Short communication

Zirconocene-catalyzed dimerization of 1-hexene: Two-stage activation and structure–catalytic performance relationship

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ABSTRACT

The dimerization of 1-hexene was catalyzed by ten zirconocenes. High catalytic productivity was achieved via a two-step activation process, namely, the treatment of the zirconocene with triisobutylaluminum (TIBA) followed by methylaluminoxane (MAO). The zirconocene $[(C_5H_4SiMe_2)_2O]ZrCl_2$ (10) exhibits a higher productivity and selectivity to dimer formation than the unsubstituted $(C_5H_5)_2ZrCl_2$ (1) complex. For the *ansa*-$[Z(C_5H_4)_2]ZrCl_2$ complexes, the catalytic activity increases as the angle between the cyclopentadienyl rings decreases. The dimerization selectivity of 10 reaches 94% when the reaction is performed using Et_2AlCl as the chlorine source needed to form the catalytic species. The possible mechanism of selective α-olefin dimerization is discussed.

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1. Introduction

The ability of zirconocene dichloride Cp_2ZrCl_2 to catalyze the transformation of α-olefins ($RCH = CH_2$, Scheme 1) to α-olefin dimers, $RCH_2CH_2C(=CH_2)R$ in the presence of a minor excess of methylaluminoxane (MAO) was discovered in the 1980s [1] and was studied by Bergman in the late 1990s [2,3]. Several aspects of metallocene-catalyzed α-olefin dimerization have been reviewed by Janiak [4,5].

The influence of the structure of zirconocene catalyst on oligomerization in the presence of significant excess of MAO has been studied earlier [6–8]. Although a thorough investigation of α-olefin dimerization is important, a systematic, comparative study of the catalytic performances of various zirconocene complexes in selective α-olefin dimerization has not yet been performed. In addition to Cp_2ZrCl_2 (1) [1–3,9], only $(n\text{-}BuC_5H_4)_2ZrCl_2$ [10], $(i\text{-}PrC_5H_4)_2ZrCl_2$ [11], $(EtC_5H_4)_2ZrCl_2$, $(tert\text{-}BuC_5H_4)_2ZrCl_2$ [6,12] and $(Me_3SiC_5H_4)_2ZrCl_2$ [12] have been studied. The results indicate that monosubstituted zirconocene dichlorides are less selective than 1 in this type of dimerization reaction.

This paper presents the first attempt to study the relationship between the zirconocene dichloride structure and its catalytic properties in α-olefin dimerization using a series of bridged and unbridged zirconocene complexes (Scheme 2). The effects of the nature of the η^5 ligand (comparison of complexes 1–3), various substituents on the Cp ligand of unbridged zirconocene dichlorides (comparison of complexes 4 and 5), and the geometries of the Cp_2Zr moiety (comparison of the *ansa*-zirconocenes 6–10) on the catalytic productivity and selectivity in α-olefin dimerization were evaluated experimentally. 1-Hexene was used as the model substrate.

2. Experimental

2.1. Zirconocene dichloride preparation

Zirconocene dichlorides 2 [13], 3 [14], 4 [15], and 5 [16]; the bridged ligands; and *ansa*-zirconocene complexes 6 [17,18], 7 [19], 9 [20], and 10 [21] were synthesized according to previously reported procedures. The preparation of complex 5 was difficult due to the low thermal stability and oxidizability of the initial ligand, cyclopentadienyl benzene 11, which made its isolation and purification complicated. Therefore, an alternative method for the synthesis of 11 was developed using the Shapiro reaction. To synthesize 5 from 11, the previously published procedure [16] was markedly modified. Likewise, the preparation of zirconocene dichloride 8 included a newly developed synthesis procedure for $CpCMe_2CMe_2Cp$ 12. Specifically, 6,6-dimethylfulvene was reacted with biphenyl sodium, an effective single-electron reducing agent, at low temperature. The experimental details for the synthesis of 5, 11 and 12 are described in the Supplementary Information (SI).

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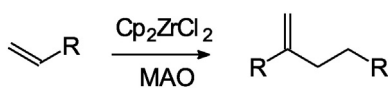
Scheme 1. α-Olefin dimerization [1–3].

2.2. Oligomerization of 1-hexene

2.2.1. Typical procedure for determining the catalytic activity in 1-hexene dimerization

1-Hexene (25 mL, 200 mmol) and a 1 M TIBA solution in hexane (2 mL, 2 mmol) were mixed in a two-necked flask prefilled with argon, which was then placed in a thermostated bath with diethylene glycol. After maintaining the external bath at 60 °C for 5 min, a solution or suspension of zirconocene dichloride (0.1 mmol) in toluene (6 mL) was added to the flask. After 20 min of stirring, a 1.5 M MAO solution (0.66 mL, 1 mmol) was added to the mixture. Samples were removed from the flask and analyzed by NMR and GC after 15 min, 30 min and 1 h.

2.2.2. Reaction mixture analysis

The integrated intensities of the vinyl proton NMR signals of 1-hexene and the reaction products were compared. GC analysis was performed using a capillary column and FID. The GC curves were calibrated using 1-hexene dimer, trimer, and tetramer samples. For experimental details, see the SI.

2.2.3. Optimization of the 2-butyl-1-octene preparation

Oligomerization was catalyzed by the activated **10** complex (0.1 mmol) in 1-hexene (25 mL, 200 mmol) at 60 °C. The optimal activation component ratio was determined experimentally to be 2 mmol of TIBA, 1 mmol of MAO, and 0.2 mmol of Et₂AlCl. The reaction time needed to achieve 100% conversion was 4 h (for ^{1}H NMR spectra of the reaction mixture see SI), and the isolated 2-butyloctene yield was 15.8 g (94%, distillation, b.p. 77–78 °C/8 Torr).

3. Results and discussion

3.1. Optimization of the catalytic procedure

Before starting the comparative study, appropriate conditions for the catalytic experiments were determined. The long induction period for α-olefin dimerization reactions catalyzed by Cp₂ZrCl₂/MAO was considered. Initially, 1-hexene dimerization was performed following

Scheme 2. Zirconocene dichlorides studied in the dimerization of 1-hexene.

the protocol described in [3] (0.05% of **1**, Al$_{MAO}$/Zr = 10, neat 1-hexene). After reaction at 20 °C for 1 h, the reaction mixture contains only the traces of the product. At 60 °C, the conversion reaches 6% in 1 h. Then, the reaction accelerates, and the 1-hexene conversion reaches 90% in 12 h (TOF of 300 h^{-1}), which is consistent with previously reported data [2,3]. Bergman showed that the induction period is reduced and the integral catalyst productivity increases up to a TOF of 1800 h^{-1} when Cp₂ZrHCl is used instead of **1** [3]. Assuming that zirconocene hydrides can be readily generated by the reaction of triisobutylaluminum (TIBA) with zirconocene dichloride [22], a two-step catalyst preparation procedure was developed. In the first step, the zirconocene dichloride was treated with 20 eq. of TIBA to generate Zr–H species (20 min at 60 °C). Although this reaction proceeds in neat 1-hexene, no 1-hexene dimerization is observed. In the second step, MAO (10 eq. relative to the zirconocene pre-catalyst) was added to the reaction mixture, and the exothermic reaction started immediately. After 1 h, the conversion, selectivity, and TOF of this benchmark experiment are 76%, 84%, and 1300 h^{-1}, respectively (run 1, Table 1).

To try and improve the dimerization selectivity, the Al$_{MAO}$/Zr ratio was varied in the experiments. The catalyst prepared with 1–2 eq. of MAO is nearly inactive; however, increasing the Al$_{MAO}$/Zr ratio substantially leads to the formation of considerable amounts of oligomers in the reaction mixture. For example, 1-hexene dimerization in the presence of 100 eq. of MAO gives the hexene dimer with 73% selectivity (run 2, Table 1).

Previously, it was reported that adding Et₂AlCl to the reaction mixture improves the selectivity of α-olefin dimerization [9]. The effectiveness of this approach when used in conjunction with a catalyst prepared by the two-step procedure was determined. The results show that the dimerization reaction is slightly more selective in the presence of 1 eq. of Et₂AlCl (87% selectivity, run 3, Table 1) than in its absence. However, increasing the amount of Et₂AlCl does not further improve the selectivity, and it results in a sharp decrease in the activity.
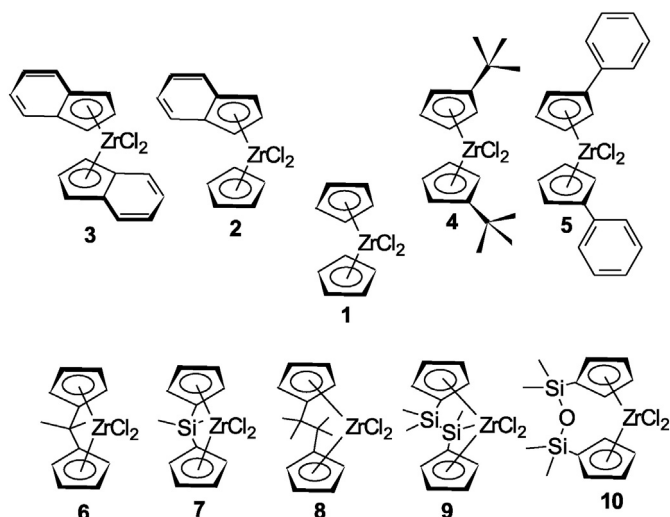
3.2. Comparison of 1-hexene oligomerization by different catalysts

The catalytic performances of zirconocene complexes **1–10**, pre-treated using the two-step activation procedure, were studied at defined conditions. The experimental results are summarized in Table 1.

Higher oligomers are predominantly formed in the presence of the moderately active cyclopentadienyl-indenyl complex **2**; the dimer content is less than 40% (run 4, Table 1). Similarly, in the case of the bis(indenyl) complex **3**, higher 1-hexene oligomers (M_w = 3900 Da) are formed (run 5, Table 1). In a previous study, considerable amounts of higher oligomers were formed in the presence of di-*tert*-butyl zirconocene dichloride **4**, even with a minor excess of MAO [12]. The results of this study are consistent with the previously published results (run 6, Table 1). Zirconocene dichloride **5** also exhibits low selectivity to the dimer, but it is significantly more active than **4** (run 7, Table 1). Presumably, this difference is due to the additional stabilization of the catalytic center in **5** by the π-donor properties of the phenyl substituents.

The target compound 2-butyl-1-octene is the major product of 1-hexene oligomerization catalyzed by the bis-cyclopentadienyl *ansa*-complexes **6–10** (runs 8–12, Table 1). The catalyst productivity, selectivity to 2-butyl-1-octene formation, and 2-hexene content in the reaction mixture depend substantially on the type and length of the bridge between the cyclopentadienyl rings. Complexes **8–10** with the longest bridges have the highest productivities, even higher than that of zirconocene dichloride **1**. However, of these metallocene catalysts, only complex **10** catalyzes the formation of 2-butyl-1-octene with a higher selectivity than **1**, making it a promising catalyst for selective dimerization.

Because the activity of **10** is higher than that of **1**, it interacts with Et₂AlCl more effectively to improve the dimerization selectivity. When

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