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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 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

Table 1

Product distribution in the zirconocene-catalyzed oligomerization of 1-hexene and selected geometric parameters of zirconocene dichlorides 1-10.



Run	Cat.	Product distribution					Selected geometric parameters (X-ray)					
		Conv., %	Dimer, wt.% in products	Olig. wt.% in products	2-Hexenes wt.% in products	Dimer, wt.% in reaction mixture	α	β	γ	d(Zr-Cp)	CGA ^a	Ref.
1	1	76	84.4	12.2	3.4	64.1	129.5	53.5	97.0	2.20	92	[23]
2	1 ^b	91	72.7	22.6	4.7	66.2	-	-	-	-	-	-
3	1 ^c	62	87.0	9.8	3.2	53.9	-	-	-	-	-	-
4	2	55	38.2	57.1	4.7	21.0	No data					
5	3	10	M _w 3900 ^d		~0.3	-	128.3	59.3	94.7	2.23	-	[24]
6	4	5	40.0	55.0	5.0	2	128.7	54.2	94.3	2.22	-	[25]
7	5	80	49.0	50.0	<1	40	129.3	56.0	95.2	2.22	-	[16]
8	6	38	83.4	8.1	8.5	31.7	116.7	71.1	100.3	2.19	108	[26]
9	7	45	86.5	7.9	5.6	38.9	125.4	60.1	98.0	2.20	100	[19]
10	8	86	81.8	13.3	4.9	70.3	125.0	55.9	97.5	2.19	95	[27]
11	9	94	76.7	20.6	2.7	72.1	131.2	51.2	95.7 98.4 ^e	2.21	90	[20]
12	10	95	88.0	9.0	3.0	83.6	130.8	51.1	98.7	2.20	89	[28]
13	10 ^c	82	91.9	5.3	2.8	75.3	-	-	-	-	-	-
14	10 ^f	100	93.7	2.8	3.5	93.7	-	-	-	-	-	-

Catalyst activation procedure: 1) TIBA, Al_{TIBA}:Zr = 20:1, 20 min; 2) MAO, Al_{MAO}:Zr = 10:1.

Conditions: neat 1-hexene, 0.05 mol% Zr, 60 °C, 1 h.

^a Coordination gap aperture.

^b $Al_{MAO}:Zr = 100:1.$

^c Et₂AlCl:Zr = 1:1.

^d By GPC.

^e Two structurally independent molecules in the crystal cell.

^f $Et_2AlCl:Zr = 2:1, 4 h.$

TIBA:MAO:Et₂AlCl:10 = 20:10:2:1, the conversion and dimerization selectivity reach 100% and 94%, respectively.

3.3. Relationship between the catalyst activity and zirconocene dichloride geometry

The key geometric parameters of the studied complexes are summarized in Table 1. A comparison of the geometric parameters of the ansa-zirconocene dichlorides 6-10 shows that the bridge type has a minor influence on the CEN–Zr–CEN (α) and Cl–Zr–Cl (γ) angles. The coordination gap aperture (CGA) concept [29,30] is widely used to draw correlations between the geometry of ring-substituted metallocene complexes and their catalytic activity. We measured the CGA value for complexes 1 and 6–10, which did not contain additional substituents in cyclopentadienyl rings (see Table 1) and showed that CGA correlates with the dihedral angle β between the cyclopentadienyl rings. An increase in the bridge length leads to a decrease in the dihedral angle β between the cyclopentadienyl rings. This dihedral angle is correlated to the catalytic activity of complexes **6–10**; as β decreases, the productivity of the metallocene catalyst increases. Of the compounds studied, complex 10, which has the longest bridge, has the highest productivity and selectivity in the 1-hexene dimerization reaction. Complex 10 is conformationally flexible; another possible reason of the high selectivity of catalytic particles derived from 10 is the coordination of MAO to the bridging oxygen atom with "freezing" of the catalyst geometry.

3.4. Mechanism of alkene dimerization

Two decades ago, Negishi found [31] that zirconocene dichloride **1** catalyzed α -olefin dimerization in the presence of Me₃Al. However, in the absence of MAO, the reaction proceeded very slowly, and the selectivity was very low. Negishi proposed that the catalytic mechanism involves the sequential insertion of two RCH = CH₂ molecules into the

Zr–C bond of the alkylzirconocene species, followed by β -hydride transfer to the monomer (M1, Scheme 3). Bergman proposed a different mechanism for α -olefin dimerization catalyzed by **1** in the presence of 1 eq. of MAO [2]. Bergman's scheme accounts for the role of MAO as an alkylating agent and as an anion moiety that stabilizes the active species. It also assumes that the zirconocene hydride Cp₂ZrH catalytic species reacts successively with two alkene molecules to form an alkene dimer after β -hydride transfer to Zr. Further research proved that chlorine must be present in the reaction mixture to achieve high dimerization selectivity; Bergman demonstrated that treating the olefin with Cp₂ZrMe₂ and 1 eq. of MAO in the absence of Cl leads exclusively to the formation of higher oligomer products [3].

Based on the two-step catalyst preparation described here, it is suggested that the catalytic species is a μ -hydride Zr–Al cluster formed by the interaction between the zirconocene dichloride and TIBA [22, 32–34]. The two simplest complexes of this type, effectively stabilized by CIMAO [35], are the *zirconium–aluminum hydride-chloride complex* **A** and *dihydride complex* **B** (Scheme 3, II). Clearly, the proportion of the dihydride **B** should increase with increasing MAO concentration because MAO captures Cl.

It is assumed that the *zirconium–aluminum hydride-chloride complex* **A** catalyzes the α -olefin dimerization reaction (Scheme 3, Line III). On the first stage n-alkyl complexes **A1** (1,2-insertion) or sec-alkyl complexes **A1'** (2,1-insertion) are formed, the latter via β -hydride transfer to Zr forms 2-hexenes, inert byproducts under current reaction conditions. This process is irreversible. On the second stage isoalkyl complex **A2** is formed. Presumably, due to the presence of the μ -Cl in **A**, the Zr center in **A** is less electrophilic and more closed than the Zr center in **B**. The insertion of a third α -olefin molecule into **A2** is less probable than the β -hydride transfer to Zr, which leads to the predominant formation of the α -olefin dimer. Thus, the μ -Cl induces the release of the α -olefin dimer from **A**. The intermediate **B** is electrophilic and sterically open enough to oligomerize an α -olefin. The observed increase in the dimerization selectivity after treating the reaction mixture with Et₂AlCl



Scheme 3. α-Olefin dimerization mechanism.

can be explained by the transformation of **B** into **A**. The formation of higher oligomer products in the presence of Cp_2ZrMe_2 and 1 eq. of MAO observed by Bergman could be due to the formation of the Cl-free *hydride-methyl complex* **C**, which is analogous to complex **B** in this study (Scheme 3, I).

Thus, the α -olefin dimerization selectivity strongly depends on the proportions of the catalytic species **A** and **B**. The proposed mechanism undoubtedly requires additional experimental and theoretical validation, which is currently being performed in our laboratory.

4. Conclusions

In this study, an effective two-step procedure for generating α -olefin dimerization catalysts was developed, and the catalytic performances of various zirconocene complexes in 1-hexene dimerization were compared. It was determined that the catalytic activity of the *ansa*-zirconocene dichlorides $Z(\eta^5-C_5H_4)_2ZrCl_2$ increases as the length of Z increases. This geometric change is accompanied by a decrease in the dihedral angle between the η^5 -cyclopentadienyl rings. The synthetically accessible bis(cyclopentadienyl) complex **10**, which contains an extended–SiMe₂OSiMe₂–bridge, exhibits higher productivity and selectivity to the dimerization product than the zirconocene dichloride **1**. By adding 2 eq. of Et₂AlCl to the catalyst prepared from **10**, 100% conversion and 94% selectivity to the 2-butyl-1-octene product can be achieved.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2016.02.013.

References

- [1] L.H. Slaugh, G.W. Schoenthal, US4658078 (1987)
- [2] J. Christoffers, R.G. Bergman, J. Am. Chem. Soc. 118 (1996) 4715–4716.
- [3] J. Christoffers, R.G. Bergman, Inorg. Chim. Acta 270 (1998) 20-27.
- [4] C. Janiak, F. Blank, Macromol. Symp. 236 (2006) 14–22.
- [5] C. Janiak, Coord. Chem. Rev. 250 (2006) 66–94.
- [6] C. Janiak, K.C.H. Lange, P. Marquardt, Macromol. Rapid Commun. 16 (1995) 643–650.
- [7] C. Janiak, K.C.H. Lange, P. Marquardt, R.-P. Krüger, R. Hanselmann, Macromol. Chem. Phys. 203 (2002) 129–138.
- [8] C. Janiak, K.C.H. Lange, P. Marquardt, J. Mol. Catal. A Chem. 180 (2002) 43–58.
- [9] K. Takeuchi, S. Fujikawa, US2011251445 (2011).
- [10] Y.V. Kissin, F.C. Schwab, J. Appl. Polym. Sci. 111 (2009) 273-280.
- [11] W.J. Heilman, Y.H. Jois, A.R. De Kraker, W. Song, US2011178348 (2011).
- [12] S. Fujikawa, K. Yokota, M. Okano, M. Tsuji, US2011207977 (2011).
- [13] M.A. Schmid, H.G. Alt, W. Milius, J. Organomet, Chem. 514 (1996) 45-49.
- [14] N. Piccollrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics 9 (1990) 3098–3105.
- [15] A.I. Licht, H.G. Alt, J. Organomet. Chem. 684 (2003) 91-104.

- [16] M.P. Thornberry, N.T. Reynolds, P.A. Deck, F.R. Fronczek, A.L. Rheingold, L.M. Liable-Sands, Organometallics 23 (2004) 1333–1339.
- [17] I.E. Nifant'ev, P.V. Ivchenko, M.V. Borzov, J. Chem. Res. (1992) 162-163 (S).
- [18] I.E. Nifant'ev, P.V. Ivchenko, Organometallics 16 (1997) 713–715.
- [19] C.S. Bajgur, W.R. Tikkanen, J.L. Petersen, Inorg. Chem. 24 (1985) 2539–2546.
- [20] K.H. Thiele, Ch. Schliessburg, K. Baumeister, K. Hassler, Z. Anorg. Allg. Chem. 622 (1996) 1806–1810.
- [21] J. Graeper, G. Paolucci, R.D. Fischer, J. Organomet. Chem. 501 (1995) 211–218.
- [22] D.E. Babushkin, V.N. Panchenko, M.N. Timofeeva, V.A. Zakharov, H.H. Brintzinger,
- Macromol. Chem. Phys. 209 (2008) 1210–1219. [23] J.Y. Corey, X.-H. Zhu, L. Brammer, N.P. Rath, Acta Crystallogr. Sect. C: Cryst. Struct.
- Commun. 51 (1995) 565–567. [24] T. Repo, M. Klinga, I. Mutikainen, Y. Su, M. Leskelä, M. Polamo, Acta Chem. Scand. 50
- (1996) 1116–1120. [25] R.A. Howie, G.P. McQuillan, D.W. Thompson, G.A. Lock, J. Organomet. Chem. 303 (1986) 213–220.
- [26] T. Koch, S. Blaurock, F.B. Somoza, A. Voigt, R. Kirmse, E. Hey-Hawkins, Organometallics 19 (2000) 2556–2563.

- [27] M. Buhl, G. Hopp, W. Philipsborn, S. Beck, M.H. Prosenc, U. Rief, H.H. Brintzinger, Organometallics 15 (1996) 778–785.
- [28] S. Ciruelos, T. Cuenca, P. Gomez-Sal, A. Manzanero, P. Royo, Organometallics 14 (1995) 177–185.
- [29] C. Janiak, U. Versteeg, K.C.H. Lange, R. Weimann, E. Hahn, J. Organomet. Chem. 501 (1995) 219–234.
- [30] C. Janiak, K.C.H. Lange, U. Versteeg, D. Lentz, P.H.M. Budzelaar, Chem. Ber. 129 (1996) 1517–1529.
- [31] D.Y. Kondakov, E. Negishi, J. Am. Chem. Soc. 117 (1995) 10771-10772.
- [32] S.M. Baldwin, J.E. Bercaw, H.H. Brintzinger, J. Am. Chem. Soc. 130 (2008) 17423–17433.
- K.P. Bryliakov, E.P. Talsi, N.V. Semikolenova, V.A. Zakharov, J. Brand, C. Alonso-Moreno, M. Bochmann, J. Organomet. Chem. 692 (2007) 859–868.
- [34] L.V. Parfenova, P.V. Kovyazin, I.E. Nifant'ev, L.M. Khalilov, U.M. Dzhemilev, Organometallics 34 (2015) 3559–3570.
- [35] M.S. Kuklin, J.T. Hirvi, M. Bochmann, M. Linnolahti, Organometallics 34 (2015) 3586–3597.