

Effects of the precatalyst structure and the Mg-containing third-component on cyclo-oligomerization of ethene

Mei Wang*, Dong Dai, Hongjun Zhu, Xiang Zhang, Licheng Sun

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Road, 158-46, Dalian 116012, PR China

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Abstract

The catalytic cyclo-oligomerization of ethene by metallocene complexes Cp_2ZrCl_2 with Et_3Al as cocatalyst in the presence of Mg-containing third-components is described. Under optimal conditions ($\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}/\text{Et}_2\text{Mg} = 1:100:10$, 150°C , $P(\text{C}_2\text{H}_4) = 1.4\text{MPa}$) the reaction afforded 51% of cyclic oligomers, including *exo*-methylene cyclopentane (41%) and a small amount of methylcyclopentane (3%), 1-methyl-1-ethylcyclopentane (4%) and vinylcyclohexane (3%), along with usual open-chain alkenes. When the π -ligand was changed to η^5 -pentamethylcyclopentadienyl and indenyl (Ind) or Cp_2TiCl_2 was used in place of Cp_2ZrCl_2 , the selectivity of *exo*-methylene cyclopentane dropped dramatically to 1–8%. In contrast, the catalytic reactions by post-metallocene complexes L^2ZrCl_2 ($\text{L}^2 = \text{salen}$, salphen) under identical conditions generated open-chain alkenes exclusively. A zirconacyclopentane mechanism is proposed to explain the products formed in cyclo-oligomerization of ethene.

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1. Introduction

Zirconocene complexes have been extensively studied as catalysts for polymerization and oligomerization of ethene. They are considered as high-performance catalysts to convert ethene into open-chain polymers or oligomers. However, their catalytic properties in another pattern of C–C linkage of small alkenes, that is, cyclo-oligomerization are unknown. Only the relevant cyclization catalyzed or promoted by zirconocene complexes were reported for some special alkenes, alkynes and dienes [1–7]. To the best of our knowledge, the cases of catalytic cyclo-oligomerization of ethene are rather scarce. Keim et al. revealed the cyclo-oligomerization of ethene in the presence of carbon monoxide or isonitriles to cyclic compounds with 3-, 5- and 6- membered rings, using Ziegler–Natta catalysts consisting of either rare earth salts or ZrCl_4 combined with EtAlCl_2 [8,9]. The cyclo-dimerization of ethene to cyclobutane catalysed by a nickel complex [10] and the

co-cyclo-dimerization of ethene/1,3-butadiene to vinylcyclobutane by titanium complexes in combination with Et_3Al [11] were described.

In our previous research, it was found that under certain reaction conditions the oligomerization of ethene, catalyzed by Cp_2ZrCl_2 and alkylaluminum co-catalysts, afforded *exo*-methylene cyclopentane (CH_2CP) along with chain oligomers [12], and that the selectivity of cyclic compounds depended on the nature and the hydrolysis extent of organoaluminum co-catalysts [13], the Al/Zr ratio, the temperature and the reaction time. Since carbocyclic compounds are useful intermediates of many fine chemicals, the exploration of novel synthetic methodology for them via stoichiometric or catalytic reactions is one of the attractive topics in organic synthesis. A further research on the effects of the structure and the metal center of precatalysts on ethene cyclo-oligomerization was made recently attempting to improve the selectivity of the cyclic oligomers and to understand more about the mechanism of the novel reaction. We report herein the contrastive results of ethene oligomerization catalyzed by the metallocene and post-metallocene precatalysts and the effects of the π -ligand, the metal center of catalysts and the Mg-containing third-components on the selectivity of cyclic compounds.

* Corresponding author. Tel.: +86-411-3702185; fax: +86-411-3702185.

E-mail address: svmbueno@vip.sina.com (M. Wang).

2. Experimental

2.1. General procedures

All reactions and operations pertinent to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Toluene was distilled prior to use from sodium/benzophenone ketyl under a nitrogen atmosphere. Ethene (polymer grade) passed over molecular sieves (4 Å). Zirconium tetrachloride, Cp_2TiCl_2 , $\text{Cp}_2^*\text{ZrCl}_2$ and Et_3Al were purchased from Signia–Aldrich, Acros, Aldrich and Fluka, respectively. The precatalysts Cp_2ZrCl_2 , $\text{Ind}_2\text{ZrCl}_2$, $(\text{salen})\text{ZrCl}_2\cdot\text{THF}$ and $(\text{salphen})\text{ZrCl}_2\cdot\text{THF}$ were prepared according to literature procedures [14,15] and characterized by IR, ^1H NMR and EA.

2.2. Oligomerization of ethene

The oligomerization reaction was carried out in a 75 ml autoclave under a constant ethene pressure of 1.4 MPa. The autoclave was heated in an oil bath to 150 °C and the contents were stirred magnetically for 2 h. After reaction, the valve of the autoclave to the ethene pipeline was closed. The autoclave was cooled, vented and weighed. The catalytic activity was calculated based on the change of the autoclave weight before and after reaction. After the reaction was quenched by an alcoholic solution saturated with NaOH, the distribution of the oligomers in the resulting solution was determined by GC analysis on an HP6890 instrument equipped with an FID detector and an HP-5 column (30 m \times 0.32 mm), and by GC/MS spectra on an HP6890GC/5973MS instrument.

3. Results and discussion

3.1. Crucial effects of the structure and the metal center of precatalysts

The catalytic reactions were carried out with various precatalysts, which differ in the part of the π -ligand and the metal center. The selected results are summarized in Table 1. In the case of zirconium complexes incorporating η^5 -cyclopentadienyl ligands (Cp) or substituted ones, η^5 -pentamethylcyclopentadienyl (Cp^*) and indenyl (Ind), the selectivity of five-membered cyclic compounds (MCP) was in the range of 6–34% for ethene oligomerization (entries 1–3). With the replacement of zirconium by titanium atom, only 1% of *exo*-methylene-cyclopentane was detected in the reaction solution by GC analysis for precatalyst Cp_2TiCl_2 (entry 6). The formation of cyclic products was thoroughly inhibited in ethene oligomerization by post-zirconocene complexes featuring N_2O_2 -salen and -salphen ligands (entries 4 and 5).

The contrastive results from the catalytic reactions show that the bevel sandwich structure of group 4 metallocene

Table 1

Effects of the structure and the metal center of precatalysts^a

Entry	Precatalyst	Catalytic activity ^b ($\times 10^{-4}$)	MCP ^{c,d} (%)	Chain alkenes ^c (%)	Chain alkenes ^c (%)
1	Cp_2ZrCl_2	2.30	34	66	56
2	$\text{Cp}_2^*\text{ZrCl}_2$	5.80	6	94	23
3	$\text{Ind}_2\text{ZrCl}_2$	5.73	8	92	62
4	$(\text{Salen})\text{ZrCl}_2\cdot\text{THF}$	4.00	–	100	53
5	$(\text{Salphen})\text{ZrCl}_2\cdot\text{THF}$	3.60	–	100	46
6	Cp_2TiCl_2	6.37	~1	>99	>99

^a Reaction conditions: precatalyst 0.05 mmol; co-catalyst Et_3Al ; Al/Zr (mol/mol) 100; $P(\text{C}_2\text{H}_4)$ 1.4 MPa; reaction temperature 150 °C (2 h); toluene 30 ml.

^b Catalytic activity: g oligomers/mol(M) h.

^c Determined by GC and GC/MS analysis with *n*-heptane as an internal standard. The rest compounds of chain alkenes in entries 1, 4–6 are oligomers with more than ten carbon atoms and jelly-like polymers were found in entries 2 and 3.

^d MCP = *exo*-methylene-cyclopentane + methylcyclopentane.

complexes is an essential factor in controlling the formation of cyclic oligomers and that the character of the metal center of the precatalyst also plays an important role in the catalysis of ethene cyclo-oligomerization. In comparison with a Cp ligand, the large π -ligands, Cp^* and Ind, in the precatalysts benefit the generation of long chain oligomers and the cyclo-oligomerization of ethene is greatly depressed, presumably brought about by the steric congestion in the metallocyclopentane, which is the key intermediate in the supposed mechanisms of ethene cyclo-oligomerization and cyclization of dienes [2,9,10]. From a catalysis point of view, the important difference in structures between group 4 metallocene and salen-type complexes is that the former is in a tetrahedral geometry, allowing the two chloride ligands to stay in adjacent coordination sites, while the latter is in a quasi-octahedral structure, forcing the two chlorides in a *trans*-arrangement. It is thus impossible for salen-type zirconium precatalysts to form a zirconacyclopentane intermediate via replacement of two chlorides. Accordingly, the catalytic reactions of ethene oligomerization by salen and salphen zirconium complexes afford open-chain alkenes exclusively.

3.2. The influence of the Mg-containing third-component on ethene cyclo-oligomerization

Inspired by the reports concerning the formation of zirconacyclopentane in the catalytic carbometalation of alkenes and nonconjugated dienes mediated by Cp_2ZrCl_2 and alkyl-magnesium reagents [2,16,17], we tried to gain an insight into the effect of the Mg-containing third-component, Et_2Mg or EtMgBr , on cyclo-oligomerization of ethene. The selected results are listed in Table 2. Zirconocene dichloride was treated with Et_2Mg or EtMgBr in toluene prior to the catalytic reaction. The following manipulation was made as described in Section 2. Under the conditions of entries 1, 7 and

Table 2
The effect of the Mg-containing third-components^a

Entry	Cp ₂ ZrCl ₂ (mmol)	Et ₃ Al (mmol)	Third-components (mmol)	Catalytic activity ($\times 10^{-4}$)	CH ₂ CP ^b (%)	CH ₃ CP ^b (%)	MECP ^b (%)	VCH ^b (%)	C ₄ –C ₈ chain alkenes ^c (%)	
1	0.05	5	–	0	2.30	26	8	4	6	54
7	0.05	5	Et ₂ Mg	0.1	2.70	30	7	6	5	44
8	0.05	5	Et ₂ Mg	0.5	2.06	41	3	4	3	39
9	0.5	5	Et ₂ Mg	1	4.63	Polymers ($M_v = 2.4 \times 10^4$)				
10	0.05	0	Et ₂ Mg	5	Null	–	–	–	–	–
11	0.05	5	EtMgBr	0.1	1.54	34	5	6	3	43
12	0.05	5	EtMgBr	0.5	Null	–	–	–	–	–

^a Et₂Mg and EtMgBr were used as the third-component. Other conditions are the same as those in Table 1.

^b CH₂CP = *exo*-methylenecyclopentane, CH₃CP = methylcyclopentane, MECP = 1-methyl-1-ethylcyclopentane, VCH = vinylcyclohexane.

^c The rest compounds of chain alkenes in entries 1, 7, 8 and 11 are oligomers with more than eight carbon atoms.

8, oligomerization of ethene afforded cyclic oligomers in a selectivity of 44–51% and the rest were C₄–C₈ chain alkenes and low-carbon alkanes. The third-component Et₂Mg indeed manifested an influence on the distribution of oligomeric products. As the amount of Et₂Mg was changed from zero to a Zr/Mg molar ratio of 1:10, the catalytic activity of Cp₂ZrCl₂ displayed no significant change, and in the meantime the selectivity of *exo*-methylenecyclopentane was increased by 15% (entry 8). Further increase in the amount of Et₂Mg to a large excess, the selectivity of cyclic oligomers was no more enhanced, presumably attributed to the poor solubility of excess Et₂Mg in toluene. When the amount of precatalyst Cp₂ZrCl₂ was raised from 0.05 to 0.5 mmol in a Cp₂ZrCl₂/Et₃Al/Et₂Mg molar ratio of 1:10:2 (entry 9), a waxy solid was obtained with viscosity-average molecular weight (M_v) of 2.4×10^4 . The addition of diethyl ether solution of EtMgBr apparently deactivated the catalytic system, accompanied by an observable improvement in the selectivity of *exo*-methylenecyclopentane (entry 11). With a Cp₂ZrCl₂/Et₃Al/EtMgBr molar ratio of 1:100:10, the system became inactive towards ethene oligomerization (entry 12).

The organic products in the solution, resulting from ethene oligomerization by Cp₂ZrCl₂/Et₃Al/Et₂Mg in a molar ratio of 1:100:2 (entry 7), were identified by GC–MS spectra. The MS spectra of the peaks at the retention time of 4.07, 4.28, 6.22 and 6.66 min in Fig. 1 are in good agreement

with the standard MS spectra of methylcyclopentane, *exo*-methylenecyclopentane, 1-methyl-1-ethylcyclopentane and vinylcyclohexane, respectively. Gas chromatographic analysis showed that the total amount of cyclic compounds accounted for 48%, being composed of 30% *exo*-methylenecyclopentane (4.283 min), 7% methylcyclopentane (4.072 min), 6% 1-methyl-1-ethylcyclopentane (6.219 min) and 5% vinylcyclohexane (6.657 min), and that the open-chain compounds include 38% C₄–C₈ linear α -alkenes (C₄²⁻ 3.235, C₆²⁻ 3.795 and C₈²⁻ 6.135 min), 8% *n*-hexane (3.841 min), a small amount of 2-hexene (3.636 min) and 1,5-hexadiene (3.749 min). The other peaks in Fig. 1 represent ethene 3.134 min), ethanol (quencher, 3.333 min), *n*-heptane (internal standard, 4.725 min) and toluene (6.037 min). No product having more than eight carbon atoms was detected by GC analysis from the resulting solution.

3.3. Discussion on the mechanism of cyclo-oligomerization of ethene by Cp₂ZrCl₂

The formation of all detected organic products can be explained by the following plausible mechanism for the cyclo-oligomerization of ethene (Scheme 1). The experimental results showed that both cyclic and chain oligomers were produced with Cp₂ZrCl₂/Et₃Al as catalyst, while without Et₃Al, the bi-component system of Cp₂ZrCl₂/Et₂Mg was

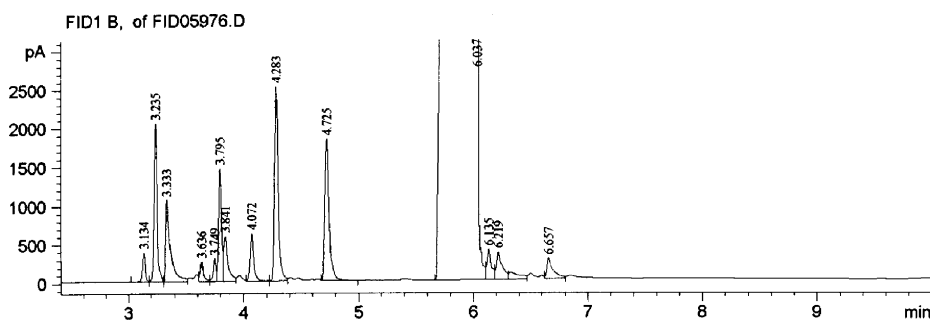
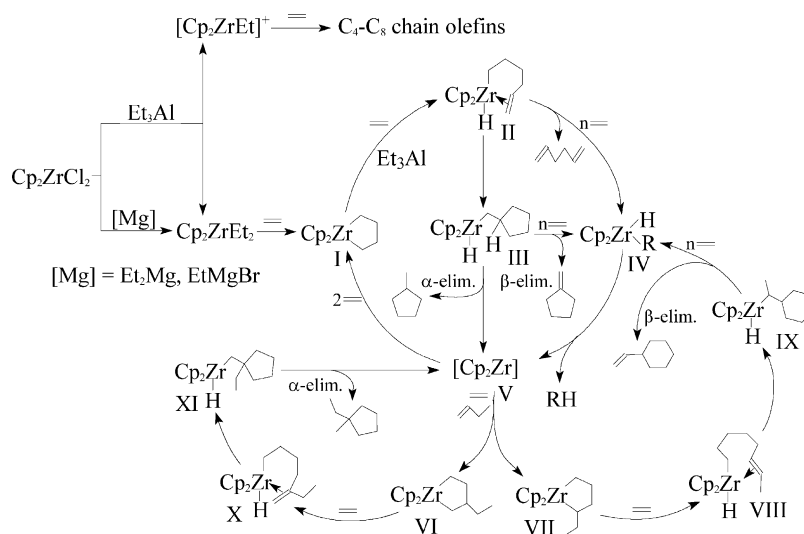


Fig. 1. GC spectrum of the resulting solution from entry 7.



Scheme 1. A plausible mechanism for ethene cyclo-oligomerization catalyzed by $\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}/[\text{Mg}]$.

inactive and no oligomeric products was formed (entry 10). With a three-component system of $\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}/\text{Et}_2\text{Mg}$, the catalytic activity did not show an apparent change compared with the results from $\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}$ system, but the selectivity of cyclic oligomers was improved. These results suggest that Et_3Al is an essential component in the system for the catalytic oligomerization of ethene and Et_2Mg plays a supplementary role only in the formation of zirconacyclopentane (I), which is a key intermediate for the formation of cyclic oligomers as described in various Zr-based catalytic reactions related to alkenes and nonconjugated dienes [18–24]. It seems that the further step from intermediate I–II is promoted or catalyzed by Et_3Al , but at this time we have no clear explanation for the role of Et_3Al in this step. Cyclic products with six carbon atoms can be formed from intermediate III, which is generated by the intramolecular insertion of intermediate II. The β - and α -elimination of III afford *exo*-methylene-cyclopentane and methylcyclopentane, respectively. The further β -elimination of II, as a by-reaction, gives a small amount of 1,5-hexadiene and an intermediate IV, which can lease low-carbon alkanes. The coordination of two molecules of ethene to the diion intermediate $[\text{Cp}_2\text{Zr}]$ (V) regenerates I to fulfill a catalytic cycle, whereas the coordination of one ethene and one 1-butene molecule constructs two kinds of substituted zirconacyclopentane VI and VII. The β -elimination of intermediate IX, derived from VII, yields vinylcyclohexane. The intermediate XI from VI has no β -hydrogen, therefore only α -elimination can occur with XI to afford 1-methyl-1-ethylcyclopentane. Although the reactions in the putative mechanism are all based on the organometallic elementary reactions: association of an alkene to the metal center, insertion of a coordinating alkene to the Zr–C or Zr–H bond as well as β - and α -elimination, more experimental proofs are needed to corroborate the mechanism for cyclo-oligomerization of ethene.

4. Conclusion

The bevel sandwich structure of group 4 metallocene complexes is an essential prerequisite for the formation of carbocyclic compounds in ethene oligomerization. Large π -ligands Cp^* and Ind greatly retard the production of cyclic compounds. The role of the Zr center of the precatalyst cannot be superseded by Ti atom for the cyclo-oligomerization of ethene. The precatalysts with N_2O_2 -salen and -salphen ligands thoroughly inhibit the generation of cyclic products. The addition of the third-component Et_2Mg or EtMgBr in a proper molar ratio of $\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}/[\text{Mg}]$ benefits the cyclo-oligomerization of ethene over the competitive chain-oligomerization.

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