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## Dehydrogenative Polymerization of New Alkylsilanes Catalyzed by $Cp_2MCl_2/Red-Al$ System (M=Ti, Hf)

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Substituted 3-phenyl-1-silabutanes, 3-chlorophenyl-1-silabutane (1), 3-tolyl-1-silabutane (2), and 3-phenoxyphenyl-1-silabutane (3), were prepared in 68-98% yield by reduction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with  $LiAlH_4$ . The dehydrogenative homopolymerization and copolymerization of the silanes were performed with  $Cp_2MCl_2/Red-Al$  (M=Ti, Hf) catalyst system. The molecular weights of the resulting polymers were in the range of 600 to 1100 (*vs* polystyrene) with degree of polymerization (DP) of 5 to 8 and polydispersity index (PDI) of 1.6 to 3.8. The monomer silanes underwent the dehydrogenative polymerization with  $Cp_2TiCl_2/Red-Al$  catalyst to produce somewhat higher molecular weight polysilanes compared with  $Cp_2HfCl_2/Red-Al$  catalyst.

### Introduction

Polysilanes with unusual optical and electronic properties have received a copious amount of attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.<sup>1-3</sup> The conventional synthetic method to get high molecular weight polysilanes to date has been the Wurtz coupling reaction of dichlorosilanes with sodium, which are intolerant of some functional groups and other limitation for controlling stereochemistry and molecular weight.

Harrod's recent discovery of the group 4 metallocene-catalyzed dehydrogenative polymerization made a large advance in polyorganosilane synthesis.<sup>4</sup> Two mechanisms have been so far suggested: (1) the oxidative addition/reductive elimination sequences *via* the intermediacy of transition-metal silylene complexes<sup>4</sup> and (2) the four-center sigma bond metathesis processes among silicon, hydrogen, and a  $d^0$  metal

center *via* the intermediacy of transition-metal silyl and hydride complexes.<sup>5</sup> The latter mechanism is strongly supported by many model reactions<sup>5</sup> and thermochemical results.<sup>6</sup> A major disadvantage of the metallocene-catalyzed dehydrogenative coupling method is to produce low molecular weights of polysilanes.<sup>4,5</sup> Considerable efforts have been made to increase the molecular weight of the polysilanes.<sup>7-10</sup>

<sup>29</sup>Si NMR technique has been useful in analyzing polysilane chain microstructure.<sup>11</sup> The structures of all polysilanes so far synthesized *via* dehydrogenative coupling method are predominantly random atactic although some diastereomeric selection was observed in the special reaction conditions.<sup>12</sup> To date, most of silanes which have been employed in the literature are arylsilanes. There are few reports on the dehydrogenative coupling of alkylsilanes.<sup>8,13</sup> To our knowledge, there is no report to date on the dehydrogenative copolymerization of alkylsilanes.

The dehydrogenative coupling route of substituted 3-phenyl-

nyl-1-silabutanes may provide the possibility of controlling the molecular weight distribution and stereochemistry of polymer as well as introducing functionality into the polymer. In this contribution, we report the dehydrogenative homopolymerization and copolymerization of substituted 3-phenyl-1-silabutanes to give poly(substituted 3-phenyl-1-silabutanes) catalyzed by metallocene complexes *in situ* generated from  $Cp_2MCl_2$  ( $M = Ti, Hf$ )/Red-Al.

## Experimental

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. Elemental analyses were performed by Advanced Analysis Center of 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. Electronic spectra were acquired using an IBM 9420 UV-vis spectrophotometer. Proton NMR spectra were recorded 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) spectrometer using  $CDCl_3$  as a reference at 77.0 ppm. Gas chromatography (GC) analyses were performed using Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5  $m \times 1/8''$  od) in conjunction with a flame ionization detector. GC/MS data were obtained using a Hewlett Packard 5890 II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm id  $\times$  30.0 m, film thickness 0.25  $\mu m$ ) 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 Ultrastaygel GPC column series (sequence 500, 10<sup>3</sup>, 10<sup>4</sup> Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standards. Data analyses were carried out using a Waters Data Module 570.  $Cp_2TiCl_2$ ,  $Cp_2HfCl_2$ , Red-Al (3.4 M in toluene), and  $LiAlH_4$  were purchased from Aldrich Chemical Co. and were used without further purification.

## Monomer Synthesis

Substituted 3-phenyl-1,1-dichloro-1-silabutanes were prepared according to the literature procedure.<sup>14</sup> The following reduction procedure is representative of the other monomers. (**Warning:** In the absence of diethyl ether solvent,  $AlCl_3$  can catalyze silane redistribution reactions to produce  $SiH_4$  which is an explosive gas upon contact with air. Therefore, the  $LiAlH_4$  reduction of the silicon chlorides should be performed in ether and quenched properly with isopropyl alcohol solution of HCl and then with water.)

**Synthesis of 3-Chlorophenyl-1-silabutane (1).** To a diethyl ether suspension of lithium aluminum hydride (3.07 g, 0.08 mol) in 70 mL of diethyl ether in a 250 mL three-necked, round-bottomed flask equipped with a reflux condenser topped with an inlet/outlet tube was slowly added 3-chlorophenyl-1,1-dichloro-1-silabutane (11.5 g, 0.04 mol) in

70 mL of diethyl ether in a pressure equalizing addition funnel. After completing addition, the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered, cooled to 0 °C, slowly quenched with HCl/isopropyl alcohol solution (20 mL/150 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 rotary vacuum evaporator. The crude product was then fractionally distilled at 64-67 °C/0.6 mmHg to yield **1** (5.04 g, 68%). Anal. Calcd for  $SiC_9H_{13}Cl$ : C, 58.51; H, 7.09. Found: C, 58.50; H, 7.38. IR (neat, KBr,  $cm^{-1}$ ): 2190 s ( $\nu SiH$ ), 910 s ( $\delta SiH$ ).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 1.09-1.27 (m, 2H,  $CH_2$ ), 1.32 (1.31) (d,  $J = 7.0$  Hz, 3H,  $CH_3$ ), 3.43 (2.88) (sextet,  $J = 7.0$  Hz, 1H, CH), 3.46 (3.41) (t,  $J = 4.0$  Hz, 3H, SiH), 7.10-7.36 (m, 4H, ArH) (isomer ratio; *ortho* : *meta* : *para* = 15 : 1 : 34).  $^{13}C\{^1H\}$  NMR ( $\delta$ ,  $CDCl_3$ , 75.5 MHz): 14.86, 15.95, 16.03 ( $SiCH_2$ ), 22.77, 24.18, 24.40 ( $CH_3$ ), 33.22, 37.24, 37.58 (CH), 124.76, 126.30, 126.91, 126.99, 127.09, 127.88, 128.53, 129.66, 131.76, 146.67, 150.40 (ArC). GC/MS, m/e (relative intensity): 184 (19) ( $M^+$ ), 169 (12), 143 (32), 141 (100), 139 (84), 125 (11), 115 (21), 105 (19), 103 (60), 102 (13), 91 (20), 78 (12), 77 (43), 75 (11), 65 (19), 63 (32), 51 (17).

**Synthesis of 3-Tolyl-1-silabutane (2).** 98% yield, bp 36-38 °C/0.6 mmHg. Anal. Calcd for  $SiC_{10}H_{16}$ : C, 73.09; H, 9.81. Found: C, 73.22; H, 9.99. IR (neat, KBr,  $cm^{-1}$ ): 2150 s ( $\nu SiH$ ), 910 s ( $\delta SiH$ ).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 1.00-1.19 (m, 2H,  $CH_2$ ), 1.32, 1.31, 1.32 (d,  $J = 7.0$  Hz, 3H,  $CH_3$ ), 2.33, 2.34, 2.35 (s, 3H,  $CH_3$ ), 3.17, 2.86, 2.87 (sextet,  $J = 7.0$  Hz, 1H, CH), 3.44, 3.40, 3.41 (t,  $J = 4.0$  Hz, 3H, SiH), 7.00-7.27 (m, 4H, ArH) (isomer ratio; *ortho* : *meta* : *para* = 23 : 35 : 42).  $^{13}C\{^1H\}$  NMR ( $\delta$ ,  $CDCl_3$ , 75.5 MHz): 15.31, 16.11, 16.12 ( $SiCH_2$ ), 19.46, 21.48, 20.98 ( $CH_3$ ), 23.71, 24.45, 24.63 ( $CH_3$ ), 32.31, 37.28, 37.61 (CH), 123.46, 124.96, 125.68, 126.25, 126.36, 126.80, 127.29, 128.25, 129.03, 130.23, 135.51 (ArC). GC/MS, m/e (relative intensity): 164 (16) ( $M^+$ ), 122 (43), 121 (66), 120 (16), 119 (100), 117 (30), 115 (26), 105 (28), 103 (11), 93 (14), 91 (69), 77 (25), 72 (12), 65 (19), 51 (12).

**Synthesis of 3-Phenoxyphenyl-1-silabutane (3).** 85 % yield, bp 90-100 °C/0.5 mmHg. Anal. Calcd for  $SiC_{15}H_{18}O$ : C, 74.32; H, 7.43. Found: C, 74.10; H, 7.42. IR (neat, KBr,  $cm^{-1}$ ): 2147 s ( $\nu SiH$ ), 918 s ( $\delta SiH$ ).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 1.18-1.37 (m, 2H,  $CH_2$ ), 1.42 (1.43) (d,  $J = 3.3$  Hz, 3H,  $CH_3$ ), 3.44 (2.99) (sextet,  $J = 3.6$  Hz, 1H, CH), 3.52 (3.50) (t,  $J = 3.9$  Hz, 3H, SiH), 6.96-7.44 (m, 9H, ArH) (isomer ratio; *ortho* : *meta* : *para* = 71 : 2 : 27).  $^{13}C\{^1H\}$  NMR ( $\delta$ ,  $CDCl_3$ , 75.5 MHz): 15.10 (16.44) ( $SiCH_2$ ), 23.47 (24.79) ( $CH_3$ ), 30.61 (37.23) (CH), 117.98, 118.68, 119.14, 119.69, 122.69, 123.05, 124.15, 127.23, 127.42, 127.83, 129.79, 130.16, 139.46, 143.30, 153.86, 155.38, 158.17 (ArC). GC/MS, m/e (relative intensity): 242 (34) ( $M^+$ ), 227 (15), 197 (100), 181 (17), 165 (5), 149 (9), 120 (9), 103 (10), 91 (17), 77 (23), 65 (5), 51 (9).

## Homopolymerization Catalyzed by $Cp_2TiCl_2$ /Red-Al

**Polymerization of 1.** The following procedure is representative of the polymerization reactions. To a Schlenk flask charged with  $Cp_2TiCl_2$  (0.20 g, 0.80 mmol) and Red-Al (24 mL, 0.80 mmol) was added slowly **1** (1.50 g, 8.00 mmol). The reaction immediately turned dark green, and the reaction medium became rapidly viscous with strong gas evolu-

tion. The mixture was stirred under a stream of nitrogen for 24 h and then heated at 90 °C until the mixture became rigid. The catalyst was allowed to oxidize by exposure to the air for a few second, and the solution was then passed rapidly through a silica gel column (70-230 mesh, 2 cm×20 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded 1.46 g (99% yield) of off-white tacky product. The polymer was dissolved in benzene, precipitated in hexane, filtered off, and dried to give white tacky product of which the physical data were very similar to that of the starting polymer. The reactive solvents (toward Si-H bond) such as alcohol, acetone, and DMSO cannot be used for the precipitation. The polymer was quite soluble in THF, ether, and benzene, and became a gum in THF. IR (neat, KBr, cm<sup>-1</sup>): 2100 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.82-1.58 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.75-2.97 (m, 1H, CH), 3.29-3.55 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.93-7.26 (m, 4H, ArH). GPC:  $\bar{M}_w=1050$ ;  $\bar{M}_n=500$ ;  $\bar{M}_w/\bar{M}_n=2.1$ .

**Polymerization of 2.** 91% yield. IR (neat, KBr, cm<sup>-1</sup>): 2105 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 1.00-1.30 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.35-2.39 (m, 3H, Ar-CH<sub>3</sub>), 2.80-2.96 (m, 1H, CH), 3.37-3.53 (m, broad overlap of SiH and SiH<sub>2</sub>), 7.02-7.27 (m, 4H, ArH). GPC:  $\bar{M}_w=1090$ ;  $\bar{M}_n=560$ ;  $\bar{M}_w/\bar{M}_n=1.9$ .

**Polymerization of 3.** 79% yield. IR (neat, KBr, cm<sup>-1</sup>): 2140 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.96-1.46 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.77-2.94 (m, 1H, CH), 3.20-3.54 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.85-7.36 (m, 9H, ArH). GPC:  $\bar{M}_w=890$ ;  $\bar{M}_n=490$ ;  $\bar{M}_w/\bar{M}_n=1.8$ . UV-vis (hexane): λ<sub>max</sub>=285 (ε=2500).

#### Homopolymerization Catalyzed by Cp<sub>2</sub>HfCl<sub>2</sub>/Red-Al

**Polymerization of 1.** The following procedure is representative of the polymerization reactions. **1** (0.17 g, 0.92 mmol) was slowly added to a Schlenk flask charged with Cp<sub>2</sub>HfCl<sub>2</sub> (24 mg, 0.06 mmol) and Red-Al (18 μL, 0.06 mmol). The reaction immediately turned light yellow, and the reaction medium became slowly viscous with moderate gas evolution. The mixture was stirred under a stream of nitrogen for 30 min and then heated at 90 °C until the mixture became rigid. The catalyst was inactivated by exposure to the air for a few second, and the solution was then passed rapidly through a silica gel column (70-230 mesh, 2 cm×20 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure gave 0.09 g (53% yield) of off-white tacky product. The polymer was dissolved in benzene, precipitated in hexane, filtered off, and dried to give white tacky product of which the physical data were very similar to that of the starting polymer. The reactive solvents such as alcohol, acetone, and DMSO cannot be used for the precipitation. The polymer was quite soluble in THF, ether, and benzene, and became a gum in THF. IR (neat, KBr, cm<sup>-1</sup>): 2150 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.63-1.02 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.47-2.98 (m, 1H, CH), 3.06-3.75 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.87-7.48 (m, 4H, ArH). GPC:  $\bar{M}_w=1030$ ;  $\bar{M}_n=450$ ;  $\bar{M}_w/\bar{M}_n=2.3$ .

**Polymerization of 2.** 32% yield. IR (neat, KBr, cm<sup>-1</sup>): 2105 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.85-1.46 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.23-2.47 (m, 3H, Ar-CH<sub>3</sub>), 2.61-2.90 (m, 1H,

CH), 3.18-3.60 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.82-7.37 (m, 4H, ArH). GPC:  $\bar{M}_w=950$ ;  $\bar{M}_n=250$ ;  $\bar{M}_w/\bar{M}_n=3.8$ .

**Polymerization of 3.** 67% yield. IR (neat, KBr, cm<sup>-1</sup>): 2108 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.84-1.64 (m, 5H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.62-2.97 (m, 1H, CH), 3.15-3.64 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.68-7.57 (m, 9H, ArH). GPC:  $\bar{M}_w=900$ ;  $\bar{M}_n=430$ ;  $\bar{M}_w/\bar{M}_n=2.1$ .

#### Copolymerization Catalyzed by Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al

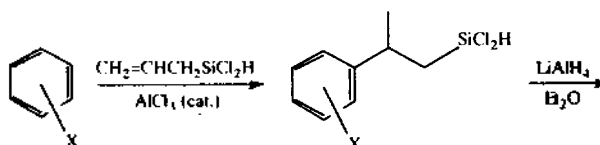
**Copolymerization of 1 and 2.** The following procedure is representative of the polymerization reactions. To a Schlenk flask charged with Cp<sub>2</sub>TiCl<sub>2</sub> (20 mg, 0.085 mmol) and Red-Al (25 μL, 0.085 mmol) was added slowly **1** (0.28 g, 1.70 mmol) and **2** (0.31 g, 1.70 mmol). The reaction immediately turned dark green, and the reaction medium became rapidly viscous with strong gas evolution. The mixture was stirred under a stream of nitrogen for 20 h and then heated at 90 °C until the mixture became rigid. The catalyst was allowed to oxidize by exposure to the air for a few second, and the solution was then passed rapidly through a silica gel column (70-230 mesh, 2 cm×20 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure afforded 0.30 g (51% yield) of off-white tacky product. The polymer was dissolved in benzene, precipitated in hexane, filtered off, and dried to give white tacky product of which the physical data were very similar to that of the starting polymer. The reactive solvents such as alcohol, acetone, and DMSO cannot be used for the precipitation. The polymer was quite soluble in THF, ether, and benzene, and became a gum in THF. IR (neat, KBr, cm<sup>-1</sup>): 2110 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.91-1.68 (m, 10H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.33 (m, 3H, CH<sub>3</sub>), 2.78-2.82 (m, 2H, CH), 3.36-3.43 (m, broad overlap of SiH and SiH<sub>2</sub>), 7.00-7.27 (m, 8H, ArH). GPC:  $\bar{M}_w=810$ ;  $\bar{M}_n=410$ ;  $\bar{M}_w/\bar{M}_n=2.0$ .

**Copolymerization of 1 and 3.** 71% yield. IR (neat, KBr, cm<sup>-1</sup>): 2120 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.97-1.52 (m, 10H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.75-2.82 (m, 2H, CH), 3.30-3.47 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.85-7.32 (m, 13H, ArH). GPC:  $\bar{M}_w=680$ ;  $\bar{M}_n=410$ ;  $\bar{M}_w/\bar{M}_n=1.7$ .

**Copolymerization of 2 and 3.** 86% yield. IR (neat, KBr, cm<sup>-1</sup>): 2110 s (νSiH). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 1.60-1.89 (m, 10H, SiCH<sub>2</sub>, CH<sub>3</sub>), 2.32 (m, 3H, Ar-CH<sub>3</sub>), 2.73-2.76 (m, 2H, CH), 3.28-3.50 (m, broad overlap of SiH and SiH<sub>2</sub>), 6.92-7.27 (m, 13H, ArH). GPC:  $\bar{M}_w=900$ ;  $\bar{M}_n=540$ ;  $\bar{M}_w/\bar{M}_n=1.7$ .

## Results

**Monomer Synthesis.** Substituted 3-phenyl-1,1-dichloro-1-silabutanes were prepared by AlCl<sub>3</sub>-catalyzed Friedel-Crafts reaction of allyldichlorosilane with substituted aryl compounds.<sup>14</sup> The monomer silanes, substituted 3-phenyl-1-silabutanes, were prepared in 68-98% yield by reaction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with LiAlH<sub>4</sub> (Eq. 1).



**Table 1.** Spectral Characteristics of Monomer Silanes

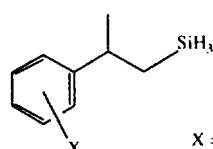
Monomer	Yield (%)	<sup>1</sup> H NMR <sup>a</sup> (Si-H, ppm)	IR <sub>Si-H</sub> (cm <sup>-1</sup> )
1	68	3.41, 3.46	2190
2	98	3.40, 3.41, 3.44	2150
3	85	3.50, 3.52	2147

<sup>a</sup>All measurements were carried out in CDCl<sub>3</sub>.

**Table 2.** Homopolymerization of Monomer Silanes with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al<sup>a</sup>

Monomer	Yield (%)	mol wt <sup>b</sup>		
		$\bar{M}_n$	$\bar{M}_w$	PDI <sup>c</sup>
1	99	1050	500	2.1
2	91	1090	560	1.9
3	79	890	490	1.8

<sup>a</sup>[Ti]/[Si]=0.10; 24 h at r.t./heating at 90 °C. <sup>b</sup>Measured with GPC vs polystyrene (in toluene). <sup>c</sup>Polydispersity index.

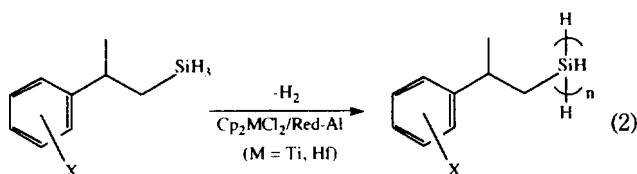


X = Cl (1), CH<sub>3</sub> (2), OPh (3)

(1)

The monomer silanes such as 3-chlorophenyl-1-silabutane (1), 3-tolyl-1-silabutane (2), and 3-phenoxyphenyl-1-silabutane (3) were purified by fractional distillation. The physical data of the monomer silanes are summarized in Table 1.

**Homopolymerization of Monomer Silanes.** Polymerization of the monomer silanes with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al catalyst system initiated immediately, as evidenced by the immediate release of hydrogen gas, and the reaction medium became rapidly viscous (Eq. 2).



(2)

To drive the reaction toward completion, the mixture was stirred at room temperature for 24 h and then heated at 90 °C until the mixture became rigid. The polymers were isolated after workup including column chromatography as off-white tacky materials which are soluble in most organic solvents. The polymerization results are shown in Table 2.

Polymerization of the monomer silanes with Cp<sub>2</sub>HfCl<sub>2</sub>/Red-Al catalyst system commenced slowly, as noticed by the moderate release of hydrogen gas, and the reaction medium became slowly viscous. To bring the reaction toward completion, the mixture was stirred at room temperature for 30 min and then heated at 90 °C until the mixture became rigid. The polymers were obtained after workup including column chromatography as off-white tacky materials which are soluble in most organic solvents. The polymerization results are given in Table 3.

**Table 3.** Homopolymerization of Monomer Silanes with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al<sup>a</sup>

Monomer	Yield (%)	mol wt <sup>b</sup>		
		$\bar{M}_n$	$\bar{M}_w$	PDI <sup>c</sup>
1	53	1030	450	2.3
2	32	950	250	3.8
3	79	900	430	2.1

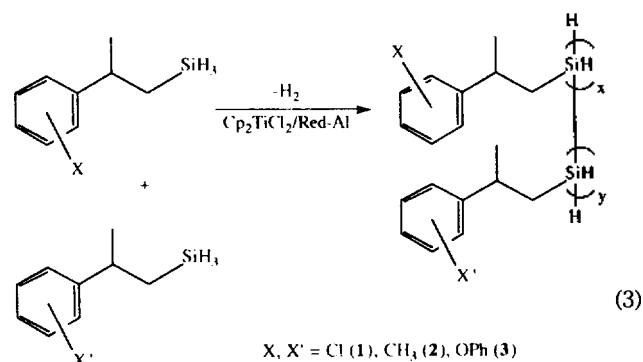
<sup>a</sup>[Hf]/[Si]=0.065; 0.5 h at r.t./heating at 90 °C. <sup>b</sup>Measured with GPC vs polystyrene (in toluene). <sup>c</sup>Polydispersity index.

**Table 4.** Copolymerization of Monomer Silanes with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al<sup>a</sup>

Monomer <sup>b</sup>	Yield (%)	mol wt <sup>c</sup>		
		$\bar{M}_n$	$\bar{M}_w$	PDI <sup>d</sup>
1 and 2	51	810	410	2.0
1 and 3	71	680	410	1.7
2 and 3	86	900	540	1.7

<sup>a</sup>[Ti]/[Si]=0.025; 24 h at r.t./heating at 90 °C. <sup>b</sup>1 : 1 mole ratio. <sup>c</sup>Measured with GPC vs polystyrene (in toluene). <sup>d</sup>Polydispersity index.

**Copolymerization of Monomer Silanes.** Copolymerization of the monomer silanes with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al catalyst system started immediately, as monitored by the immediate release of hydrogen gas, and the reaction medium became rapidly viscous (Eq. 3).



(3)

X, X' = Cl (1), CH<sub>3</sub> (2), OPh (3)

To reach completion, the mixture was stirred at room temperature for 24 h and then heated at 90 °C until the mixture became rigid. The polymers were acquired after workup including column chromatography as off-white tacky materials which are soluble in most organic solvents. The polymerization results are shown in Table 4.

## Discussion

The chemical shifts and coupling constants associated with the protons of the Si-H bonds in the <sup>1</sup>H NMR spectra of the monomer silanes are in the ranges of 3.4-3.6 ppm and 3.9-4.0 Hz, respectively. The variation of chemical shifts of the Si-H bonds with substituents is a little albeit 3 with -OPh group shifts somewhat more toward downfield. The

Si-H stretching bands in the IR spectra of the silanes are in the 2140-2190  $\text{cm}^{-1}$  range. **1** with -Cl group shifts toward somewhat higher frequency. The spectral data appear to be little affected by the substituents and were in good agreement with other alkylsilanes reported in the literature.

While the molecular weights of polysilanes produced by the dehydrogenative coupling reaction are lower than those produced *via* Wurtz coupling of dichlorosilanes, this method is more tolerant of functional groups. The Wurtz coupling method might not be proper to polymerize chlorine-substituted silanes due to possible cross-linking in toluene refluxing condition.<sup>1</sup> Although  $\text{Cp}_2\text{ZrMe}_2$ ,<sup>4</sup>  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ ,<sup>5</sup> and  $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ <sup>12b</sup> are known to be the active catalysts for the dehydrogenative polymerization of primary silanes, we wanted to employ a new catalyst system,  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  (M=Ti, Hf)<sup>9</sup> which was recently found to give predominantly linear, higher molecular weight of polysilanes than any other catalyst system in neat polymerization condition (low molecular weight of oligosilanes produced more as the amount of used solvent increased, resulting in decrease of molecular weight of polysilane), because the present monomer silanes, substituted 3-phenyl-1-silabutanes, are sterically hindered. Sterically hindered silanes were known to be very slow to polymerize and to give low molecular weights of oligosilanes.<sup>5</sup> Thus, in order to accelerate the rate of polymerization, both higher catalyst concentration (*i.e.*, 10 mol% for Ti and 6.5 mol% for Hf in the homopolymerization; 2.5 mol% for Ti in the copolymerization) than usual concentration range of 0.5-1.0 mol% and heating to 90 °C were employed in the polymerization. As anticipated from steric ground, the present hindered silanes dehydrogenatively polymerize slower than less hindered silane (*e.g.*, phenethylsilane). However, substitution on the phenyl ring results in similar rates for the methyl, phenoxy and chloro substituents due probably to presence of an ethylene spacer between Si and phenyl ring. In addition, the isomers appeared to polymerize in similar rates for the same reason. These results suggest that steric effect influences the rate of polymerization more than electronic effect in the present dehydrogenative polymerization.

As expected from the reactivity of  $d^0$  metallocene hydrides toward silanes, the monomer silanes with  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  catalyst system dehydrogenatively homopolymerize faster than with  $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$  catalyst system. The polymers reported here apparently show no sign of cross-linking due to coupling of the substituted chlorine and of the backbone Si-H bonds of polymer chains, evidenced by <sup>1</sup>H NMR, IR, and GPC. UV-vis spectrum in hexane of poly(3-phenoxyphenyl-1-silabutane) showed  $\lambda_{\text{max}} = 285$  ( $\epsilon = 2500$ ) which is in the normal range of polysilane.<sup>1</sup>

Although the molecular weights determined by GPC (*vs* polystyrene standard) are not directly comparable for various substituted polysilanes,<sup>1</sup> it appears that the polymers of substituted 3-phenyl-1-silabutanes are lower degree of polymerization than those obtained from phenylsilane, but are approximately of the similar degree of polymerization as those obtained from benzylsilane<sup>9</sup> or *n*-butylsilane.<sup>13</sup> As seen in the proton NMR and IR spectral data (see Experimental), the change of the chemical shifts and frequencies of Si-H bonds from monomer silanes to polysilanes are minor. The resonances corresponding to SiH and SiH<sub>2</sub> could not be discrimi-

nated due to their overlap. As shown in Table 2 through 4, the polymers with degree of polymerization (DP) of 5 to 8 and with polydispersity index (PDI) of 1.6-3.8 were obtained.  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  system produced somewhat higher molecular weights of polysilane than  $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$  system, opposite trend to the polymerization of phenylsilane with  $\text{Cp}_2\text{MCl}_2/\text{RLi}$  system.<sup>15</sup> In comparison, the dehydrogenative polymerization of the monomer silanes with  $\text{Cp}_2\text{MCl}_2$  (M=Ti, Hf)/*n*-BuLi catalyst system is currently underway. We are not presently certain of the percentage of cyclic and linear oligomers in the polymers. We expect some degree of diastereomeric selection in the polymerization, especially at the Si-Si coupling step *via* sigma bond metathesis,<sup>5</sup> due to the presence of 2-methyl group of the substituted 3-phenyl-1-silabutanes. To find out the percentage of cyclic and linear oligomers in the polymers and the degree of diastereomeric selection in the polymerization using chromatography and <sup>29</sup>Si NMR techniques is currently in progress and will be the subject of a future paper.

## Conclusion

This work describes the preparation and the dehydrogenative homopolymerization and copolymerization of new alkylsilanes, substituted 3-phenyl-1-silabutanes, catalyzed by  $\text{Cp}_2\text{MCl}_2$  (M=Ti, Hf)/Red-Al combined system. The polymers with degree of polymerization (DP) of 5 to 8 were obtained. The dehydrogenative polymerization of the monomer silanes with  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$  catalyst system occurred at a faster rate and produced higher molecular weights of polysilane than that with  $\text{Cp}_2\text{HfCl}_2/\text{Red-Al}$  catalyst system, opposite trend to the polymerization of phenylsilane with  $\text{Cp}_2\text{MCl}_2/\text{RLi}$  system.

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## The Adsorption Energetics and Geometry of Ketene Physisorbed on Ag(111)\*

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Ketene ( $\text{CH}_2\text{CO}$ ) adsorption on Ag(111) has been studied in ultrahigh vacuum using electron energy loss spectroscopy and temperature programmed desorption. Ketene adsorbs molecularly on Ag(111) at temperatures below 126 K. The coverage increases linearly with exposure until saturation. No multilayer formation and no shift in desorption temperature with coverage were observed, indicating a lack of attractive interaction between adsorbate molecules. The desorption activation energy is estimated to be 7.8 kcal/mol by assuming first order kinetics and a pre-exponential factor of  $10^{13} \text{ sec}^{-1}$ . The adsorption geometry of ketene on the surface is determined from the relative intensities of the vibrational energy loss peaks. The CCO axis of  $\text{CH}_2\text{CO}$  is found to be almost parallel to ( $\sim 4^\circ$  away from) the surface and the molecular plane is almost perpendicular to the surface ( $\sim 3^\circ$  tilt).

### Introduction

Ketene,  $\text{CH}_2\text{CO}$ , is a convenient source of methylene which has been postulated as an important intermediate in the Fischer-Tropsch synthesis of hydrocarbons.<sup>1</sup> To isolate and unambiguously identify methylene, an unstable species, on transition metal surfaces has been the goal for a number of experiments under ultrahigh vacuum conditions.<sup>2,3</sup> As a precursor to methylene, ketene adsorption on single crystal surfaces needs to be characterized and understood.

McBreen *et al.*<sup>4</sup> observed that ketene adsorbs molecularly on Fe(110) at 120 K, but dissociates to CO and bridge-bonded methylene at 390 K. On the other hand, Radloff *et al.*<sup>5</sup> reported that on Pt(111) at low exposures, ketene adsorbs dissociatively at 100 K. The only products found by temperature programmed desorption (TPD) were  $\text{H}_2$  and CO, with

carbon left on the surface. At high exposures, ketene and ethylene were detected in the TPD experiment in addition to  $\text{H}_2$  and CO. Similar to the Pt(111) observations, ketene adsorption at 105 K on Ru(001)<sup>6</sup> occurs both molecularly and dissociatively depending on the exposure. The desorption products here are  $\text{H}_2$ , CO, and  $\text{CO}_2$  with no hydrocarbon detected.

One of the main reasons for studying physisorbed or weakly chemisorbed molecule is that properties of the adsorbed molecules can be compared with the properties of the gas-phase molecules. Insight into the nature of the adsorbate-substrate interaction and molecular processes on surfaces can be gained from such comparisons. In particular, surface photochemical reaction of a weakly adsorbed molecule may be similar to gas-phase reactions in terms of mechanism and energetics<sup>7-9</sup> provided that the surface only weakly perturbs the molecular properties.

A TPD study would allow the determination of adsorption energy. The extent of perturbation of the adsorbate molecules by the surface can be further revealed from the change of

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