Redistribution/Dehydrocoupling of Endocrine \(n\)-Bu\(_3\)SnH to Polystannanes Catalyzed by Group 4 Metallocene Complexes

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Abstract

Trialkyltin \(n\)-Bu\(_3\)SnH, an endocrine disruptor, was slowly converted by the catalytic action of group 4 \(\text{Cp}_2\)MCl\(_2\)/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, hexabutyldistannane 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\(^3\). 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\(^3\). 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 synthesizes 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) by Wurtz-type coupling of \(n\)-Bu\(_2\)SnCl\(_2\) using molten Na metal\(^12\) and by hydrostannolysis of \(n\)-Bu\(_2\)Sn (CH\(_2\)CH\(_2\)OEt)NMe\(_2\) 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 (\(M_n\) ~70,000)\(^14\)-\(^16\). Subsequently, Corey and coworker also described the similar dehydrocatenation of \(n\)-Bu\(_2\)SnH\(_2\) catalyzed by the \(\text{Cp}_2\)MCl\(_2\)/n-BuLi (M = Zr, Hf) combination\(^14\). The \(\text{Cp}_2\)MCl\(_2\)/Red-Al (M = Ti, Zr, Hf) combination catalyst and the \(\text{M(CO)}_6\) (M = Cr, Mo, W) catalyst have been developed in our laboratory for dehydrocatenation of hydrosilanes to polysilanes\(^15\)-\(^17\). 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 \(n\)-Bu\(_2\)SnH\(_2\) promoted by the \(\text{Cp}_2\)MCl\(_2\)/Red-Al (M = Zr, Hf), producing cross-linked insoluble polystannanes and non-cross-linked soluble oligostannanes\(^17\). Here we report the redistribution/dehydrocatenation of \(n\)-Bu\(_2\)SnH to polystannanes catalyzed by the group 4 \(\text{Cp}_2\)MCl\(_2\)/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. \( \text{Cp}_2\text{MCl}_3 \) (\( M = \text{Ti, Zr, Hf} \)), \( n\)-\( \text{Bu}_3\text{SnCl} \), 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); \(^1\)H NMR (d, CDCl\(_3\)/CH\(_2\)Cl\(_2\)) 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 \( \mu \)m) 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 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. Infrared 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 CDCl\(_3\)/CH\(_2\)Cl\(_2\) 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 \( \mu \)m) 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 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 \( \text{Cp}_2\text{MCl}_3/\text{Red-Al} \) (\( M = \text{Ti, Zr, Hf} \))

The following procedure is the representative of redistribution/dehydrocoupling of \( n\)-\( \text{Bu}_3\text{SnH} \) with the group 4 metalloocene \( \text{Cp}_2\text{MCl}_3/\text{Red-Al} \) (\( M = \text{Ti, Zr, Hf} \)) combination catalysis. \( n\)-\( \text{Bu}_3\text{SnH} \) (0.50 g, 0.86 mmol) was added to a Schlenk flask containing \( \text{in situ-generated} \) dark purple catalytic mixture of \( \text{Cp}_2\text{TiCl}_3 \) (6.5 mg, 0.026 mmol) and Red-Al (6.7 \( \mu \)L, 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 eluent 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 (nSn-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\(^{-1}\)): 177 (100, BuSnH).}

3. Results and Discussion

Dehydrocatenation of \( n\)-\( \text{Bu}_3\text{SnH} \) with 3 mol% of the \( \text{Cp}_2\text{MCl}_3/\text{Red-Al} \) (\( M = \text{Ti, Zr, Hf} \)) 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).

\[
\text{n-Bu}_3\text{SnH} \xrightarrow{H_2} (\text{n-Bu}_3\text{Sn}) _2 + H(\text{n-Bu}_3\text{Sn})_2 \to H(\text{n-Bu}_3\text{Sn})_2 + (\text{n-Bu}_3\text{Sn}) _2 \to (\text{n-Bu}_3\text{Sn})_4
\]

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 metalloocene combinations are given in Table 1.

The IR spectra of the polymeric solids exhibit a very
A weak νSn-H band at 1808 cm⁻¹. The ¹H NMR spectra of (n-Bu₂Sn₃) show resonances centered at 0.85, 1.26, 1.50 ppm assigned to CH₃, CH₂CH₃, and Sn-CH₂, respectively. The IR spectra of the hexabutyldistannane do not exhibit a νSn-H band at 1808 cm⁻¹. The mass spectrum of the hexabutyldistannane shows fragmentations of 581 (0.5, M⁺), 425 (8, Bu₃SnOSnBu⁻), 289 (30, Bu₂Sn⁻), 233 (42, Bu₂Sn⁺), 177 (100, BuSnH⁺), and 133 (95, CH₂Sn⁻). The clear pale yellow oily products were clearly identified as hexabutyldistannane by comparing with ¹H NMR, IR, MS spectral data of authentic sample independently prepared according to the literature procedure. However, as seen in the MS fragmentation pattern, the hexabutyldistannane was contaminated with small amount of (n-Bu₂Sn)O. It is well known that (n-Bu₂Sn) can be easily oxidized to (n-Bu₂Sn)O in the presence of moisture.

We initially expected that the catalytic dehydrocoupling of the sterically bulky n-Bu₂SnH by the group 4 could occur hardly to produce single product (n-Bu₂Sn)₂ because the dehydrocoupling reactivity of hydrosilanes is well known to decrease drastically in the order of primary > secondary >> tertiary. As seen in Table 1 and Table 2, the group 4 metalloocene combination catalysts in the dehydrocoupling of n-Bu₂SnH produce the expected product, (n-Bu₂Sn)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 and the oligomerization of disilanes, catalyzed by inorganic hydrides (e.g. NaH, KH, etc). Corriu et al. suggested a mechanism via the intermediacy of a pentacoordinated hydrosilyl anion, 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 linkages, catalyzed by Red-Al.

We believe that a small portion of n-Bu₂SnH may be disproportionated into n-BuSnH and n-Bu₂SnH₂ in the presence of Red-Al, n-Bu₂SnH may be immediately dehydrocoupled with n-Bu₂SnH₂ may be immediately dehydrocoupled with n-Bu₂SnH₂ to produce soluble copolystannane, (n-BuSnH), which backbone Sn-H may subsequently undergo the cross-linking process. The endocrine possibility of the polystannanes is under investigation.

Table 1. Characterization of catalytic redistribution/dehydrocoupling of n-Bu₂SnH with group 4 transition metal complexes

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% yield</th>
<th>Sn₂⁺</th>
<th>Sn⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂TiCl₂/Red-Al</td>
<td>77</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Cp₂TiCl₂/n-BuLi</td>
<td>65</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Cp₂ZrCl₂/Red-Al</td>
<td>81</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Cp₂HCl₂/Red-Al</td>
<td>82</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

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

4. Conclusions

The sterically bulky n-Bu₂SnH, an endocrine disruptor, was slowly transformed by the group 4 Cp₃MCl/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, hexabutyldistannane 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 oligo-
tannane possessing partial backbone Sn-H bonds which then underwent an extensive cross-linking reaction of backbone Sn-H bonds, leading to an insoluble polys-tannane. This provides first exciting example of redistribution/dehydrocoupling of a tertiary stannane catalyzed by early transition metalloccenes.

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References


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