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Oligomerization and simultaneous cyclization of ethylene to methylenecyclopentane catalyzed by zirconocene complexes

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Abstract

The oligomerization of ethylene catalyzed by Cp_2ZrL_2 (L = Cl, Me, OC_6H_4-Me-*p*) with ethylaluminoxane or Et_3Al as cocatalyst (Al/Zr = 100, 150°C, $P(C_2H_4) = 1.4$ MPa) afforded not only common chain oligomers but also a cyclic oligomer, methylenecyclopentane. The selectivity of methylenecyclopentane reached 39% under optimal conditions. The addition of C_5H_5N to the catalytic system of Cp_2ZrCl_2/Et_3Al was capable of further improving the selectivity of methylenecyclopentane to 43%. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ethylene oligomerization; Zirconocene complexes; Cyclization; Methylenecyclopentane

1. Introduction

Zirconocene/aluminoxane catalysts have attracted intense interest due to their catalytic activity and special stereoselectivity in the polymerization of α-olefins. Recently, the development of homogeneous catalytic chemistry of zirconocenes has been extended to the field of fine chemical synthesis, e.g. selective oligomerization of α-olefins, enantioselective reaction of monosubstituted alkenes and monocyclization of α,ω-dienes, by using low Al/Zr ratios or combining zirconocenes with other cocatalysts [1]. In contrast to methylaluminoxane (MAO), the use of other higher alkylaluminoxanes as cocatalysts has been much less frequently reported in the literature [2].

In our attempts to tune Cp_2ZrL_2 (L = Cl, Me, OC_6H_4Me-*p*)/ethylaluminoxane (EAO) to be a catalytic system for the oligomerization of ethylene to low-carbon linear α-olefins, we found that in addition to common oligomers, the oligomerization of ethylene catalyzed by Cp_2ZrL_2 with EAO or Et_3Al as cocatalyst also afforded an unexpected cyclic product, methylenecyclopentane (MCP). The selectivity of MCP, affected by aging and reaction temperature, the Al/Zr ratio and the hydrolysis extent of Et_3Al, reached 39% under optimal conditions. The addition of C_5H_5N as a third component to the catalytic system of Cp_2ZrCl_2/Et_3Al was capable of further improving the selectivity of MCP to 43%. As far as we know, this is the first example of catalytic formation of a cyclic product direct from ethylene oligomerization. The oligomerization and simultaneous cyclization of ethylene occurring in one-pot really provides a potential convenient access to five-membered carbocyclic compounds, which are very useful building blocks for organic synthesis [3].

2. Results and discussion

Pretreatment of Cp_2ZrCl_2 (0.025 mmol) with EAO (Al/Zr = 100) in anhydrous toluene (20°C, 30 min), followed by exposure to ethylene (1.4 MPa, 150°C, 2 h) gave not only chain oligomers in 72% yield, but also an unusual monocyclic product, methylenecyclopentane in 28% yield based on GC analysis. Intrigued by this surprising lead, we examined the oligomerization of ethylene with other zirconocene complexes as procatalysts under identical conditions of temperature, pressure and Al/Zr ratio. Some representative results are sum-

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marized in Table 1. In the case of Cp_2ZrL_2/EAO, MCP was obtained in 17–28% yield. The replacement of EAO with Et_3Al gave even higher selectivity to MCP (39%). In contrast, when the hydrolysis extent of Et_3Al changed from 1 to 2 (H_2O/Et_3Al), the selectivity to MCP dropped to 12%. The reaction of ethylene catalyzed by Ind_2ZrCl_2 with EAO as cocatalyst mainly gave polymers, and with Et_3Al gave only 8% of MCP. If zirconocene complexes were replaced by simple zirconium complexes without η^5-cyclopentadienyl ligands, such as $ZrCl_4$, $ZrCl_2(OR)_2$ and $ZrCl_2(acac)_2$, with either EAO, Et_3Al or Et_2AlCl as cocatalyst, chain olefins were produced selectively [4]. Chain oligomers are also the exclusive products for the oligomerization of ethylene catalyzed by the previously reported non-zirconocene compounds, ZrR_4, $Zr(OR)_4$ and $Zr(OCOR)_4$, in combination with alkylaluminum chloride [5]. These contrasting results distinguish catalysis with metallocenes from that with non-metallocenes, implying that zirconocene complexes may perform a different behavior from the simple zirconium catalysts in the oligomerization of ethylene and that the pseudo-sandwich structure of zirconocene complexes plays an important role in the formation of the cyclic oligomer.

Both aging and reaction temperature prove to be important factors in optimizing the selectivity for MCP (Table 2). For example, the selectivity of MCP increased from 3 to 31% as the reaction temperature rose from 120 to 165°C, while Cp_2ZrCl_2/EAO was pretreated at 60°C. The selectivity of MCP also depends on the Al/Zr ratio. Under the identical reaction conditions, when the Al/Zr ratio was 25:1, the oligomerization of ethylene gave 1-hexene in 55% yield, and the selectivity of MCP was only 3%. With an increase of the Al/Zr ratio from 40:1 to 100:1 the selectivity of MCP grew from 8 to 27%. Further enhancement of the Al/Zr ratio to 200:1 did not show an evident effect on the selectivity of the cyclic oligomer.

To confirm the structure of the cyclic product, we collected the reaction mixture and distilled it carefully. A fraction containing 56% of the cyclic oligomer and 44% of toluene was obtained and the sample was characterized by GC–IR, GC–MS, ^1H- and ^{13}C-NMR spectra. With the exception of the signals of toluene, the data obtained were identical to the structure of methylenecyclopentane.

The formation of a significant portion of MCP in ethylene oligomerization catalyzed by Cp_2ZrL_2/EAO prompted us to investigate the reaction of 1,5-hexadi-

Table 1
Activities and product distributions for selected catalytic systems [a]

Catalytic system	Catalytic activity (kg mol^{-1} (Zr) h^{-1})	MCP (%) [d]	$C_{4\sim10}$ chain olefins (%) [d]	$\geq C_{12}$ chain olefins (%) [d]
Cp_2ZrMe_2/EAO	21	17	42	41
$Cp_2Zr(OC_6H_4\text{-}p\text{-}Me)_2$/EAO	37	17	36	47
Cp_2ZrCl_2/EAO [b]	66	28	35	37
Cp_2ZrCl_2/Et_3Al [b]	65	39	39	22
$Cp_2ZrCl_2/Et_3Al/C_5H_5N$ [b,c]	31	43	33	24
Ind_2ZrCl_2/Et_3Al [b]	57	8	62	30

[a] Reaction conditions: Zr = 0.05 mmol; Al/Zr = 100; aging temperature 100°C (30 min); reaction temperature 150°C (2 h); $P(C_2H_4) = 1.4$ MPa; toluene 30 ml.

[b] Zr = 0.025 mmol; aging temperature 20°C.

[c] With third component: $Al/Zr/C_5H_5N = 100:1:1$.

[d] Determined by GC analysis (SE-30, 30 m × 0.25 mm) with internal standard (*n*-heptane).

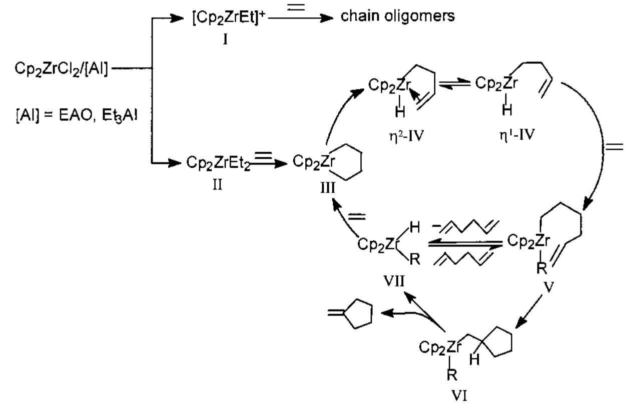
Table 2
Activities and product distributions for selected reaction conditions [a]

Aging temperature (°C)	Reaction temperature (°C)	EAO/Zr (mol/mol)	Catalytic activity (kg mol^{-1} (Zr) h^{-1})	MCP (%) [c]	$C_{4\sim10}$ chain olefins (%) [c]	$\geq C_{12}$ chain olefins (%) [c]
60 [b]	120	100:1	21	3	27	70
60 [b]	165	100:1	28	31	43	26
150	150	100:1	43	15	49	36
20	150	100:1	39	27	34	39
20	150	40:1	36	8	48	38
20	150	25:1	14	3	64	33

[a] Other reaction conditions are the same as those in Table 1.

[b] With third component: $Al/Zr/Ph_2PCH_2COONa = 100:1:1$.

[c] Determined by GC analysis.



Scheme 1. Proposed catalytic cycle for oligomerization and cyclization of ethylene

ene in the presence of the same catalyst. Zirconium-catalyzed monocyclization of 1,5-hexadiene to five-membered cyclic compounds has been reported by Waymouth using a three-component catalyst of $Cp^*_2ZrMe_2/AlMe_3/B(C_6F_5)_3$, Bazan using $[C_5H_5BPh]_2$-$ZrCl_2$/MAO and Walther using $[(Siam)ZrCl_3]_2$ (Siam = *N*,*N*′-bis(trimethylsilyl)benzamidinate)/MAO and $[(Ph_3SiO)_2ZrMe_2(bpy)](tol)_2$/MAO as catalysts [6]. In the latter two cases, methylenecyclopentane was selectively produced in the reactions, while under comparable conditions the use of Cp_2ZrCl_2 afforded 19% of MCP and 14% of methylcyclopentene and methylcyclopentane [6c]. Our studies showed that the monocyclization of 1,5-hexadiene could be catalyzed by Cp_2ZrCl_2/EAO at 150°C, yielding 58% of MCP and 21% of methylcyclopentene, along with a small amount of dimer and trimer of 1,5-hexadiene. In comparison with the Cp_2ZrCl_2/MAO catalyst, the catalytic system of Cp_2ZrCl_2/EAO has a preference for monocyclic products to chain oligomers.

We assume that in the oligomerization of ethylene two types of active species [7], the neutral diethylzirconocene intermediate (II) and the monoethylzirconocene cation (I) [8], are formed competitively. The former leads to MCP and the latter results in normal chain oligomers. The intermediacy of metallacyclopentane (III), previously postulated for zirconocene-catalyzed dimerization and carbometalation of α-olefins and alkynes [9–11], and for chromium-catalyzed trimerization of ethylene [12], might be involved in the construction of the cyclic oligomer. A very small amount of 1,5-hexadiene in the oligomeric mixture has been identified by GC and GC–MS. This result can be interpreted in terms of the mechanism shown in Scheme 1 based on well-known fundamental processes and our experimental results. The intermediate (V) could undergo two competitive reactions: (i) intramolecular insertion of the end double bond to afford a (cyclopentylmethyl)zirconocene (VI) [6a], and (ii) β-elimination to give 1,5-hexadiene and hydridozirconocene (VII). It is rational that the free 1,5-hexadiene thus formed in the reaction is prone to quickly re-form the intermediate (V) by coordination and insertion to the hydridozirconocene (VII). Therefore, after reaction and hydrolysis, a very small amount of 1,5-hexadiene was present in the reaction mixture. The experimental results supposed that ethylzirconocene species formed by the reaction of Cp_2ZrCl_2 and EAO render the oligomerization of ethylene via a different pathway from that catalyzed by Cp_2ZrCl_2 and MAO. The different reactivities between the ethyl- and methylzirconocene species may be caused by the β-Me in the ethyl group, which readily undergoes β-H elimination. More experimental supports are needed to further clarify the proposed Scheme 1.

3. Conclusions

In conclusion, we have found a catalytic cyclization reaction concurring with ethylene oligomerization catalyzed by a zirconocene/EAO or /Et_3Al system. Although the selectivity to methylenecyclopentane is not very high, the moderate yield already shows a potential of this unique cyclization reaction as a convenient way to prepare substituted cyclopentanes, which can be used as intermediates for the production of some fine chemicals, and to offer feed stock for the production of cycloolefin copolymers with interesting properties. Our further studies underway are directed at optimizing the catalytic system and reaction conditions to improve the selectivity of methylenecyclopentane and at acquiring a better understanding of the mechanism of the novel cyclization reaction concurring with ethylene oligomerization.

4. Experimental

4.1. General methods

All reactions and operations were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Ethylene was purified by passage through a column of molecular sieve (4 Å). Triethyl aluminum was carefully distilled in vacuo and then partially hydrolyzed by the reaction with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene at 0 ~ 5°C. Toluene was distilled from sodium/benzophenone ketyl prior to use. Zirconium tetrachloride was purchased from Merck–Schuchardt. Other commercially available reagents, C_5H_5N, HOC_6H_4Me-*p* and $Al_2(SO_4)_3 \cdot 18H_2O$ were used without further purification. Complexes Cp_2ZrCl_2 [13], Cp_2ZrMe_2 [14] and $Cp_2Zr(OC_6H_4\text{-}Me\text{-}p)_2$ [15] were prepared according to literature methods.

The following spectrometers were used to detect the structure of methylenecyclopentane: NMR, JEDLFX-90Q NMR spectrometer; GC–MS, HP6890GC/5973MS; GC–IR, HP5890II/Bio-Rad FT S-65A.

4.2. Ethylene oligomerization

Ethylene oligomerization experiments using the various catalyst precursors were carried out by the following general procedure. A 75 ml autoclave, equipped with a magnetic stirring bar, was dried in vacuo at 200°C for 30 min, cooled to room temperature and filled with pre-purified dinitrogen. A toluene solution of EAO, in a calculated molar ratio of 100:1 (EAO:precatalyst), was added to a Schlenk bottle, which was charged with 0.025 or 0.05 mmol of precatalyst and 15 ml of toluene. All suspended substances were dissolved after being stirred for a few minutes. The solution was transferred into the autoclave and the Schlenk bottle was washed three times with 5 ml of toluene. After 30 min of pre-reaction, 1.4 MPa of ethylene was introduced to the autoclave and the system was heated to the reaction temperature for 2 h. After reaction, the autoclave was closed and cooled in ice-water for 30 min. The autoclave was vented and weighed. The weight of products was calculated by the weight difference of the autoclave before and after reaction. The catalytic system was quenched by addition of 1 ml of NaOH/EtOH saturated solution. The product distribution was determined by GC analysis of the obtained solution with *n*-heptane as internal standard.

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