

## Disproportionation/Dehydrocoupling of Endocrine Disruptor, Tributyltin Hydride to Polystannanes Using Cp'<sub>2</sub>TiCl<sub>2</sub>/N-Selectride (Cp' = Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*) Catalyst

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### Abstract

Tributyltin hydride (*n*-Bu<sub>3</sub>SnH), an endocrine disruptor, was slowly polymerized by the group 4 Cp'<sub>2</sub>TiCl<sub>2</sub>/N-selectride (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*) catalyst combination to give two phases of products: one is an insoluble cross-linked solid, polystannane in 3-25% yield as minor product *via* disproportionation/dehydrocoupling combination process, and the other is an oil, hexabutylstannane in 65-90% yield as major product *via* simple dehydrocoupling process. Disproportionation/dehydrocoupling process first produced a low-molecular-weight oligostannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, resulting in the formation of an insoluble polystannane. The disproportionation/dehydrocoupling of a tertiary hydrostannane mediated by early transition metallocene/inorganic hydride is quite unusual and applicable.

**Key words:** Disproportionation, Dehydrocoupling, Polystannane, Titanocene, N-Selectride, Endocrine Disruptor

### 1. Introduction

Inorganic polymers, which typically have main group Si, Ge, Sn, B, Al, N, P, O, S elements in the polymer backbone chain, as substitutes for organic polymers are widely used for industrial applications<sup>[1]</sup>. Among them, polysilanes possessing unique optoelectronic and physicochemical properties addressed to sigma-bonding electron conjugation along the silicon-silicon polymer backbone have attracted a great deal of attention<sup>[2]</sup>. The conventional Wurtz type reductive coupling reaction of organodichlorosilanes to polysilanes using an alkali metal dispersion (mainly, Na, K) in toluene-refluxing temperature has a few drawbacks such as required extremely dangerous reaction condition, low yield, low reproducibility, etc<sup>[3]</sup>. An alternative for synthesizing polysilanes without mediation of a transition metal complex has been described<sup>[4]</sup>. Harrod's recent discov-

ery of a group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes to polysilanes, provided the novel way to prepare polysilanes<sup>[5]</sup>. Many attempts have been successfully made to improve the dehydrocoupling routes in terms of yield, molecular weight, molecular weight distribution, thermal stability, etc.<sup>[6-11]</sup>.

Unlike to polysilanes, polystannane, a tin analogue of polysilane, has not been investigated until recently because of its synthetic difficulties and toxicity. The synthesis of poly(*n*-butylstannane)s by Wurtz-type reductive coupling of *n*-Bu<sub>2</sub>SnCl<sub>2</sub> in molten Na metal<sup>[12]</sup> and by hydrostannolysis of *n*-Bu<sub>2</sub>Sn(CH<sub>2</sub>CH<sub>2</sub>OEt)NMe<sub>2</sub> in the presence of DIBAL-H<sup>[13]</sup> have been reported. Recently, Tilley *et al.* reported the dehydrocoupling of secondary stannanes with the group 4 zirconocene complex catalyst, producing soluble mixtures of cyclic oligostannanes (~50%) and linear polystannanes (*M<sub>w</sub>* ~70,000)<sup>[14a,b]</sup>. Subsequently, Corey and coworker also described the similar dehydrocoupling of *n*-Bu<sub>2</sub>SnH<sub>2</sub> catalyzed by the Cp<sub>2</sub>MCl<sub>2</sub>/*n*-BuLi (M = Zr, Hf) combination<sup>[14c]</sup>.

The Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr, Hf) combination catalyst and the M(CO)<sub>6</sub> (M = Cr, Mo, W) catalyst have been discovered in our laboratory for the effective

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dehydrocoupling of hydrosilanes to polysilanes<sup>[11,15]</sup>. Trialkyltin compounds are well known endocrine disruptors or environmental hormones unlike trialkylsilane/trialkylgermane compounds<sup>[16]</sup>. Organic tin compounds have been widely used as stabilizer-catalyst-antibacterial. We already reported the disproportionation/dehydrocoupling of *n*-Bu<sub>2</sub>SnH<sub>2</sub> promoted by the Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M= Zr, Hf), producing cross-linked insoluble polystannanes and non-cross-linked soluble oligostannanes<sup>[17]</sup>. Here we report the disproportionation/dehydrocoupling of sterically bulky tertiary alkyltin hydride, *n*-Bu<sub>3</sub>SnH to polystannanes and distannane, catalyzed by the group 4 Cp'<sub>2</sub>TiCl<sub>2</sub>/N-selectride (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*) combination.

## 2. Experimental Section

### 2.1. Materials

All reactions and manipulations were carried out under prepurified/predried nitrogen or argon atmosphere using Schlenk techniques. Dry, oxygen-free solvents were used throughout to prevent the inactivation of organometallic catalyst. Glasswares were flame-dried or oven-dried prior to use. Cp'<sub>2</sub>TiCl<sub>2</sub> (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*), *n*-Bu<sub>3</sub>SnCl, and N-selectride (sodium tri-*sec*-butylborohydride; NaB[CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>]<sub>3</sub>H, 1.0 M in THF) were purchased from Aldrich Chemical Co. and were used as received. *n*-Bu<sub>3</sub>SnH [IR (neat, KBr, cm<sup>-1</sup>): 1808 s (ν<sub>Sn-H</sub>); <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.88 (t, *J*=7.3 Hz, 9H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.25 (m, 12H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.59 (m, 6H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 5.22 (m, 1H, Sn-H)] was prepared by reduction of *n*-Bu<sub>3</sub>SnCl with LiAlH<sub>4</sub> in diethyl ether, and used immediately<sup>[18]</sup>. *n*-Bu<sub>3</sub>SnH is a light-sensitive toxic compound which is an endocrine disruptor.

### 2.2. Instrumentation

Infrared spectra were acquired 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. 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. Thermogravimetric analysis (TGA) of the polymer sample was performed on a Per-

kin-Elmer 7 Series thermal analysis system under an argon flow. The polymer sample was heated from 25 to 900°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.

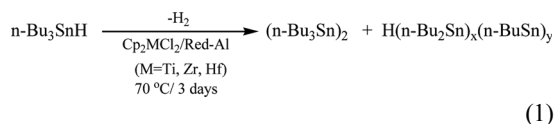
### 2.2. Redistribution/Dehydrocoupling of *n*-Bu<sub>3</sub>SnH Catalyzed by Cp'<sub>2</sub>TiCl<sub>2</sub>/N-selective (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*)

The following procedure is the representative of disproportionation/dehydrocoupling of *n*-Bu<sub>3</sub>SnH with the group 4 metallocene Cp'<sub>2</sub>TiCl<sub>2</sub>/N-selectride (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*) combination catalyst. *n*-Bu<sub>3</sub>SnH (0.50 g, 0.86 mmol) was added to a Schlenk flask containing *in situ*-generated dark purple catalytic mixture of Cp<sub>2</sub>TiCl<sub>2</sub> (6.5 mg, 0.026 mmol) and N-selectride (52 μL, 0.052 mmol) which was protected from fluorescent room light because the products might be photochemically sensitive. The violet reaction mixture was heated at 70°C to turn green instantly, and the reaction medium became slowly viscous. The catalyst was inactivated after 72 hrs by exposure to the air for a few minutes. The translucent viscous yellow-orange material was washed well with dry THF and dried at reduced pressure to give 85 mg (17% yield) of a pale yellow solid which was insoluble in most organic solvents. The combined washing solutions were pumped to dryness and the resulting oil was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm × 2 cm) with 100 mL of hexane used as the eluent. The effluent was evaporated *in vacuo* to yield 0.384 g (77% yield) of a clear pale yellow oil. For the solid: IR (KBr pellet, cm<sup>-1</sup>): 1808 w (ν<sub>Sn-H</sub>); TGA ceramic residue yield: 38% at 400°C and 33% at 900°C (grey solid), onset temperature for decomposition = 300°C. For the oil: IR (neat, KBr cm<sup>-1</sup>): ν<sub>Sn-H</sub>-absent; <sup>1</sup>H NMR (d, CDCl<sub>3</sub>, MHz): 0.85 (t, *J*=7.3 Hz, 18H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.26 (m, 24H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.50 (m, 12H, Sn-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>); GC/MS, m/e (relative intensity): 581 (0.5, M<sup>+</sup>), 425 (8, Bu<sub>3</sub>SnOSnBu<sup>+</sup>), 289 (30, Bu<sub>3</sub>Sn<sup>+</sup>), 233 (42, Bu<sub>2</sub>Sn<sup>+</sup>), 177 (100, BuSnH<sup>+</sup>), 133 (95, CH<sub>2</sub>Sn<sup>+</sup>).

## 3. Results and Discussion

Dehydrocoupling of *n*-Bu<sub>3</sub>SnH with 3 mol% of the Cp<sub>2</sub>TiCl<sub>2</sub>/Red-Al (Cp' = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp;

Me<sub>5</sub>C<sub>5</sub>, Cp\*) combination catalysts occurred very slowly at ambient temperature, and upon heating at 70°C the reaction mixture became slowly viscous over 3 days (eq 1).



The products were isolated in high yield as two phases after workup including washing and flash chromatography. Hexabutyldistannane (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>, was obtained in 65-90% yield as a clear pale yellow oil. Polystannane was acquired in 3-25% yield as a pale yellow solid which was insoluble in most organic solvents. The TGA ceramic residue yield at 900°C of the insoluble solids were *ca.* 33%. The disproportionation/dehydrocoupling reactions of *n*-Bu<sub>3</sub>SnH with the group 4 titanocene combinations are summarized in Table 1.

The IR spectra of the polymeric solids exhibit a very weak ν<sub>Sn-H</sub> band at 1808 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of (*n*-Bu<sub>3</sub>Sn)<sub>2</sub> show resonances centered at 0.85, 1.26, 1.50 ppm assigned to CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>, and Sn-CH<sub>2</sub>, respectively. The IR spectra of the hexabutyldistannane do not exhibit a ν<sub>Sn-H</sub> band at 1808 cm<sup>-1</sup>. The mass spectrum of the hexabutyldistannane shows fragmentations of 581 (0.5, M<sup>+</sup>), 425 (8, Bu<sub>3</sub>SnOSnBu<sup>+</sup>), 289 (30, Bu<sub>3</sub>Sn<sup>+</sup>), 233 (42, Bu<sub>2</sub>Sn<sup>+</sup>), 177 (100, BuSnH<sup>+</sup>), and 133 (95, CH<sub>2</sub>Sn<sup>+</sup>). The clear pale yellow oily products were clearly identified as hexabutyldistannane by comparing with <sup>1</sup>H NMR, IR, MS spectral data of authentic sample independently prepared according to the literature procedure.<sup>19</sup> However, as seen in the MS fragmentation pattern, the hexabutyldistannane was contaminated with small amount of (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>O. It is well known that (*n*-

Bu<sub>3</sub>Sn)<sub>2</sub> can be easily oxidized to (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>O in the presence of moisture<sup>19</sup>.

We initially expected that the catalytic dehydrocoupling of the sterically bulky *n*-Bu<sub>3</sub>SnH by the group 4 could occur hardly to produce single product (*n*-Bu<sub>3</sub>Sn)<sub>2</sub> because the dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >> tertiary<sup>110</sup>. As seen in Table 1, the group 4 titanocene combination catalysts in the dehydrocoupling of *n*-Bu<sub>3</sub>SnH produce the expected product, (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>, as a major product along with the disproportionation/dehydrocoupling product, cross-linked insoluble polystannane, as a minor product. Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the exchange reaction of di- and trihydrosilanes<sup>20a</sup> and the oligomerization of disilanes<sup>20b</sup>, catalyzed by inorganic hydrides (*e.g.* NaH, KH, *etc.*). Corriu *et al.* suggested a mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion<sup>20c</sup>, which is formed by addition of hydride (H<sup>-</sup>) on the silanes. We recently described an intriguing redistribution of bis- and tris(silyl)methanes with Si-C-Si linkage(s), catalyzed by Red-Al<sup>20d</sup>. N-selectride (sodium tri-*sec*-butylborohydride; NaB[CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>]<sub>3</sub>H) should work in the same way. In this case, 2 equiv N-selectride is need for the activation of 1 equiv titanocene dichloride while 1 equiv Red-Al is need for the activation of 1 equiv titanocene dichloride

We believe that a small portion of *n*-Bu<sub>3</sub>SnH may be redistributed into *n*-Bu<sub>3</sub>SnH and *n*-Bu<sub>2</sub>SnH<sub>2</sub> in the presence of Red-Al, *n*-Bu<sub>3</sub>SnH<sub>3</sub> may be immediately dehydrocoupled with *n*-Bu<sub>2</sub>SnH<sub>2</sub> may be immediately dehydrocoupled with *n*-Bu<sub>2</sub>SnH<sub>2</sub> to produce soluble copolystannane, (*n*-Bu<sub>2</sub>Sn)<sub>*y*</sub>(*n*-Bu(H)Sn)<sub>*z*</sub> of which the backbone Sn-H may subsequently undergo the cross-linking process due to the nature of very reactive Sn-H bonds. PhGeH<sub>3</sub> and PhSnH<sub>3</sub> are known to undergo the dehydrocoupling process, catalyzed by the group 4 metallocenes to give the cross-linked polymers unlike PhSiH<sub>3</sub><sup>21,22</sup>. We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using solid-state <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy and other analytical techniques. The TGA ceramic residue yield at 400°C of Tilley's soluble poly(di-*n*-butylstannanes) is 18% with onset temperature for decomposition of 255°C<sup>14</sup>, whereas the TGA ceramic residue yield at 400°C of our

**Table 1.** Characterization of catalytic disproportionation/dehydrocoupling of *n*-Bu<sub>3</sub>SnH with titanocene combination<sup>a</sup>

Catalyst	% yield	
	Sn <sub>2</sub> <sup>b</sup>	Sn <sub>x</sub> <sup>c</sup>
Cp <sub>2</sub> TiCl <sub>2</sub> /N-selectride	77	17
Cp <sub>2</sub> TiCl <sub>2</sub> / <i>n</i> -BuLi	65	25
CpCp*TiCl <sub>2</sub> /N-selectride	84	11
(MeCp) <sub>2</sub> TiCl <sub>2</sub> /N-selectride	79	16
Cp* <sub>2</sub> TiCl <sub>2</sub> /N-selectride	90	3

<sup>a</sup>[M]/[Sn]=0.03; heating at 70°C for 3 days. <sup>b</sup>Yield of THF-soluble product. <sup>c</sup>Yield of THF-insoluble product.

insoluble poly(*di-n*-butylstannane) is 38% with onset temperature for decomposition of 300°C. The TGA data of our insoluble polystannanes show that the ceramic residue yields are consistently lower than the theoretical yields (*i.e.* Sn/SnC<sub>8</sub>H<sub>18</sub>=51%), probably due to loss of some volatile tin-constituents formed under the thermolysis conditions although the polystannanes have a cross-linked network structure. The endocrine possibility of the polystannanes is under investigation<sup>[23]</sup>. Hexabutylstannane and trialkyltin hydride have been used in the organic synthesis as a radical initiator<sup>[24]</sup>.

#### 4. Conclusions

The sterically bulky *n*-Bu<sub>3</sub>SnH, an endocrine disruptor, was slowly converted by the group 4 Cp\*<sub>2</sub>TiCl<sub>2</sub>/N-selectride (Cp\* = C<sub>5</sub>H<sub>5</sub>, Cp; Me-C<sub>5</sub>H<sub>4</sub>, Me-Cp; Me<sub>5</sub>C<sub>5</sub>, Cp\*) to produce two phases of products: one is an insoluble cross-linked solid, polystannane in 3-25% yield as minor product *via* disproportionation/ dehydrocoupling combination process, and the other is an oil, hexabutylstannane in 65-90% yield as major product *via* simple dehydrocoupling process. One might naturally think that the disproportionation/dehydrocoupling process first produced a low-molecular-weight oligostannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, leading to an insoluble polystannane formation. This provides a rare example of disproportionation/dehydrocoupling of a tertiary stannane catalyzed by early transition metallocenes.

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