Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

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



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ARTICLE INFO

Article history: Received 30 January 2016 Received in revised form 12 February 2016 Accepted 13 February 2016 Available online 16 February 2016

Keywords: Zirconocenes Single-site catalysts Coordination oligomerization Hydrides

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 Et₂AlCl 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 Cp₂ZrCl₂ to catalyze the transformation of α -olefins (RCH = CH₂, Scheme 1) to α -olefin dimers, RCH₂CH₂C(=CH₂)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 Cp₂ZrCl₂ (1) [1–3,9], only (*n*-BuC₅H₄)₂ZrCl₂ [10], (*i*-PrC₅H₄)₂ZrCl₂ [11], (EtC₅H₄)₂ZrCl₂ (*i*+ert-BuC₅H₄)₂ZrCl₂ [6,12] and (Me₃SiC₅H₄)₂ZrCl₂ [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

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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 Cp₂Zr 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 CpCMe₂CMe₂Cp **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 ¹H 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 1hexene). 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 Et_2AlCl 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 Et_2AlCl (87% selectivity, run 3, Table 1) than in its absence. However, increasing the amount of Et_2AlCl 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 ($M_w = 3900 \text{ Da}$) 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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