

Catalytic Dehydrocoupling of Bis(1-sila-3-butyl)benzene and 2-Phenyl-1,3-disilapropane by Zirconocene Catalysts

Hee-Gweon Woo* and Sun-Jung Song

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

Received July 26, 1996

The catalytic dehydrocoupling of bis(1-sila-3-butyl)benzene, **1** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts yielded a mixture of oily and solid polymers. While the catalytic dehydrocoupling of 2-phenyl-1,3-disilapropane, **2** by $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst produced a mixture of oily and solid polymers, the catalytic redistribution/dehydrocoupling of **2** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ combination catalyst gave oily polymer. The dehydrocoupling of **1** and **2**, unless the prior silane redistribution occurs, seems to initially produce a low-molecular-weight polymer, which then undergoes an extensive cross-linking reaction of backbone Si-H bonds, leading to an insoluble polymer.

Introduction

Inorganic polymers with various superior properties over organic polymers have been used for many special applications.¹ *Inter alia*, polysilanes with unusual optical and electronic properties due to electron-conjugation along the silicon backbone have particularly received extensive attentions as SiC ceramic precursors,^{2a} luminescent materials,^{2b} deep-UV photoresists,^{2c} electroconductors,^{2d} and photoinitiators.^{2e-f} The conventional synthetic method of polysilanes is the Wurtz coupling reaction of organodichlorosilanes using an alkali metal dispersion in toluene-refluxing temperature, which is intolerant of some functional groups, lack of reproducibility, and dangerous due to the strongly reduced reaction conditions.³ Other synthetic methods include anionic polymerization of masked disilenes,^{4a} ring-opening polymerization of cyclic oligosilanes,^{4b} electroreductive polymerization of organodichlorosilanes,^{4c} sonochemical polymerization of organodichlorosilanes,^{4d} and electrochemical polymerization of hydrosilanes.^{4e}

Harrod recently discovered an alternative group 4 metallocene-catalyzed dehydropolymerization leading to great progress in poly(organosilane) synthesis.⁵ A major handicap of this synthetic method is the production of low-molecular-weight polysilanes which affects mechanical and optical properties.^{5,6} Intensive efforts have been made to increase the molecular weight of the polysilanes by studying the polymerization mechanism, by varying reaction conditions, and by adding either an additive or a cross-linking agent.⁵⁻¹⁰

Tilley *et al.* described the catalytic dehydropolymerization of bis- and tris(silyl)arenes to highly cross-linked polysilanes by $(\text{CpCp}^*\text{ZrH}_2)_2$ and $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$.⁷ We reported the dehydropolymerization of aryl-substituted alkylsilanes catalyzed by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Hf).¹¹ We recently reported the catalytic redistribution/dehydrocoupling of 2-phenyl-1,3-disilapropane by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Hf) and the catalytic dehydropolymerization of bis(silyl)alkylbenzenes by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{MCl}_2/n\text{-BuLi}$ combination catalysts (M = Ti, Hf).¹² In this paper, we wish to report the catalytic dehydrocoupling of bis(1-sila-3-butyl)benzene, **1** and 2-phenyl-1,3-disilapropane, **2** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and by $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts to compare their catalytic effects on the different type of bis(silyl)alkylbenzenes with the

other group 4 metallocene catalysts.

Experimental Section

All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Approximate distances between silicon atoms of silanes with two silyl groups were obtained by using CS Chem 3D Pro™ program (version 3.0) developed by the Cambridge Soft Corporation operating on a Power Macintosh personal computer. 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 recorded on a Varian Gemini 300 spectrometer using $\text{CDCl}_3/\text{CHCl}_3$ 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) spectrometer with CDCl_3 as a reference at 77.0 ppm. Solid-state proton NMR spectra were obtained using Bruker MSL 200 spectrometer by the Solid-state NMR Center of the Korea Basic Science Institute, Seoul, Korea. The line widths at half-height ($\Delta\nu_{1/2}$) of the proton signals are reported in Hz. 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 m, film thickness 0.25 μm) connected to a Hewlett-Packard 5972A mass selective detector. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene and separately eluted from an Ultrastayragel GPC column series (sequence 500, 10³, 10⁴ Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 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 °C at a rate of 20 °C/min. Ceramic residue yield is reported as the percentage of the sample remaining after completion of the heating cycle. Differential scanning calorimetry (DSC) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. Polymer sample was heated at 20 °C/min. X-ray powder diffraction measurements were obtained using an APD 3600 X-ray powder diffractometer. Cp_2ZrCl_2 , Red-Al (or Vitride; sodium bis(2-methoxyethoxy) aluminum hydride; 3.4 M in toluene) and *n*-butyllithium (2.67 M solution in hexane) were purchased from Aldrich Chemical Co. and were used without further purification. The bis(silyl)alkylbenzenes **1** and **2** were prepared according to the literature procedure.¹²

Dehydropolymerization of 1 Catalyzed by Cp_2ZrCl_2 /*n*-BuLi. **1** (0.33 g, 1.48 mmol) was slowly added to a Schlenk flask charged with Cp_2ZrCl_2 (8.8 mg, 0.03 mmol) and *n*-BuLi (23 μL of a 2.67 M solution in hexane, 0.06 mmol). The reaction mixture immediately turned light brown, and the reaction medium became rapidly gelatinous with violent gas evolution. After 1 day, the catalyst was inactivated by exposure to the air for a few hours. The yellow gelatinous material was washed several times with toluene and diethyl ether and dried at reduced pressure to give 0.165 g (50% yield) of off-white solid which was insoluble in most organic solvents. 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 \times 2 cm). The column was rinsed with 200 mL of toluene. The colorless effluent was evaporated to dryness to yield 0.122 g (37% yield) of a very viscous clear oil which was soluble in most organic solvents. For the solid: Anal. Calcd for $(\text{Si}_2\text{C}_{12}\text{H}_{18})_n$: C, 65.98; H, 8.31. Found: C, 64.85; H, 9.17; Solid-state ^1H NMR (δ , 200 MHz): 0.75 ($\Delta\nu_{1/2}$ =430 Hz, 10H, SiCH_2 and CH_3), 3.03 ($\Delta\nu_{1/2}$ =360 Hz, 5.2H, CH and SiH), 6.60 ($\Delta\nu_{1/2}$ =245 Hz, 4H, ArH); TGA ceramic residue yield: 67% (black solid). For the very viscous oil: IR (neat, KBr, cm^{-1}): 2148 s (ν_{SiH}); ^1H 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, 4.2H, SiH), 6.98-7.32 (m, 4H, ArH); GPC: M_w =1070, M_n =850. TGA ceramic residue yield: 8% (black solid).

Dehydropolymerization of 1 Catalyzed by Cp_2ZrCl_2 /Red-Al. **1** (0.33 g, 1.48 mmol) was slowly injected to a Schlenk flask containing Cp_2ZrCl_2 (8.8 mg, 0.03 mmol) and Red-Al (8.8 μL , 0.034 mmol). The reaction mixture instantly turned light brown, and the reaction medium became quickly gelatinous with rapid gas evolution. The catalyst was inactivated 24 h later by exposure to the air for a few hours. The yellow gelatinous material was washed well with toluene and diethyl ether and dried at reduced pressure to give 0.173 g (52% yield) of off-white solid which was insoluble in most organic solvents. 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 \times 2 cm) with 200 mL of toluene used as the eluent. The removal of volatiles yielded 0.125 g (38% yield) of a very viscous clear oil which was soluble in most organic solvents. For the solid: Anal. Calcd for $(\text{Si}_2\text{C}_{12}\text{H}_{18})_n$: C, 65.98; H, 8.31. Found: C, 64.81; H, 9.19; Solid-state ^1H NMR (δ , 200 MHz): 0.75 ($\Delta\nu_{1/2}$ =430 Hz, 10H, SiCH_2 and CH_3), 3.03 ($\Delta\nu_{1/2}$ =360

Hz, 5.2H, CH and SiH), 6.60 ($\Delta\nu_{1/2}$ =245 Hz, 4H, ArH); TGA ceramic residue yield: 64% (black solid). For the very viscous oil: IR (neat, KBr, cm^{-1}): 2148 s (ν_{SiH}); ^1H 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, 4.2H, SiH), 6.98-7.32 (m, 4H, ArH); GPC: M_w =1090, M_n =890. TGA ceramic residue yield: 9% (black solid).

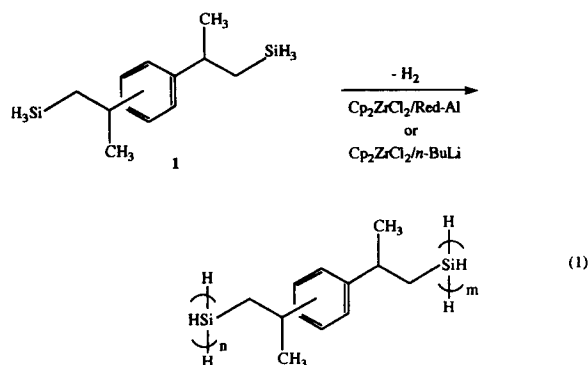
Dehydropolymerization of 2 Catalyzed by Cp_2ZrCl_2 /*n*-BuLi. To a Schlenk flask charged with Cp_2ZrCl_2 (49.7 mg, 0.17 mmol) and *n*-BuLi (0.13 mL of a 2.67 M solution in hexane, 0.35 mmol) was injected slowly **2** (1.31 g, 8.55 mmol). The reaction mixture immediately turned light brown, and the reaction medium became swiftly gelatinous with vigorous gas evolution. After 24 h, the catalyst was destroyed by exposure to the air for a few hours. The yellow gelatinous material was washed several times with toluene and diethyl ether and dried at reduced pressure to give 1.25 g (95% yield) of off-white solid which was insoluble in most organic solvents. The combined washing solutions were concentrated at reduced pressure and then passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm \times 2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated at reduced pressure to yield 0.012 g (1% yield) of a very viscous opaque oil which was soluble in most organic solvents. For the solid: Anal. Calcd for $(\text{Si}_2\text{C}_7\text{H}_8)_n$: C, 56.69; H, 5.44. Found: C, 54.90; H, 6.16; Solid-state ^1H NMR (δ , 200 MHz): 3.21 ($\Delta\nu_{1/2}$ =208 Hz, 3.85H, CH and SiH), 6.03 ($\Delta\nu_{1/2}$ =140 Hz, 5H, ArH); TGA ceramic residue yield: 73% (black solid). For the very viscous oil: IR (neat, KBr, cm^{-1}): 2150 s (ν_{SiH}); ^1H NMR (δ , CDCl_3 , 300 MHz): 1.8-2.2 (m, 1H, CH), 3.0-4.5 (m, 4.1H, SiH), 6.5-7.5 (m, 5H, ArH); GPC: M_w =9020, M_n =1050. TGA ceramic residue yield: 14% (black solid).

Dehydrocoupling of 2 Catalyzed by Cp_2ZrCl_2 /Red-Al. **2** (2.0 g, 13.1 mmol) was drop by drop added to a Schlenk flask loaded with Cp_2ZrCl_2 (15.5 mg, 0.053 mmol) and Red-Al (17.0 μL , 0.058 mmol). (*Warning! The addition order, addition rate, and catalyst concentration should be adhered, or a violent explosion with fire will be occurred.*) The reaction mixture immediately turned light brown, and the reaction medium became viscous with intense gas evolution. After 8 h, the catalyst was killed by exposure to the air. The low-boiling products were isolated by bulb-to-bulb vacuum distillation: the low-boiling products were identified to be benzylsilane (**3**, 3%), dibenzylsilane (**4**, 1%), 2,4-diphenyl-1,3-disilabutane (**5**, 5%), 2,4-diphenyl-1,3,5-trisilapentane (**6**, 60%), 2,5-diphenyl-1,3,4,6-tetrasilahexane (**7**, 5%), and unidentified products (26%). The remaining high-boiling mixture was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm \times 2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.50 g (25% yield) of a viscous opaque oil. IR (neat, KBr, cm^{-1}): 3022 w, 2922 m, 2852 w (ν_{CH}), 2148 s (ν_{SiH}), 1594 w, 1492 m, 1450 w, 1032 m, 922 s (δ_{SiH}), 878 m, 696 s; ^1H NMR (δ , CDCl_3 , 300 MHz): 1.2-2.5 (m, CH), 3.6-4.4 (m, SiH), 6.5-7.5 (m, ArH); GPC: M_w =750, M_n =510. TGA ceramic residue yield: 2% (black solid).

Results and Discussion

Although Cp_2MMe_2 ($\text{M}=\text{Ti}, \text{Zr}$),⁵ $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$,⁶ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ ¹³ are known to be the active catalysts for the dehydropolymerization of primary silanes and $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ and $(\text{CpCp}^*\text{ZrH}_2)_2$ were the most active catalyst previously examined,⁶ we decided to employ a novel combination catalyst, $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$),¹⁴ 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.^{5,6}

Dehydropolymerization of **1** with 2 mol% of the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts initiated immediately, as monitored by the immediate release of hydrogen gas, and the reaction medium became rapidly gelatinous (eq 1).



The polymers were isolated in >85% total yield as two phases after workup including washing and column chromatography. The first part of the polymers was obtained in 50-52% yield as an off-white solid which was insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solids was in the range of 64-67%. The second part of the polymers was acquired in 37-38% yield as a very viscous clear oil which was soluble in most organic solvents. The TGA ceramic residue yield of the soluble oils ranged from 8% to 9%. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the oily polymers were in range of 1070-1090 and 850-890, respectively. The characterization data are summarized in Table 1.

The solid-state ^1H NMR spectra of the insoluble solid polysilanes showed only a single, broad ($\Delta\nu_{1/2}=360$ Hz) peaks centered at ca. 3.0 ppm assigned to the C-H and Si-H resonances. The ^1H NMR spectra of the soluble oily polysilanes apparently show nearly one broad unresolved mountain-like resonances centered at ca. 3.4 ppm. The IR spectra of the polysilanes exhibit an intense SiH band at ca. 2140 cm^{-1} .

Dehydropolymerization of **2** with 2 mol% of the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst commenced immediately, as moni-

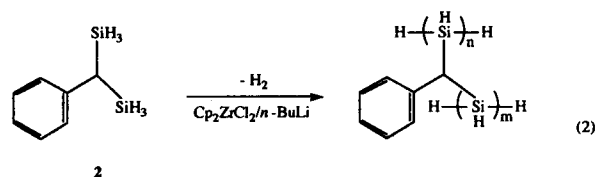


Table 1. Characterization of Catalytic Dehydrocoupling of **1** with Zirconocene Combination Catalysts^a

Catalyst	% yield	mol wt ^b		% ceramic residue yield ^c
		M_w	M_n	
$\text{Cp}_2\text{ZrCl}_2/$ $n\text{-BuLi}$	50 (solid)	—	—	67
$\text{Cp}_2\text{ZrCl}_2/$ $n\text{-BuLi}$	37 (oil)	1070	850	8
$\text{Cp}_2\text{ZrCl}_2/$ Red-Al	52 (solid)	—	—	64
$\text{Cp}_2\text{ZrCl}_2/$ Red-Al	38 (oil)	1090	890	9

^a $[\text{Zr}]/[\text{Si}]=0.02$; at ambient temperature for 24 h. ^bMeasured with GPC (vs polystyrene) in toluene. ^cMeasured with TGA up to 800 $^\circ\text{C}$.

Table 2. Characterization of Catalytic Dehydrocoupling of **2** with Zirconocene Combination Catalysts

Catalyst	% yield	mol wt ^c		% ceramic residue yield ^d
		M_w	M_n	
$\text{Cp}_2\text{ZrCl}_2/$ $n\text{-BuLi}$ ^a	95 (solid)	—	—	73
$\text{Cp}_2\text{ZrCl}_2/$ $n\text{-BuLi}$	1 (oil)	9020	1050	14
$\text{Cp}_2\text{ZrCl}_2/$ Red-Al ^b	25 (oil)	750	510	2

^a $[\text{Zr}]/[\text{Si}]=0.02$; at ambient temperature for 24 h. ^b $[\text{Zr}]/[\text{Si}]=0.004$; at ambient temperature for 8 h. ^cMeasured with GPC (vs polystyrene) in toluene. ^dMeasured with TGA up to 800 $^\circ\text{C}$.

tored by the instant evolution of hydrogen gas, and the reaction medium became promptly gelatinous (eq 2).

The polymer was isolated in 96% total yield as two phases after workup including washing and column chromatography. The first part of the polysilane was obtained in 95% yield as an off-white solid which was insoluble in most organic solvents. The TGA ceramic residue yield of the insoluble solids was 73%. The second part of the polysilane was acquired in 1% yield as a very viscous opaque oil which was soluble in most organic solvents. The TGA ceramic residue yield of the soluble oil was 14%. The M_w and M_n of the oily polymer were 9020 and 1050, respectively. The characterization data are given in Table 2.

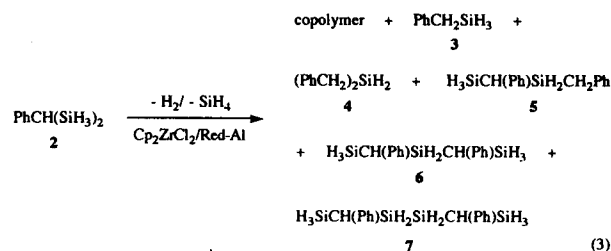
The solid-state ^1H NMR spectrum of the insoluble polysilane showed only a single, broad ($\Delta\nu_{1/2}=208$ Hz) peaks centered at ca. 3.2 ppm assigned to the C-H and Si-H resonances. The ^1H NMR spectrum of the soluble polysilane apparently shows nearly one broad unresolved mountain-like resonances centered at ca. 4.0 ppm. The IR spectrum of the polysilane exhibits an intense ν_{SiH} band at ca. 2145 cm^{-1} .

We found from the above results that the expected structures of polysilanes are obtained without appreciable side reactions from the catalytic dehydropolymerization of **1** by $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalysts and from the catalytic dehydropolymerization of **2** with $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst. As shown in Table 1, two combination catalysts in the dehydropolymerization of **1** produce the polysilanes with similar molecular weights and percent ceramic residue yield in the similar polymerization yield. Interestingly, as shown in Table 1 and 2, with the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ combination catalyst, the molecular weight

and percent ceramic residue yield of the polysilane prepared from the catalytic dehydropolymerization of **2** were higher than those of the polysilanes prepared from the catalytic dehydropolymerization of **1**. Compared to the other group 4 metallocene combination catalysts,^{12a} zirconocene combination catalysts produced the polysilanes with the similar molecular weights and percent ceramic residue yield as the titanocene and hafnocene combination catalysts in the catalytic dehydropolymerization of **1**. Zirconocene combination catalyst produced the oily polysilane with the higher molecular weights than the titanocene and hafnocene combination catalysts in the dehydropolymerization of **2** catalyzed by $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$. Differential scanning calorimetry (DSC) for these solid polymers did not show the presence of a glass transition temperature (T_g) between 25 and 400 °C. X-ray powder pattern ($2\theta=5\text{-}80^\circ$) for the solid polymers were featureless, which suggests that the polymers adopt an amorphous, glass-like structure. The carbon analyses were consistently lower than the calculated values due presumably to SiC formation leading to incomplete carbon combustion. The cross-linked solid polysilanes were not pyrophoric and were found to be quite stable at air atmosphere for a long period: the noticeable growth of Si-O stretching bands by oxidation of the Si-Si bonds was not observed for several months. Thermogravimetric analysis (TGA) of these insoluble polysilanes remained unchanged after and before irradiation for 2 h using a medium-pressure mercury lamp, indicating that the solid polymers are not appreciably photodegradable. The TGA data of the insoluble polysilanes showed that the ceramic residue yields were consistently higher than the theoretical yields (i.e., $2\text{SiC}/\text{Si}_2\text{C}_{12}\text{H}_{18}=36.6\%$ for **1**; $2\text{SiC}/\text{Si}_2\text{C}_7\text{H}_8=53.8\%$ for **2**), probably due to extra free carbon formation, promoted by the crosslinking, along with SiC formation under the pyrolysis conditions. 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. Catalytic dehydropolymerization of *ortho*-, *meta*-, *para*-bis(silyl)phenylenes with the Si-Si distance of approximately 3.22, 5.57, and 6.43 Å, respectively,¹⁵ is known to produce a soluble polysilane for the *ortho*-bis(silyl)phenylene and an insoluble polysilane for the *meta*- and *para*-bis(silyl)phenylenes.^{7a} In addition, the catalytic dehydropolymerization of the 1,2-diphenyldisilane with the Si-Si distance of approximately 2.22 Å produces a soluble polysilane.⁸ In contrast, the catalytic dehydropolymerization of the bis(silyl)alkylbenzenes **1** and **2** with the Si-Si distance of approximately 3.07, and 10.92 Å, respectively, produces insoluble polysilanes. It is now evident that the orientation of the two silyl groups as well as the Si-Si distance in a silane with two silyl groups are an important factor to yield an extensive network structure of polysilane.

The catalytic dehydrocoupling of **2** by 0.4 mol% of the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ combination catalyst yielded a complex mixture of products by redistribution/dehydrocoupling reactions of **2**. We first expected that the catalytic dehydrocoupling of **2** by the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ and $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ catalyst systems could give the same type of polysilane because both catalyst systems are known to produce same catalytic species in the presence of silane,^{5,6,13} but they gave totally different

products (*vide infra*). Redistribution/dehydrocoupling of **2** with the $\text{Cp}_2\text{ZrCl}_2/\text{Red-Al}$ catalyst system commenced immediately and the reaction medium became slowly viscous (eq. 3).



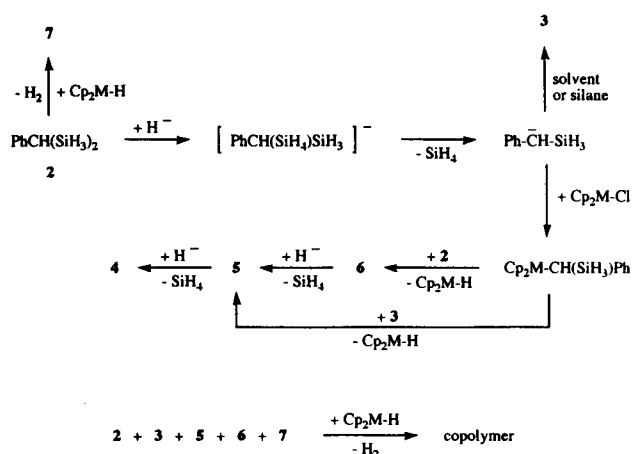
The volatiles **3-7** were isolated by bulb-to-bulb vacuum distillation and then subject to GC/MS analysis.^{12b} The polymer was isolated in 28% yield as a viscous opaque oil after workup including column chromatography. The TGA ceramic residue yield of the polymer was 2%. The weight average molecular weight and number average molecular weight of the polymer 750 and 510, respectively. The ¹H NMR spectrum of the polymer apparently shows a set of broad unresolved mountain-like peaks in the region of 3.6-4.4 ppm assigned to the Si-H resonances. The IR spectrum of the polymer shows an intense Si-H band at around 2150 cm⁻¹. We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using high-resolution ¹³C and ²⁹Si NMR spectroscopy and other analytical techniques.

Although enough experimental data are not currently in our hands, some comments on the catalytic redistribution/dehydrocoupling mechanism of **2** by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ combination catalyst seem appropriate. We propose a mechanism involving the preferential attack of the hydride on the less hindered silicon with formation of a pentacoordinated anionic species which collapses to give an α -silyl carbanion intermediate and SiH₄ gas. The α -silyl carbanion may then pick up a hydrogen from the hydrogen source (e.g., silane or solvent) to yield **3** or may react with a metallocene chloride to produce its metallocene derivative which will then undergo a σ -bond metathesis reaction with **2** and **3** to give a Si-C coupling product, **6** and **5**, respectively. **6** may sequentially lose SiH₄ gas by the action of a hydride ion producing **4** and **5**. The resulting silanes might then undergo dehydrocoupling to yield a copolymer (Scheme 1).

One may expect that the secondary silyl groups of the silanes **4-7** should seldom undergo dehydrocoupling due to their steric bulkiness. The dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order primary > secondary > tertiary.^{5,6} One may note that the redistribution of **2** could only occur prior to the dehydrocoupling when the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ is used as a catalyst, but the dehydrocoupling could occur without redistribution when the $\text{Cp}_2\text{MCl}_2/n\text{-BuLi}$ used as a catalyst. This provides an example of forming different types of polymers, depending on the combination of metallocene and anionic additive.

Conclusions

The monomeric silanes bis(1-sila-3-butyl)benzene **1** was



Scheme 1. Postulated mechanism for catalytic dehydrocoupling of **2** by $Cp_2ZrCl_2/Red-Al$.

dehydrocoupled by the $Cp_2ZrCl_2/Red-Al$ and $Cp_2ZrCl_2/n-BuLi$ combination catalysts to produce two phases of polymers: one is a highly cross-linked insoluble solid, and the other is noncross-linked or slightly cross-linked soluble oil and could be a precursor for the solid polymer. 2-phenyl-1,3-disilapropane **2** was dehydrocoupled by the $Cp_2ZrCl_2/n-BuLi$ combination catalyst, similarly yielding two phases of polymers. By contrast, the catalytic reaction of **2** with the $Cp_2ZrCl_2/Red-Al$ combination catalyst produced a soluble polymer *via* redistribution/dehydrocoupling process. A plausible mechanism for the formation of the soluble polymer was provided.

Acknowledgment. This research was supported by the Korea Science and Engineering Foundation (1996). H.G.W. especially thanks the Dow Corning Ltd. for a contribution.

References

- Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.
- (a) Yajima, S.; Omori, M.; Hayashi, J.; Okamura, K.; Matsuzawa, T.; Liaw, C. F. *Chem. Lett.* **1976**, 551. (b) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342. (c) Griffing, B. F.; West, R. *Polym. Eng. Sci.* **1983**, *23*, 947. (d) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. S. V.; Srinivasan, H. Y. *J. Am. Chem. Soc.* **1981**, *103*, 7352. (e) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (f) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
- (a) Trefonas, P., III; Damewood, J. R., Jr.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318. (b) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601. (c) Fujino, M.; Hisaki, T.; Fujiki, M.; Matsumoto, N. *Macromolecules* **1992**, *25*, 1079.
- (a) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494. (b) Matyjaszewski, K.; Cypriak, M.; Frey, H.; Hrkach, J.; Kim, H. K.; Moeller, M.; Ruehl, K.; White, M. J. *Macromol. Sci.-Chem.* **1991**, *A28*, 1151. (c) Hengge, E.; Litscher, G. K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 370. (d) Matyjaszewski, K.; Greszta, D.; Hrkach, J. S.; Kim, H. K. *Macromolecules* **1995**, *28*, 59. (e) Kimata, Y.; Suzuki, H.; Satoh, S.; Kuriyama, A. *Organometallics* **1995**, *14*, 2506.
- (a) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804. (b) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (c) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (d) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897. (e) Woo, H.-G.; Harrod, J. F.; Hénique, J.; Samuel, E. *Organometallics* **1993**, *12*, 2883. (f) Britten, J.; Mu, Y.; Harrod, J. F.; Polowin, J.; Baird, M. C.; Samuel, E. *Organometallics* **1993**, *12*, 2672.
- (a) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (d) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (e) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700.
- (a) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (b) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487.
- (a) Harrod, J. F. In *Transformation of Organometallics into Common and Exotic Materials, Design and Activation*; Laine, R. M., Ed.; NATO ASI Series E: Appl. Sci. no. 141; Martinus Nijhoff Publishers: Amsterdam, 1988; p 103. (b) Mu, Y.; Harrod, J. F. In *Inorganic and Organometallic Polymers and Oligomers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991; p 23.
- (a) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548. (b) Dioumaev, V. K.; Harrod, J. F. Submitted for publication.
- (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (b) Imori, T.; Tilley, T. D. *Polyhedron* **1994**, *13*, 2231.
- Woo, H.-G.; Kim, S.-Y.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Organometallics* **1995**, *14*, 2415.
- (a) Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Cho, E. J.; Yeon, S. H.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1109. (b) Woo, H.-G.; Song, S.-J.; You, H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1996**, *17*, 475.
- Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121.
- Woo, H.-G.; Harrod, J. F. Unpublished results.
- Woo, H.-G., Ph.D. Thesis, University of California at San Diego, CA, 1990.