

## Titanocene-Catalyzed Dehydrocoupling of Ethylene Disilanes

Hee-Gweon Woo\*, Sun-Jung Song, Mi-Kyung Han,  
Eun Jeong Cho†, and Il Nam Jung†

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

*†Organometallic Chemistry Laboratory,  
Korea Institute of Science & Technology,  
P.O. Box 131 Cheongryang,  
Seoul 130-650, Korea*

*Received September 1, 1995*

Inorganic polymers with various superior properties as compared with organic polymers have been used for many special applications.<sup>1</sup> Polysilanes with unusual optical and electronic properties due to  $\sigma$ -conjugation along the silicon backbone have particularly received extensive attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.<sup>2-4</sup> 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 recently discovered group 4 metallocene catalyzed dehydropolymerization leading to great progress in poly(organosilane) synthesis.<sup>5</sup> A major disadvantage of the metallocene-catalyzed dehydrocoupling method is the production of low-molecular-weight polysilanes.<sup>5,6</sup> Considerable efforts have been made to increase the molecular weight of the polysilanes by variation of reaction temperature, addition rate, solvent, catalyst, and monomer and by addition of either additive or cross-linking agent.<sup>7-10</sup> Higher-molecular-weight polysilanes is more useful to the application.<sup>2</sup> The dehydropolymerization of bis and tris(silyl)arenes was reported to produce highly cross-linked polysilanes.<sup>7a</sup>

We very recently reported the dehydropolymerization of aryl-substituted alkylsilanes catalyzed by group 4 metallocene complexes generated *in situ* from  $Cp_2MCl_2/Red-Al$ .<sup>11</sup> Hydrosilation has been employed 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> Here we report the dehydrocoupling of other types of ethylene disilanes such as 2,5-disila-7-octene and 2,5-disilahexane catalyzed by titanocene complex generated *in situ* from  $Cp_2TiCl_2/Red-Al$ .

### 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 before

use. 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  $CDCl_3/CHCl_3$  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  $\times$  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.  $\times$  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 Ultrastayragel 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 standard. Data analyses were carried out using a Waters Data Module 570. Number average molecular weights ( $M_n$ ) were determined by vapor pressure osmometry (VPO) in HPLC-grade chloroform using a Wescan Model 233100 osmometer.  $Cp_2TiCl_2$ , Red-Al (3.4 M in toluene), and  $LiAlH_4$  were purchased from Aldrich Chemical Co. and were used without further purification.

**Monomer Synthesis.** 2,2,5,5-Tetrachloro-2,5-disila-7-octene and 2,2,5,5-tetrachloro-2,5-disilahexane 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 an isopropyl alcohol solution of aqueous HCl and then with water.*)

**Synthesis of 2,5-Disila-7-octene (1).** To a diethyl ether suspension of lithium aluminum hydride (1.52 g, 0.04 mol) in 40 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 2,2,5,5-tetrachloro-2,5-disila-7-octene (5.64 g, 0.02 mol) in a pressure-equalizing addition funnel. After addition was completed, the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered, cooled to 0 °C, 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 130 °C/760 mmHg to yield **1** (1.13 g, 97%).<sup>14</sup> IR (neat, KBr,  $cm^{-1}$ ): 3010 m ( $\nu=CH$ ), 1610 m ( $\nu C=C$ ), 2100 s ( $\nu SiH$ ), 944 s ( $\delta SiH$ ). GC/MS, m/e (relative intensity): 144( $M^+$ ) (1), 115 (14), 103 (100), 87 (5), 75 (60), 71 (15), 59 (5), 57 (11).

**Synthesis of 2,5-Disilahexane (2).** 82% yield; bp 40-42 °C/760 mmHg. IR (neat, KBr,  $cm^{-1}$ ): 2950 m ( $\nu CH$ ), 2110 s ( $\nu SiH$ ), 940 s ( $\delta SiH$ ). <sup>1</sup>H NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 0.18 (t,  $J=4.0$  Hz, 6H,  $CH_3$ ), 0.75 (t,  $J=4.0$  Hz, 4H,  $CH_2CH_2$ ), 3.75 (m, 4H,  $SiH_2$ ). GC/MS, m/e (relative intensity): 119 ( $M^+$ ) (1), 117 (7), 103 (9), 89 (19), 88 (19), 73 (37), 72 (100), 71

(13), 59 (14).

**Hydrogenation and Dehydrocoupling of 1 Catalyzed by  $Cp_2TiCl_2/Red-Al$ .** To a Schlenk flask charged with  $Cp_2TiCl_2$  (8.0 mg, 0.021 mmol) and Red-Al (5.2  $\mu$ L, 0.020 mmol) was added slowly **1** (0.20 g, 1.39 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 remained undisturbed under nitrogen atmosphere for 30 days, which turned out to be a mixture of 2,5-disila-7-octane and oligomers (judged by GC analysis and  $^1H$  NMR spectroscopy). The catalyst was destroyed 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 $\times$ 2 cm) with 200 mL of toluene as the eluent. The effluent was evaporated to dryness to yield 0.04 g (20% yield) of a clear oil. IR (neat, KBr,  $cm^{-1}$ ): 2126 s ( $\nu$ SiH).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 0.0-2.0 (m, SiCH<sub>2</sub> and SiCH<sub>3</sub>), 3.5-4.0 (m, SiH), 5.5-6.5 (m, CH<sub>2</sub>=CH).  $M_n$ =410 (by VPO). The molecular weight distribution of the oil could not be obtained because of overlap of the low-molecular-weight oil peaks with the toluene (solvent) peak in the GPC.

**Dehydrocoupling of 2 Catalyzed by  $Cp_2TiCl_2/Red-Al$ .** To a Schlenk flask loaded with  $Cp_2TiCl_2$  (8.0 mg, 0.021 mmol) and Red-Al (5.2  $\mu$ L, 0.020 mmol) was added slowly **2** (0.22 g, 1.86 mmol). The reaction mixture instantly turned dark green, but the reaction medium became slowly viscous with gas evolution. After 24 h, the catalyst was allowed to oxidize 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 $\times$ 2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded 0.06 g (27% yield) of a clear viscous oil. IR (neat, KBr,  $cm^{-1}$ ): 2126 s ( $\nu$ SiH).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ , 300 MHz): 0.0-0.3 (m, 6H, SiCH<sub>3</sub>), 0.5-1.0 (m, 4H, CH<sub>2</sub>), 3.5-3.9 (m, SiH); GPC:  $M_w$ =2030,  $M_n$ =770.

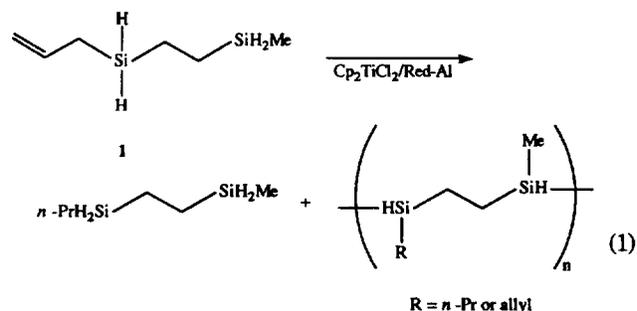
## Result and Discussion

2,2,5,5-Tetrachloro-2,5-disila-7-octene and 2,2,5,5-tetrachloro-2,5-disilahexane were prepared by  $H_2PtCl_6$ -catalyzed hydrosilation reaction of vinylmethylchlorosilane with allyldichlorosilane and methylchlorosilane, respectively.<sup>14</sup> The monomeric silanes **1** and **2** were prepared in 97 and 82% yields, respectively, by reaction of the corresponding chlorosilanes with  $LiAlH_4$ . The Si-H stretching bands in IR spectra of the silanes are in the 2100-2110  $cm^{-1}$  range.

Although  $Cp_2MMe_2$  ( $M=Ti, Zr$ ),<sup>5</sup>  $Cp_2Zr[Si(SiMe_3)_3]Me$ ,<sup>6</sup> and  $Cp_2ZrCl_2/n-BuLi$ <sup>15</sup> are known to be the active catalysts for the dehydrocoupling of primary silanes and  $CpCp^*Zr[Si(SiMe_3)_3]Me$  and  $(CpCp^*ZrH_2)_2$  were the most active catalyst previously examined,<sup>6</sup> we wanted to employ a novel catalyst system,  $Cp_2MCl_2/Red-Al$  ( $M=Ti, Zr$ ),<sup>9</sup> 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.<sup>6</sup>

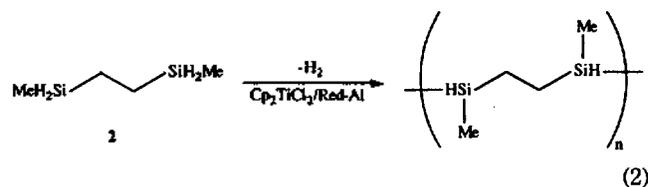
Dehydrocoupling of **1** with 1.5 mol%  $Cp_2TiCl_2/Red-Al$  catalyst system was very sluggish, as judged by GC analyses

(eq. 1).



The hydrogen gas release was too much minimized to hinder the observation with the naked eye because of the allyl group, acting as hydrogen sponge, of **1**. The reaction mixture contained 2,5-disilaoctane (a hydrogenation product) and oligomers 30 days later, judged by GC analysis and  $^1H$  NMR spectroscopy. The oligomer was obtained as a clear oil in 20% yield after workup including column chromatography. The molecular weight ( $M_n$ ), determined by vapor pressure osmometry (VPO), was 410. The low isolated yield is due probably to the sterically bulky nature of **1**. The  $^1H$  NMR spectrum of the oil suggests that the oligomer might be a co-oligomer of **1** and 2,5-disilaoctane. The IR spectrum of the polysilane exhibited an intense  $\nu$ Si-H band at 2126  $cm^{-1}$ . The hydrogenation seemed to be predominantly occurred over the Si-Si coupling reaction. The hydrosilation accompanied with Si-Si coupling reaction will greatly contribute to the molecular weight increase of the oil. Harrod and coworkers used cyclohexene and cyclooctene as hydrogen sponge to increase the rate of titanocene-catalyzed dehydrocoupling of phenylsilane, but hydrosilation was not observed at all.<sup>5b</sup> From the facts, hydrosilation is unlikely to be occurred, but its possibility cannot be completely ruled out.

Dehydrocoupling of **2** with 1 mol%  $Cp_2TiCl_2/Red-Al$  catalyst system was slow, as monitored by the weak release of hydrogen gas, and the reaction medium became slowly viscous over 24 h (eq. 2).



Insoluble polymer to be formed by an extensive cross-linking reaction of backbone Si-H bonds was not obtained due presumably to the sterically bulky nature of **2** unlike the dehydrocoupling of bis(1-sila-3-butyl)benzene, producing an extensively cross-linked polysilane.<sup>1b</sup> The polymer was obtained as a clear viscous oil in 27% yield after workup including column chromatography. The low polymerization yield is due probably to the volatility and sterically bulky nature of **2**. The weight average molecular weight  $M_w$  and number average molecular weight  $M_n$  of the viscous oil were 2030 and 770, respectively. The  $^1H$  NMR spectrum of the polysilane apparently showed nearly one broad unresolved mountain-like resonances centered at ca. 3.7 ppm. The IR spectrum of the polysilane exhibited an intense  $\nu$ Si-H band at 2126  $cm^{-1}$ . The polysilane could be a non-cross-linked

or slightly cross-linked polymer. Thus, it is apparently essential to the production of a high-molecular-weight polysilane that a disilane should have at least one  $\text{SiH}_3$  moiety. The sterically less bulky silane **2** produced the higher-molecular-weight dehydrocoupling product when compared to **1**. The allyl group on **1** could not accelerate the reaction rate unlike the titanocene-catalyzed dehydrocoupling of phenylsilane in the presence of cyclohexene.<sup>5b</sup> The dehydrocoupling study of other types of alkylene disilanes using various transition metal catalysts is in progress and will be reported in the near future.

In conclusion, this work describes the preparation and dehydrocoupling of ethylene disilanes, 2,5-disila-7-octene **1** and 2,5-disilahexane **2**, catalyzed by titanocene complex generated *in situ* from  $\text{Cp}_2\text{TiCl}_2/\text{Red-Al}$ . The silanes **1** hydrogenated and/or dehydrocoupled to produce cooligomer ( $M_n=410$ ) of **1** and 2,5-disilaoctane with a slim chance of hydrosilation. The silanes **2** dehydrocoupled to produce a non-cross-linked or slightly cross-linked polysilane with an average molecular weight  $M_w$  of 2030 and a polydispersity of 2.6.

**Acknowledgment.** This research was supported in part by the Non-directed Research Fund, Korea Research Foundation (1995) and in part by the Korea Science and Engineering Foundation (1995).

## References

1. Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.
2. Miller, R. D.; Michl, J. *Chem. Rev.* 1989, 89, 1359.
3. West, R. *J. Organomet. Chem.* 1986, 300, 327.
4. Ziegler, J. M.; Fearon, F. W. G. *Silicon-based Polymer Science*; American Chemical Society: Washington, DC, 1990.
5. (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.
6. (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, K. M.; Waymouth, R. M. *Organometallics* 1993, 12, 4700.
7. (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.
8. (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.
9. Woo, H.-G.; Dioumaev, V.; Harrod, J. F. Manuscript in preparation.
10. Tilley, T. D. *Acc. Chem. Res.* 1993, 26, 22.
11. (a) Woo, H.-G.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* 1995, 16(1), 58. (b) Woo, H.-G.; Kim, S.-Y.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Organometallics* 1995, 14, 2415.
12. Seyferth, D.; Koppetsch, G. E.; Wood, T. G.; Tracy, H. J.; Robison, J. L.; Czubarow, P.; Tasi, M.; Woo, H.-G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, 34(1), 223.
13. Corriu, R. J. P.; Enders, M.; Huille, S.; Moreau, J. J. E. *Chem. Mater.* 1994, 6, 15.
14. Jung, I. N.; Yu, B. R.; Lee, B. W.; Suk, M. Y. *Korean Patent Application* 1993, 93-26069.
15. Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* 1993, 12, 1121.

## Synthesis and Characterization of $(\text{L})\text{Zr}(\text{L})_2\text{Zr}(\text{L})$ . ( $\text{L} = \text{CpCo}\{\text{P}(\text{=O})(\text{OMe})_2\}_2\{\text{P}(\text{=O})(\text{OMe})(\text{O})\}$ )

lee Yeung Cho, Hwan Jin Yeo\*, and Jong Hwa Jeong\*

Department of Chemistry,  
Kyungpook National University,  
Taegu 702-701, Korea

Received September 6, 1995

The anionic Cobalt(III)-based oxygen tripod  $\text{LO}_E$  ( $\text{LO}_E = [\text{CpCo}\{\text{P}(\text{=O})(\text{OEt})_2\}_3]^-$ ), developed by Klaui and coworkers, can form stable complexes with various transition metals.<sup>1</sup> The synthesis and X-ray structures of  $\text{Zr}(\text{LO}_E)\text{Cl}_3$  and  $\text{U}(\text{LO}_E)_2\text{Cl}_2$  have been reported,<sup>2</sup> which are expected as the starting compounds to examine the property of the oxygen tripod ligand compared to Cp or Cp derivatives. So we have attempted to obtain  $\text{Zr}(\text{LO}_E)_2\text{Cl}_2$  ( $\text{LO}_E = [\text{CpCo}\{\text{P}(\text{=O})(\text{OMe})_2\}_3]^-$ ) from the feasible reaction of  $\text{ZrCl}_4$  with 2 equivalent  $\text{NaLO}_E$ . However,  $(\text{L})\text{Zr}(\text{L})_2\text{Zr}(\text{L})$  has been isolated surprisingly at room temperature, which is the second example of the unusual dimer in an unusual bridging fashion of tripod ligand shown in  $(\text{LO}_E)_2\text{Y}[\text{CpCo}\{\text{P}(\text{=O})(\text{OEt})_2\}_2\{\text{P}(\text{=O})(\text{OEt})(\text{O})\}]_2\text{Y}$  ( $\text{LO}_E$ ) formed at high temperature.<sup>3</sup> Herein we report the preparation and X-ray structure of the title compound.

## Experimental

All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature. Solvents were purified by standard methods and were freshly dried and distilled prior to use.  $\text{ZrCl}_4$  was purchased from Aldrich Co. and used as received.  $\text{LO}_E$  was prepared by the literature method.<sup>4</sup>

<sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained in  $\text{CDCl}_3$  and referenced to internal deuterated solvent and recalculated relative to TMS and to external 85%  $\text{H}_3\text{PO}_4$  on a Bruker AM-300 spectrometer. Chemical analyses were carried out by