

8. **2**:  $^1\text{H}$  NMR (300 MHz  $\text{CD}_3\text{OD}$ ):  $\delta$  1.26 (d,  $J=5.7$  Hz, 3H); 4.12 (bs, 2H).  
**3**:  $^1\text{H}$  NMR (300 MHz  $\text{CDCl}_3$ ):  $\delta$  1.45 (d,  $J=6.0$  Hz, 3H); 2.08 (s, 3H); 4.39 (d,  $J=7.2$  Hz, 1H); 5.28 (m, 1H); 11.04 (bs, 1H).  
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## Catalytic Dehydropolymerization of 3-Aryl-1-silabutanes by $\text{Cr}(\text{CO})_6$

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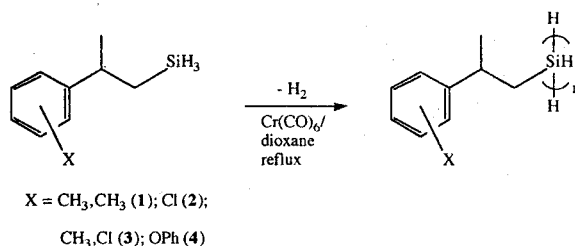
A great deal of attention has recently been focused on the synthesis of polysilanes with unusual optical and electronic properties due to  $\sigma$ -conjugation along the silicon backbone. Polysilanes have been used for many special applications such as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.<sup>1</sup> The conventional synthetic method to currently get high-molecular-weight polysilanes has been the Wurtz coupling reaction of dichlorosilanes using alkali metals, which are intolerant of some functional groups, lack of reproducibility, and have some limitations for controlling stereochemistry and molecular weight distributions.

Harrod's recent discovery of group 4 metallocene-catalyzed dehydropolymerization led to great progress in poly(organo-silane) synthesis.<sup>2</sup> A major handicap of the metallocene-catalyzed dehydrocoupling method is the production of low-molecular-weight polysilanes which affects mechanical and optical properties.<sup>2,3</sup> Intensive efforts have been made to increase the molecular weight of the polysilanes by a broad screening of various early transition metallocenes,<sup>4</sup> by studies on the reaction intermediates and mechanism,<sup>5</sup> and by employing versatile silanes.<sup>6,7</sup>

Harrod *et al.* unsuccessfully attempted the catalytic dehydropolymerization of phenylsilane by group VI metallocenes.<sup>4a</sup> Tilley *et al.* described the preparation and dehydropolymerization of chromium tricarbonyl derivative of benzylsilane by using group IV metallocene catalyst.<sup>8</sup> We reported earlier the dehydropolymerization of 3-aryl-1-silabutanes catalyzed by group IV metallocene  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ .<sup>9</sup> To our knowledge, group VI metal hexacarbonyl complexes have never been used for the dehydropolymerization of silanes. Although  $\text{Cp}_2\text{MMe}_2$  ( $\text{M}=\text{Ti}, \text{Zr}$ ),<sup>2</sup>  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ ,<sup>3a-d</sup> and  $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ <sup>10</sup> 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,<sup>3a-d</sup> we wanted to employ a novel catalyst,  $\text{Cr}(\text{CO})_6$  to compare with  $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$  ( $\text{M}=\text{Ti}, \text{Hf}$ ),<sup>9</sup> which

was recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system.<sup>11</sup> In this communication we wish to report the catalytic dehydropolymerization of 3-aryl-1-silabutanes by group VI transition metal hexacarbonyl complex  $\text{Cr}(\text{CO})_6$ .

In a typical experiment, dioxane (4 mL) was added to a Schlenk flask charged with  $\text{Cr}(\text{CO})_6$  (62 mg, 0.28 mmol) and 3-(2,5-dimethylphenyl)-1-silabutane **1** (1.0 g, 5.6 mmol). The reaction mixture was heated at dioxane-refluxing temperature for 3 days. The green viscous 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 diethyl ether.



The removal of volatiles at reduced pressure yielded 0.88 g (88% yield) of off-white tacky product.<sup>12</sup> Similarly, the dehydropolymerization of the other 3-aryl-1-silabutanes such as 3-(chlorophenyl)-1-silabutane **2**, 3-(chloro-*p*-tolyl)-1-silabutane **3**, and 3-(phenoxyphenyl)-1-silabutane **4** was also carried out to give the corresponding polysilanes as off-white tacky products.<sup>13</sup>

The results are summarized in Table 1.

Dehydropolymerization of **1-4** catalyzed by  $\text{Cr}(\text{CO})_6$  was not occurred at room temperature probably due to the low solubility of  $\text{Cr}(\text{CO})_6$  in dioxane, but the reaction medium became rapidly viscous upon being heated at dioxane-refluxing temperature. All of the resulting polysilanes were soluble in most organic solvents. Compared with dehydropolymerization of **1-4** catalyzed by group IV metallocenes, the polymerization yields and the spectroscopic data of polysilanes produced with  $\text{Cr}(\text{CO})_6$  were almost same.<sup>11-13</sup> This fact implies that the polysilanes produced by the dehydropolymerization of **1-4** with group IV metallocenes and  $\text{Cr}(\text{CO})_6$  must have the similar structures. However, the weight average molecular weights of the polysilanes produced with  $\text{Cr}(\text{CO})_6$  were much higher (by up to five times) than those produced with group IV metallocenes.

**Table 1.** GPC Characterization of Polymerization of Monomer Silanes with  $\text{Cr}(\text{CO})_6$ <sup>a</sup>

Monomer	Yield (%)	mol wt <sup>b</sup>		
		$\bar{M}_w$	$\bar{M}_n$	PDI <sup>c</sup>
<b>1</b>	88	5810	630	9.2
<b>2</b>	80	4150	1340	3.1
<b>3</b>	90	2140	1010	2.1
<b>4</b>	92	1110	280	4.0

<sup>a</sup>  $[\text{Cr}]/[\text{Si}]=0.05$ ; refluxing in dioxane for 3 days. <sup>b</sup> Measured with GPC in toluene (*vs* polystyrene). <sup>c</sup> Polydispersity index,  $\bar{M}_w/\bar{M}_n$ .

Although enough experimental data are not currently available, some comments on the catalytic dehydrocoupling mechanism of **1-4** by  $\text{Cr}(\text{CO})_6$  seem appropriate. The dehydrocoupling polymerization might possibly occur *via*: (A) oxidative addition/reductive elimination sequences,<sup>2,3f,10</sup> (B) the intermediacy of silylene complexes,<sup>2c</sup> (C) free radical process,<sup>2b</sup> and (D) four-center heterolytic M-Si/M-H transposition ( $\sigma$ -bond metathesis) process.<sup>3a-d,5</sup> For  $d^0$  group IV metallocene-catalyzed dehydropolymerization of silanes, the mechanism **D** is most widely accepted. For late transition metal complex-catalyzed dehydrocoupling of silanes, the mechanism **A** is most widely accepted. However, for the electron-rich early transition metal complex  $\text{Cr}(\text{CO})_6$ -catalyzed dehydrocoupling of silanes, all of the mechanism **A-D** might be possible. A two-electron, three-center M-H-Si interaction is observed in the photochemical reactions of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$  with tertiary silanes.<sup>14</sup> In addition, the selective photohydrosilation of trimethylsilane to 1,3-dienes catalyzed by  $\text{Cr}(\text{CO})_6$  was reported.<sup>15</sup> Berry and co-workers have reported that reaction of hexamethylsilacyclopropane with  $\text{CpMo}(\text{CO})_3\text{H}$  gave a silylene insertion product *via* radical chain mechanism.<sup>16</sup> We are uncertain which mechanism should dominate for the catalytic dehydropolymerization of silanes by  $\text{Cr}(\text{CO})_6$ . The detailed study on the dehydropolymerization mechanism is in progress and will be reported in the future.

In conclusion, this work describes the catalytic dehydropolymerization of 3-aryl-1-silabutanes **1-4** by  $\text{Cr}(\text{CO})_6$ . Compared with dehydropolymerization of **1-4** with group IV metallocenes, the polymerization yields and the spectroscopic data of that with  $\text{Cr}(\text{CO})_6$  were almost same. However, the weight average molecular weights of the polysilanes produced with  $\text{Cr}(\text{CO})_6$  were much higher (by up to five times) than those produced with group IV metallocenes. The possible mechanisms for the dehydropolymerization were discussed.

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- Poly (**1**): IR (neat, KBr,  $\text{cm}^{-1}$ ): 2105 s ( $\nu\text{SiH}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.80-1.50 (m, 5H,  $\text{SiCH}_2$ ,  $\text{CH}_3$ ), 2.10-2.40 (m, 6H, Ar- $\text{CH}_3$ ), 2.92-3.26 (m, 1H, CH), 3.26-3.72 (m, SiH), 6.77-7.40 (m, 3H, ArH); GPC:  $M_w=5810$ ,  $M_n=630$ ;  $M_w/M_n=9.2$ .
- Poly (**2**): 80% yield; IR (neat, KBr,  $\text{cm}^{-1}$ ): 2100 s ( $\nu\text{SiH}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.82-1.58 (m, 5H,  $\text{SiCH}_2$ ,  $\text{CH}_3$ ), 2.75-2.97 (m, 1H, CH), 3.29-3.55 (m, SiH), 6.93-7.26 (m, 4H, ArH); GPC:  $M_w=4150$ ,  $M_n=1340$ ;  $M_w/M_n=3.1$ . Poly (**3**): 90% yield; IR (neat, KBr,  $\text{cm}^{-1}$ ): 2108 s ( $\nu\text{SiH}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.78-1.49 (m, 5H,  $\text{SiCH}_2$ ,  $\text{CH}_3$ ), 2.09-2.49 (m, 3H, Ar- $\text{CH}_3$ ), 3.31-3.43 (m, 1H, CH), 3.43-3.62 (m, SiH), 6.78-7.38 (m, 3H, ArH); GPC:  $M_w=2140$ ,  $M_n=1010$ ;  $M_w/M_n=2.1$ . Poly (**4**): 92% yield; IR (neat, KBr,  $\text{cm}^{-1}$ ): 2140 s ( $\nu\text{SiH}$ );  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz): 0.96-1.46 (m, 5H,  $\text{SiCH}_2$ ,  $\text{CH}_3$ ), 2.77-2.94 (m, 1H, CH), 3.20-3.54 (m, SiH), 6.85-7.36 (m, 9H, ArH); GPC:  $M_w=1110$ ,  $M_n=280$ ;  $M_w/M_n=4.0$ .
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