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Catalytic Properties of Zirconocene-Based Systems in 1-Hexene Oligomerization and Structure of Metal Hydride Reaction Centers

Lyudmila V. Parfenova [1,*], Pavel V. Kovyazin [1], Almira Kh. Bikmeeva [1], Eldar R. Palatov [1], Pavel V. Ivchenko [2,3], Ilya E. Nifant'ev [2,3], Leonard M. Khalilov [1]

[1] Institute of Petrochemistry and Catalysis, Ufa Federal Research Center, Russian Academy of Sciences, 450075 Ufa, prosp. Oktyabrya, 141, Russian Federation;
[2] Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, 1-3 Leninskiye Gory, Russian Federation;
[3] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 119991 Moscow, Russian Federation
* Correspondence: luda_parfenova@ipc-ras.ru; Tel.: +7-347-284-3527

Abstract: In spite of large-scale investigations of homogeneous single-site metallocene catalysts and systems based on them, the problem of controlling their activity, chemo- and stereoselectivity with the aim of developing efficient methods for the preparation of practically useful products of alkenes transformation, such as dimers, oligomers, and polymers, still remains topical. Here we studied catalytic activity of differently structured zirconocenes (10 examples of cyclopentadienyl and indenyl complexes) and co-catalysts activating the system, namely $HAlBu^i_2$, MMAO-12 or $(Ph_3C)[B(C_6F_5)_4]$ at low activator/Zr ratios in 1-hexene oligomerization reaction. The influence of catalyst structure and system composition on alkene conversion, type of products formed and reaction stereoselectivity was investigated. The composition of hydride intermediates forming in the systems L_2ZrCl_2 (L_2= ansa-Me_2CCp_2)-$HAlBu^i_2$-activator was studied by NMR and the participation of biszirconium hydride complex as the precursor of catalytically active sites of the alkene dimerization reaction was shown.

Keywords: zirconocenes; metal hydrides; methylaluminoxane; perfluorophenyl borates; alkene dimerization; oligomerization; nuclear magnetic resonance

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1. Introduction

Catalytic systems based on metallocenes, organoaluminum compounds (OACs) and activators are well known and have been studied for almost 70 years [1]. A large scale of research is related to the possibility of efficient synthesis of practically important products – alkene dimers and oligomers as well as polymers widely known as polyalphaolefins (PAO) [2-7]. The use of metallocene complexes in these reactions allowed to transfer the classical Ziegler-Natta catalysis from heterogeneous to homogeneous medium, while the highly active and stereoselective single-site catalysts for the polymerization of unsaturated compounds became more controllable, and a detailed study of the mechanism of the process became possible. The high activity, chemo- and stereoselectivity of the metallocene complexes is a consequence of their structural features. They most efficiently ensure the stability of electronic and steric environment of transition metal atom due to the high energy of metal-ligand bond and vary the electrophilicity and geometry of catalytically active centers due to the large structural modification possibilities of π-ligand. Thus, it has been shown that the electronic and steric factor of the ligand, the nature of the activator, and the reaction conditions [8-15] determine the productivity and selectivity of catalytic systems.

Interest in the mechanisms of action of homogeneous single-site catalysts, which are constantly being improved and added due to new facts [16-22], is not diminishing. One of the trends in this field is becoming research on the role of hydride intermediates in alkene transformation processes, especially dimerization and oligomerization reactions [6, 7, 23-31], whose mechanism of action remains an open question.

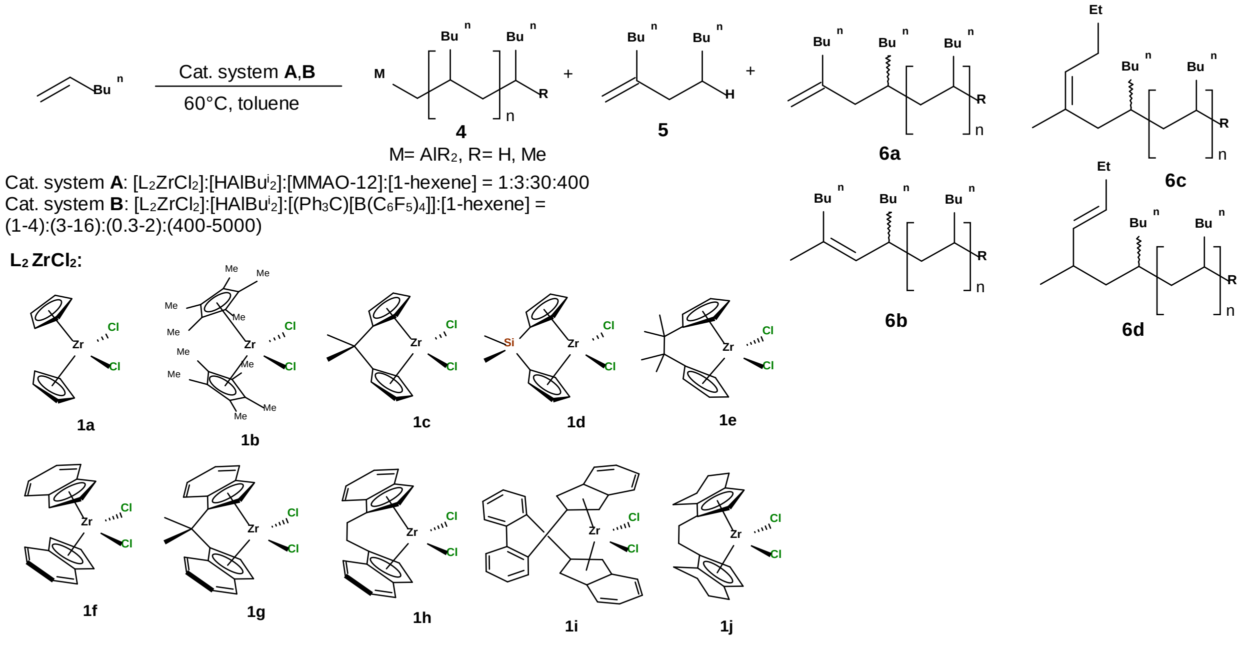
Our interest to the structural features and reactivity of IV subgroup metal hydrides is conditioned by the latest data obtained in the course of investigation of alkene transformation reactions under the action of zirconocene dichloride Cp_2ZrCl_2 or zirconocene dihydride $[Cp_2ZrH_2]_2$ and OACs in the presence of aluminum- or boron-containing activators [32-35]. The formation of bimetallic Zr,Zr-hydride intermediate in these systems was found and its ability to serve as the precursor of the specific and selective catalytic active species of alkene dimerization was shown.

2. Results and Discussion

2.1. Catalytic effect of L_2ZrCl_2-$HAlBu^i_2$-activator systems in 1-hexene oligomerization

The catalytic effect of complexes **1a-j** in the oligomerization reaction in the presence of $HAlBu^i_2$ and the activators MMAO-12 and $[Ph_3C][B(C_6F_5)_4]$ was studied. We used isobutylalane $HAlBu^i_2$ as a co-catalyst similar to $AlBu^i_3$ [6, 7, 26-28, 30] as an initiator for the formation of zirconocene hydrides, which act as catalytic active centres in these reactions [29, 30, 33-35]. Reagent ratios were chosen on the basis of our earlier works [33-35]. During the reaction under selected conditions the conversion of 1-hexene was about 99% in 1-3 h in most of the experiments performed. Decrease of alkene conversion up to 85% was observed in the reaction catalyzed by complex **1e** in the presence of MMAO-12. 1-Hexene dimer (**5**) and oligomers (**6**) of different structure are formed as main reaction products via the chain termination process by β-H elimination mechanism [36] (Scheme 1, Figures S1, S2). The presence of oligomers with various double bond positions may be due to the migration of zirconium cation via generation of allyl complexes [37, 28]. Small amounts of M-C bonded oligomers **4** were generally observed in systems containing MMAO-12. In the same systems oligomers with a methyl starting group were found.

It was shown that in the system based on zirconocene dichloride and $[Ph_3C][B(C_6F_5)_4]$ when the reaction is carried out in toluene the best result is achieved at lower content of the activator relative to Zr complex. Thus, Cp_2ZrCl_2 catalyzes the oligomerization reaction at [Zr]:[B]=1:(0.3-1) ratio. At [Zr]:[B]=1:0.3 the catalytic system is more selective in the dimerization direction (Table 1, entries 1, 4). Increase of $[Ph_3C][B(C_6F_5)_4]$ concentration in range 0.3-1 eq. causes growth the proportion of heavier oligomer with n=1-5. At the same time the selectivity of the reaction decreases as follows from the GC-MS and NMR spectra of the products which are a mixture of stereoisomers and isomers of the double bond position. In the NMR ^{13}C spectra of the oligomers obtained under these conditions, internal double bond signals are present in the δ_C 124-131 ppm region. When the reaction is carried out at the ratio [Zr]:[B]=1:2 the alkylation products - hexyl-substituted toluene is observed. An increase in the relative content of zirconocene and $HAlBu^i_2$ provides the formation of heavier products with bimodal distribution (Mw 5571 and 1578 Da) along with dimers and light oligomers (Table 1, entry 4). In the presence of MMAO-12, this system shows greater activity and selectivity towards the formation of dimers (entry 5) [31].



Scheme 1. Alkene transformations in the presence of catalytic systems L_2ZrCl_2-$HAlBu^i_2$-activator.

In the presence of complexes **1c** and **1e** with hydrocarbon-bridged cyclopentadienyl ligands, dimer **5** is formed in >94% yield (entries 8,9,12). The activity and chemoselectivity of complex **1e** appeared to be higher with activator $[Ph_3C][B(C_6F_5)_4]$ (94% dimer) compared to MMAO-12 (78% dimer) (entries 12,13).

Significant differences in the activator action were also found when the reaction was carried out in the presence of Me_2Si-bound complex **1d** (entries 10, 11). For example, application of MMAO-12 promoted the formation of dimerization product **5** in yield up to 80%, whereas application of $[Ph_3C][B(C_6F_5)_4]$ resulted in preferential formation of oligomers **6** of atactic structure, including heavy ones with a predominant value Mw 6130.

Carrying out the reaction in the presence of bulky pentamethylcyclopentadienyl complex **1b** gives mainly oligomers **6** whose mass distribution depends on the type of activator used (entries 6, 7). Under the action of $[Ph_3C][B(C_6F_5)_4]$ activator mainly short-chain oligomers with vinylidene end group are formed (according to ^{13}C NMR spectra). The heavy fraction obtained in the presence of MMAO-12 contains oligomers with a bimodal distribution (M_w 5605 and 861 Da). Moreover, here the amount of heavy oligomers is much higher than in the experiment with the sterically non-hindered complex Cp_2ZrCl_2. This indicates a significant predominance of chain growth rate over chain termination under these conditions, which may be due to the steric factor of catalytically active centres preventing β-H elimination or chain transfer to monomer or OAC. The steric factor appears to be generated here not only by the pentamethylsubstituted ligand on Zr but also by the bulk MAO counterion.

The appearance of indeneyl ligands (**1f**) including those bonded by bridges (**1g-j**) in the complexes also leads to an increased yield of oligomeric products, both in the case of MMAO-12 and $[Ph_3C][B(C_6F_5)_4]$ (entries 14-27). The reaction catalyzed by $Me_2CInd_2ZrCl_2$ (**1g**) mainly provides dimers and light oligomers with n=1-4 (entries 17-19). Heavy oligomers are formed in the system based on *rac*-$H_4C_2Ind_2ZrCl_2$ (**1h**), $[Ph_3C][B(C_6F_5)_4]$ or MMAO-12 (entries 20, 21). Hydrogenation of benzene rings of ligand in **1h** complex and transfer to **1j** provides considerable decrease of catalytic system activity - alkene conversion on 90-99% level is achieved during 3 h of reaction (entries 25-27). Moreover, the oligomeric products obtained in these experiments have, as a rule, a multimodal distribution.

For the isolated higher hexene oligomers the isotacticities in mmmm% were determined using ^{13}C NMR spectroscopy [37-40]. The most stereoselective were zirconocenes with indenyl ligands. For example, complexes **1f, 1g** and **1h** showed isotacticities of 67, 93 and 71% mmmm respectively (Table 1, entries 16, 17 and 20) (Figures S3, S4). The stereoselectivity of the catalytic systems based on zirconocenes **1i** and **1j** was below 58%mmmm. It is important to note here the dependence of the stereoselectivity on the nature of the activator used. Under the action of **1f** complex an oligomer with isotacticity of 67% was obtained in the presence of MMAO-12, while $[Ph_3C][B(C_6F_5)_4]$ provided an atactic product. The opposite picture was observed for complex **1g** with bound ligands: the highest stereoselectivity was achieved in the presence of $[Ph_3C][B(C_6F_5)_4]$. The complex $H_4C_2Ind_2ZrCl_2$ (**1h**) allows to obtain isotactic oligohexenes (61-71%mmmm) regardless of the activator type. For complexes **1i** and **1j** some increase in stereoselectivity in the presence of MMAO-12 was found. The observed dependence indicates a fine tuning of catalytically active centres in homogeneous Ziegler-Natta type systems. Probably, the stereocontrol may be carried out not only by the ligand on the transition metal atom (site control) or the growing chain (chain control), but also by the activator residing in the active centre and determining its structure and dynamics along with other factors. As stated earlier [12], the complete separation of cation-anion pair can increase the activity of the system, but lead to the loss of stereoselectivity. Strong cation-anion interactions could minimize the epimerization of the last inserted molecule, thereby increasing stereoselectivity, but at the same time cause a decrease in activity as a result of monomer coordination hinderance. PDI values close to 1 in most of the experiments suggest that the process proceeds in the living mode.

Thus, it has been shown that dimerization direction is realized with the participation of Zr complexes with sterically non-hindered cyclopentadienyl ligands (L= Cp, *ansa*-Me_2CCp_2, *ansa*-$(Me_2C)_2Cp_2$, *ansa*-Me_2SiCp_2), whereas the oligomerization is determined by the action of complexes with bulky cyclopentadienyl (L= C_5Me_5, *rac*-$H_4C_2[THInd]_2$) or electron-withdrawing indenyl (L= Ind, Me_2CInd_2, $H_4C_2Ind_2$, $BIPh(Ind)_2$) substituents. The difference in the behavior of the complexes would be primarily determined by the composition of the intermediates and their reactivity. It was supposed that hydride bimetallic intermediates may act as the active centers of dimerization and oligomerization reaction [29, 30, 33-35]. Our previous NMR study of the reaction of Cp_2ZrCl_2 or $[Cp_2ZrH_2]_2$ with OACs showed the occurrence of Zr,Zr-hydride complexes, which activation by MMAO-12 or organoboron compounds ($[Ph_3C][B(C_6F_5)_4]$, $B(C_6F_5)_3$) affords active species responsible for dimer formation [32-35].

Table 1. Catalytic activity and chemoselectivity of systems L_2ZrCl_2-$HAlBu^i_2$-activator in the reaction with 1-hexene in toluene, 60°C.

Entry	Catalytic systems		Mole ratio [Zr]:[$HAlBu^i_2$]:[activator]:[1-alkene]	Time, min	Alkene conversion, %	Light fraction yield, wt.%	Light fraction product composition, % (GC-MS)						Heavy fraction yield, wt.% (GPC)	M_W, Da	M_N, Da	M_W/M_N	Tacticity, mmmm%	Oligomer structural type
	Complex	Activator					5	6										
								n=1	n=2	n=3	n=4	n=5						
1	Cp_2ZrCl_2 **(1a)**	$(Ph_3C)[B(C_6F_5)_4]$	1:3:0.3:400	60	95	98	61	21	10	6	2	-	2	6211	6129	1.01	atactic	**6b-d**
2			1:3:1:400		>99	99	30	28	20	10	8	4	-					
3			1:3:2:400		>99[b]								33	5277	5208	1.01		
4			4:16:1:400		>99	88	61	5	12	8	8	5	2 10	5571 1578	5459 1211	1.02 1.30		
5		MMAO-12 [31]	1:3:30:400	5	98		97						-					
6	$(C_5Me_5)_2ZrCl_2$ **(1b)**	$(Ph_3C)[B(C_6F_5)_4]$	4:16:1:400	180	99	44	0	27	18	30	24		55	1109	933	1.19	atactic	**6a**
7		MMAO-12	1:3:30:400	60	99	3	28	23	17	16	16		71 26	5605 861	5906 798	1.05 1.08	atactic	**4, 6a**[e]
8	$Me_2CCpZrCl_2$ **(1c)**	$(Ph_3C)[B(C_6F_5)_4]$	4:16:1:400	60	>99		95	4					-					
9		MMAO-12	1:3:30:400	60	>99		94	6					-					
10	$Me_2SiCp_2ZrCl_2$ **(1d)**	$(Ph_3C)[B(C_6F_5)_4]$	4:16:1:400	180	>99	5	17	28	15	21	18		89 6	6130 2769	6041 2672	1.02 1.04	atactic	**6a, 6d**
11		MMAO-12	1:3:30:400	60	>99	99	80	16	4				-					
12	$(Me_2C)_2CpZrCl_2$ **(1e)**	$(Ph_3C)[B(C_6F_5)_4]$	4:16:1:400	60	>99	99	98	1					-					
13		MMAO-12	1:3:30:400	60	85		78	7					-					
14	Ind_2ZrCl_2 **(1f)**	$(Ph_3C)[B(C_6F_5)_4]$	1:3:0.3:400	180	>99	96	7	23	32	21	17		3	6307	6200	1.02	atactic	**6a-d**
15			4:16:1:400	60	>99	63	0	22	20	26	31		36	988	869	1.14	atactic	**6a**
16		MMAO-12	1:3:30:400	60	>99	27	6	15	17	19	43		72	2182	1599	1.36	isotactic (67%)	**4, 6a,d**
17	*rac*-$Me_2CInd_2ZrCl_2$ **(1g)**	$(Ph_3C)[B(C_6F_5)_4]$	1:3:0.3:400	60	97	70	22	21	20	19	18		27	6359	6291	1.01	isotactic (93%)	**6d**
18			4:16:1:400	60	>99	72	79	10	5	4	2		24 3	5585 903	5144 871	1.08 1.04	isotactic (76%)	**6a-d**
19		MMAO-12	1:3:30:400	60	>99	55	4	33	33	18	12		44	1081	927	1.17	atactic	**4, 6a-d**[e]
20	*rac*-$H_4C_2Ind_2ZrCl_2$ **(1h)**	$(Ph_3C)[B(C_6F_5)_4]$	4:16:1:400	60	>99								99	6396	6285	1.02	isotactic (71%)	**6a-d**
21		MMAO-12	1:3:30:400	60	>99	5	7	22	22	24	25		94	6347	6287	1.01	isotactic (61%)	**4, 6a,d**
22	$BIPh(Ind)_2ZrCl_2$	$(Ph_3C)[B(C_6F_5)_4]$	1:3:0.3:400	180	47[c]	25	13	49	23	15			22	6037	6125	1.01		

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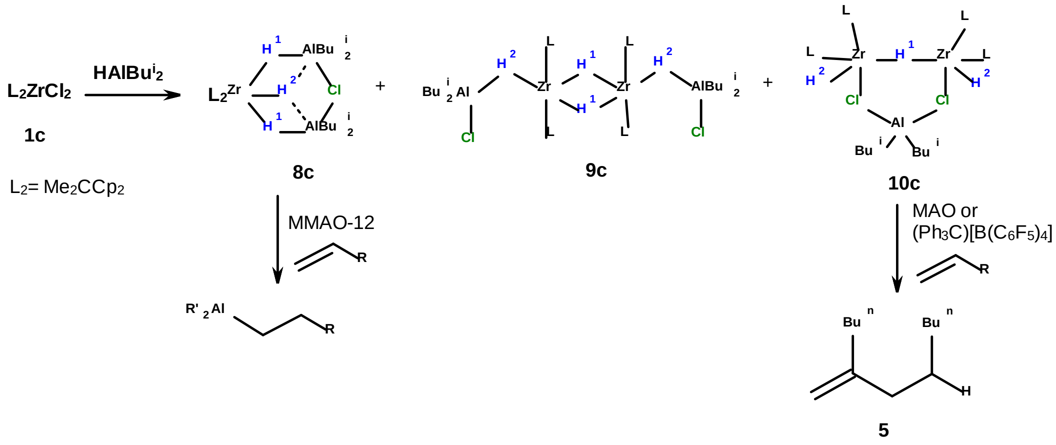
23	(**1i**)		4:16:1:400	60	>99[c]	59	7	21	26	14	32		40	1096	1003	1.09	isotactic (33%)	**6a**
24		MMAO-12	1:3:30:400	60	>99[c]	9	3	20	25	23	29		20 70	5742 2159	5657 1532	1.02 1.4	isotactic (45%)	**4, 6a**[e]
25	*rac*-H_4C_2[THInd]$_2$ZrCl_2 (**1j**)	(Ph$_3$C)[B(C_6F_5)$_4$]	1:3:0.3:400	180	89[d]	69	13	18	20	15	14	12	10 10	6131 960	6048 909	1.02 1.06		
26			4:16:1:400	180	>99	11	29	19	18	17	17		88	5530	5033	1.10	isotactic (38%)	**6a-d**
27		MMAO-12	1:3:30:400	180	95	8	11	24	24	23	18		38 19 30	6159 3145 2074	6103 3114 1971	1.01 1.01 1.06	isotactic (58%)	**6a-d**

[a] Hydrometalation products (3%), monoalkylsubstituted toluene (12%) and dialkylsubstituted toluene (8%) were detected in the mixture; [b] Monoalkylsubstituted toluene (77%), dialkylsubstituted toluene (19%) and trialkylsubstituted toluene (4%) were detected; [c] tetramers - "dimer of dimers" (15%) are formed in the presence of both activators; [d] yield of oligomers with n=6 up to 7%; [e] Me starting group.

2.1. NMR study of catalytic systems $Me_2CCp_2ZrCl_2$-$HAlBu^i_2$-activator

To establish the effect of the transition metal ligand environment on the structure and reactivity of hydride intermediates, we have studied systems consisting of zirconocene with *ansa*-cyclopentadienyl ligands **1c**, $HAlBu^i_2$, MMAO-12 or ionic activator $[Ph_3C][B(C_6F_5)_4]$.

It was found that the composition of the reaction mixture formed in the course of the reaction of $Me_2CCp_2ZrCl_2$ with $HAlBu^i_2$ depends largely on the ratio of the starting reagents. For example, in the ^1H NMR spectrum of the mixture of **1c** and $HAlBu^i_2$ taken in the molar ratio [Zr]:[Al]=1:3, signals of hydride atoms are registered at δ_H -1.44 (H^1) and 1.29-1.43 ppm (H^2) correlated with each other in the COSY HH experiment (at 250 K) (Figures S5, S6). The ratio of signal intensities H^1:H^{Cp}:H^{Cp} was 2:4:4. The NOESY spectrum exhibited opposite phase cross-peaks of these protons with Cp-ring signals at δ_H 6.11 and 5.19 ppm, and a isopropylidene bridge methyl group signal at δ_H 1.03 ppm (Figure S7). At 298 K, the hydride atom signals were significantly broadened and peaks corresponding to the chemical exchange between H^1, H^2, $HAlBu^i_2$ monomer and oligomers were registered in the NOESY spectra (Figure S8). On the basis of these results and literature data for similar molecules with other π-ligands [41-44] the observed signals were assigned to the trihydride complex **8c** as the most probable structure (Scheme 2, Table 2). Moreover, the C_{2v} symmetry of the complex also corresponds to the observed NMR pattern.



Scheme 2. Reaction of $Me_2CCp_2ZrCl_2$ with $HAlBu^i_2$, activators and alkene.

Under conditions of $HAlBu^i_2$ deficiency (ratio [Zr]:[Al]=1:1.7) the upfield signals at δ_H -1.10 (H^1) and -0.81 (H^2) ppm, correlated with each other in the COSY HH spectrum, was recorded in addition to the signals of unreacted complex **1c** (Figures S10, S11). The downfield part of the spectrum contained signals of four non-equivalent protons of the cyclopentadienyl ligand at δ_H 6.28, 6.23, 5.66, and 5.37 ppm. The observed decrease in the symmetry of the structure, the ratio of H^1:H^2:H^{Cp}:H^{Cp}:H^{Cp}:H^{Cp} signal intensities equal to 1:1:2:2:2:2, and the literature data [42, 44] allow to identify the structure as **9c**. Also, a triplet signal at δ_H -3.58 ppm with low intensity was observed in the ^1H NMR spectrum, correlating with a doublet signal at δ_H -1.34 ppm in the COSY HH spectra (Figure S10). The spin-spin coupling constants J=17.9 Hz for these signals are typical of the biszirconium structures $[Cp_2ZrH_2 \cdot Cp_2ZrHCl \cdot ClAlR_2]$ we found earlier [32-35]. Therefore, these resonance lines were attributed to the **10c** complex.

The addition of MMAO-12 to the mixture obtained in the reaction of $Me_2CCp_2ZrCl_2$ and $HAlBu^i_2$ at a ratio of 1:(3-8) and containing the trihydride intermediate **8c** leads to the broadening of both hydride atom signals and cyclopentadienyl ring signals of complex **8c** (Figures 1, S13), which may indicate its association with methylaluminoxane. According to theoretical data, zirconium hydride complexes have a high affinity for this activator and are able to produce stable adducts [45]. In addition, the high tendency of methylalumoxane is known to absorb hydrides which, when exchanged with methyl groups, give H-substituted MAO [46]. This was also confirmed in our studies: in the NOESY spectra of the mixture of MMAO-12 and $HAlBu^i_2$ a negative effect was observed for methyl groups at -0.14 ppm, isobutyl groups at 0.56 and 1.29 ppm, and H-Al(MAO) signals at 3.30-4.30 ppm (Figures S11, S12), indicating that these groups belong to the macromolecule. It also follows from the NOESY spectra that the association of **8c** with MAO preserves the possibility of hydride exchange with H-Al(MAO) (Figure S14).

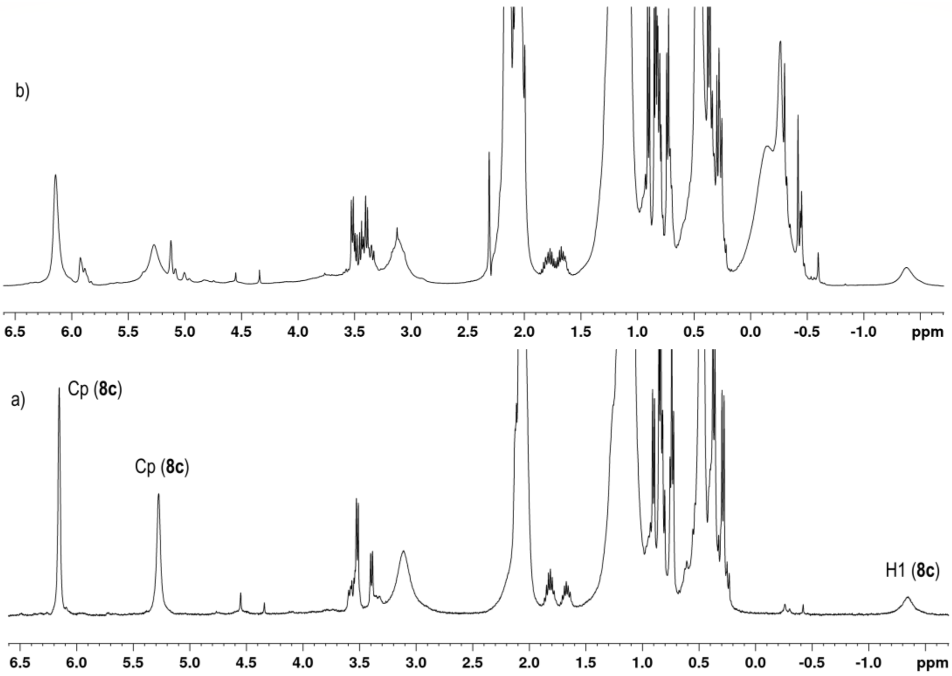


Figure 1. ^{1}H NMR of system $Me_2CCp_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ − MMAO-12 in C_7D_8 (298 K): a) [Zr]:[Al]:[Al_{MAO}] = 1:8:0; b) [Zr]:[Al]:[Al_{MAO}] = 1:8:11.

Table 2. ^{1}H and ^{13}C NMR (δ, ppm, 400.13 MHz (^{1}H), 100.62 (^{13}C)) of complexes **8c**–**10c** in $C_6D_5CD_3$.

Complex	Activator	T, K	δ_H Cp	δ_C Cp	δ_H H^1	δ_H H^2
8c		250 K	6.11 (s, 4H) 5.19 (s, 4H) 1.03 (s, 12H)	110.9 110.3 100.8 36.8 22.3	-1.44 (br.s, 2H)	1.29-1.43 (br.s, 1H)
9c			6.28 (s, 2H) 6.23 (s, 2H) 5.66 (s, 2H) 5.37 (s, 2H) 1.15 (NOESY) 1.12 (NOESY)		-1.10 (br.s, 1H)	-0.81 (br.s, 1H)
10c		298 K			-3.58 (t, 17.9 Hz, 1H)	-1.34 (d, 17.9 Hz, 2H)
10c·MAO	MMAO-12	298 K	6.12 (NOESY) 5.67 (NOESY) 5.42 (NOESY) 4.85 (NOESY) 0.98 (NOESY)	119.6 108.7 101.2 98.2 21.1	-3.57 (t, 17.6 Hz, 2/3H) -3.71 (t, 18.0 Hz, 1/3H)	-1.32 (d, 17.6 Hz, 2H) -0.56 − 0.15 (MAO)
10c[a]	$[Ph_3C][B(C_6F_5)_4]$	298 K			-3.59 (t, 18.3 Hz, 2H)	-1.34 (d, 18.3 Hz, 2H)

[a] The complex was observed after the addition of $[Ph_3C][B(C_6F_5)_4]$.

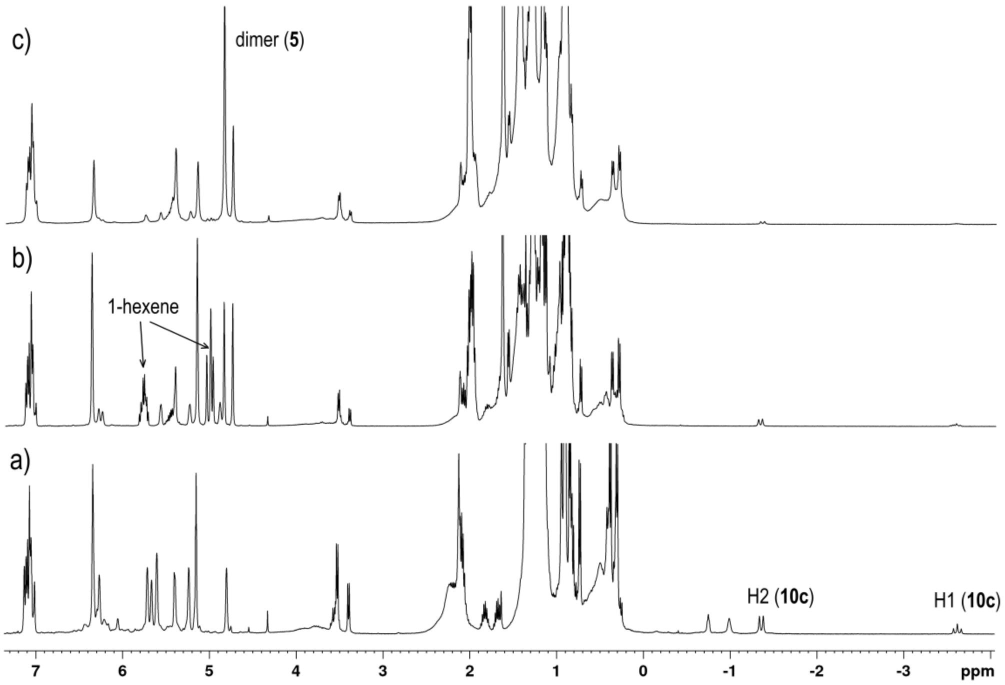


Figure 2. NMR monitoring of the reaction of hydride complexes with 1-hexene in $C_6D_5CD_3$ (intensity of upfield signals is increased): (a) system $Me_2CCp_2ZrCl_2$ (**1c**) − $HAlBu^{i}_2$ – $(Ph_3C)[B(C_6F_5)_4]$, [Zr]:[Al]:[B] = 1:1:0.1; (b) [Zr]:[Al]:[B]:[1-alkene] = 1:1:0.1:1.5, 5 min; (c) [Zr]:[Al]:[B]:[1-alkene] = 1:1:0.1:1.5, after keeping the ampoule at 60 °C for 5 minutes.

Under conditions of $HAlBu^{i}_2$ deficiency, when complexes **9c** and **10c** exist in the catalytic system, the addition of MMAO-12 is accompanied by the appearance of a heavy fraction and a doubling of the triplet at δH -3.58 ppm belonging to **10c**, whereas the signals of complex **9c** remain virtually unchanged (Figures S15, S16). The negative NOE effect indicates an increase in the molecular weight of the complex, which may be due to the formation of a stable **10c·MAO** conjugate similar to the biscyclopentadienyl complex [33, 35] (Figure S17).

Addition of $[Ph_3C][B(C_6F_5)_4]$ to complex **8c** formed in the system $Me_2CCp_2ZrCl_2$–$HAlBu^{i}_2$ (1:1) leads to a change in equilibrium due to the reaction of $HAlBu^{i}_2$ with organoboron reagent, resulting in the recovery of the original zirconocene dichloride and the appearance of complexes **9c** and **10c** (Figures S18, S19). With time the signals of complex **9c** disappeared in the NMR spectrum.

To clarify the reactivity of the complexes towards the alkene, 1-hexene was added to the systems containing various intermediates in different ratios. After addition of alkene to the reaction media with **10c·MAO** conjugate the appearance of hydrometalation products were observed (Figure S19). The formation of dimers was detected only in systems containing **10c** intermediate when the reaction mixture was heated to 60°C for several minutes (Figure 2).

Thus, the NMR study of systems **1c**-$HAlBu^{i}_2$-activator demonstrated the formation of various hydride clusters, among which the biszirconium hydride intermediate $[L_2ZrH_2{\cdot}L_2ZrHCl{\cdot}ClAlR_2]$ may be the precursor of the active centers which determine the dimerization direction.

3. Materials and Methods

3.1. General Procedures

All operations for organometallic compounds were performed under argon according to Schlenk technique. Complexes Cp_2ZrCl_2 (**1a**) [47], $Me_2CCpZrCl_2$ (**1c**) [48], $Me_2SiCp_2ZrCl_2$ (**1d**) [49], $(Me_2C)_2CpZrCl_2$ (**1e**) [50], Ind_2ZrCl_2 (**1f**) [51], *rac*- $Me_2C(Ind)_2ZrCl_2$ (**1g**) [52], BIPh(Ind)$ZrCl_2$(**1i**) [53] were synthesized from $ZrCl_4$. Commercially available $(C_5Me_5)_2ZrCl_2$ (**1b**) (97%, Acros), *rac*-$C_2H_4Ind_2ZrCl_2$ (**1h**) (Strem), *rac*-$C_2H_4(THInd)_2ZrCl_2$ (**1j**) (97%, Merck), $HAlBu^{i}_2$ (99%, Merck), MMAO-12 (7% wt Al in toluene, Merck), $(Ph_3C)[B(C_6F_5)_4]$ (97%, Abcr), 1-hexene (97%, Acros) were involved into the reactions. The solvents (THF, toluene, benzene) were dried over $AlBu^{i}_3$ and distilled immediately prior to use.

CAUTION: pyrophoric nature of aluminum alkyl and hydride compounds require special safety precautions in their handling.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^{1}H), 100.62 MHz (^{13}C)) (Bruker, Rheinstetten, Germany). As the solvents and the internal standards, C_7D_8 and $CDCl_3$ were employed. 1D and 2D NMR spectra (COSY HH, HSQC, HMBC, NOESY) were recorded using standard Bruker pulse sequences.

The analysis of the oligo(1-hexenes) by NMR spectroscopy was carried out according to Refs. [36-39].

The ratio of the light and heavy fractions, the Mw and Mn of oligo(1-hexenes) were determined on a SHIMADZU gel permeation chromatograph, with a RID-20A detector equipped with a PSS column, toluene was used as a solvent at a flow rate of 1 ml/min. The measurements were carried out at 25°C, the standard was polystyrene.

The light products were analyzed using a gas chromatograph-mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Tokyo, Japan) equipped with the GC-2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan).

*3.2. Reaction of L_2ZrCl_2 (**1a-j**) with $HAlBu^{i}_2$, MMAO-12 or $(Ph_3C)[B(C_6F_5)_4]$ and 1-hexene*

A flask with a magnetic stirrer was filled under argon with 10 mg (0.018-0.034 mmol) of L_2ZrCl_2, 0.01-0.018 mL (0.055-0.103 mmol) of $HAlBu^{i}_2$, 0.23-0.44 mL (0.55-1.02 mmol) of MMAO-12, 0.002-0.004 mL (0.018-0.034 mmol) of 1-hexene and 0.5 mL of C_7D_8. For organoboron activator $(Ph_3C)[B(C_6F_5)_4]$ the following amounts were used: 10 mg (0.018-0.034 mmol) of L_2MCl_2, 0.0097-0.018 mL (0.0546-0.103 mmol) of $HAlBu^{i}_2$, 4-63 mg (0.0045-0.0684 mmol) of $(Ph_3C)[B(C_6F_5)_4]$, 0.002-1.7 mL (0.018-13.7 mmol) of 1-hexene and 0.5 mL of toluene. The reaction was carried out with stirring at temperature 60°C. After 60 and 180 min, samples (0.1 mL) were syringed into tubes filled with argon, and the samples were decomposed with 10% HCl or DCl at 0°C. Products were extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4. The yields of products were determined by GC/MS.

3.3. NMR study of the reaction of $Me_2CCp_2ZrCl_2$ with $HAlBu^{i}_2$ and activator (MMAO-12, $(Ph_3C)[B(C_6F_5)_4]$)

NMR tube was charged with 0.029-0.045 mmol (9.8-15 mg) of $Me_2CCp_2ZrCl_2$ and C_7D_8 in an argon-filled glovebox. The tube was cooled to 0°C and 0.03-0.25 mmol (3.8-36 mg) of $HAlBu^{i}_2$ was added dropwise. The mixture was stirred and the formation of complexes **8-10** was monitored by NMR. Then 0.17-0.34 mmol (65.4-0.131 mg) of MMAO-12 or 0.005-0.022 mmol (4.7-20 mg) of $(Ph_3C)[B(C_6F_5)_4]$ were added.

5. Conclusions

To reveal the regularity of metallocene-AOC-activator catalytic systems action we studied activity, chemo- and stereoselectivity of η^5-zirconium complexes in the presence of $HAlBu^{i}_2$, MMAO-12 or $[Ph_3C][B(C_6F_5)_4]$ in 1-hexene oligomerization. Depending on the composition of the catalytic system, the formation of 1-hexene vinylidene dimer and oligomers, 1,2-insertion products with different double bond positions, were observed.

The dimerization pathway is realized, as a rule, in the presence of Zr complexes with sterically non-hindered cyclopentadienyl ligands (L= Cp, *ansa*-Me_2CCp_2, *ansa*-$(Me_2C)_2Cp_2$, *ansa*-Me_2SiCp_2). The use of zirconocenes with bulky cyclopentadienyl (L= C_5Me_5, *rac*-$H_4C_2[THInd]_2$) or electron-withdrawing indenyl (L= Ind, Me_2CInd_2, $H_4C_2Ind_2$, BIPh(Ind)$_2$) substituents resulted in the formation of oligomers.

Indenyl complexes (L= Ind, Me_2CInd_2, $H_4C_2[Ind]_2$) showed the highest values of isotacticity at 67, 93, 71%mmmm, respectively. Moreover, stereoselectivity was notably dependent on the type of activator, suggesting a significant influence of the co-catalyst on the stereoregulation process in the course of alkene coordination by the catalytically active species.

Considerable differences in catalyst action are indicative of the realization of dimerization and oligomerization processes through different active centers, including hydride intermediates. On the example of the reaction of *ansa*-$Me_2CCp_2ZrCl_2$ with $HAlBu^{i}_2$ and activators the composition of hydride intermediates was studied by NMR spectroscopy. As a result, biszirconium complex of type $[L_2ZrH_2{\cdot}L_2ZrHCl{\cdot}ClAlR_2]$ which is the precursor of catalytically active centers of the alkene dimerization was found.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figures S1-S20: NMR spectra of reaction products and intermediates.

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