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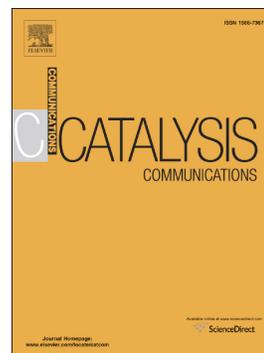
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Diastereoselective Synthesis of Functionally Substituted Alkene Dimers and Oligomers, Catalysed by Chiral Zirconocenes

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Abstract

The research addresses the reaction of terminal alkenes and propene with AlR_3 (R = Me, Et) in the presence of chiral Zr complexes, *rac*-[Y(η^5-C$_9$H$_{10}$)$_2$]ZrCl$_2$ (Y = C$_2$H$_4$, SiMe$_2$) or (NMI)$_2$ZrCl$_2$ (NMI- η^5–neomenthylindenyl), and methylaluminoxane. The effect of reaction conditions, catalyst and trialkylalane structure on the substrate conversion and the reaction chemo- and stereoselectivity has been studied. The reaction predominantly goes via the stage of alkene methyl(ethyl)zirconation with subsequent introduction of substrate molecules into the Zr-C bond. As a result, a diastereoselective one-pot method for the synthesis of functionally substituted linear terminal alkene dimers and propene oligomers was developed.

Keywords: dimers, oligomers, zirconocenes, carbometalation

1. Introduction

Catalytic systems based on titanium-group metallocenes and methylaluminoxane (MAO) are widely used for alkene polymerization [1], di- and oligomerization [2]-[4]. By varying the electronic and spatial structures of the ligand in the transition metal complexes, one can control the activity and stereoselectivity of these catalytic systems [5], [6]. There are few publications on the use of chiral metallocene complexes in the stereoselective synthesis of alkene oligomers. For example, the synthesis of saturated stereoregular optically active oligomers of propene catalyzed by *ansa*-zirconocene-based system, (R)-[$C_2H_4(\eta^5$-$C_9H_{10})_2$]ZrMe$_2$/MAO/H$_2$ (the molar ratio [Zr] : [MAO] = 1:3), has been reported [7], [8]. Enantiomerically enriched propene and butene oligomers containing a methylene double bond were obtained with the use of catalytic system (S)-[$C_2H_4(\eta^5$-$C_9H_{10})_2$]Zr(O-acetyl-(R)-mandelate)$_2$/MAO (the molar ratio [Zr] : [MAO] = 1:100) [9]. The reactions give saturated or unsaturated hydrocarbons, where it may be difficult to introduce additional functional groups needed for their further application as synthons. The enantiomerically and diastereomerically pure methyl-substituted primary alcohols were obtained in the reaction of propene with ZnEt$_2$ and MAO catalyzed by enantiomerically pure zirconocenes (the molar ratio [Zr]:[MAO]:[ZnEt$_2$] = 1:1000:(1800-5000)) followed by subsequent oxidation [11], [12]. Functionally substituted products of 1-hexene oligomerization containing up to six units were synthesized using *ansa*-η^5-complexes as catalysts [13], [14]. Thus, the stereoselective oligomerization of alkenes appears to be a promising method, because it could provide one-pot route to stereomerically pure moieties of practically useful compounds for medicinal chemistry and industry [3], [4], [15]-[18] (Scheme 1). Meanwhile, the existing syntheses of these structural units are multistage and occur via gradual attachment of monomer units (see, for example, Ref. [19]-[26]).

Scheme 1.
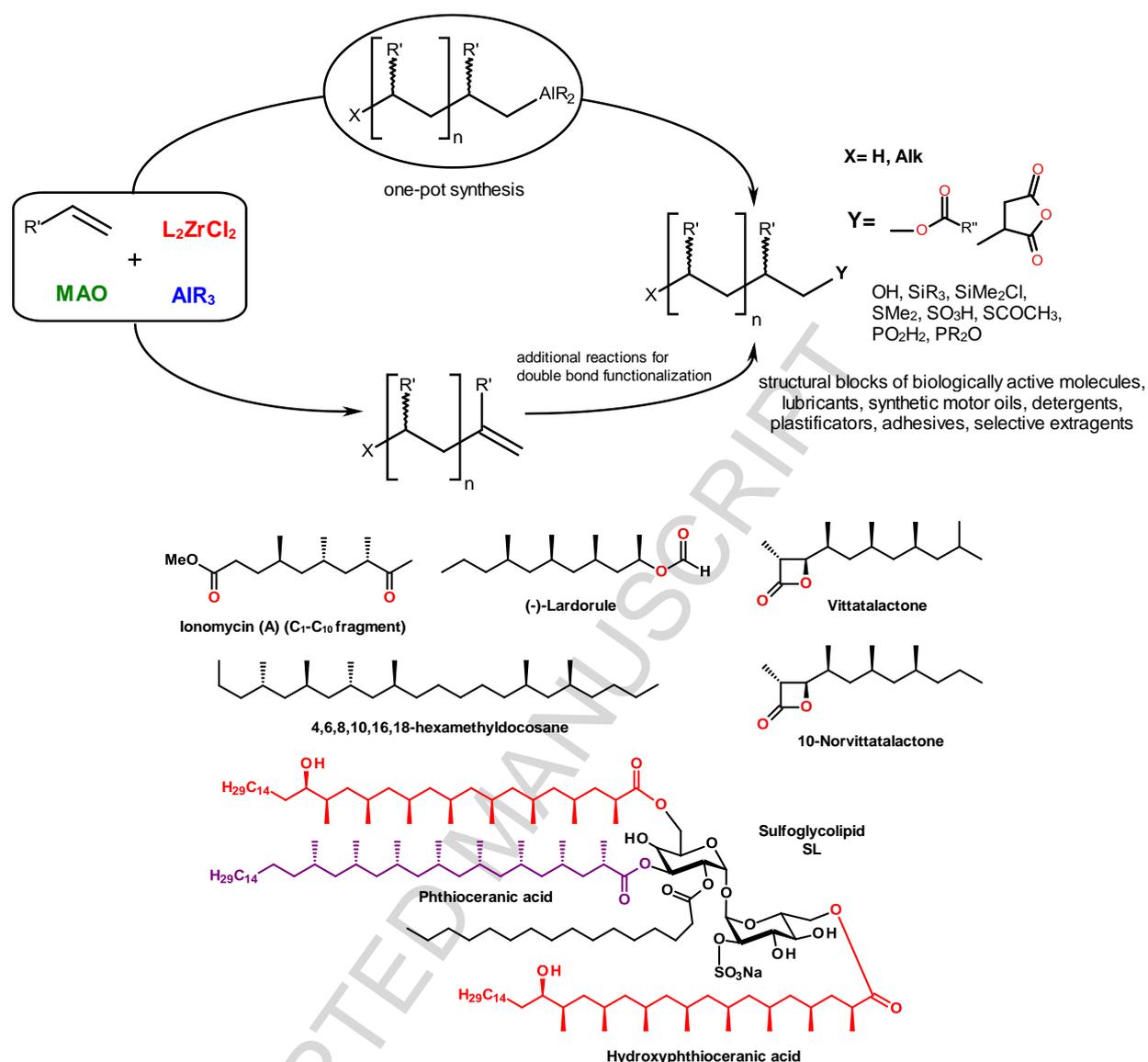
Thus, in order to develop the method for the one-pot synthesis of functionalized linear terminal alkene and propene oligomers we studied the effect of the catalyst and trialkylalane structures, as well as the reaction conditions on the catalytic system activity, chemo- and stereoselectivity. As the stereoselective catalysts for the preparation of alkene oligomers, we used both conformationally rigid *ansa*-complexes, *rac*-[Y(η^5-C$_9$H$_{10}$)$_2$]ZrCl$_2$ (Y= C$_2$H$_4$ (**1**), SiMe$_2$ (**2**)), and conformationally mobile *bis*(η^5–1–neomenthylindenyl)zirconium dichloride (**3**) (Scheme 2).

2. Experimental

General procedures. All operations for organometallic compounds were performed under argon according to Schlenk technique. The zirconocenes **1-3** were prepared using the standard procedures from ZrCl$_4$ (99.5%, Aldrich) (*rac*-**1** [27], *rac*-**2** [28], **3** [29]). The solvents (hexane, toluene) were distilled from i-Bu$_2$AlH immediately prior to use; THF and diethyl ether were

dried and distilled from sodium/benzophenone before use. Dichloromethane was dried over P_2O_5. Commercially available 98% $AlEt_3$, 97% $AlMe_3$ (Aldrich) and MMAO-12 (7 wt% Al in toluene, Sigma-Aldrich) were involved into the reactions. Terminal alkenes 1-hexene (97%, Acros), 1-octene (99%, Acros), 1-decene (97%, Acros) and propylene (≥99%, Sigma-Aldrich) were used.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^1H), 100.62 MHz (^{13}C)). As the solvent and the internal standard, $CDCl_3$ was employed. 1D and 2D NMR spectra (COSY HH, HSQC, HMBC) were recorded using standard Bruker pulse sequences. Chromatographic analysis was carried out on a CARLO ERBA 1150 instrument in a helium flow, a 50000×0.32 mm column, ULTRA-1 stationary phase, and a flame ionization detector. The deuterated products were analyzed by GC/MS on an automated QP 2010 Ultra GC/MS assembled with a TD-20 Shimadzu thermal desorber.

Reaction of 1-alkenes with AlR_3 (R= Me, Et) in the presence of complexes 1-3 and MAO.

A 50 mL glass reactor mounted on a magnetic stirrer and filled with argon was charged with catalyst (**1-3**) (0.0075 mmol), CH_2Cl_2 or $C_6H_5CH_3$ (10 ml), alkene **4a-c** (1.5 mmol), AlR_3 (1.5 mmol) and MMAO-12 (0.3 mmol). In the case of propene (**4d**), the reaction media was bubbled with alkene at 0°C, brought to room temperature and stirred for 24 hours under a propene atmosphere (1 bar). The reaction was carried out at 20°C with continuous stirring for 72 hours. After completion of the reaction, a part of the reaction mixture was quenched with 10% DCl at 0°C. The products were extracted with benzene and filtered, and the organic layer was dried with Na_2SO_4. The product yield (**5-8**) was determined by analyzing the hydrolysis and deuterolysis products by GLC and GC/MS.

The remaining reaction mixture was cooled to 0°C and oxidized by bubbling O_2 for 2 h, then kept in an oxygen atmosphere for 24 hours more. The products were quenched with HCl and extracted by diethyl ether, and the organic layer was dried with Na_2SO_4, filtered, and concentrated. Functionally substituted di- and oligomers (**9**, **10**) were isolated by column chromatography on silica gel using a 7 : 1 hexane : diethyl ether system. Alcohols **9** (**n=1**) were isolated by column chromatography on silica gel in a 4 : 1 hexane : diethyl ether system. The organic fractions were dried over Na_2SO_4.

Synthesis of silylated derivatives of propene oligomer alcohols. A 20 mL glass reactor mounted on a magnetic stirrer and filled with argon was charged with 5 ml of toluene and 20 mg of hydroxy- substituted propene oligomers **9-IId** or **10d** (0.06-0.095 mmol). At 0°C, 0.1 ml (0.25 mmol) of BuLi (2.5 M in hexane) was added dropwise to the solution. The resulting solution was brought to room temperature and stirred for 30 minutes. Then the reactor was cooled to 0°C and

0.04 ml (0.3 mmol) of Me$_3$SiCl was added dropwise. The resulting mixture was brought to room temperature and stirred for 3 hours. After that, the reaction mixture was decomposed with water; the organic layer was collected and dried over Na$_2$SO$_4$. Compounds **13**, **14** were obtained and analyzed by GLC and GC-MS.

3. Results and Discussion

The reaction of alkenes with AlR$_3$ in the presence of 0.5 mol% of complexes **1**-**3** and MAO yields carbometalation products and functionally substituted dimers and oligomers (Scheme 2, Table 1). The resulting oligomers may be both functionally substituted organoaluminum compounds (**5**, **6**), as shown by mass-spectroscopic analysis of the deuterolysis products (**11**, **12**), and higher branched alkenes with a methylene double bond (**7**, **8**). In this work, we mainly used a small amount of MAO (40 equiv.) [13], [14]. This gives rise to organoaluminum derivatives (**5**, **6**), which are subsequently oxidized to give methyl- or ethyl-substituted primary alcohols **9** and **10** containing 2 to 7 monomer units (Scheme 2). A higher content of MAO (200-250 equiv.) in the L$_2$ZrCl$_2$-AlR$_3$-MAO-alkene system results in the formation of α-olefin oligomers with a terminal double bond (**7** and **8**).

Scheme 2. Reaction of alkenes with AlR$_3$ (R= Me, Et) in the presence of complexes 1-3 and MAO.
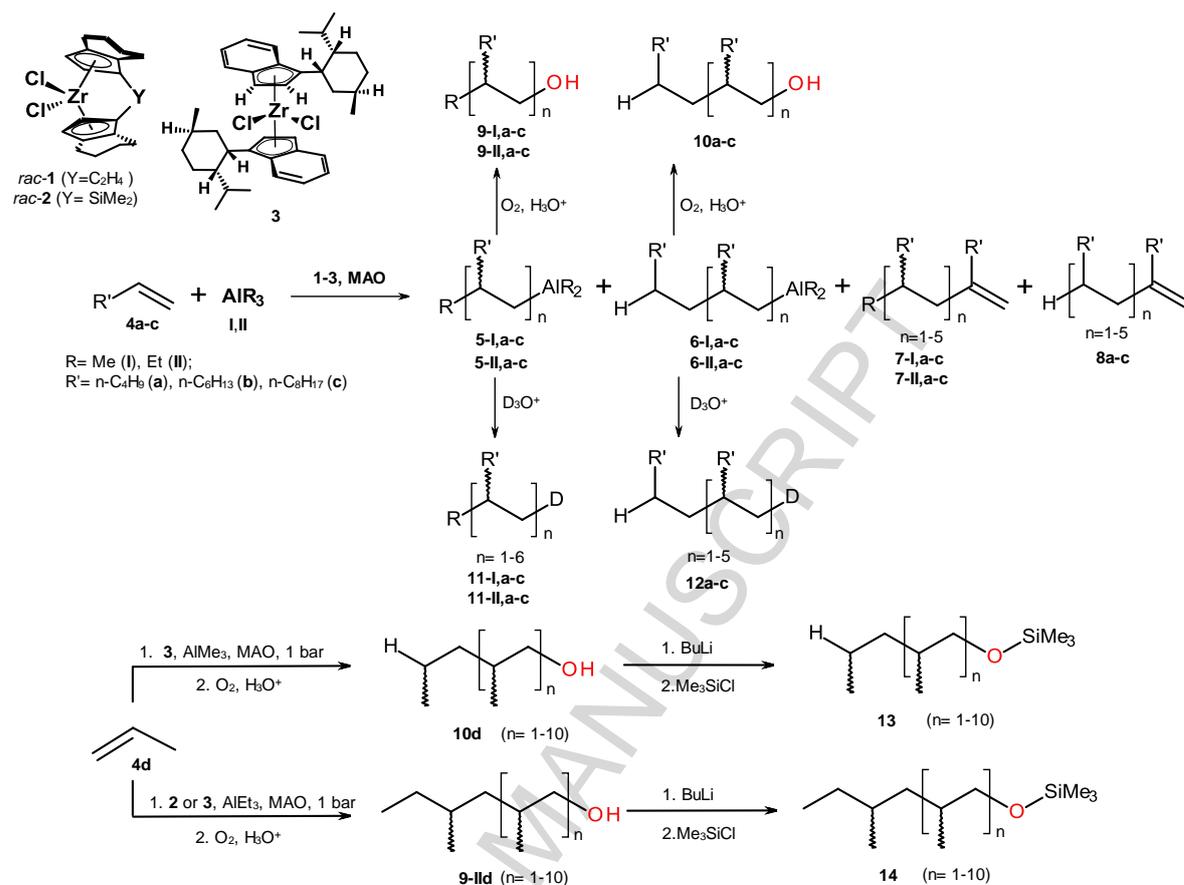
The reaction of alkenes **4a,b** with AlMe$_3$ in the presence of *ansa*-complex **1** and MAO goes with high conversion of the substrate (98-99%) and provides mainly functionalized methyl-substituted dimers and oligomers **5-Ia,b** (n=2-6, totally 50-67%), functionalized dimers and oligomers **6-Ia,b** (n=2-6, totally 12-19%), carboalumination products **5-Ia,b** (n=1, <11%) and adducts **7-Ia,b** with a methylene double bond (n=2-6, totally 15-25%) (Table 1, entries 1-4). The reaction with 1-decene (**4c**) gives the same set of products, but runs with less conversion.

Table 1
Oligomerization of linear alkenes in the presence of complexes **1-3**, AlR$_3$ and MAO (molar ratio [Zr]:[substrate]:[AlR$_3$]:[MAO]=1:200:200:40, 72 h, 20°C)

Entry	AlR$_3$	Catalyst	1-Alkene	Solvent	Conversion	Mole ratio of products[a,b], %			
						5	**6**	**7**[c]	**8**
						n			
1	AlMe$_3$	**1**	**4a**	CH$_2$Cl$_2$	99	1	11		
						2	7	3	3
						3	7	3	3
						4	20	10	5
						5	10	4	3
						6	6	3	1
2				toluene	99	1	1		

Entry	Additive	Substrate	Ligand	Solvent	Yield	n				
						2	12			
						3	13	4	6	
						4	13	2	7	
						5	12	3	6	
						6	11	3	6	
3			**4b**	CH$_2$Cl$_2$	98	1	10			
						2	7	3	1	
						3	12	3	3	
						4	14	4	5	
						5	13	3	4	
						6	10	3	3	
4				Toluene	99	1	10			
						2	22	8	2	
						3	18	5	1	
						4	15	3		
						5	7	2		
						6	5	1		
5			**4c**	CH$_2$Cl$_2$	52	1	11			
						2	8	3	1	
						3	9	5	3	
						4	5	4	3	
6				toluene	51	1	4	6		
						2	7	4	7	1
						3	8	1	5	
						4	3	1	4	
7		**2**	**4b**	CH$_2$Cl$_2$	85	1	16			
						2	26	10	1	
						3	11	1	1	
						4	6	1	1	
						5	9	1	<1	
8				Toluene[d]	99	1	40			
						2	26	1	17	
						3	7	<1	7	
9		**3**[d]	**4a**	CH$_2$Cl$_2$	94	1	41	6	3	-
						2	27	2	2	1
						3	6	1	1	-
						4	3	-	-	-
						5	1	-	-	-
10				toluene	98	1	60			
						2	28			
						3	8			
						4	2			
11			**4b**	CH$_2$Cl$_2$	92	1	64			7
						2	18			3
12				toluene	80	1	10	1	1	
						2	27		20	6
						3	7		6	
						4	1		1	
13			**4c**	CH$_2$Cl$_2$	95	1	67			
						2	7	1	5	7
						3	4	1	2	1
14				Toluene	99	1	47			
						2	41		3	
						3	7		1	
15	AlEt$_3$	**1**	**4a**	CH$_2$Cl$_2$	99	1	14	2	<1	
						2	15	1	<1	
						3	18	3	<1	
						4	12	5		
						5	9	3		
						6	6	2		

Entry			Solvent	Conv.	n				
					7	5	2		
16			toluene	99	1	<1			
					2	36	2		
					3	32	2		
					4	14	1		
					5	6	<1		
					6	3	<1		
17		4b	CH$_2$Cl$_2$	99	1	59			
					2	24	2		
					3	10	<1		
					4	3			
18			toluene	72	1	30	13		
					2	19			
					3	7			
					4	3			
19		4c	CH$_2$Cl$_2$	90	1	61	8		
					2	13	3	<1	
					3	3	<1		
20			toluene	40	1	11	6		
					2	7	5	4	<1
					3	4	2		
21	2	4a	toluene	99	1	<1			
					2	23	2		5
					3	20	1		
					4	20	1		
					5	13	1		
					6	11	1		
22	3^d	4a	CH$_2$Cl$_2$	99	1	54			
					2	30	5	4	6
23			toluene	78	1	4	2		
					2	39	2	3	3
					3	14	2	2	2
					4	4	1		
24		4b	CH$_2$Cl$_2$	92	1	35	2		
					2	20	12	2	7
					3	4	5	1	4
25			toluene	75	1	4	2		
					2	8	3	5	3
					3	12	6	8	6
					4	6	4	3	5

^{a} Determined by GC of deuterolysis products.

^{b} *de%* was determined by ^{13}C NMR of products **9, 10**.

^{c} The content of product **7** (n = 0) was <1%.

^{d} 2 mol% of catalyst.

Dimethylsilylene bridged zirconocene catalyst **2** showed less activity in the reaction, however, it possesses better selectivity towards the dimer **5-I** (Table 1, entry 7).

The reaction of alkenes with AlMe$_3$ in the presence of 40 equiv. of MAO and conformationally mobile complex **3** involves high conversion of the substrate (80-99%) and affords predominantly the carboalumination products (Table 1, entries 9-11,13). The replacement of dichloromethane by toluene in this system increases the yield of 1-octene and 1-decene dimers (entries 12, 14).

The using of AlEt$_3$ in the studied reaction leads to ethyl-substituted alkene oligomers for the whole range of tested catalysts and substrates. Ethyl-substituted functionalized derivatives **5-**

II (n=2-7) prevail in the case of conformationally rigid catalysts **1** and **2** (Table 1, entries 15-21). Reaction, catalyzed by complex **3**, goes with less selectively and gives a wider range of oligomeric products (entries 22-25). It should be noted that addition of MAO to the catalytic systems containing AlEt$_3$ almost completely stops the cycloalumination pathway, which in the absence of the activator is usually the main direction of the reaction [30]-[33]. The use of dichloromethane as the solvent and either *ansa*-complex **1** or conformationally mobile complex **3** as the catalyst was found to result in the 92-99% conversion of the substrates and predominant formation of carbometalation products **5-II** (n=1, 35-61%) (Table 1, entries 17, 19, 22, 24), whereas the chemoselectivity of the oligomer formation decreases. The replacement of dichloromethane by toluene in these systems decreases the alkene conversion, but enhances the chemoselectivity towards the formation of ethyl-substituted oligomers (entries 16, 18, 20, 21, 23, 25).

Alcohols **9, 10** obtained by oxidation and hydrolysis of products **5,6** formed in the reaction of α-olefins with AlR$_3$ catalyzed by complexes **1-3** and MAO were analyzed by mass spectrometry and NMR spectroscopy. It was found that the reaction of alkenes with AlR$_3$ in the presence of conformationally rigid *ansa*-complexes **1** and **2** and MAO furnishes functionally substituted dimers and oligomers with high diastereomeric purity of ~99% *de*. Thus, the ^{13}C NMR spectra of dimers **9-I** obtained with the catalytic systems based on conformationally rigid complexes **1** and **2** exhibit signals of one diastereomer (Fig. 10b, SI). The result is consistent with published data on high stereoselectivity of *ansa*-complexes in alkene polymerization [5], [6]. Unlike *ansa*-complexes, the use of conformationally flexible complex **3** as the catalyst leads to the formation of functionally substituted oligomers **6** and **7** with up to five units, with dimers being the predominant components and with low diastereoselectivity (not more than 5% *de*). Indeed, the ^{13}C NMR spectrum of compounds **9 I,II** obtained after oxidation of the reaction mixture shows doubled signals for the (*RR*+*SS*) and (*RS*+*SR*) diastereomers (Fig.10a, SI), which attests to the loss of diaselectivity upon the insertion of a second alkene molecule into the carbometallation product formed in the first stage of the reaction.

Thus, comparison of the conformationally mobile and rigid complexes demonstrates that complexes with rigid geometry exhibit higher selectivity towards oligomerization. Moreover, the use of *ansa*- complexes results in high process diastereoselectivity.

The reaction of propene (**4d**) with trialkylalanes in the presence of chosen catalysts **1**-**3** and MAO affords functionally substituted oligomers with up to 11 units (Scheme 2). Conformationally mobile complex **3** catalyzes the reaction of propene with AlMe$_3$ at room temperature in 24 h ([Zr]: [AlR$_3$]:[MAO]=1:200:40, pressure of propene 1 bar) to give propene oligomers **10d** with the catalytic activity of 133 g$_{oligomer}$·mol$_{Zr}^{-1}$·h^{-1}. Oligopropenes obtained in

this reaction have an n-propyl starting group, as was also observed for the *ansa*-zirconocene-MAO systems studied previously [7]-[9], indicating that the early stages of the process is hydrometalation, which occurs due to the catalytically active sites containing a Zr-H bond (Scheme 3). Conformationally rigid complexes **1** and **2** proved to be catalytically inert under the same conditions. The replacement of AlMe$_3$ by AlEt$_3$ in the η^5-L$_2$ZrCl$_2$-AlR$_3$-MAO-alkene systems makes it possible to perform propene oligomerization in the presence of *ansa*-complex **2**, the catalytic activity of which is 340 g$_{oligomer}$·mol$_{Zr}^{-1}$·h^{-1}. The activity of complex **3** under these conditions is lower, namely, 154 g$_{oligomer}$·mol$_{Zr}^{-1}$·h^{-1}. When propene reacts with AlEt$_3$ in the presence of complexes **2** and **3**, the first stage is propene carbometalation, which is followed by formation of substrate insertion products (**9-II,d**).

The ^{13}C NMR of oxidized products **9-IId**, **10d** (Fig. 11, SI) and mass spectra of their silylated derivatives**Error! Reference source not found.** (Fig. 1) indicate the low diastereoselectivity of the reactions catalyzed by complex **3**, whereas high regio- and diastereoselectivity are inherent to the catalytic system based on the zirconocenes with fixed geometry (Fig. 1b).

The variety of products obtained in the studied reaction can be explained by the mechanism presented in Scheme 3. Thus, the formation of Me(Et)-substituted oligomers **5** and **7** is due to the existence of active centers with a Zr-C bond, which carbometalate the alkenes [15],[16], gradually increasing the oligomeric chain. The chain termination occurs as a result of the transmetalation by AlR$_3$ or due to the β-C-H activation providing hydrocarbons with a methylene double bond. The latter process is a source of intermediates with an active Zr-H bond, which hydrometalate the substrate and give products **6** and **8** with an *n*-alkyl starting group. It should be noted as well that in systems with AlEt$_3$, the addition of small amounts of MAO probably reduced the rate of β-C-H activation, since we did not observe cyclomelation products, for which a hydride transfer with ethane release and the formation of zirconacyclopropane is required [33]; in addition, this fact is confirmed by a larger proportion of ethylated oligomers in the reaction products.
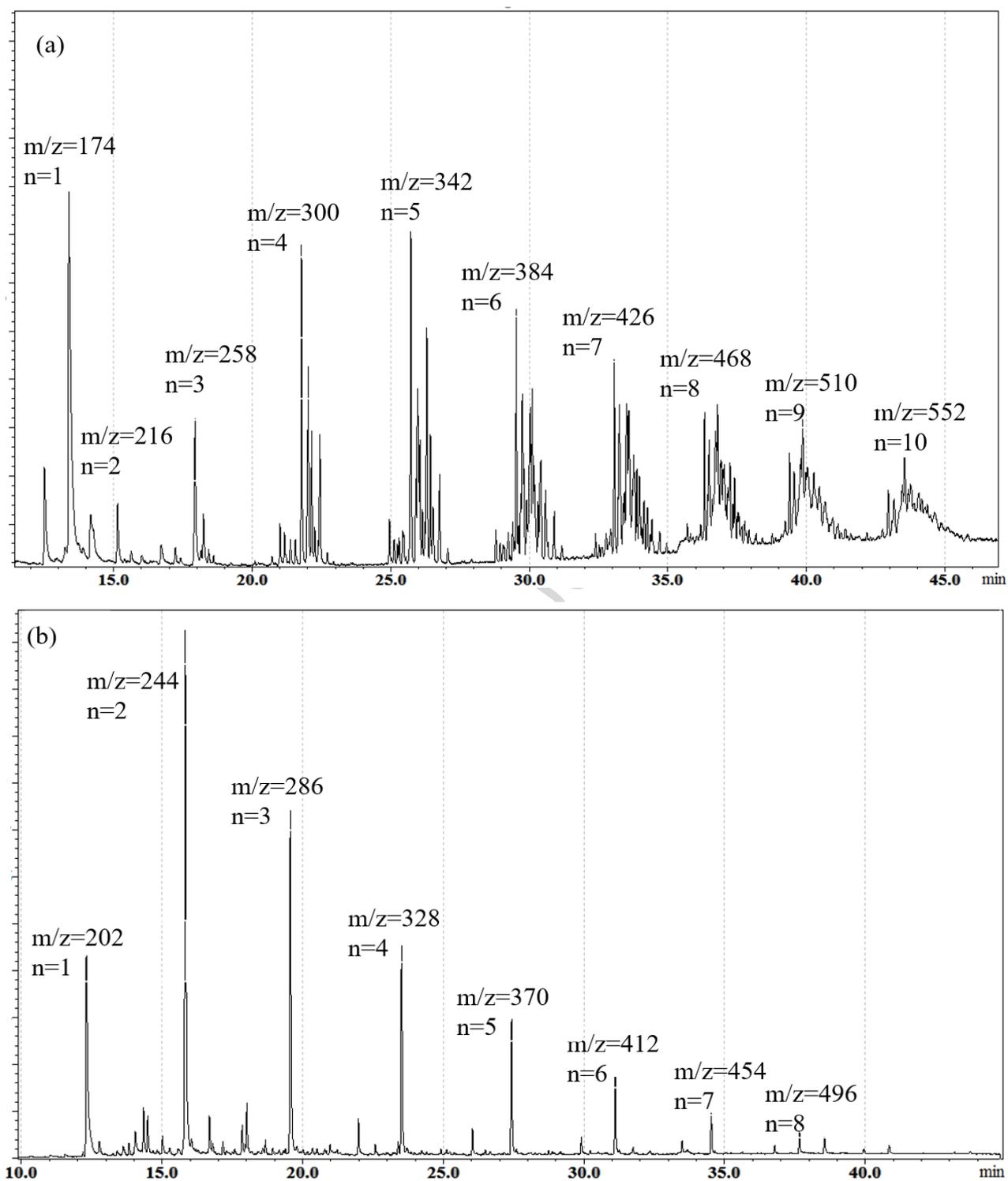
Fig. 1. Chromatogram of silylated derivatives **13,14**: (a) reaction of $AlMe_3$ with propene catalyzed by complex **3**; (b) reaction of $AlEt_3$ with propene catalyzed by complex **2**

Scheme 3. Probable mechanism of reaction of alkenes with AlR$_3$ (R= Me, Et) in the presence of complexes 1-3 and MAO.
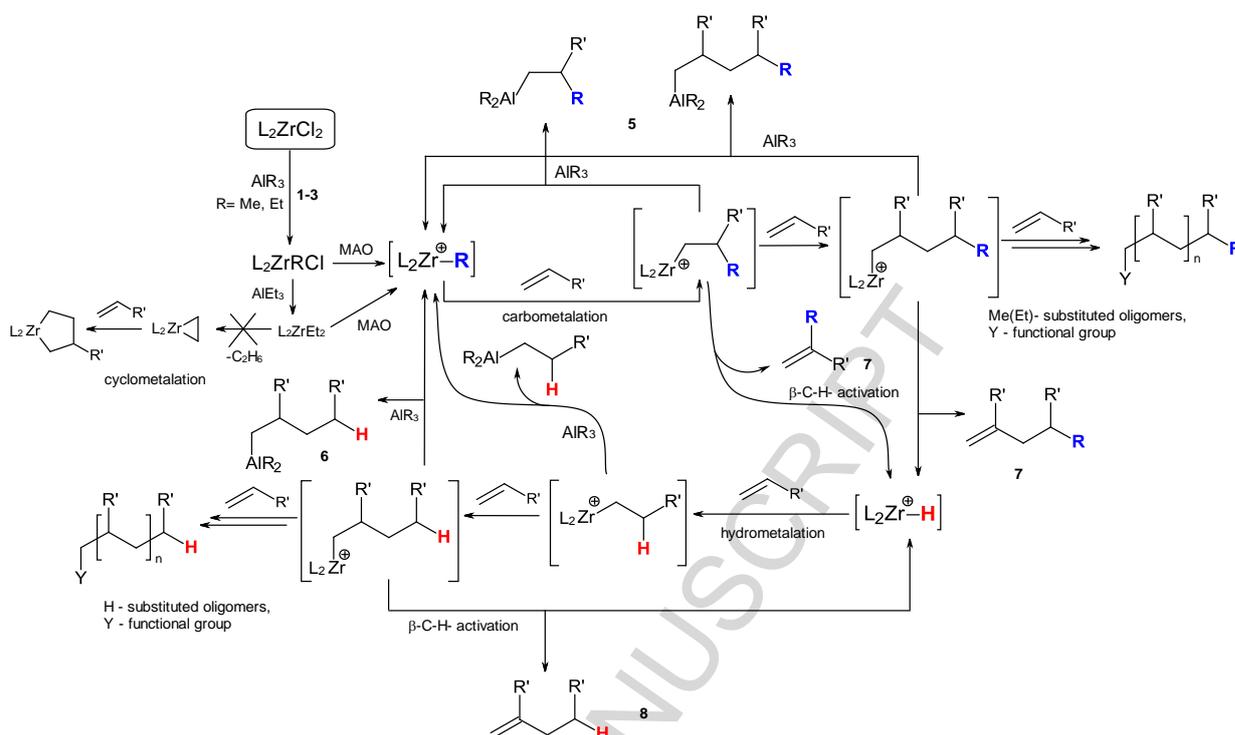
If we consider diastereoselectivity, then in the case of conformationally flexible catalyst **3**, the subsequent insertion of substrate molecules into the carbometallation product is not stereoselective (equal amounts of *R* and *S*): this means that the stereoselectivity of alkene coordination is controlled via configuration of the catalytically active site to which the substrate is coordinated (site control) rather than via the end group control (Scheme 4). For example, if A and B are the possible conformers of the catalytically active sites produced by complex **3** [13], the insertion of the first alkene molecule into the Zr-C bond proves to be faster than the transition to another conformer: this accounts for good enantioselectivity of the methylalumination (up to 70%*ee*) [34]. The branched alkyl chain formed at zirconium apparently changes the rate of transformation of one conformer to another (e.g., A to B), so that the rates of insertion of a second molecule and ligand rotation become comparable; hence, the *re* and *si* coordinations of the alkene are equally probable. In the case of the complex with the fixed geometry (C, Scheme 4), the conformational transition is impossible; this accounts for high diastereoselectivity of the dimerization and oligomerization.

Scheme 4. Conformational mobility of ligands in complexes 1-3 and diastereoselectivity of alkene insertion.
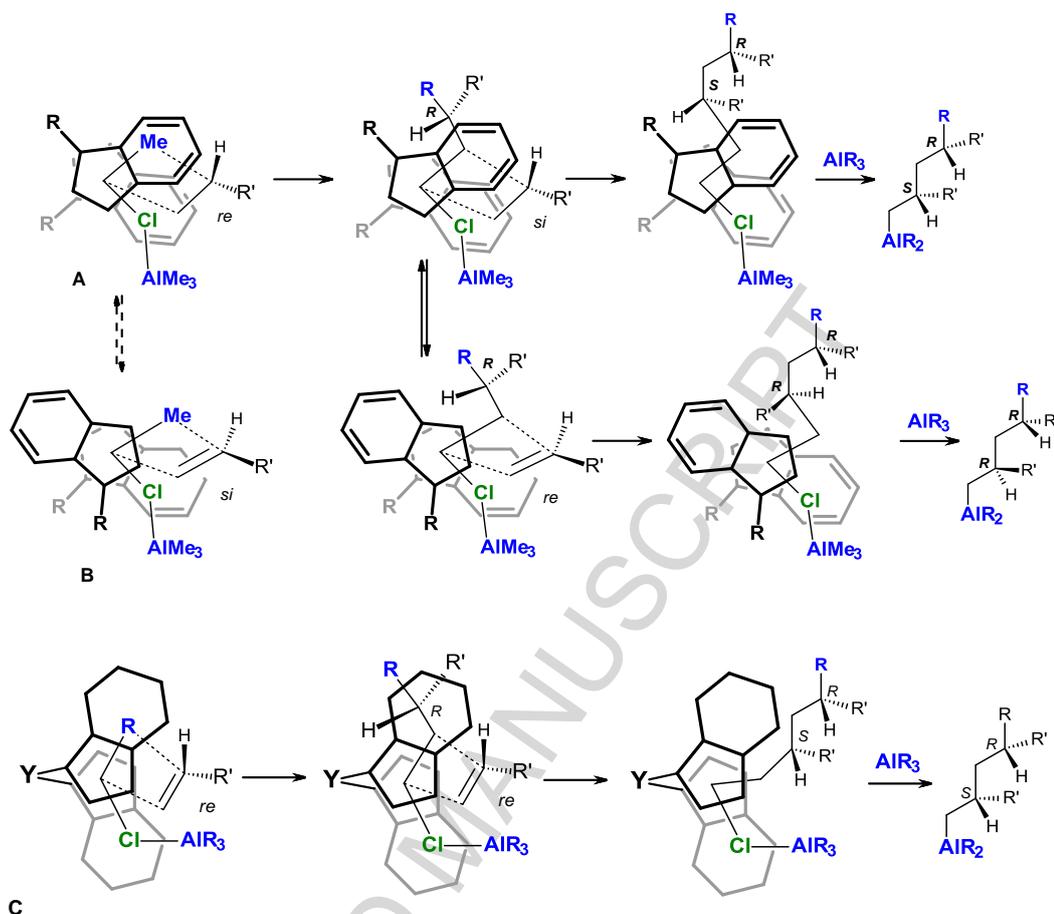
4. Conclusions

In a study of the reaction between terminal alkenes and AlR_3 (R = Me, Et) in the presence of chiral Zr complexes, rac-[Y(η^5-C_9H_{10})$_2$]ZrCl$_2$ (Y = C_2H_4, SiMe$_2$) or (NMI)$_2$ZrCl$_2$ (NMI- η^5– neomenthylindenyl), the conditions that provide chemo- and diastereoselective formation of functionally substituted oligomers were found. Comparison of the catalysts showed that complexes with rigid geometry possess higher selectivity towards oligomerization, whereas conformationally flexible complex provides carbometalation products to a greater extent. Moreover, the use of *ansa-* complexes results in high process diastereoselectivity. Thus, we showed the possibility of using Ziegler-Natta type catalytic systems for one-pot diastereoselective synthesis of functionally substituted linear alkene dimers and propene oligomers. This strategy could be subsequently used for the synthesis of a broad range of chiral stereoregular molecules suitable as building blocks for the preparation of biologically active compounds.

Acknowledgements

Supplementary data to this article can be found online at

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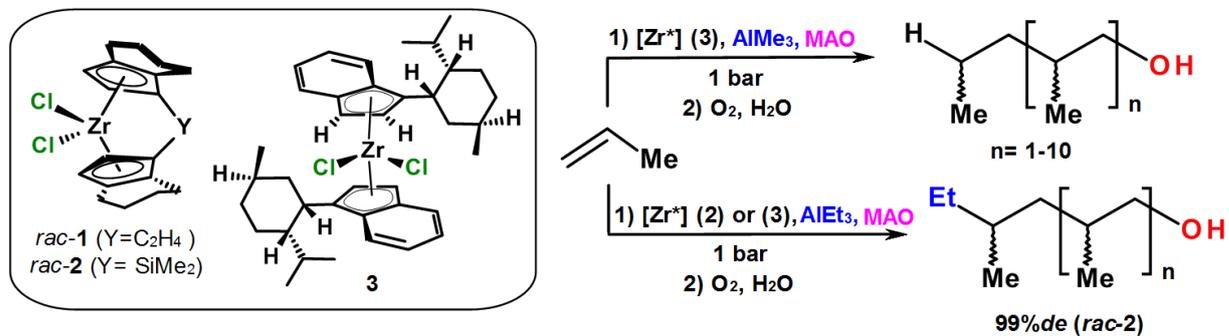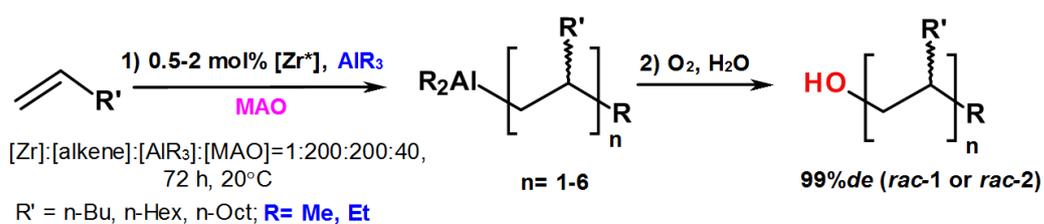
Graphical Abstract

Highlights

- Reaction of alkenes with AlR$_3$ (R = Me, Et) catalyzed by chiral Zr complexes and MAO was studied
- Ansa- zirconocenes with rigid geometry possess high chemo- and diastereoselectivity
- Diastereomerically pure functionalized alkene dimers and propene oligomers were obtained