Dehydropolymerization of Bis(silyl)alkylbenzenes to Highly Cross-Linked Polysilanes, Catalyzed by Group 4 Metallocene Complex

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Bis(silyl)alkylbenzenes such as bis(1-sila-*sec*-butyl)benzene (**1**) and 2-phenyl-1,3-disilapropane (**2**) were prepared in high yields by reduction of the corresponding chlorosilanes with $LiAlH_4$. The dehydropolymerization of **1** and **2** was carried out with group 4 metallocene complexes generated *in situ* from Cp_2MCl_2/Red-Al and Cp_2MCl_2/*n*-BuLi (M=Ti, Hf), producing two phases of polymers. The TGA residue yields of the insoluble polymers were in the range of 64-74%. The molecular weights of the soluble polymers produced ranged from 700 to 5000 (M_w *vs* polystyrene) and from 500 to 900 (M_n *vs* polystyrene). The dehydropolymerization of **1** and **2** seemed to initially produce a low-molecular-weight polymer, which then underwent an extensive cross-linking reaction of backbone Si-H bonds, leading to an insoluble polymer.

Introduction

Polysilanes with unusual optical and electronic properties due to σ-conjugation along the silicon backbone have received extensive attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.[1~3] The conventional synthetic method to get high-molecular-weight polysilanes to date has been the Wurtz coupling reaction of dichlorosilanes using alkali metals, which are intolerant of some functional groups, lack of reproducibility, and have other limitations for controlling stereochemistry and molecular weight.

Harrod's recent discovery of group 4 metallocene catalyzed dehydropolymerization led to great progress in poly(organosilane) synthesis.[4] A major disadvantage of the metallocene-catalyzed dehydrocoupling method is the production of low molecular weights of polysilanes.[4,5] Copious efforts have been made to increase the molecular weight of the polysilanes.[6~9]

To date, silanes which have been appeared in the literature have been mostly arylsilanes. There are few reports on the dehydrocoupling of alkylsilanes.[7,10] We reported the dehydropolymerization of aryl-substituted alkylsilanes catalyzed by group 4 metallocene complex.[11] Woo *et al.* reported the dehydropolymerization of bis- and tris(silyl)arenes to produce highly cross-linked polysilanes.[6a] To our knowledge, the dehydropolymerization of bis(silyl)alkylbenzenes has not been reported to date. Higher-molecular-weight polysilanes is known to be more useful to the application.[1] Here we report the dehydropolymerization of bis(silyl)alkylbenzenes to highly cross-linked polysilanes catalyzed by group 4 metallocene complexes.

Experimental Section

General Considerations. All reactions and manipula-

tions were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recored on a Varian Gemini 300 spectrometer using $CDCl_3$/$CHCl_3$ as a reference at 7.24 ppm downfield from TMS. Carbon-13 NMR spectra were obtained using a Varian Gemini 300 (operating at 75.5 MHz) spectometer using $CDCl_3$ as a reference at 77.0 ppm. Gas chromatography (GC) analyses were performed using a Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5 m×1/8″ in. o.d.) in conjunction with a flame ionization detector. GC/MS data were obtained using a Hewlett-Packard 5890II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm i.d.×30.0 cm, film thickness 0.25 μm) connected to a Hewlett-Packard 5972A mass selective detector. Gel permeation chromatography (GPC) was carried out on a Waters Milipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene and seperately eluted from an Ultrastyragel GPC column series (sequence 500, 10^3, 10^4 Å column). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Molule 570. Thermogravimetric analysis (TGA) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. The polymer sample was heated from 25 to 800 ℃ at a rate of 20 ℃/min. Ceramic residue yield is reported as the percentage of the sample remaining after completion of the heating cycle. Differential scanning calorimetry (DSC) of polymer sample was performed on a Perkin Elmer 7 Series Thermal Analysis

System under an argon flow. Polymer sample was heated at 20 ℃/min. Melting point was determined on a Thomas Hoover Unimelt apparatus and is uncorrected. X-ray powder diffraction measurements were obtained using an APD 3600 X-ray powder diffractometer. Cp$_2$TiCl$_2$, Cp$_2$HfCl$_2$, Red-Al (3.4 M in toluene), n-butyllithium (2.67 M solution in hexane) and LiAlH$_4$ were purchased from Aldrich Chemical Co. and were used without further purification.

Monomer Synthesis. α,α-Bis(chlorosilyl)toluene[12a] and bis(1,1-dichloro-1-sila-*sec*-butyl)benzene[12b] were prepared according to the literature procedure. The following reduction procedure is representative of the other monomers. (*Warning! In the absence of diethyl ether solvent, AlCl$_3$ can catalyzed silane redistribution reactions to produce SiH$_4$ which is an explosive gas upon contact with air. Therfore, the LiAlH$_4$ reduction of the silicon chlorides should be performed in ether and quenched properly with an isopropyl alchol solution of aqueous HCl and then with water.*)

Synthesis of Bis(1-sila-sec-butyl)benzene (1). To a diethyl ether suspension of lithium aluminum hydride (6.1 g, 0.16 mol) in 150 mL of diethyl ether in a 500 mL three-necked, round-bottomed flask equipped with a refulx condenser topped with an inlet/outlet tube was slowly added bis(1,1-dichloro-1-sila-*sec*-butyl) benzene (17.2 g, 0.04 mol) in 100 mL of diethyl ether in a pressure-equalizing addition funnel. After addition was completed, the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered, cooled to 0 ℃, slowly quenched with a HCl/isopropyl alcohol solution (30 mL/200 mL), and then poured into ice-water. The resulting slurry was extracted with diethyl ether. The combined ether phases were washed twice with water, dried over anhydrous MgSO$_4$, and concentrated on a rotary vacuum evaporator. The solution was then fractionally distilled at 65-66 ℃/0.6 mmHg to yield 1 (8.72 g, 98%). Anal. Calcd for Si$_2$C$_{12}$H$_{22}$: C, 64.80; H, 9.97. Found: C, 64.90; H, 10.20. Isomer ratio (by GLC): meta : para＝2 : 3. IR (neat, KBr, cm^{-1}): 2147 s (vSiH), 932 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.14-1.25 (m, 2H, SiCH$_2$), 1.38 (1.39) (d, J＝6.9 Hz, 3H, CH$_3$), 2.63 (sextet, J＝7.2 Hz, 2H, CH), 3.46 (t, J＝3.6 Hz, 6H, SiH), 7.07-7.30 (m, 4H, ArH). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 75.5 MHz): 16.30 (CH$_3$), 24.50 (SiCH$_2$), 37.40 (37.90) (CH), 122.00, 125.00, 126.50, 128.50, 146.0, 148.30 (ArC). GC/MS, m/e (relative intensity): meta isomer 222 (M$^+$) (22), 177 (47), 163 (5), 149 (100), 147 (50), 135 (33), 133 (61), 131 (16), 107 (54), 105 (20), 91 (13), 73 (17); para isomer 222 (M$^+$) (19), 207 (6), 177 (100), 149 (21), 147 (24), 133 (41), 131 (14), 107 (21), 105 (12), 91 (10), 73 (18).

Synthesis of 2-Phenyl-1,3-disilapropane (2). 85% yield; bp 173-174 ℃/760 mmHg. Anal. Calcd for Si$_2$C$_7$H$_{12}$: C, 54.50; H, 7.84. Found: C, 54.30; H, 8.17. IR (neat, KBr, cm^{-1}): 2115 s (vSiH), 930 s (δSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 2.15 (hep, J＝4.0 Hz, 1H, CH), 4.01 (d, J＝4.0 Hz, 6H, SiH$_3$), 7.30-7.44 (m, 5H, ArH). GC/MS, m/e (relative intensity): meta isomer 152 (M$^+$) (40), 121 (53), 120 (100), 119 (38), 105 (33), 93 (19), 91 (15), 53 (12).

Polymerization of 1 Catalyzed by Cp$_2$TiCl$_2$/Red-Al. To a Schlenk flask charged with Cp$_2$TiCl$_2$ (16 mg, 0.04 mmol) and Red-Al (8.8 μL, 0.034 mmol) was added slowly 1 (0.33 g, 1.48 mmol). The reaction mixture immediately turned dark green, and the reaction medium became rapidly gelatinous with violent gas evolution. The mixture remained

undisturbed under a stream of nitrogen for 24 h. The catalyst was destroyed by exposure to the air for a few hours. The yellow gelatinous meterial was washed several times with toluene and diethyl ether and dried at reduced pressure to give 0.18 g (55% yield) of off-white solid (mp>300 ℃; TGA ceramic residue yield 64% (black solid)) which was insoluble in most organic solvent. The combined washing solutions were concentrated on a rotary vacuum evaporator and then passed rapidly through a silica gel column (70-230 mesh, 15 cm×2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.12 g (36% yield) of a very viscous clear oil which was soluble in most organic solvents. IR (KBr pellet, cm^{-1}): 2140 s (vSiH) for solid. For the very viscous clear oil: IR (neat, KBr, cm^{-1}): 2148 s (vSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.08-1.23 (m, 4H, SiCH$_2$), 1.24-1.38 (m, 6H, CH$_3$), 2.85-2.95 (m, 2H, CH), 3.37-3.48 (m, SiH), 6.98-7.32 (m, 4H, ArH); GPC: M_w＝1050, M_n＝820.

Polymerization of 1 Catalyzed by Cp$_2$HfCl$_2$/Red-Al. To a Schlenk flask charged with Cp$_2$HfCl$_2$ (8.0 mg, 0.02 mmol) and Red-Al (5.2 μL, 0.02 mmol) was added slowly 1 (0.23 g, 1.03 mmol). The reaction mixture immediately turned light yellow, and the reaction medium became rapidly gelatinous with violent gas evolution upon heating at 90 ℃ for 20 min. The catalyst was destroyed by exposure to the air for a few hours. The pale yellow gelatinous meterial was washed several times with toluene and diethyl ether and dried at reduced pressure to give 0.09 g (39% yield) of off-white solid (mp>300 ℃; TGA ceramic residue yield 67% (black solid)) which was insoluble in most organic solvent. The combined washing solutions were concentrated on a rotary vacuum evaporator and then passed rapidly through a reverse phase silica gel column (70-230 mesh, 15 cm×2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.52 g (60% yield) of a viscous clear oil which was soluble in most organic solvents. IR (KBr pellet, cm^{-1}): 2140 s (vSiH) for solid. For the very viscous clear oil: IR (neat, KBr, cm^{-1}): 2150 s (vSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.08-1.23 (m, 4H, SiCH$_2$), 1.24-1.38 (m, 6H, CH$_3$), 2.85-2.95 (m, 2H, CH), 3.37-3.48 (m, SiH), 6.98-7.32 (m, 4H, ArH); GPC: M_w＝720, M_n＝590.

Polymerization of 2 Catalyzed by Cp$_2$TiCl$_2$/n-BuLi. To a Schlenk flask loaded with Cp$_2$TiCl$_2$ (42.3 mg, 0.17 mmol) and n-BuLi (0.13 mL of a 2.67 M solution in hexane, 0.35 mmol) was added slowly 2 (1.32 g, 8.55 mmol). The reaction mixture immediately turned dark green, and the reaction medium became rapidly gelatinous with vigorous gas evolution. After 24 h, the catalyst was destroyed by exposure to the air for a few hours. The yellow gelatinous meterial was washed several times with toluene and diethyl ether and dried at reduced pressure to give 1.08 g (82% yield) of pale yellow solid (Anal. Calcd for (Si$_2$C$_7$H$_8$)$_n$: C, 56. 69; H, 5.44. Found: C, 51.60; H, 6.14; mp>300 ℃; TGA ceramic residue yield 72% (black solid)) which was insoluble in most organic solvent. The combined washing solutions were concentrated on a rotary vacuum evaporator and then passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm×2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.17 g (13% yield) of a very viscous opaque oil which was soluble in most organic solvents. IR (KBr pel-

let, cm^{-1}): 2114 s (vSiH) for solid. For the very viscous oil: IR (neat, KBr, cm^{-1}): 2117 s (vSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.8-2.2 (m, CH), 3.0-4.5 (m, SiH), 6.5-7.5 (m, ArH); GPC: M_w=4120, M_n=820.

Polymerization of 2 Catalyzed by Cp$_2$HfCl$_2$/n-BuLi.

To a Schlenk flask loaded with Cp$_2$HfCl$_2$ (64.5 mg, 0.17 mmol) and n-BuLi (0.13 mL of a 2.67 M solution in hexane, 0.35 mmol) was added slowly 2 (1.32 g, 8.55 mmol). The reaction mixture immediately turned yellow, and the reaction medium became rapidly gelatinous with vigorous gas evolution upon heating at 90 ℃ for 20 min. The catalyst was destroyed by exposure to the air for a few hours. The yellow gelatinous meterial was washed several times with toluene and diethyl ether and dried at reduced pressure to give 1.05 g (80% yield) of pale yellow solid (mp>300 ℃; TGA ceramic residue yield 74% (black solid)) which was insoluble in most organic solvent. The combined washing solutions were concentrated on a rotary vacuum evaporator and then passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm×2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.18 g (14% yield) of a very viscous opaque oil which was soluble in most organic solvents. IR (KBr pellet, cm^{-1}): 2112 s (vSiH) for solid. For the very viscous oil: IR (neat, KBr, cm^{-1}): 2115 s (vSiH). ^{1}H NMR (δ, CDCl$_3$, 300 MHz): 1.8-2.2 (m, CH), 3.0-4.5 (m, SiH), 6.5-7.5 (m, ArH); GPC: M_w=5010, M_n=850.

Results and Discussion

α,α-Bis(chlorosilyl)tolune[12a] and bis(1,1-dichloro-1-sila-*sec*-butyl)benzene[12b] were prepared by AlCl$_3$-catalyzed Friedel-Crafts reation of allyldichlorosilane with benzene and by Cu/Cd-catalyzed direct reaction of elemental silicon with α,α-dichlorotoluene in the presence of HCl gas. The monomeric silanes 1 and 2 were prepared in 98 and 85% yields, respectively, by reaction of the corresponding chlorosilanes with LiAlH$_4$. The chemical shifts and coupling constants associated with the protons of the Si-H bonds in the ^{1}H NMR spectra of the silanes are in the ranges of 3.4-4.0 ppm and 3.6-4.0 Hz, respectively. The Si-H stretching bands in the IR spectra of the silanes are in the 2110-2140 cm^{-1} range.

Although Cp$_2$MMe$_2$ (M=Ti, Zr),[4] Cp$_2$Zr[Si(SiMe$_3$)$_3$]Me,[5] and Cp$_2$ZrCl$_2$/n-BuLi[13] are known to be the active catalysts for the dehydropolymerization of primary silanes and CpCp*Zr[Si(SiMe$_3$)$_3$]Me and (CpCp*ZrH$_2$)$_2$ were the most active catalyst previously examined,[5] we wanted to employ a novel catalyst system, Cp$_2$MCl$_2$/Red-Al(M=Ti, Hf),[8] which was recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system, because the monomeric silanes 1 and 2 are sterically hindered. Sterically hindered silanes were known to be very slow to polymerize and to give low-molecular-weight oligosilanes.[5]
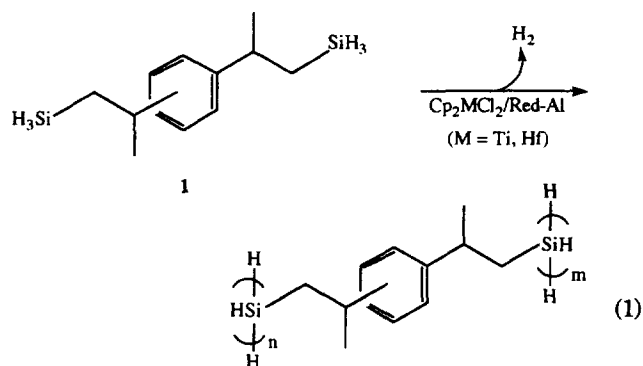
Dehydropolymerization of 1 with 2 mol% Cp$_2$TiCl$_2$/Red-Al catalyst system was immediately initiated, as monitored by the immediate release of hydrogen gas, and the reaction medium became rapidly gelatinous (eq. 1).

Dehydropolymerization of 1 with 2 mol% Cp$_2$HfCl$_2$/Red-Al catalyst system also began immediately, as evidenced by the immediate discharge of hydrogen gas, but the reaction was

Table 1. GPC and TGA Characterization of Dehydropolymerization of Monnomeric Silanes 1 and 2 with Group 4 Metallocene Complexes[a]

Monomer	Catalyst	Percent yield	mol wt[b] M_w	M_n	Residue yield (%)[c]
1	Cp$_2$TiCl$_2$/	55(solid)	—		64
	Red-Al	36(oil)	1050	820	—
1	Cp$_2$HfCl$_2$/	39(solid)	—		67
	Red-Al	60(oil)	720	590	—
2	Cp$_2$TiCl$_2$/	82(solid)	—		72
	n-BuLi	13(oil)	4120	820	—
2	Cp$_2$HfCl$_2$/	80(solid)	—		74
	n-BuLi	14(oil)	5010	850	—

[a][M]/[Si]=0.02. For Ti, stirring at room temperature for 24 h; for Hf, heating at 90 ℃ for 20 min. [b]Measured with GPC (vs polistyrene) in toluene. [c]TGA residue yield at 800 ℃.

(1)

slow and the reaction medium became rapidly gelatinous upon being heated at 90 ℃. The polymer was acquired in total >90% yield as two phases after workup including washing and column chromatography. The first part of polymer was obtained in 55% yield for Ti and 39% yield for Hf as off-white solids (mp>300 ℃), respectively, which were insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solid was 64% for Ti and 67% for Hf, respectively. The second part of polymer was accquired in 36% yield for Ti and 60% yield for Hf as very viscous clear oils, respectively, which were soluble in most organic solvents. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the oily polymers were 1050 and 820 for Ti and 720 and 590 for Hf, respectively (Table 1).

Dehydropolymerization of 2 with Cp$_2$MCl$_2$/Red-Al(M=Ti, Hf) catalyst system yielded a complex mixture of products by both redistribution and dehydrocoupling reaction of 2.[14] Dehydropolymerization of 2 with 2 mol% Cp$_2$TiCl$_2$/n-BuLi catalyst system commenced immediately, as monitored by the immediate discharge of hydrogen gas, and the reaction

(2)

2
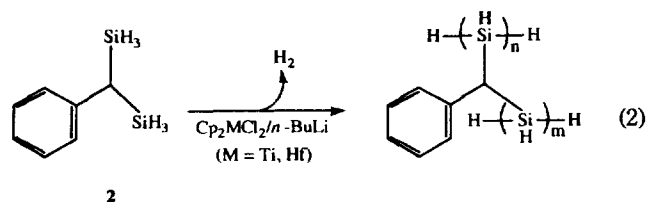
medium became rapidly gelatinous (eq. 2).

Dehydropolymerization of **2** with 2 mol% Cp_2HfCl_2/*n*-BuLi catalyst system also started immediately, as evidenced by the immediate release of hydrogen gas, but the reaction was slow and the reaction medium became repidly gelatinous upon being heated at 90 °C. The polymer was acquired in total >90% yield as two phases after workup including washing and column chromatography. The first part of polymer was obtained in 82% yield for Ti and 80% yield for Hf as pale yellow solids (mp >300 °C), respectively, which were insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solid was 72% for Ti and 74% for Hf, respectively. The second part of polymer was accquired in 13% yield for Ti and 14% yield for Hf as very viscous opaque oils, respectively, which were soluble in most organic solvents. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the oily polymers were 4120 and 820 for Ti and 5010 and 850 for Hf, respectively (Table 1). The ^1H NMR spectra of the soluble polysilanes prepared apparently show nearly one broad unresolved mountain-like resonances centered at *ca.* 3.4 ppm for **1** and 4.0 ppm for **2**. The IR spectra of all of the polysilanes produced here exhibit an intense $vSi-H$ band in the 2110-2150 cm^{-1} range. We found from the results that the expected polysilanes from the dehydropolymerization of **2** with Cp_2MCl_2 /*n*-BuLi catalyst system are obtained without redistribution. Differential scanning calorimetry (DSC) for these polymers did not show the existence of a glass transition temperature (Tg) between 25 and 350 °C. X-ray powder pattern analysis(2 θ = 5-80°) of the solid polymer was featureless, which suggests that the polymer adopt an amorphous, glasslike structure. The solid polysilanes were found to be quite stable at air atmosphere for a long period: the growth of $vSi-O$ stretching bands (*i.e.*, oxidation of the Si-Si bonds) was not observed for several months. We are not sure at this moment why the dehydropolymerization with Cp_2MCl_2/*n*-BuLi gave the higher degree of cross-linking than that with Cp_2MCl_2 /Red-Al (Table 1). We think that the difference is due probably to the difference in the characteristic dehydrocoupling reactivity[15] of the silanes **1** and **2** beacause both catalyst systems are known to produce same catalytic species in the presence of silane.[5,13] One might naturally think that the polymerization first produced a low-molecular-weight polymer which then underwent an extensive cross-linking reaction of backbone Si-H bonds, leading to an insoluble polymer. The bis(silyl)alkylbenzenes **1** and **2** could be employed as a cross-linking agent in the dehydropolymerization of other primary silanes. The solid polymers could be used in the preparation of silicon carbide and SiC-metal composite ceramic materials which might be used as catalyst operating at high temperature. The study is in progress and will be reported in the future.

In conclusion, this work describes the preparation and dehydropolymerization of new bis(silyl)alkylbenzenes, bis(1-sila-*sec*-butyl)benzene **1** and 2-phenyl-1,3-disilapropane **2**, catalyzed by group 4 metallocene complexes generated *in situ* from Cp_2MCl_2/Red-Al and Cp_2MCl_2/*n*-BuLi (M = Ti, Hf), respectively. The monomeric silanes **1** and **2** dehydrocoupled to produce two phases of polymers: one is a highly cross-linked insoluble solid, and the other is non-cross-linked or slightly cross-linked soluble oil and could be a precursor for the solid.

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