

Preliminary communication

# Tin-bridged *ansa*-metallocenes of zirconium: synthesis and catalytic performance in olefin polymerization

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Received 31 October 1995

## Abstract

The first tin-bridged zirconocenes  $[(CH_3)_2Sn(C_5H_4)_2]Zr\{N(CH_3)_2\}_2$  (**3**) and  $Sn\{(C_5H_4)_2Zr\{N(CH_3)_2\}_2\}_2$  (**4**) have been obtained from tetrakis(dimethylamido)zirconium (**1**) and the CH-acidic ligands  $(CH_3)_2Sn(C_5H_5)_2$  (**2a**) and  $Sn(C_5H_5)_4$  (**2b**), respectively. The *ansa*-zirconocene **3** is formed in quantitative yield, **4** in 81% yield. The bi- and trimetallic complexes **3** (ZrSn) and **4** (Zr<sub>2</sub>Sn) polymerize ethylene more efficiently than the well-known silicon-bridged analogue of **3** (Si instead of Sn).

**Keywords:** Tin-bridged zirconocenes; Olefine polymerization

## 1. Introduction

Since the discovery of *ansa*-metallocenes/MAO-systems (MAO = methylalumoxane) as highly active polymerization catalysts, intense studies have focused on (i) optimizing the catalytic performance and stereoselectivity [1], (ii) understanding the mechanistic features [2], and (iii) the development of new polymers [3]. Not only do the substituents of the indenyl ligands strongly influence the catalytic behaviour [1]; there is also an effect of the bridge ligands on the polymerization performance since they determine the rigidity of the ligand sphere and thus influence structural properties (e.g. aperture gap) [4]. A rough comparison of carbon- and silicon-linked metallocenes shows that the silanediyl-bridged derivatives (-SiR<sub>2</sub>-) are particularly active and produce polymers with highest molecular weight and/or higher stereospecificity [4]. Although these differences have been examined, only a few studies [5] are available on metallocenes with bridges containing atoms of higher homologues of carbon and silicon. We present a most efficient synthetic approach to new tin-linked

bis(cyclopentadienyl) complexes of zirconium and report on its ethylene-polymerization behaviour.

## 2. Synthesis

Because of the facile cleavage of Sn–Cp bonds, the standard transmetallation strategy proved unfavourable for the synthesis of tin-functionalized metallocenes. However, homoleptic metal amides  $M(NR_2)_4$  ( $M = Ti, Zr, Hf; R = \text{alkyl}$ ) turned out to be excellent precursors of metallocenes and halfsandwich complexes via deprotonation of C–H acidic ligands with concurrent liberation of amines [6,7]. The reactions of tetrakis(dimethylamido)zirconium,  $Zr(NMe_2)_4$  (**1**), with the tin-based ligands  $(CH_3)_2Sn(C_5H_5)_2$  (**2a**) and  $Sn(C_5H_5)_4$  (**2b**), respectively, were carried out in an argon atmosphere using Schlenk and glove-box techniques [8]. The addition of ligand **2a** to a solution of the metal amide **1** at  $-78^\circ\text{C}$  and subsequent heating to  $50^\circ\text{C}$  affords the corresponding *ansa*-zirconocene in quantitative yield. After evaporation of the volatile materials, the novel complex **3** was obtained as a moisture-sensitive yellow powder [9] (Scheme 1).

The reaction is monitored by the characteristic NMR signals [8] of the ligand **2a**. As the yellow color of the reaction mixture intensifies, the resonances at  $\delta = 5.96$  and  $-0.21$  ppm (ligand **2a**) decrease significantly. In

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Table 1  
Slurry polymerization of Ethylene with new Sn-bridged *ansa*-Metallocenes<sup>a</sup>

Metallocene	amt. Met. ( $\mu\text{mol}$ )	Productivity (kg of PE/mmol of Zr, h)	Viscosity number ( $\text{cm}^3 \text{g}^{-1}$ )
3	4.4	6.84	240
4	9.5	3.86	914
For comparison $\text{Me}_2\text{SiCp}_2\text{Zr}(\text{NMe}_2)_2$ (5) <sup>c</sup>	13.6	3.54	74

<sup>a</sup> Polymerization conditions: diesel oil (b.p. 100–120°C), 7 bars ethylene, 70°C, Zr:Al = 1:600 (methylalumoxane 10% in toluene purchased from Witco).

the complex 3 the triplets of the  $\pi$ -bonded cyclopentadienyl protons are observed at  $\delta = 5.75$  and 6.64 ppm, showing typical tin satellites ( $^3J(^{117/119}\text{Sn}^1\text{H}_\alpha) = 11.6$  Hz,  $^4J(^{117/119}\text{Sn}^1\text{H}_\beta) = 14.7$  Hz). These values are similar to the signals of the silanediyl-functionalized metallocene ( $\delta = 6.50$  and 5.77 ppm) [7]. The  $\text{Sn}(\text{CH}_3)_2$  group shows a sharp resonance at  $\delta = 0.28$  ppm surrounded by tin satellites ( $^2J(^{119}\text{Sn}^1\text{H}) = 63.5$  Hz and  $^2J(^{117}\text{Sn}^1\text{H}) = 60.4$  Hz). The simple habitus of the proton and carbon NMR spectra correspond to a symmetrical ligand sphere ( $C_{2v}$ -symmetry), as expected by the structure of its silicon congener. The chemical shift of the tin bridge amounts to  $\delta(^{119}\text{Sn}) = -79.4$  ppm, which differs by approximately 100 ppm from the free tin ligand 2a ( $\delta(^{119}\text{Sn}) = 23.0$  ppm).

The spirocyclic *ansa*-metallocene 4 is prepared from two equivalents of the metal amide 1 with tetrakis(cyclopentadienyl)tin (2b) [8]. The trimetallic Zr<sub>2</sub>Sn-complex was obtained in 81% yield after recrystallization from n-hexane. The bright yellow complex has a limited solubility in unpolar hydrocarbons. The protons of the cyclopentadienyl rings exhibit the AA'BB' coupling pattern ( $\delta = 5.92, 6.62$  ppm) in combination with the tin coupling ( $^3J(^{117/119}\text{Sn}^1\text{H}_\alpha) = 15.9$  Hz and  $^4J(^{117/119}\text{Sn}^1\text{H}_\beta) = 17.7$  Hz); no singlet indicating a non-bonded cyclopentadienyl substituent ( $\delta = 5.80$  ppm ligand 2b) is seen. The tin NMR resonance shifts from  $\delta(^{119}\text{Sn}) = -24.7$  ppm (2b) to  $\delta(^{119}\text{Sn}) = -137.9$  ppm (4), resembling tetravinyl- and tetraphenyltin [10].

### 3. Polymerization of ethylene using compounds 3,4 and $\text{Me}_2\text{SiCp}_2\text{Zr}(\text{NMe}_2)_2$ (5)

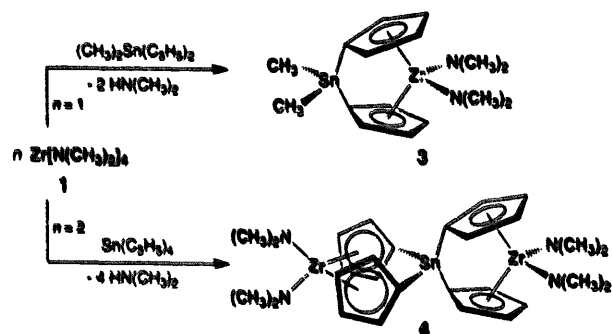
We polymerized ethylene using standard conditions (Table 1). All complexes were activated similar to the dichloro metallocenes using methylalumoxane as the cocatalyst. The dinuclear complex 4 exhibit only 50% of the activity of the mononuclear complex 3 where the molecular weight (viscosity number) produced by 4 is in the range of a high molecular weight polyethylene. Comparing the productivity of 3 and 4 it seems that only one center of 4 is active during polymerization. The activities of the Sn- and Si-bridged mononuclear complexes 3 and 5 are comparable. The rate of chain termination decreases significantly with changing the linking metal from silicon to tin, especially in the case of the binuclear complex 4. These effects will stimulate further polymerization kinetics and theoretical studies for a deeper understanding.

### 4. Conclusion

The metal–amide route yields unprecedented tin-bridged zirconocene derivatives without SnC–bond cleavage. This methodology is clearly superior over the common metal–halide reactions since the latter require (nucleophilic) anionic ligand precursors that can attack bonds between carbon and heavier main-group elements.

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Scheme 1.

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