

## Dehydrocoupling of Ethylene Disilanes Catalyzed by Group 4 Metallocene Combination

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Inorganic polymers such as polycarbosilanes and polysilanes have been employed for many special applications.<sup>1</sup> Polycarbosilanes have been used as SiC ceramic precursor. Polysilanes possess peculiar optoelectronic properties due to  $\sigma$ -conjugation along the silicon backbone and have received great attention as silicon-containing ceramic precursors,<sup>2a</sup> luminescent materials,<sup>2b</sup> deep-UV positive photoresists,<sup>2c</sup> electroconductors,<sup>2d</sup> and photoinitiators.<sup>2e-f</sup> The conventional synthetic method to prepare high-molecular-weight polysilanes is the Wurtz coupling reaction of dichlorosilanes using an alkali metal dispersion in either toluene-refluxing temperature<sup>3</sup> or supersonic activation.<sup>4</sup> However, the heterogeneous reductive dehalocoupling method has some limitations such as intolerance of some functional groups, lack of reproducibility, and difficulties in controlling stereochemistry and molecular weight.<sup>5</sup> Recently, the group 4 metallocene-catalyzed dehydrocoupling of hydrosilanes to polysilanes was discovered.<sup>6</sup> Considerable efforts have been made to increase the molecular weight of the polysilanes in the homogeneous catalytic dehydrocoupling of hydrosilanes.<sup>7-10</sup>

We reported the dehydropolymerization of various hydrosilanes catalyzed by group 4 metallocene complexes generated *in situ* from Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al combination.<sup>11</sup> Hydrosilation has been used to increase the molecular weight of polysilanes containing both Si-H and olefin moieties.<sup>12</sup> Corriu *et al.* recently accounted the tunable dehydropolymerization of an ethylene disilane, 1,4-disilapentane to highly cross-linked insoluble polysilane as a silicon carbide precursor.<sup>13</sup> We preliminarily noted the hydrogenation/dehydrocoupling of ethylene disilanes catalyzed by the Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al combination.<sup>14a</sup> Here we report the hydrogenation/hydrosilation/dehydrocoupling of 2,5-disilaoct-7-ene (**1**) and the dehydrocoupling of 2,5-disilahexane (**2**), catalyzed by group 4 metallocene complexes generated *in situ* from Cp<sub>2</sub>MCl<sub>2</sub>/Hydride [Cp' =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>(Cp),  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>(Cp<sup>\*</sup>); M = Ti, Zr, Hf; Hydride = Red-Al, N-Selectride] combination.

### Experimental Section

**General Considerations.** 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 prior to use.

Infrared spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using CDCl<sub>3</sub>/CHCl<sub>3</sub> as a reference at 7.24 ppm downfield from TMS. 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 5890 II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm i.d. × 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>, 10<sup>5</sup> 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. Cp<sub>2</sub>TiCl<sub>2</sub>, Cp<sub>2</sub>ZrCl<sub>2</sub>, Cp<sub>2</sub>HfCl<sub>2</sub>, Red-Al (3.4 M in toluene), and N-Selectride (1.0 M in THF) were purchased from Aldrich Chemical Co. and were used without further purification. Ethylene disilanes (**1** and **2**),<sup>14</sup> CpCp<sup>\*</sup>ZrCl<sub>2</sub><sup>15</sup> and Cp<sup>\*</sup><sub>2</sub>ZrCl<sub>2</sub><sup>16</sup> were prepared according to the literature procedure.

**Dehydrocoupling of **1** Catalyzed by Cp<sub>2</sub>TiCl<sub>2</sub>/Hydride (Hydride=Red-Al, N-Selectride).** As a typical experiment of the catalytic dehydrocoupling of **1** with Cp<sub>2</sub>TiCl<sub>2</sub>/Hydride, to a Schlenk flask containing Cp<sub>2</sub>TiCl<sub>2</sub> (5.2 mg, 0.021 mmol) and Red-Al (5.2  $\mu$ L, 0.020 mmol) was added **1** (0.30 g, 2.1 mmol). The reaction mixture immediately turned dark green, but the dehydrocoupling reaction seemed to occur at an extremely slow rate (judged by GC analyses). The mixture was then heated at 70 °C under nitrogen atmosphere for 5 days, which turned out to be a mixture of 2,5-disilaoctane and oligomers (judged by GC analysis and <sup>1</sup>H NMR spectroscopy). The catalyst was deactivated by exposure to the air for a few minutes, and the solution was then passed rapidly through a silica gel column (70-230 mesh, 20 cm × 2 cm) with 200 mL of toluene as the eluent. The effluent was evaporated to dryness at reduced pressure to yield 0.09 g, (30% yield) of a clear oil. IR (neat, KBr, cm<sup>-1</sup>): 1608 w ( $\nu_{C=C}$ ), 2123 s ( $\nu_{Si-H}$ ). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 0.0-

2.3 (m, CH<sub>2</sub>, SiCH<sub>2</sub> and SiCH<sub>3</sub>), 3.4-4.0 (m, SiH), 5.5-6.5 (m, CH<sub>2</sub>=CH): GPC:  $M_w = 860$ ,  $M_n = 510$  (polydispersity =  $M_w/M_n = 1.7$ ).

**Dehydrocoupling of 1 Catalyzed by Cp<sub>2</sub>MCl<sub>2</sub>/Hydride (Cp' = Cp, Cp\*; M = Zr, Hf; Hydride = Red-Al, N-Selectride).** As a representative experiment of the catalytic dehydrocoupling of 1 with Cp<sub>2</sub>MCl<sub>2</sub>/Hydride, 1 (0.30 g, 2.1 mmol) was charged to a Schlenk flask containing Cp<sub>2</sub>ZrCl<sub>2</sub> (6.1 mg, 0.021 mmol) and Red-Al (5.2 μL, 0.020 mmol). The reaction mixture immediately turned dark brown, but the dehydrocoupling reaction seemed to take place at a slow rate (judged by GC analyses). The mixture was then heated at 70 °C under nitrogen atmosphere for 5 days, which resulted in the formation of a mixture of 2,5-disilaoctane and polymers (judged by GC analysis and <sup>1</sup>H NMR spectroscopy). The catalyst was allowed to oxidize by exposure to the air for a few minutes, and the solution was then subject to flash column chromatography through a silica gel column (70-230 mesh, 20 cm × 2 cm) with 200 mL of toluene as the eluent. The volatiles were removed under reduced pressure to yield 0.17 g (57% yield) of a clear oil. IR (neat, KBr, cm<sup>-1</sup>): 2125 s (ν<sub>Si-H</sub>). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.0-2.3 (m, CH<sub>2</sub>, SiCH<sub>2</sub> and SiCH<sub>3</sub>), 3.4-4.0 (m, SiH): GPC:  $M_w = 1640$ ,  $M_n = 910$  (polydispersity =  $M_w/M_n = 1.8$ ).

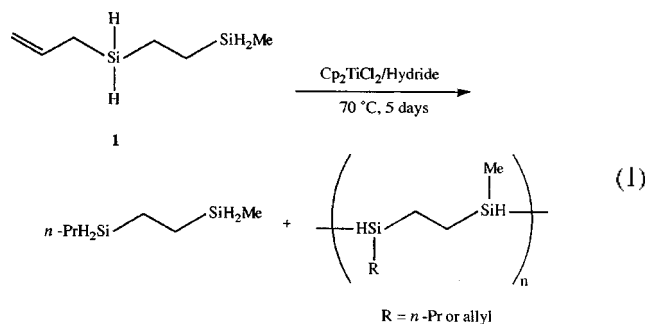
**Dehydrocoupling of 2 Catalyzed by Cp<sub>2</sub>MCl<sub>2</sub>/Hydride (Cp' = Cp, Cp\*; M = Ti, Zr, Hf; Hydride = Red-Al, N-Selectride).** The following procedure is the representative of the catalytic dehydrocoupling of 2 with Cp<sub>2</sub>MCl<sub>2</sub>/Hydride. To a Schlenk flask loaded with Cp<sub>2</sub>TiCl<sub>2</sub> (5.2 mg, 0.021 mmol) and Red-Al (5.2 μL, 0.020 mmol) was syringed slowly 2 (0.25 g, 2.1 mmol). The reaction mixture instantly turned dark green, but the reaction medium became slowly viscous with weak gas evolution. After 2 days, the catalyst was destroyed by exposure to the air for a few minutes. The solution was then passed rapidly through a silica gel column (70-230 mesh, 20 cm × 2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles *in vacuo* on rotary evaporator yielded 0.095 g (38% yield) of a clear viscous oil. IR (neat, KBr, cm<sup>-1</sup>): 2126 s (ν<sub>Si-H</sub>). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.0-0.3 (m, 6H, SiCH<sub>3</sub>), 0.5-1.0 (m, 4H, CH<sub>2</sub>), 3.5-4.0 (m, SiH): GPC:  $M_w = 2060$ ,  $M_n = 890$  ( $M_w/M_n = 2.3$ ).

## Results and Discussion

Among the catalysts, previously examined for the dehydrocoupling of primary silanes, CpCp\*Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]Me and (CpCp\*ZrH<sub>2</sub>)<sub>2</sub> are known to be the most active catalysts.<sup>7,8</sup> Instead, we decided to use novel, handy *in situ* catalyst system, Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Hf),<sup>10c,11</sup> which was recently discovered to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system. Sterically hindered silanes such as monomeric disilanes 1 and 2 are known to be very slow to polymerize and to give low-molecular-weight oligosilanes.<sup>6,7</sup>

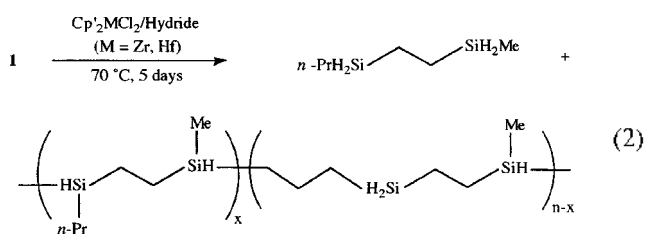
Dehydrocoupling of 1 with Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al catalyst is extremely sluggish at ambient temperature as seen in our preliminary study.<sup>14a</sup> Thus, the dehydrocoupling reaction mix-

ture of 1 with 1.0 mol % Cp<sub>2</sub>TiCl<sub>2</sub>/Hydride (Hydride = Red-Al, N-Selectride) catalyst was heated at 70 °C for 5 days (eq. 1).



The hydrogen gas release was too minimized to prevent the observation with the very naked eye because of existence of the allyl group, acting as a hydrogen sponge, of 1. The reaction mixture contained 2,5-disilaoctane (a hydrogenation product of 1) and oligomers 5 days later, judged by GC analysis and <sup>1</sup>H NMR spectroscopy. The oligomers were obtained as a clear oil in 28% (for N-Selectride) and 30% (for Red-Al) yield, respectively, after workup including flash column chromatography. The weight average molecular weight ( $M_w$ ) and number average molecular weight ( $M_n$ ) of the viscous oils were 830 and 500 (for N-Selectride) and 860 and 510 (for Red-Al), respectively. The difference of catalytic activity between Red-Al and N-Selectride in the presence of Cp<sub>2</sub>TiCl<sub>2</sub> was found to be negligible. The results are summarized in Table 1. The low isolated yields are due probably to the sterically bulky nature of 1. The <sup>1</sup>H NMR spectra of the oils showed the small vinyl resonances at 5.5-6.5 ppm and hint that the oligomer might be a cooligomer of 1 and 2,5-disilaoctane. The IR spectra of the oligomers exhibited an intense ν<sub>Si-H</sub> band at 2123 cm<sup>-1</sup> and a weak ν<sub>C=C</sub> band at 1608 cm<sup>-1</sup>. The hydrogenation seems to predominantly occur over the Si-Si coupling reaction during the catalytic reaction. Harrod and coworkers used cyclohexene and cyclooctene as hydrogen sponge to increase the rate of titanocene-catalyzed dehydrocoupling of phenylsilane, but hydrosilylation was not observed at all.<sup>6b</sup> From the facts described above, hydrosilylation in the presence of Cp<sub>2</sub>TiCl<sub>2</sub>/Hydride catalyst is unlikely to occur, although its possibility cannot be completely ruled out.

Dehydrocoupling of 1 with 1.0 mol% Cp<sub>2</sub>MCl<sub>2</sub>/Hydride [Cp' = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> (Cp), η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> (Cp\*); M = Zr, Hf; Hydride = Red-Al, N-Selectride] catalyst was carried out at 70 °C for 5 days (eq. 2).



The reaction mixture contained 2,5-disilaoctane and poly-

**Table 1.** Catalytic Dehydrocoupling of **1** with Cp<sub>2</sub>MCl<sub>2</sub>/Hydride Combination<sup>a</sup>

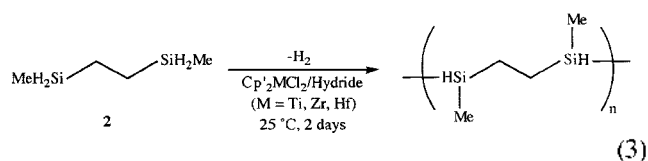
Catalyst	% Yield of dehydrocoupling	Mol. wt. <sup>b</sup>	
		<i>M<sub>w</sub></i>	<i>M<sub>n</sub></i>
Cp <sub>2</sub> TiCl <sub>2</sub> /Red-Al	30	860	510
Cp <sub>2</sub> ZrCl <sub>2</sub> /Red-Al	57	1640	910
CpCp*ZrCl <sub>2</sub> /Red-Al	68	1790	960
Cp* <sub>2</sub> ZrCl <sub>2</sub> /Red-Al	10	730	490
Cp <sub>2</sub> HfCl <sub>2</sub> /Red-Al	40	2010	1190
Cp <sub>2</sub> TiCl <sub>2</sub> /N-Selectride	28	830	500
Cp <sub>2</sub> ZrCl <sub>2</sub> /N-Selectride	51	1590	890
Cp <sub>2</sub> HfCl <sub>2</sub> /N-Selectride	36	1910	1130

<sup>a</sup>Reaction conditions: [M] = 0.01, [Red-Al] = 0.01, [N-Selectride] = 0.02, [1] = 1.0; heating at 70 °C for 5 days. <sup>b</sup>Measured with GPC (vs polystyrene) in toluene.

mers after 5 days, judged by <sup>1</sup>H NMR spectroscopy. The polymers were obtained as viscous oil in 10–68% yields, after workup including flash column chromatography. The *M<sub>w</sub>* and *M<sub>n</sub>* of the viscous oils were in the range of 730–2010 and 490–1190, respectively. The dehydrocoupling data are summarized in Table 1.

The polymerization yields were in the order of Red-Al > N-Selectride: CpCp\*Zr > Cp<sub>2</sub>Zr > Cp<sub>2</sub>Hf > Cp\*<sub>2</sub>Zr. The polymer molecular weights were in the order of Red-Al > N-Selectride: Cp<sub>2</sub>Hf > CpCp\*Zr > Cp<sub>2</sub>Zr > Cp\*<sub>2</sub>Zr. The proper replacement of Cp by Cp\* can increase solubility and can prevent the aggregation of metallocene hydrides, resulting in the increment of their catalytic activity. However, the excessive replacement of Cp by Cp\* will eventually hamper the reaction rate. The structure of the product by Cp\*<sub>2</sub>ZrCl<sub>2</sub>/Red-Al seems to be similar to those by the other zirconocene/hydride combinations, based on their <sup>1</sup>H NMR and IR spectra. The catalytic reaction with hafnocene was slower, but the resulting molecular weight was higher than with zirconocene. The <sup>1</sup>H NMR spectra of the viscous oils did not show the resonances corresponding to allyl group. The IR spectra of the polymers exhibited an intense ν<sub>Si-H</sub> band at 2125 cm<sup>-1</sup>. However, the ν<sub>C=C</sub> band around at 1600 cm<sup>-1</sup> was not appreciably observed in the IR spectra. The hydrogenation and hydrosilation appeared to occur in the presence of the zirconocene and hafnocene catalysts. The hydrosilation accompanied with Si-Si coupling reaction may contribute to the molecular weight increase of the viscous oils. Unlike the case of Cp<sub>2</sub>TiCl<sub>2</sub>/Hydride, the absence of allyl group in the <sup>1</sup>H NMR and IR spectra and the increased molecular weights of the polymers in the case of Cp<sub>2</sub>MCl<sub>2</sub>/Hydride (M = Zr, Hf) suggest that the copolymer might be formed by both hydrosilation of **1** and dehydrocoupling of 2,5-disilaoctane as seen in eq. 2. Harrod *et al.* found that cyclohexene and cyclooctene were hydrosilated upon [-SiH(Ph)-]<sub>n</sub> to form a copolysilane in the zirconocene-catalyzed dehydropolymerization of phenylsilane.<sup>6b</sup>

Dehydrocoupling of **2** with 1 mol % Cp<sub>2</sub>MCl<sub>2</sub>/Hydride (Cp' = Cp, Cp\*; M = Ti, Zr, Hf; Hydride = Red-Al, N-Selectride) catalyst was slow at room temperature, as monitored by the weak release of hydrogen gas, and the reaction medium became slowly viscous over 2 days (eq. 3).

**Table 2.** Catalytic Dehydrocoupling of **2** with Cp<sub>2</sub>MCl<sub>2</sub>/Hydride Combination<sup>a</sup>

Catalyst	% Yield of dehydrocoupling	Mol. wt. <sup>b</sup>	
		<i>M<sub>w</sub></i>	<i>M<sub>n</sub></i>
Cp <sub>2</sub> TiCl <sub>2</sub> /Red-Al	38	2060	890
Cp <sub>2</sub> ZrCl <sub>2</sub> /Red-Al	44	2140	960
CpCp*ZrCl <sub>2</sub> /Red-Al	50	2410	1160
Cp* <sub>2</sub> ZrCl <sub>2</sub> /Red-Al	7	910	510
Cp <sub>2</sub> HfCl <sub>2</sub> /Red-Al	26	2610	1174
Cp <sub>2</sub> TiCl <sub>2</sub> /N-Selectride	34	2030	880
Cp <sub>2</sub> ZrCl <sub>2</sub> /N-Selectride	40	2090	890
Cp <sub>2</sub> HfCl <sub>2</sub> /N-Selectride	23	2590	1150

<sup>a</sup>Reaction conditions: [M] = 0.01, [Red-Al] = 0.01, [N-Selectride] = 0.02, [2] = 1.0; stirring at 25 °C for 2 days. <sup>b</sup>Measured with GPC (vs polystyrene) in toluene.

Insoluble polymer to be formed by an extensive cross-linking reaction of backbone Si-H bonds was not obtained due presumably to the steric bulkiness of **2** unlike the dehydropolymerization of bis(1-sila-3-butyl)benzene, producing an extensively cross-linked polysilane.<sup>11b</sup> The polymers were obtained as a clear viscous oil in 7–50% yields after workup including flash column chromatography. The dehydrocoupling data are provided in Table 2.

The low polymerization yields are due probably to the volatility and steric bulkiness of **2**. The *M<sub>w</sub>* and *M<sub>n</sub>* of the viscous oils were in the range of 910–2610 and 510–1170, respectively. The polymerization yields were in the order of Red-Al > N-Selectride: CpCp\*Zr > Cp<sub>2</sub>Zr > Cp<sub>2</sub>Ti > Cp<sub>2</sub>Hf > Cp\*<sub>2</sub>Zr. The polymer molecular weights were in the order of Red-Al > N-Selectride: Cp<sub>2</sub>Hf > CpCp\*Zr > Cp<sub>2</sub>Zr > Cp<sub>2</sub>Ti > Cp\*<sub>2</sub>Zr. Similarly as in the dehydrocoupling of **1**, the proper replacement of Cp by Cp\* increased the catalytic activity, but the excessive replacement of Cp by Cp\* hampered the reaction rate. The catalytic reaction with hafnocene was slower, but the resulting molecular weight was higher than with titanocene and zirconocenes. The <sup>1</sup>H NMR spectra of the polysilanes apparently showed nearly one broad unresolved mountain-like resonances centered at *ca.* 3.7 ppm. The IR spectra of the polysilanes exhibited an intense ν<sub>Si-H</sub> band at 2126 cm<sup>-1</sup>. The polysilanes could be the non-cross-linked or slightly cross-linked polymers. Thus, it is apparently essential to the production of a high-molecular-weight polysilane that a disilane should have at least one SiH<sub>3</sub> moiety instead of SiH<sub>2</sub>Me moiety. The sterically less bulky silane **2** produced the higher-molecular-weight dehydrocoupling product when compared to **1**. The internal allyl group on **1** could not accelerate the reaction rate unlike the titanocene-catalyzed dehydropolymerization of phenylsilane in the presence of external cyclohexene.<sup>6b</sup>

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