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Preparation and Catalytic Activity of Boron-Substituted Zirconocenes

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Abstract. Borylated zirconocenes of the type $(L_2B-C_5H_4)_2ZrCl_2$ and $(L_2B-C_5H_4)(C_5H_5)ZrCl_2$ are readily available in two steps. In the polymerization of ethylene and propylene in the presence of $AlEt_3$ or methylalumoxan (MAO), these zirconocenes are more active than the unsubstituted reagent Cp_2ZrCl_2 .

Introduction

Metallocenes have emerged as an important class of catalysts in organic synthesis and in polymer chemistry [1]. For example, a variety of titanocene- and zirconocene-based catalysts are useful in enantioselective organic transformations [2] and in the polymerization of ethylene and propylene [3]. In the area of ethylene/propylene polymerization certain zirconocenes in the presence of a large excess of methylalumoxan (MAO) are highly efficient catalysts, cationic zirconium species probably being the active species. MAO-free polymerizations are also possible by employing alkylzirconocenes in the presence of reagents such as $(C_6F_5)_3B$ or $[Ph_3C]^+[(C_6F_5)_4B]^-$ which induce the formation of zirconium cations necessary for polymer initiation and propagation [4].

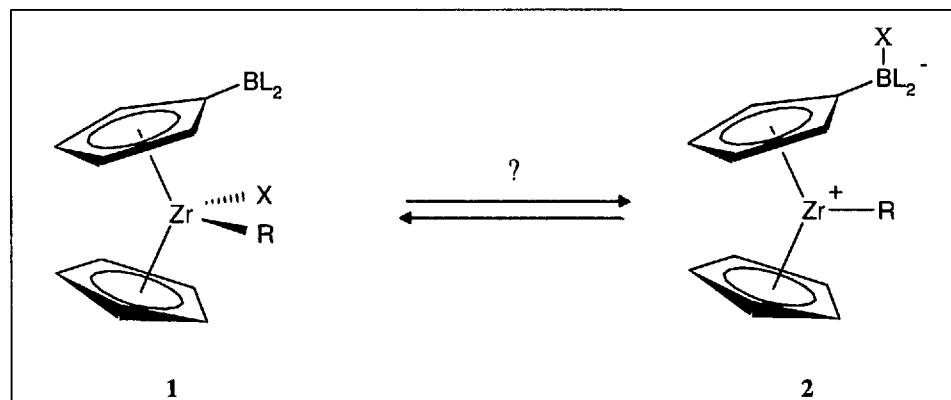
We envisioned a different strategy in this currently fast developing field. Accordingly, borylated zirconocenes of the

type **1** in a bridged or non-bridged form could be in equilibrium with the corresponding cationic form **2** under the proper conditions (*Scheme 1*). Here we present our initial efforts directed towards exploring this novel class of zirconocenes.

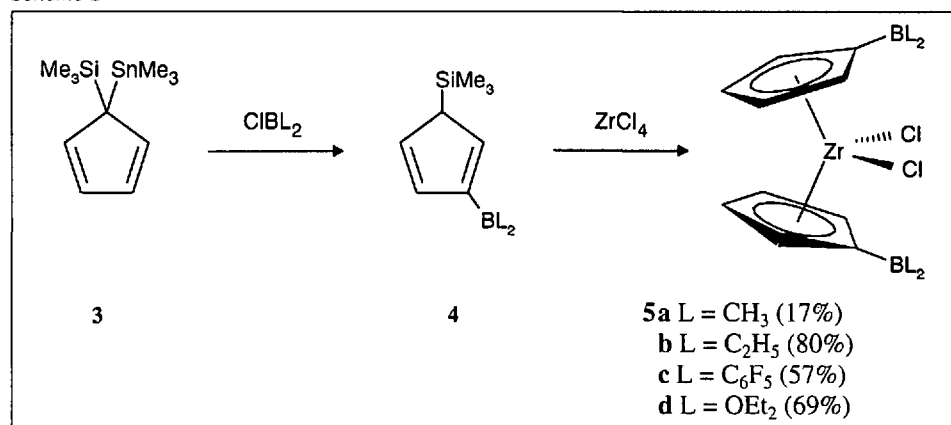
Results

Using the known Sn/B-exchange reaction of stannylated cyclopentadienes first described by *Jutzi* and *Seufert* [5], we reacted the Si/Sn-derivative **3** [6] with borylating agents $CIBL_2$. The products **4** were then treated with $ZrCl_4$ in a Si/Zr-exchange reaction [7] to form the desired borylated zirconocenes **5** in good yield (total yield over two steps is given in the parentheses) (*Scheme 2*).

Scheme 1

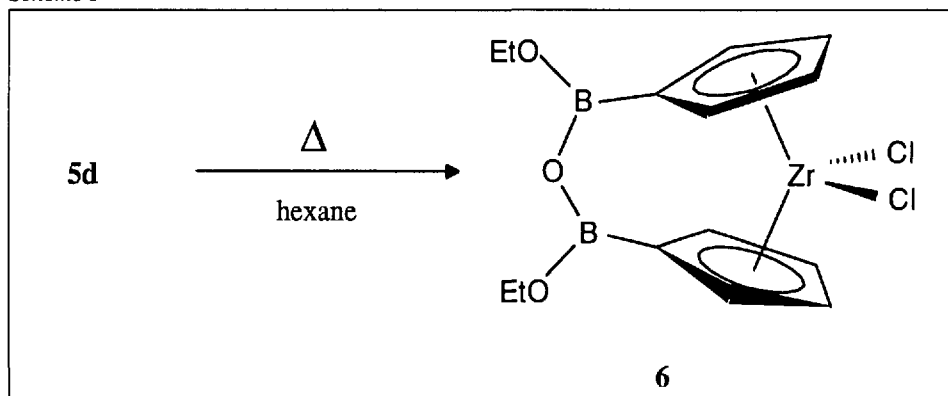


Scheme 2

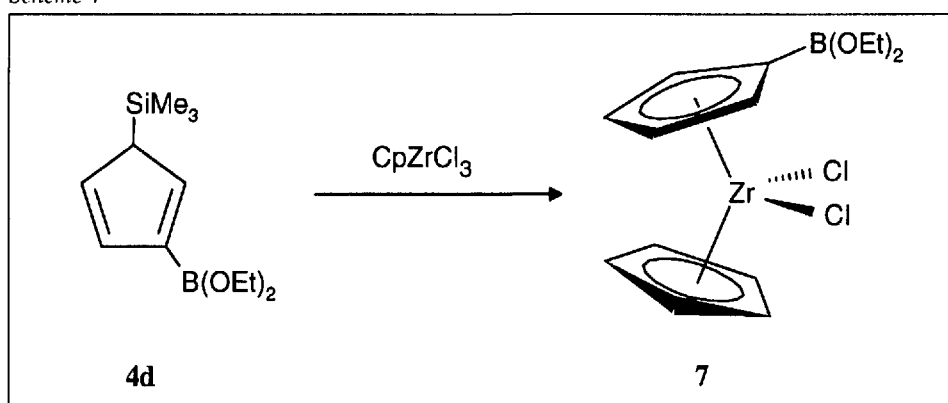


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Scheme 3



Scheme 4



Upon refluxing compound **5d** in hexane, the boron-bridged zirconocene **6** was formed (Scheme 3).

The generality of our synthetic approach was expanded further by reacting compounds **4** with CpZrCl_3 , leading to zirconocenes having only one borylated cyclopentadienyl ligand, as in compound **7** [8] (Scheme 4).

All zirconocenes were characterized by NMR spectroscopy, and in several cases suitable crystals for X-ray structural analyses were obtained. The crystal structures of compounds **5b** and **6** [9] are shown in Figs. 1 and 2, respectively.

Preliminary studies of olefin polymerization with and without MAO show that the presence of boron moieties increases catalytic activity relative to the use of unsubstituted Cp_2ZrCl_2 . For example, in a 200 ml reactor for polypropylene formation in the presence of MAO (120 ml toluene as solvent; $1 \cdot 10^{-5}$ mol catalyst; Al : Zr = 10000 : 1; pressure 2 bar; temperature $+40^\circ$), the rate of propene-uptake turned out to depend on the nature of the zirconocene: Cp_2ZrCl_2 (40 ml/min), **5a** (120 ml/min), and **6** (490 ml/min). As expected, all polypropylene samples were atactic and of low molecular weight ($M_w(\text{GPC})$ ca. 1500).

In the case of ethylene polymerization in the presence of AlEt_3 , Cp_2ZrCl_2 failed to initiate polymerization [10]. In contrast, **5c** (Al : Zr = 25 : 1) initiates rapid polymerization of ethylene, productivity being $1.6 \cdot 10^6$ g/mol [Zr] · h. This is comparable to the activities that we observed with the system $\text{Cp}_2\text{ZrCl}_2/\text{AlEt}_3/\text{B}(\text{C}_6\text{F}_5)_3$ which we prepared and tested according to Chien and coworkers [11], who employed various *ansa*-zirconocene dichlorides for propene polymerization. The polymer produced by **5c** has a $M_w(\text{GPC})$ of around 1 million and a melting point of $133\text{--}135^\circ$. Cp_2ZrCl_2 produced a polymer of significant lower molecular weight ($M_w(\text{GPC}) = 170\,000$) with a lower melting point ($127\text{--}129^\circ$).

Discussion

A simple and flexible method for the preparation of borylated zirconocenes has been developed. Initial studies of the catalytic properties of these compounds in ethylene and propylene polymerization in the presence of AlEt_3 or MAO clearly indicate increased activities relative to the use of unsubstituted Cp_2ZrCl_2 . Further studies are therefore meaningful, especially with respect to the application of our synthetic method in the preparation of

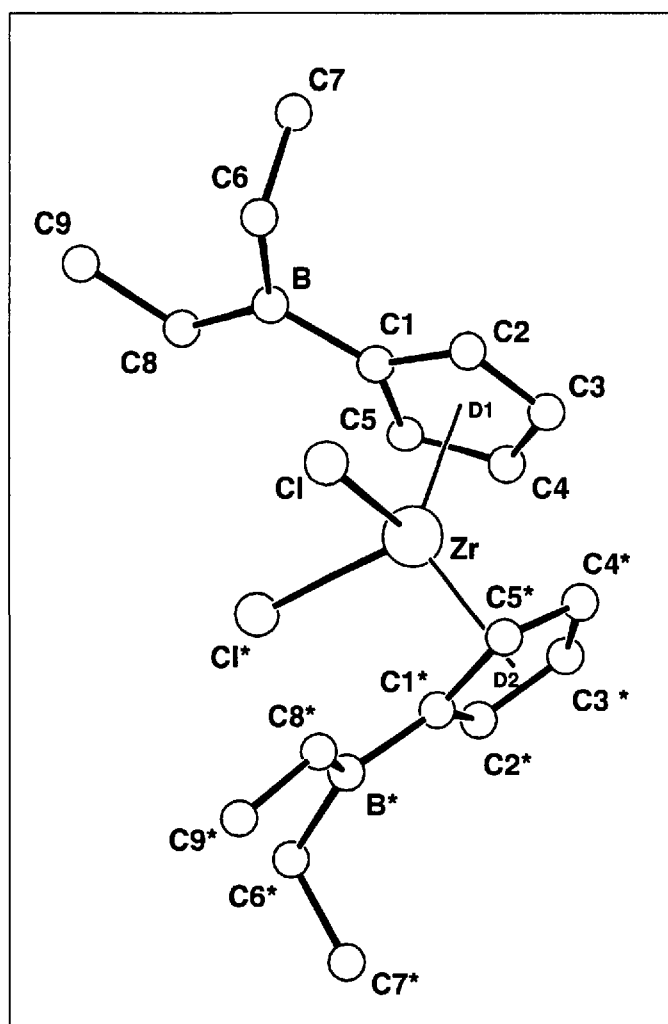


Fig. 1. Crystal structure of **5b**

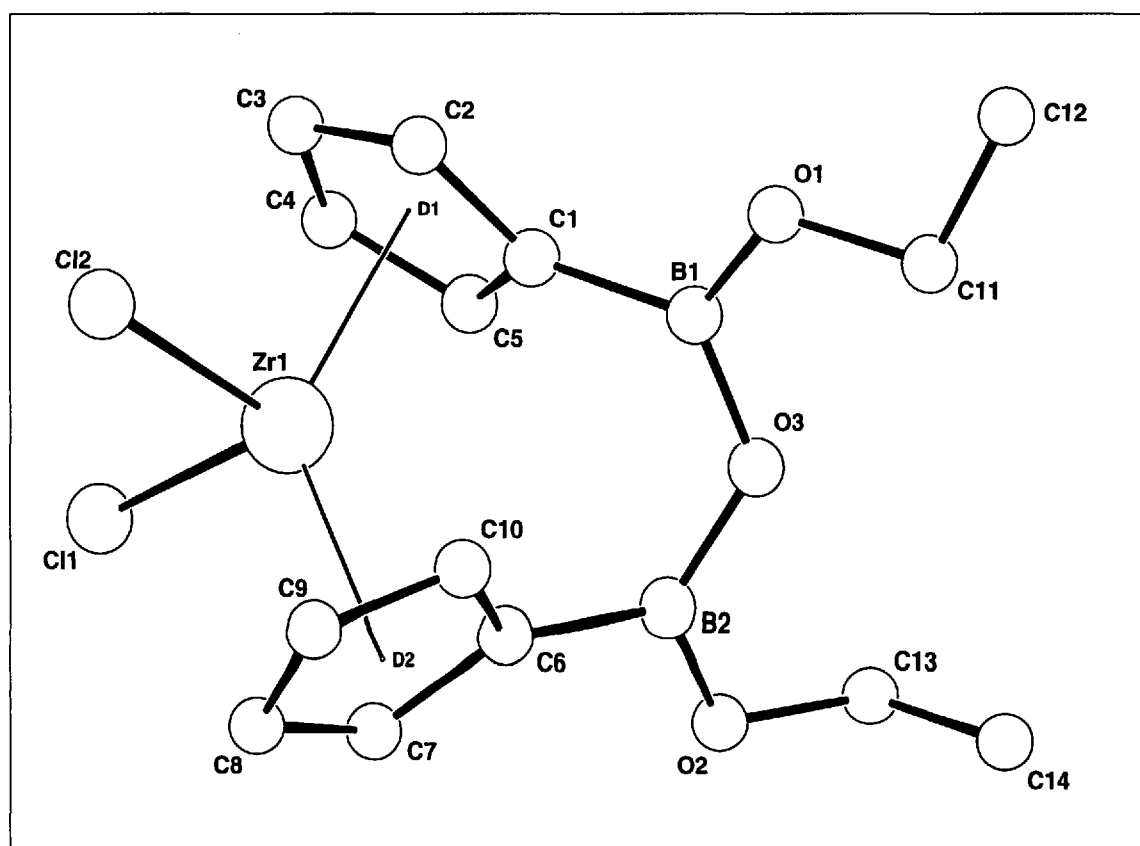


Fig. 2. Crystal structure of 6

borylated *ansa*-type zirconocenes, including those derivatives in which boron forms the bridge.

Experimental

Synthesis of Ligands. In a typical experiment, 1.89 g (18.1 mmol) chlorodiethylborane was added at r.t. with stirring to 5.44 g (18.1 mmol) of the cyclopentadiene **3**. After 4–6 h the product was isolated by fractional distillation, giving 3.34 g (16.2 mmol, 90%) of diethyl(trimethylsilylcyclopentadienyl)borane **4b**, b.p. 42°/0.4 mbar as a slightly yellow liquid.

The other ligands were prepared analogously, **4c** being recrystallized from hexane. In the case of **4a**, the synthesis was according to [12], yielding 24% of product.

Synthesis of Complexes. In a typical experiment, 1.76 g (8.52 mmol) of ligand **4b** was added dropwise at r.t. to a suspension of 0.970 g (4.16 mmol) of zirconium tetrachloride in 40 ml of toluene. After stirring of 2 h at 60° and at r.t. over night, the almost clear solution was filtered and concentrated *in vacuo*. At –30° colourless crystals were formed, which were separated, washed with cold hexane and dried. Yield: 1.59 g (3.70 mmol, 89%).

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