (s, 8H, PhCH_2CH_2), 2.54 (s, 8H, benzylic ring- CH_2), 2.70-2.76 (m, 2H, SiCH_2CH_2), 6.79 (s, 1H, aryl- H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 5.12 (SiCH_3), 22.46 (SiCH_2), 23.09, 23.56 (PhCH_2CH_2), 26.19 (SiCH_2CH_2), 26.42, 29.98 (benzylic ring- CH_2), 126.34, 133.45, 134.34, 135.83, 137.77, 143.60 (aryl-carbons); HRMS (m/z) calcd for $\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{Si}$ (M^+), 326.1024; found, 326.1004. Data for **4a**: mp: decomposed slowly at 230 °C; $^1\text{H NMR}$ (300 MHz, benzene- d_6) δ 0.43 (s, 6H, SiCH_3), 1.04 (t, $J = 3$ Hz, 4H, SiCH_2), 1.66 (s, 8H, ring- CH_2), 2.61 (s, 8H, benzylic ring- CH_2), 2.72 (t, $J = 3$ Hz, 4H, SiCH_2CH_2); $^{13}\text{C NMR}$ (75 MHz, benzene- d_6) δ 4.59 (SiCH_3), 20.87 (SiCH_2), 21.00 (ring- CH_2), 23.67 (SiCH_2CH_2), 27.16 (benzylic ring- CH_2), 132.17, 137.21 (aryl-carbons); Anal. Calcd. for $\text{C}_{20}\text{H}_{30}\text{Cl}_4\text{Si}_2$: C, 51.28; H, 6.46. Found: C, 51.40; H, 6.52.

Reaction of the mixture of 2 and 2' with 1b. Using the same procedure as above, the reaction of a 2 : 1 mixture of **2** and **2'** (2.80 g, 15.0 mmol), and **1b** (2.42 g, 15.0 mmol) in the presence of AlCl_3 (0.2 g, 1.5 mmol) gave a 1 : 5.6 mixture (2.4 g) of **3b** and **3b'**, and **4b** (1.45 g). Compound **4b** was purified by the recrystallization of toluene solution. The results obtained from the other reactions using various mole ratio of **1b** and **2** are summarized in Table I, in details.

Data for **3b**: $^1\text{H NMR}$ (300 MHz, benzene- d_6) δ 1.33 (t, J

= 3.39 Hz, 2H, SiCH_2), 2.37 (s, 8H, ring- CH_2), 2.62 (s, 8H, benzylic ring- CH_2), 2.64-2.67 (m, 2H, SiCH_2CH_2), 6.58 (s, 1H, aryl- H); $^{13}\text{C NMR}$ (75 MHz, benzene- d_6) δ 23.38, 23.69 (ring- CH_2), 24.02 (SiCH_2CH_2), 25.25, 30.39 (benzylic- CH_2), 29.40 (SiCH_2), 126.76, 133.47, 134.15, 135.55 (aryl-carbons); HRMS (m/z) calcd for $\text{C}_{16}\text{H}_{21}\text{Cl}_3\text{Si}$ (M^+), 346.0478; found, 346.0475. Data for **3b'**: $^1\text{H NMR}$ (300 MHz, benzene- d_6) δ 1.63 (t, $J = 4.90$ Hz, 2H, SiCH_2), 2.37 (s, 8H, ring- CH_2), 2.62 (s, 8H, benzylic ring- CH_2), 2.64-2.67 (m, 2H, SiCH_2CH_2), 6.87 (s, 1H, aryl- H); $^{13}\text{C NMR}$ (75 MHz, benzene- d_6) δ 23.38, 23.44, 23.69, 25.12 (ring- CH_2), 25.25, 26.58, 30.39 (benzylic ring- CH_2), 26.46 (SiCH_2CH_2), 27.19 (SiCH_2), 126.80, 131.65, 132.04, 133.47, 134.16, 136.35 (aryl-carbons); HRMS (m/z) calcd for $\text{Si}_1\text{C}_{16}\text{H}_{21}\text{Cl}_3$ (M^+), 346.0478; found, 346.0478. Data for **4b**: mp: decomposed slowly at 260 °C; $^1\text{H NMR}$ (300 MHz, benzene- d_6) δ 1.19 (t, $J = 4.5$ Hz, 4H, SiCH_2), 1.59 (s, 8H, ring- CH_2), 2.46 (s, 8H, benzylic- CH_2), 2.68 (t, $J = 3.9$ Hz, 4H, SiCH_2CH_2); $^{13}\text{C NMR}$ (75 MHz) δ 20.65 (ring- CH_2), 23.33 (SiCH_2CH_2), 23.49 (benzylic ring- CH_2), 27.01 (SiCH_2), 132.30, 136.31 (aryl-carbons); Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{Cl}_6\text{Si}_2$: C, 42.45; H, 4.75. Found: C, 42.80; H, 4.82.

X-ray Structure Determination. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine-centered reflections in the 2θ range of from 15° to 25°. The variations of intensities were monitored by a repeated check of intensities of three reflections every 1 h during the data collection period. A direct method successfully located all the non-hydrogen atoms (SHELXS-97). The program, SHELXL-97, was used to refine the structure. Hydrogen atoms were included in the structure factor calculation using a riding model. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-188534). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

- Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379.
- Ishikawa, M.; Ohshita, J.; Nalwa, H. S. *Organic Conductive Molecules and Polymers*; Wiley: New York, 1997; Vol. 2.
- Mauhart, S. A.; Adachi, A.; Sakamaki, K.; Okita, K.; Ohshita, J.; Ohno, T.; Hamaguchi, T.; Kunai, A.; Kido, J. *J. Organomet. Chem.* **1999**, *592*, 52.
- Boek, H.; Ansari, M.; Nagel, N.; Claridge, R. F. C. *J. Organomet. Chem.* **1995**, *501*, 53.
- Boek, H.; Ansari, M.; Nagel, N.; Claridge, R. F. C. *J. Organomet. Chem.* **1996**, *521*, 51.
- Kaim, W.; Boek, H. *Chem. Ber.* **1978**, *111*, 3585.
- Song, Y. S.; Kong, S. D.; Khan, S. A.; Yoo, B. R.; Jung, I. N. *Organometallics* **2001**, *20*, 5586.
- Lee, B. W.; Yoo, B. R.; Kim, S. I.; Jung, I. N. *Organometallics* **1994**, *13*, 1312.
- Cho, E. J.; Lee, V.; Yoo, B. R.; Jung, I. N.; Sohn, H.; Powell, D.

- R.; West, R. *Organometallics* **1997**, *16*, 4200.
10. Cho, E. J.; Lee, V.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1997**, *548*, 237.
11. Yoo, B. R.; Kim, J. H.; Lee, H. J.; Lee, K. B.; Jung, I. N. *J. Organomet. Chem.* **2000**, *605*, 239.
12. Ahn, S.; Song, Y. S.; Yoo, B. R.; Jung, I. N. *Organometallics* **2000**, *19*, 2777.
13. See a review: Jung, I. N.; Yoo, B. R. *Adv. Organomet. Chem.* **2000**, *41*, 145.
14. Jung, I. N.; Yoo, B. R.; Cho, E. J. Unpublished results.
15. (a) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317. (b) Linstead, R. P.; Millidge, A. F.; Thomas, L. S.; Walpole, A. L. *J. Chem. Soc.* **1937**, 1146.
16. Shadmanov, K. M. *Dokl. Akad. Nauk Uz. SSR.* **1963**, *20*(11), 26; *Chem. Abstr.* **1964**, *61*, 4286f.
17. (a) Thomas, C. A. *Anhydrous Aluminum Chloride in Organic Chemistry*, Reinhold: New York, 1941. (b) Alkylation under extremely anhydrous conditions using 99.99% $AlCl_3$ undergoes very slowly.
18. Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.
19. Kresge, A. J.; Tobin, J. B. *Angew. Chem. Int. Ed.* **1993**, *32*, 721.
20. Eabon, C.; Bott, R. W. *Organometallic Compounds of the Group II Elements*; MacDiarmid, A. G., Ed.; Dekker: New York, 1968; Vol. 1, Part 1, pp 359-437.
21. (a) Roberts, R. M.; Khalaf, A. A. *Friedel-Crafts Alkylation Chemistry*; Marcel Dkker, Inc.: New York and Basel, 1984. (b) Olah, G. A. *Friedel-Crafts and Related Reactions*; John Wiley & Sons: New York-London-Sydney, 1963; Volumes I-IV.
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