

Redistribution/Dehydrocoupling of Endocrine *n*-Bu₃SnH to Polystannanes Catalyzed by Group 4 Metallocene Complexes

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Abstract

Trialkyltin *n*-Bu₃SnH, an endocrine disruptor, was slowly converted by the catalytic action of group 4 Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) to produce two phases of products: one is an insoluble cross-linked solid, polystannane in 7-23% yield as minor product *via* redistribution/dehydrocoupling combination process, and the other is an oil, hexabutylstannane in 69-90% yield as major product *via* simple dehydrocoupling process. Redistribution/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. This is the first exciting example of redistribution/dehydrocoupling of a tertiary hydrostannane catalyzed by early transition metallocenes.

Key words : Redistribution, Dehydrocoupling, Polystannane, Metallocene, Catalyst, Endocrine

1. Introduction

Inorganic polymers as substitutes for organic polymers are very important for diverse industrial applications^[1]. Especially polysilanes with unique optoelectronic and chemical properties attributed to sigma-electron conjugation along the silicon polymer backbone have received a great deal of attention^[2]. The conventional Wurtz coupling reaction of organodichlorosilanes to polysilanes using an alkali metal dispersion in toluene-refluxing temperature has several disadvantages including extreme reaction condition, low yield, etc.^[3] An alternative for synthesizing polysilanes without resort to a transition metal catalyst have been reported^[4]. Harrod's recent discovery of a group 4 metallocene-catalyzed dehydropolymerization of hydrosilanes, paved the new way to synthesize polysilanes^[5]. Great efforts have been made to improve the dehydropolymerization method^[6-11]. By comparison, polystannane, a tin analogue of polysilane, has not been studied until quite recently

because of its synthetic difficulties. The synthesis of poly(di-*n*-butylstannane)s by Wurtz-type coupling of *n*-Bu₂SnCl₂ using molten Na metal^[12] and by hydrostannolysis of *n*-Bu₂Sn(CH₂CH₂OEt)NMe₂ in the presence of DIBAL-H^[13] have been reported. Recently, Tilley *et al.* described the catalytic dehydrocatenation of secondary stannanes with the group 4 zirconocene complexes, producing soluble mixtures of cyclic oligostannanes (~50%) and linear polystannanes (*M_w* ~70,000)^[14a,b]. Subsequently, Corey and coworker also described the similar dehydrocatenation of *n*-Bu₂SnH₂ catalyzed by the Cp₂MCl₂/*n*-BuLi (M = Zr, Hf) combination^[14c]. The Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination catalyst and the M(CO)₆ (M = Cr, Mo, W) catalyst have been developed in our laboratory for dehydrocatenation of hydrosilanes to polysilanes^[11,15]. Trialkyltin compounds are well known endocrine disruptors or environmental hormones unlike trialkylsilane compounds^[16]. Organic tin compounds have been used as stabilizer-catalyst-antibacterial. We reported the redistribution/dehydrocatenation of *n*-Bu₂SnH₂ promoted by the Cp₂MCl₂/Red-Al (M = Zr, Hf), producing cross-linked insoluble polystannanes and non-cross-linked soluble oligostannanes^[17]. Here we report the redistribution/dehydrocatenation of *n*-Bu₃SnH to polystannanes catalyzed by the group 4 Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) combination.

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2. Experimental

2.1. Materials

All reactions and manipulations were carried out under prepurified nitrogen or argon gas using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glasswares were flame-dried or oven-dried before use. Cp_2MCl_2 (M = Ti, Zr, Hf), $n\text{-Bu}_3\text{SnCl}$, and Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; 3.4 M in toluene) were purchased from Aldrich Chemical Co. and were used without further purification. $n\text{-Bu}_3\text{SnH}$ [IR (neat, KBr, cm^{-1}): 1808 s (nSn-H); ^1H NMR (d, CDCl_3 , 300 MHz): 0.88 (t, $J=7.3$ Hz, 9H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.25 (m, 12H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.59 (m, 6H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 5.22 (m, 1H, Sn-H)] was prepared prior to use by reduction of $n\text{-Bu}_3\text{SnCl}$ with LiAlH_4 in diethyl ether^[18]. $n\text{-Bu}_3\text{SnH}$ is a light-sensitive compound.

2.2. Instrumentation

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 $\text{CDCl}_3/\text{CHCl}_3$ 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. \times 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 Perkin-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.

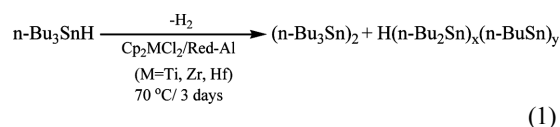
2.3. Redistribution/Dehydrocoupling of $n\text{-Bu}_3\text{SnH}$ Catalyzed by $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Zr, Hf).

The following procedure is the representative of redistribution/dehydrocoupling of $n\text{-Bu}_3\text{SnH}$ with the group 4 metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M = Ti, Zr, Hf) combination catalysis. $n\text{-Bu}_3\text{SnH}$ (0.50 g, 0.86 mmol) was added to a Schlenk flask containing *in situ-generated* dark purple catalytic mixture of Cp_2TiCl_2 (6.5 mg, 0.026 mmol) and Red-Al (6.7 μL , 0.026 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 \times 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^{-1}): 1808 w (vSn-H); 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^{-1}): vSiH-absent; ^1H NMR (d, CDCl_3 , MHz): 0.85 (t, $J=7.3$ Hz, 18H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.26 (m, 24H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.50 (m, 12H, Sn- $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$); GC/MS, m/e (relative intensity): 581 (0.5, M^+), 425 (8, $\text{Bu}_3\text{SnOSnBu}^+$), 289 (30, Bu_3Sn^+), 233 (42, Bu_2Sn^+), 177 (100, BuSnH^+), 133 (95, CH_2Sn^+).

3. Results and Discussion

Dehydrocatenation of $n\text{-Bu}_3\text{SnH}$ with 3 mol% of the $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ (M=Ti, Zr, Hf) combination catalysts took place 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 ($n\text{-Bu}_3\text{Sn}$)₂, was obtained in 77-82% yield as a clear pale yellow oil. Polystannane was acquired in 13-17% 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 redistribution/dehydrocoupling reactions of $n\text{-Bu}_3\text{SnH}$ with the group 4 metallocene combinations are given in Table 1.

The IR spectra of the polymeric solids exhibit a very

Table 1. Characterization of catalytic redistribution/dehydrocoupling of *n*-Bu₃SnH with group 4 transition metal complexes^a

Catalyst	% yield	
	Sn ₂ ^b	Sn _x ^c
Cp ₂ TiCl ₂ /Red-Al	77	17
Cp ₂ TiCl ₂ / <i>n</i> -BuLi	65	25
Cp ₂ ZrCl ₂ /Red-Al	81	14
Cp ₂ HfCl ₂ /Red-Al	82	13

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

weak $\nu_{\text{Sn-H}}$ band at 1808 cm⁻¹. The ¹H NMR spectra of (*n*-Bu₃Sn)₂ show resonances centered at 0.85, 1.26, 1.50 ppm assigned to CH₃, CH₂CH₂, and Sn-CH₂, respectively. The IR spectra of the hexabutylidistannane do not exhibit a $\nu_{\text{Sn-H}}$ band at 1808 cm⁻¹. The mass spectrum of the hexabutylidistannane shows fragmentations of 581 (0.5, M⁺), 425 (8, Bu₃SnOSnBu⁺), 289 (30, Bu₃Sn⁺), 233 (42, Bu₂Sn⁺), 177 (100, BuSnH⁺), and 133 (95, CH₂Sn⁺). The clear pale yellow oily products were clearly identified as hexabutylidistannane by comparing with ¹H NMR, IR, MS spectral data of authentic sample independently prepared according to the literature procedure.¹⁹ However, as seen in the MS fragmentation pattern, the hexabutylidistannane was contaminated with small amount of (*n*-Bu₃Sn)₂O. It is well known that (*n*-Bu₃Sn)₂ can be easily oxidized to (*n*-Bu₃Sn)₂O in the presence of moisture¹⁹.

We initially expected that the catalytic dehydrocoupling of the sterically bulky *n*-Bu₃SnH by the group 4 could occur hardly to produce single product (*n*-Bu₃Sn)₂ because the dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >> tertiary¹⁰. As seen in Table 1 and Table 2, the group 4 metallocene combination catalysts in the dehydrocoupling of *n*-Bu₃SnH produce the expected product, (*n*-Bu₃Sn)₂, as a major product along with the redistribution/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^[20a] and the oligomerization of disilanes^[20b], catalyzed by inorganic hydrides (*e.g.* NaH, KH, *etc.*). Corriu *et al.* suggested a mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion^[20c],

which is formed by addition of hydride (H⁻) 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^[20d].

We believe that a small portion of *n*-Bu₃SnH may be disproportionated into *n*-BuSn₃H and *n*-Bu₂SnH₂ in the presence of Red-Al, *n*-BuSnH₃ may be immediately dehydrocoupled with *n*-Bu₂SnH₂ may be immediately dehydrocoupled with *n*-Bu₂SnH₂ to produce soluble copolystannane, (*n*-Bu₂Sn)_y(*n*-Bu(H)Sn)_z of which the backbone Sn-H may subsequently undergo the cross-linking process due to the nature of very reactive Sn-H bonds. PhGeH₃ and PhSnH₃ are known to undergo the dehydrocoupling process, catalyzed by the group 4 metallocenes to give the cross-linked polymers unlike PhSiH₃^[21,22]. We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using solid-state ¹³C and ¹¹⁹Sn 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,¹⁴ whereas the TGA ceramic residue yield at 400°C of our 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/SnC₈H₁₈=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.^[23] Hexabutylidistannane and trialkyltin hydride have been used in the organic synthesis as a radical initiator.^[24]

4. Conclusions

The sterically bulky *n*-Bu₃SnH, an endocrine disruptor, was slowly transformed by the group 4 Cp₂MCl₂/Red-Al (M = Ti, Zr, Hf) to produce two phases of products: one is an insoluble cross-linked solid, polystannane in 7-23% yield as minor product *via* redistribution/dehydrocoupling combination process, and the other is an oil, hexabutylidistannane in 69-90% yield as major product *via* simple dehydrocoupling process. One might naturally think that the redistribution/dehydrocoupling process first produced a low-molecular-weight oligos-

tannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, leading to an insoluble polysilane. This provides first exciting example of redistribution/dehydrocoupling of a tertiary stannane catalyzed by early transition metallocenes.

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