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Alkene and Olefin Functionalization by Organoaluminum Compounds, Catalyzed with Zirconocenes: Mechanisms and Prospects

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Additional information is available at the end of the chapter

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Abstract

Alkene and olefin functionalization via addition of electro- or nucleophilic reagents is one of the convenient synthetic methods for the insertion of heteroatoms into organic molecules. The use of organometallic reagents in these reactions in combination with the specific catalysts provides high substrate conversion and process selectivity. The introduction of this approach into the chemistry of organoaluminum compounds leads to the development of chemo-, regio- and stereoselective catalytic methods of alkene and olefin functionalization. The chapter focuses on the modern concepts of the alkene hydro-, carbo- and cycloaluminum mechanisms, that is, the experimental and theoretical data on the intermediate structures involved in the product formation, the effects of the catalyst and organoaluminum compound structure, reaction conditions on the activity and selectivity of the bimetallic systems. The prospects of the development of enantioselective methods using these catalytic systems for the alkene and olefin transformations are considered.

Keywords: hydrometalation, carbometalation, cyclometalation, zirconocenes, organoaluminum compounds, reaction mechanism, asymmetric catalysis


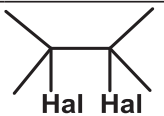
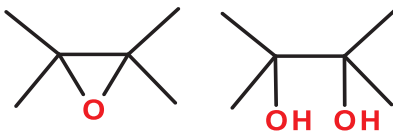
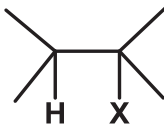
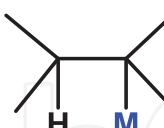

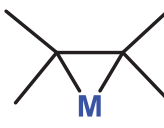
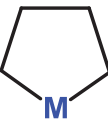
1. Introduction

Insertion of various functional groups into the molecules is one of the central problems of organic chemistry. In this regard, alkene and olefin double bonds are often considered as possible

reactive centers for the construction of C-heteroatom fragments. The classic functionalization methods are based on the addition reaction of electro- or nucleophilic reagents toward the unsaturated substrates, for example, halogenation, oxidation, hydrohalogenation, hydroboration, hydroamination, hydrosilylation, hydro- and carbometalation, etc. (Table 1).

Each type of functionalization goes under specific conditions and involves various reagents and catalysts, which obviously affects the mechanisms of the processes and product structure. Thus, this chapter is focused on the reactions of alkenes with organometallic compounds as the effective routes for the synthesis of numerous classes of organic compounds.

Reactions of alkenes with organometallic reagents run with high substrate conversion and selectivity due to the generation of active intermediates with C-metal bonds (Table 1), further modification of which provides a wide range of products. The organoaluminum compounds (OACs) occupied a strong position in the chemistry of alkenes and olefins [1–11]. The acyclic and cyclic products bearing organoaluminum moiety obtained as a result of hydro-, carbo- and cycloalumination require no further separation and could be readily modified to alcohols,

Substrate	Reagent	Product
	Hal ₂	
	[O]	
	H-X X = Hal, OH, SO ₄ , NR ₂ , BR ₂ , SiR ₃ , PO(OR) ₂ etc.	
	M-H M = Li, Mg, Al, Zn, Zr, etc. Catalysts: [Ti], [Zr], [Co], [Ni]	 hydrometalation
	M-R M = Li, Mg, Al, Zn, Zr, etc. R = Alk, Ar, Allyl Catalysts: [Cu], [Ti], [Zr], [Ni], [Fe], [Co]	 carbometalation
	M-R M = Mg, Al, Zr etc. R = Alk, Alkenyl Catalysts: [Ti], [Zr], [Hf]	 cycloalumination
		

Section 2.1.

M = Al (OAC)

Catalysts:

 $(\eta^5\text{-L})_2\text{ZrCl}_2$

Sections 2.2, 3

M = Al (OAC)

Catalysts:

 $(\eta^5\text{-L})_2\text{ZrCl}_2$

Sections 2.2, 3

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Catalysts:

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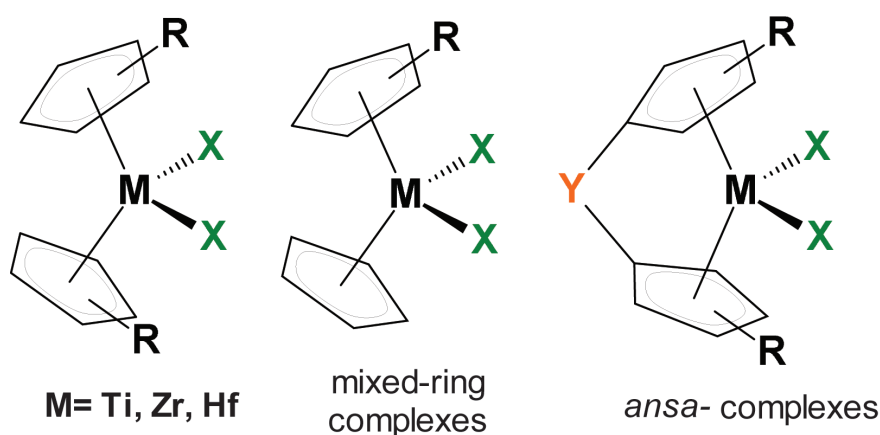
Table 1. Alkene and olefin functionalization via addition reactions.

halides, heterocycles, carbocycles and others [9, 12–18]. For example, the well-known Ziegler-Alfol process for the synthesis of higher and linear primary alcohols from ethylene [12] has been realized in the industrial scale.

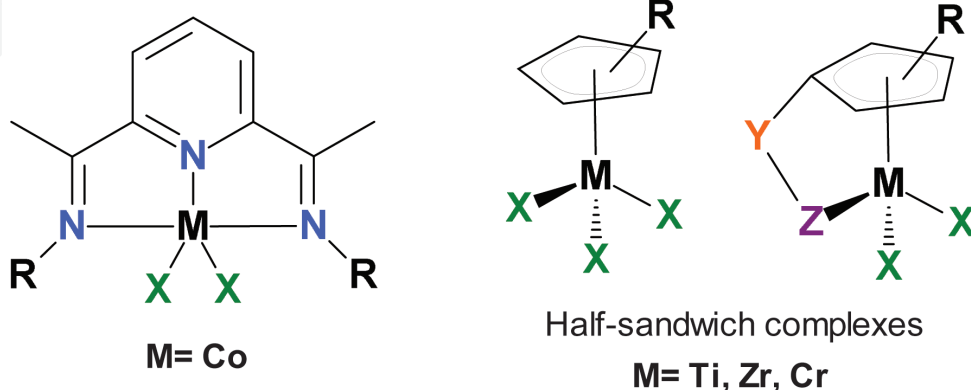
The application of transition metal complexes as catalysts enables the reactions of OAC and alkenes to proceed under mild conditions with chemo- and stereoselectivity control. Among the complexes Group IV transition metals played a significant role in the development of alkene functionalization methods using OAC. Structural types of catalysts can be varied from metal salts to metallocenes and postmetallocenes (**Scheme 1**). The special milestone in this research is the discovery of metallocene catalysis, which serves as an effective tool for the stereochemistry regulation via η^5 -ligand structure variation and provides an opportunity to a comprehensive study of the reaction mechanisms.

The future development of these methods needs understanding the reaction mechanisms: how the OAC nature, reaction conditions, catalyst and alkene structure regulate the substrate conversion, chemo- and enantioselectivity; what kinds of intermediates define the process pathways. Among the mechanistic studies much attention has been paid to the catalytic systems

η^5 - Complexes (metallocenes):



Postmetallocenes:



Scheme 1. Structural types of transition metal complexes applied as catalysts in alkene hydro-, carbo- and cycloalumination.

based on zirconocenes due to several reasons. First, a broad range of catalytic reactions can be implemented in these systems, from hydro-, carbo- and cyclometalation to polymerization of unsaturated compounds. Second, these systems are convenient for fundamental investigations, since η^5 -ligands bound to zirconium atoms act like magnetic probes indicating the electronic state of the transition metal atom and reflecting the molecule symmetry. Third, the reaction times and intermediate lifetimes appear to be convenient for nuclear magnetic resonance (NMR) monitoring, which is the most informative method for the studies of homogeneous catalytic reactions. Moreover, the systems are substantially free of paramagnetic species, which, for example, in the case of titanium complexes, preclude observation of the genesis of intermediates due to pronounced NMR signal broadening.

Thus, the chapter presents the results on the experimental and theoretical studies of the mechanisms of alkene hydro-, carbo- and cyclometalation by organoaluminum compounds (AlR_3 and XAlBu^i), catalyzed with zirconium η^5 -complexes. The factors that determine the intermediate reactivity and, consequently, the activity of the catalytic systems, reaction pathway and enantioselectivity are considered. The prospects of the development of stereoselective methods using these catalytic systems for the alkene and olefin transformations are discussed.

2. Mechanisms of alkene functionalization, catalyzed by zirconium η^5 -complexes

2.1. Mechanism of zirconocene catalysis in alkene hydroalumination

The catalytic alkene hydroalumination has found wide application as an efficient regio- and stereoselective method for the double and triple bond reduction providing important syntheses for organic and organometallic chemistry [4, 13–15]. Various transition metal complexes can be used as the catalysts of the reaction, however, the compounds based on the metals with no vacant d orbital show much less activity in the reaction (e.g., Cu, Zn vs. Ti, Zr, Co, Ni) [16–21]. Moreover, the significant effect of the OAC nature and ligand structure on the hydrometalation product yield has been shown [22, 23].

Studies on the catalytic activity of the systems $\text{L}_2\text{ZrCl}_2\text{-XAlBu}^i_2$ ($\text{L} = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, Ind, C_5Me_5 ; $\text{L}_2 = \text{rac-Me}_2\text{C(2-Me-4-Bu}^t\text{-C}_5\text{H}_2)_2$, $\text{meso-Me}_2\text{C(2-Me-4-Bu}^t\text{-C}_5\text{H}_2)_2$, $\text{rac-Me}_2\text{C(3-Bu}^t\text{-C}_5\text{H}_3)_2$, $\text{rac-Me}_2\text{C(Ind)}_2$, $\text{rac-Me}_2\text{Si(Ind)}_2$ and $\text{rac-C}_2\text{H}_4(\text{Ind})_2$; $\text{X} = \text{H, Cl, Bu}^i$) in the alkene hydroalumination [22, 23] showed that the most active catalytic systems are those based on the Zr complexes with sterically hindered ligands in combination with HAlBu^i_2 (**Figure 1**). Catalysts with less bulky ligands are most active in the reaction of alkenes with AlBu^i_3 or ClAlBu^i_2 .

The reaction mechanism (e.g., see [16–21]) implies the generation of transition metal hydride L_nMH formed upon σ -ligand exchange; then this species coordinates alkene to give an alkyl derivative. In the last step, as a result of the transmetalation of alkyl fragment from M to Al, the organoaluminum product is formed and the transition metal hydride is recovered (**Scheme 2**).

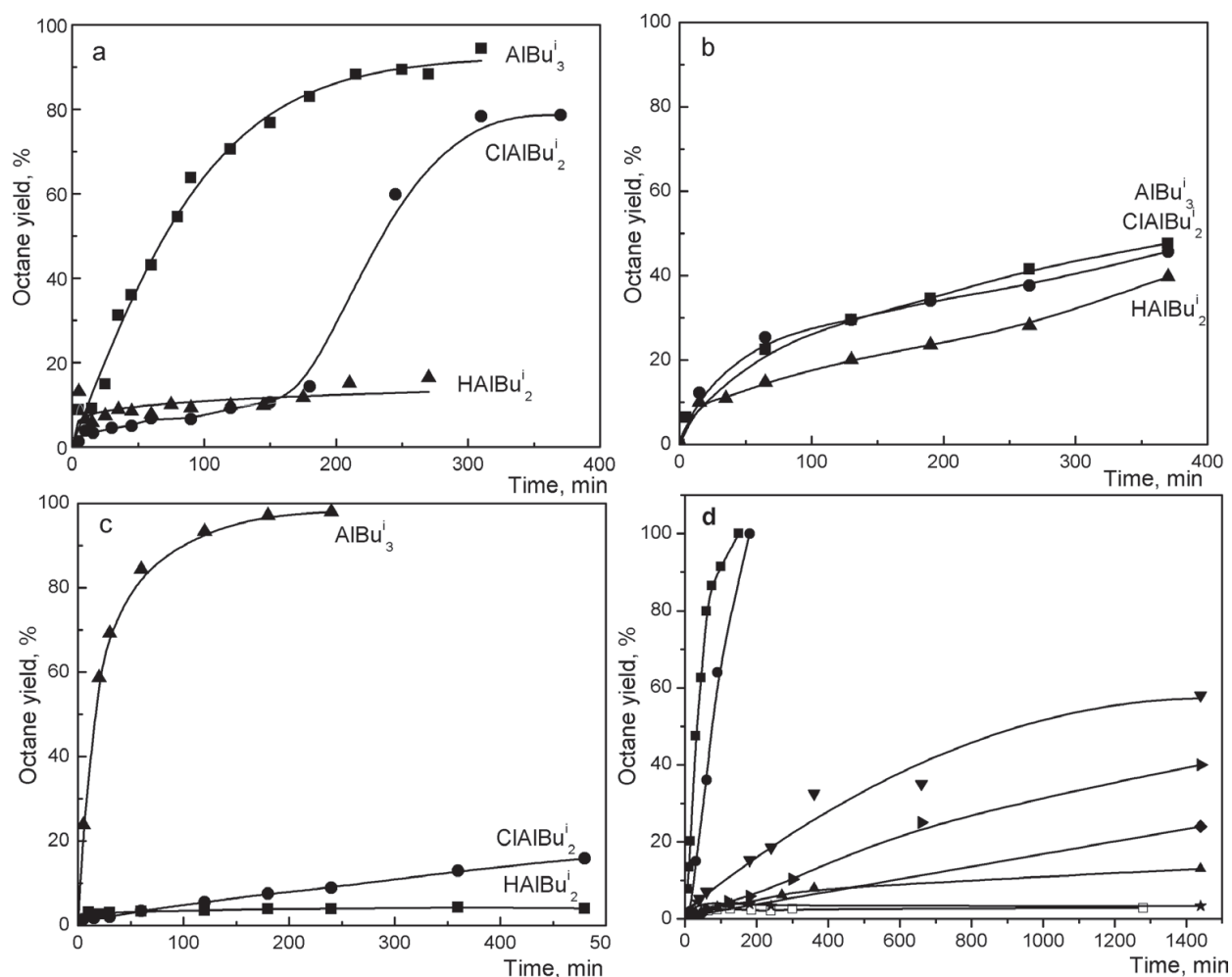
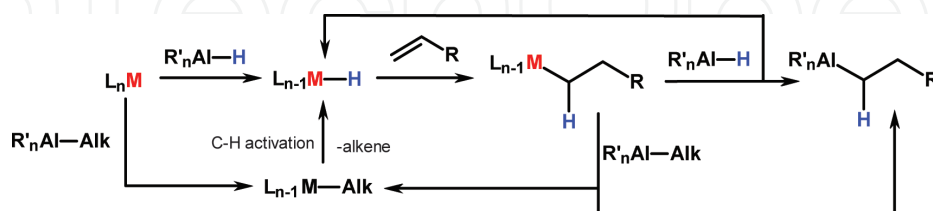


Figure 1. The effect of η^5 -ligand and OAC structure on octane yield in the reaction of 1-octene hydroalumination (molar ratio L_2ZrCl_2 :AOC:alkene 1:60:50, C_6H_6 , $t = 20^\circ C$). (a) $L = Cp$; (b) $L = Ind$; (c) $L = CpMe_3$; (d) $rac-Me_2C(2-Me-4-Bu^t-C_5H_2)_2ZrCl_2 + HAIBu^i_2$ (■), $rac-Me_2C(3-Bu^t-C_5H_3)_2ZrCl_2 + HAIBu^i_2$ (●), $rac-C_2H_4(Ind)_2ZrCl_2 + HAIBu^i_2$ (▼), $rac-Me_2C(Ind)_2ZrCl_2 + HAIBu^i_2$ (►), $rac-Me_2Si(Ind)_2ZrCl_2 + HAIBu^i_2$ (◆), $rac-Me_2C(2-Me-4-Bu^t-C_5H_2)_2ZrCl_2 + AlBu^i_3$ (□), $rac-C_2H_4(Ind)_2ZrCl_2 + AlBu^i_3$ (*), $meso-Me_2C(2-Me-4-Bu^t-C_5H_2)_2ZrCl_2 + HAIBu^i_2$ (▲).

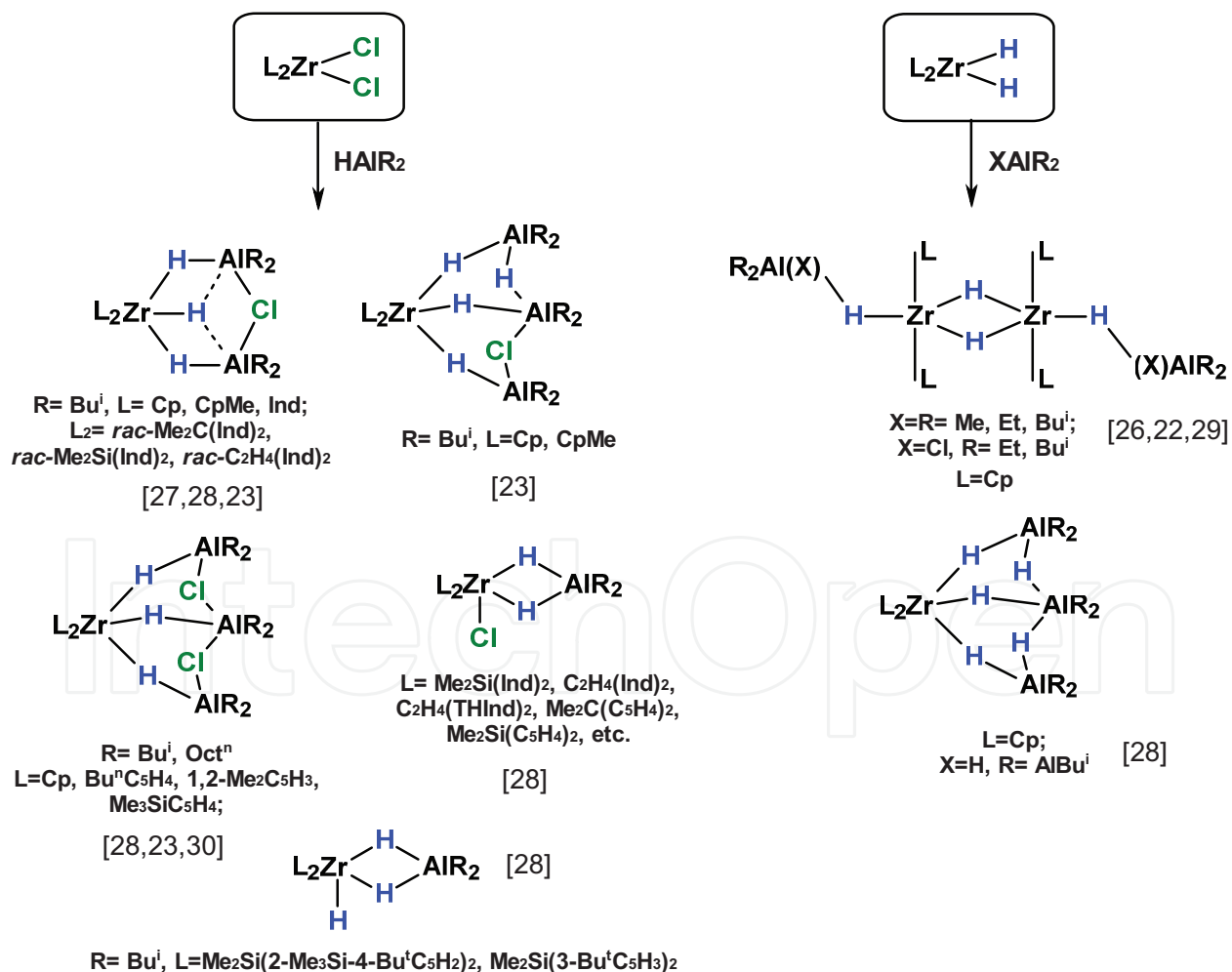


Scheme 2. Generalized scheme of catalytic alkene hydrometalation.

Furthermore, a large number of various bimetallic hydride complexes were identified in reactions of metal chlorides, hydrides and alkyl derivatives with OAC (see, e.g., reviews [24, 25]) that gave an idea on the involvement of such a type of complexes as key intermediates in the hydrometalation reaction. The structural types of the hydride Zr, Al-complexes, which could

be observed in the reactions of zirconocenes with aluminum hydrides or alkylaluminums, are presented in **Scheme 3**.

Our studies on the olefin hydroalumination by XAlBu^i_2 ($\text{X} = \text{H}, \text{Cl}, \text{Bu}^i$), catalyzed with Zr η^5 -complexes, using the quantum chemical methods [31, 32], chemical kinetics [33] and NMR [22, 23], showed that the reaction is a complex multi-step process (**Scheme 4**). The use of zirconocenes with less electron-donating and sterically hindered ligands provides the stable Zr, Al-hydride clusters $\text{L}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}^i_2)_2(\mu\text{-Cl})$ (**6**) ($\text{L} = \text{Cp}, \text{CpMe}, \text{Ind}$; $\text{L}_2 = \text{rac-Me}_2\text{C}(\text{Ind})_2$, $\text{rac-Me}_2\text{Si}(\text{Ind})_2$, $\text{rac-C}_2\text{H}_4(\text{Ind})_2$), $\text{L}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}^i_2)_3(\mu\text{-Cl})(\mu\text{-H})$ (**7**), $\text{L}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}^i_2)_3(\mu\text{-Cl})_2$ (**8**) ($\text{L} = \text{Cp}, \text{CpMe}$), which tend to form bridging Zr—H—Al bonds, and, hence, these complexes have low activity in the reaction with alkene. Moreover, intra- and intermolecular exchange between the hydride atoms in these clusters and $[\text{HAlBu}^i]_n$ oligomers were found. Thus, the complexes exist in equilibrium with each other and HAlBu^i_2 self-associates, while the intermolecular exchange involves the OAC monomer and occurs via dissociation of bimetallic complexes



Scheme 3. Structural types of some hydride Zr, Al-complexes [22, 23, 26–30].



Scheme 4. Mechanism of alkene hydroalumination by XAlBu^i , ($\text{X} = \text{H}, \text{Cl}, \text{Bu}^i$), catalyzed with Zr η^5 -complexes.

(**Figure 2**). Increasing of the $[\text{HALBu}_2^i]_n$ concentration, that is, realization the catalytic conditions, shifts the equilibrium toward low active large clusters into which the alkene insertion is hampered due to their competing intermolecular exchange with OAC oligomers.

Reaction of Cp_2ZrCl_2 with AlBu_3 goes via alkyl chloride exchange and isobutylene elimination, which give the intermediates $\text{Cp}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}_2)(\text{AlBu}_3)$ and $\text{Cp}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}_2)_2(\mu\text{-Cl})$. The absence of fast exchange between these hydride clusters increases the lifetime of the active sites with free Zr—H bond, and this is responsible for the high activity of the $\text{Cp}_2\text{ZrCl}_2\text{-AlBu}_3$ catalytic system toward alkene [23].

High yields of hydroalumination products in the reactions of alkenes with HAlBu_2 , catalyzed by Zr complexes with bulky ligands ($\text{L} = \text{CpMe}_5$, $\text{rac-Me}_2\text{C}(\text{2-Me-4-Bu}^t\text{-C}_5\text{H}_2)_2$, $\text{rac-Me}_2\text{C}(\text{3-Bu}^t\text{-C}_5\text{H}_3)_2$) are caused by the formation of Zr, Al-bimetallic active sites (**4**) containing a $[\text{L}_2\text{ZrH}_3]$ moiety with a free Zr-H bond, in which the steric hindrance in the ligand prevents the formation of

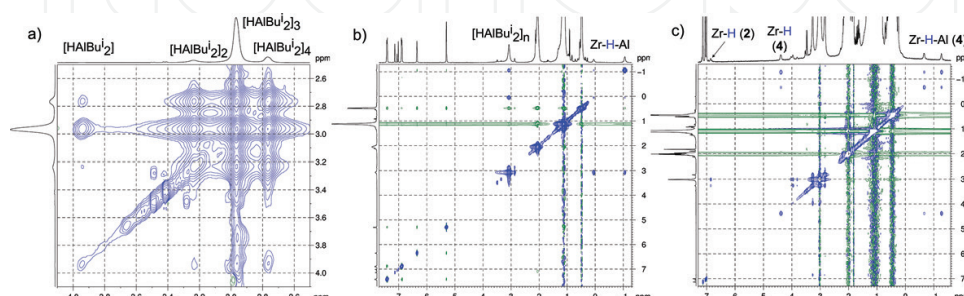


Figure 2. EXSY spectra of (a) HALBu_i^1 in C_6D_6 (3.3 mol/L, 300 K, $\tau = 0.3$ s); (b) system $\text{Ind}_2\text{ZrCl}_2\text{--HALBu}_i^1(1:12)$ in d_8 -toluene at 275 K ($\tau = 0.3$ s); (c) system $(\text{CpMe}_5)_2\text{ZrCl}_2\text{--HALBu}_i^1(1:26)$ in d_8 -toluene at 265 K ($\tau = 0.3$ s). Diagonal and cross-peaks of the same phase demonstrate the existence of chemical exchange.

low-active intermediates. The *meso*-isomer of the sterically hindered cyclopentadienyl complex $\text{Me}_2\text{C}(2\text{-Me-4-Bu}^t\text{-C}_5\text{H}_2)_2\text{ZrCl}_2$ gives the intermediate with the shielded free Zr–H bond, which makes the catalytic system inactive [23].

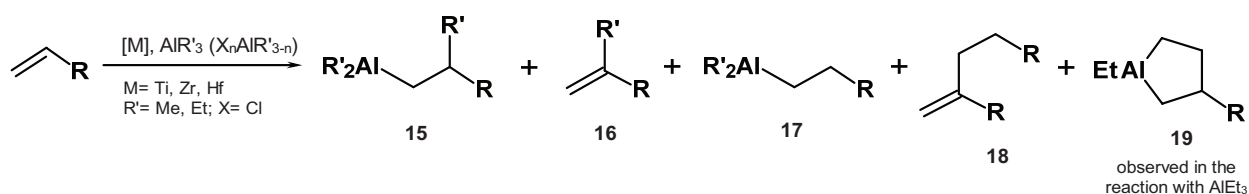
Thus, the $\text{L}_2\text{ZrCl}_2\text{-XAlBu}_2$ systems provide Zr, Al-hydride complexes with Zr–H–Zr and Zr–H–Al-bridged bonds in which intra- and intermolecular hydride exchange between Zr and Al, controlled by the steric factor of the η^5 -ligand, OAC nature and by the reaction conditions (reactant ratio), plays the key role in the catalytic process. The energy of cleavage of these bridging bonds and the ability of the complex to have initially a free Zr–H bond are the factors determining the activity of Zr, Al-hydride intermediates in the alkene hydroalumination.

2.2. Mechanisms of zirconocene catalysis in alkene carbo- and cycloalumination

Catalytic alkene and acetylene carbo- and cycloalumination are convenient one-pot synthetic routes to the acyclic and cyclic OACs that could be converted into alcohols, halides, heterocycles, carbocycles and others [2–11]. The using of enantiomerically pure complexes as the catalysts affords the asymmetric induction in the reactions. Thus, the method of Zr-catalyzed asymmetric carboalumination of alkenes-ZACA-reaction has been developed [7–11, 34], which was applied to the synthesis of a number of biologically active compounds. The involvement of methylaluminoxane (MAO) [35–38] or other Lewis acidic cocatalysts [39] substantially increases the activity of the catalytic systems providing alkene dimers, oligomers and polymers.

Summarizing the information on the study of the reaction of alkenes with alkylaluminums ($\text{R} = \text{Me, Et}$) in the presence of metal complexes [40–46], it should be noted that the process can give various products depending on the reagent nature, catalyst structure and reaction conditions (**Scheme 5**): saturated and unsaturated alkylated products (**15** and **16**), hydrometallation products (**17**), dimers (**18**) and cyclic OACs (**19**). As shown in **Tables 2** and **3** [46], the use of chlorinated solvent altogether with Zr catalysts, which contain bulky ligand (CpMe_5), increases the yield of carbometallation products **15**. The dimers **18** predominate in the reaction of alkenes with AlMe_3 , catalyzed by zirconocenes with Cp and CpMe ligands. The maximal yields of cyclic OAC **19** were observed in the reaction that runs in hydrocarbon solvent and in the presence of Zr complexes substituted with Cp, CpMe, CpMe_5 and Ind ligands.

Obviously, the reaction pathways are determined by the catalytically active sites of a definite type. Thus, bimetallic Zr, Al-alkyl complexes $\text{L}_2\text{ZrR}(\mu\text{-Cl})\text{AlR}_n\text{Cl}_{3-n}$ in the reaction of zirconocenes with alkylaluminums were found [47–52] and the complexes were suggested as key intermediates of olefin β -alkylation (**Scheme 6**). Using of strong Lewis acids, for example, MAO or perfluoroaryl boranes enhances the catalytic system productivity by several orders



Scheme 5. Reaction of alkenes with AlR_3 ($\text{R} = \text{Me, Et}$) in the presence of metal complexes.

L_2ZrCl_2	Solvent	Hexene-1 conversion, %	Product yield, %			
			15	16	17	18
Cp_2ZrCl_2	CH_2Cl_2	92	3	14	7	68
	$C_6H_5CH_3$	69	3	21	7	38
$(CpMe)_2ZrCl_2$	CH_2Cl_2	84	11	14	7	52
	$C_6H_5CH_3$	39	9	9	9	12
$(CpMe_3)_2ZrCl_2$	CH_2Cl_2	68	53	8	7	-
	$C_6H_5CH_3$	44	15	14	14	1
Ind_2ZrCl_2	CH_2Cl_2	87	28	18	8	33
	$C_6H_5CH_3$	70	38	14	10	8

Table 2. Effect of catalyst structure and solvent on the product yields in the reaction of hexene-1 with $AlMe_3$, catalyzed by L_2ZrCl_2 (mole ratio $AlMe_3$:alkene: L_2ZrCl_2 = 60:50:1, reaction time 24 h, 22°C).

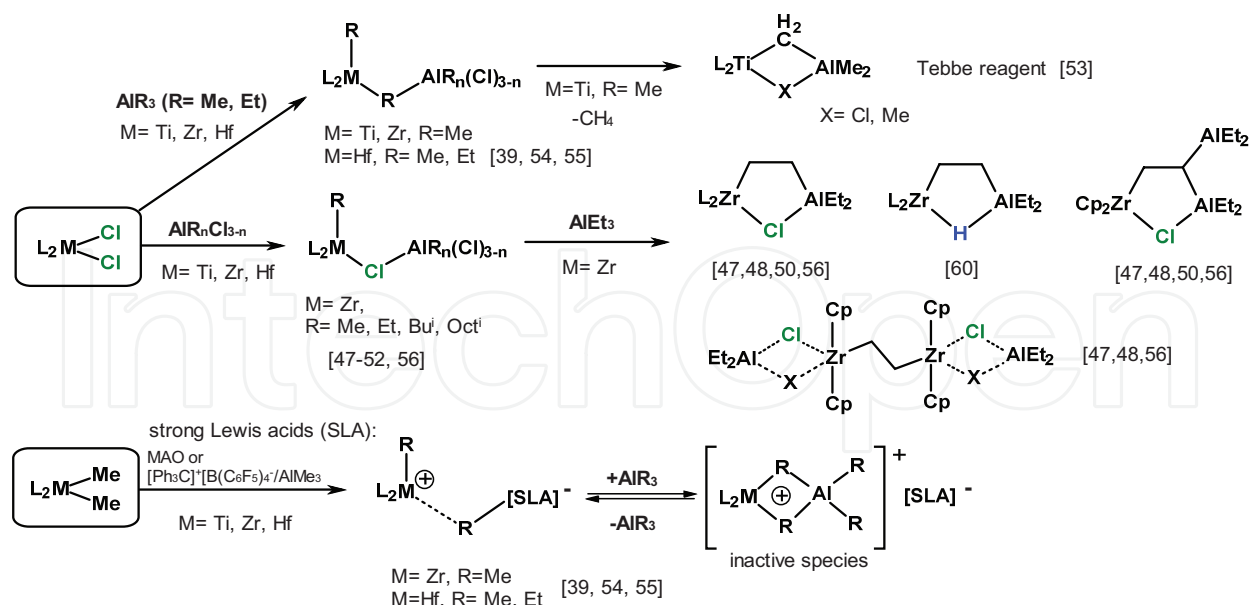
due to the generation of highly active cationic species, which are formed as a result of the ionic pair dissociation [39, 54, 55].

Further transformations of the neutral alkyl bimetallic complexes via α -C-H (Ti) or β -C-H (Zr) activation gives the stable structures with $M-CH_2-Al$, $M-CH_2CHR-Al$ or $M-CH_2CH_2-M$ bridges. Five-membered bimetallic complex $L_2ZrCH_2CH_2(\mu-Cl)AlEt_2$ was found to be the intermediate that is responsible for the cycloalumination pathway [50, 56, 57].

The Me-group exchange between Zr and Al atoms in the complexes $L_2ZrMe(\mu-Cl)AlMe_3$ has been observed by the means of dynamic 2D NMR spectroscopy [58, 59] (**Figure 3a**). Moreover, the exchange between the magnetically nonequivalent hydrogens, which belong to the opposite parts of *ansa*-ligand in the complex $Me_2SiInd_2ZrMe(\mu-Cl)AlMe_3$, was found (**Figure 3b**). This dynamic picture could be explained by the intermolecular exchange

L_2ZrCl_2	Solvent	Hexene-1 conversion, %	Product yield, %				
			15	16	17	18	19
Cp_2ZrCl_2	CH_2Cl_2	96	16	16	13	<1	51
	C_6H_6	91	24	2	2	–	63
$(CpMe)_2ZrCl_2$	CH_2Cl_2	98	16	9	10	–	62
	C_6H_6	97	6	10	12	–	69
$(CpMe_3)_2ZrCl_2$	CH_2Cl_2	99	48	13	10	7	21
	C_6H_6	96	15	2	5	–	74
Ind_2ZrCl_2	CH_2Cl_2	93	36	3	7	2	45
	C_6H_6	99	25	–	<1	<1	74

Table 3. Effect of catalyst structure and solvent on the product yields in the reaction of hexene-1 with $AlEt_3$, catalyzed by L_2ZrCl_2 (mole ratio $AlEt_3$:alkene: L_2ZrCl_2 = 60:50:1, reaction time 24 h, 22°C).



Scheme 6. Bimetallic Zr, Al-intermediates in the reaction of zirconocenes with alkylaluminums [39, 47–56].

between the diastereomers of the complex, containing a stereogenic center on the transition metal atom, via $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$.

On the basis of these investigations, we proposed the mechanism, where the alkyl chloride bimetallic complex associated with the AlR_3 molecule is the starting point of the several catalytic cycles, carbo-, cyclometalation, hydrometalation and dimerization (**Scheme 7**). The zirconocenes with more electron-deficient η^5 -ligands in combination with chlorinated solvents provide a greater concentration of a key intermediate, which speeds up all the pathways, ensuring the high conversion of a substrate. The sterical hindrances in η^5 -ligand and solvation by chlorine containing solvents delay the processes of C–H activation in the methylalkyl substituted intermediate increasing the cabometalation product yield.

As shown in **Figure 4**, dynamic processes are also characteristic to the five-membered bimetallic complex $\text{L}_2\text{ZrCH}_2\text{CH}_2(\mu\text{-Cl})\text{AlEt}_2$. Thus, we found intermolecular exchange by

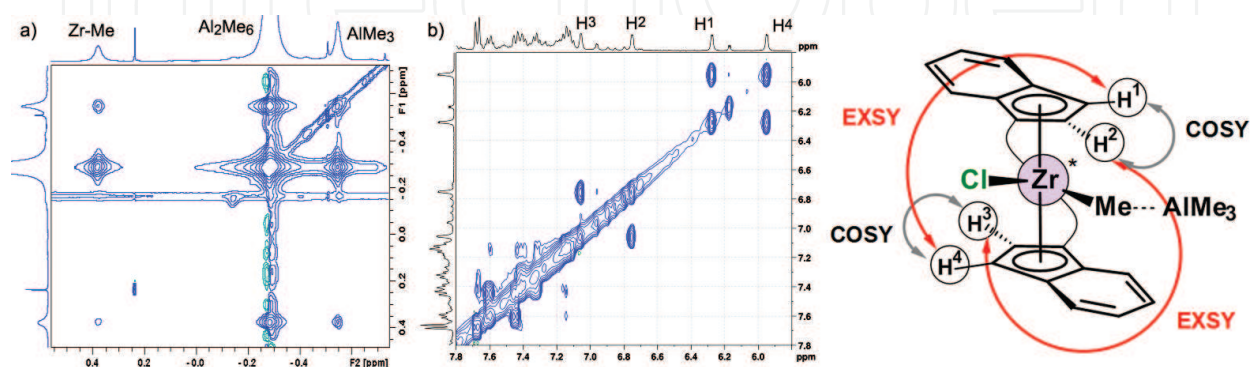


Figure 3. EXSY spectra of (a) system $\text{Cp}_2\text{ZrCl}_2-(\text{AlMe}_3)_2$ in CD_2Cl_2 at 300 K ($\tau = 0.3$ s); (b) system $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2-(\text{AlMe}_3)_2$ in CD_2Cl_2 at 300 K ($\tau = 0.3$ s).

hydrogens in the pairs H^1-H^4 and H^2-H^3 of *ansa*-ligand, as well as between the H-atoms of Zr-CH₂ and Al-CH₂ groups. The exchange may exist due to the equilibrium between the five-membered complex diastereomers, which apparently goes via the zirconacyclopentane structure.

Another evidence of the zirconacyclopentane generation in the systems $L_2ZrCl_2-AlEt_3$ could be the observation of diastereomeric five-membered bimetallic complexes $CpCp'ZrCH_2CH_2(\mu-H)AlEt_2$ ($Cp' = \eta^5-(1\text{-neomenthyl-4,5,6,7-tetrahydroindenyl})$) [60], the formation is possible due to realization of two parallel stages—two types of β -C-H activation in L_2ZrEt_2 (**Scheme 7**): (i) elimination of ethane to give zirconacyclopentane and (ii) formation of Et_2AlH from Et_3Al and L_2ZrHEt with loss of ethylene.

Moreover, our density functional theory (DFT) calculations showed that equilibrium between zirconacyclopentane (**23**) and bimetallic five-membered Zr, Al-complex (**22**) is thermodynamically probable; however, it is shifted toward the bimetallic intermediate [61]. Analysis of the reactions between the complexes and olefins demonstrated that zirconacyclopentane is more reactive toward the substrate than the intermediate **22** (**Scheme 7**). The insertion of olefin into **22** is accompanied by removal of the $ClAlEt_2$ molecule from the zirconium coordination sphere. The interaction of olefins with zirconacyclopentane and bimetallic five-membered Zr, Al-complex provides zirconacyclopentane structures, which is involvement in the cyclometalation process, has been proposed earlier [62, 63]. Transmetalation of zirconacyclopentane

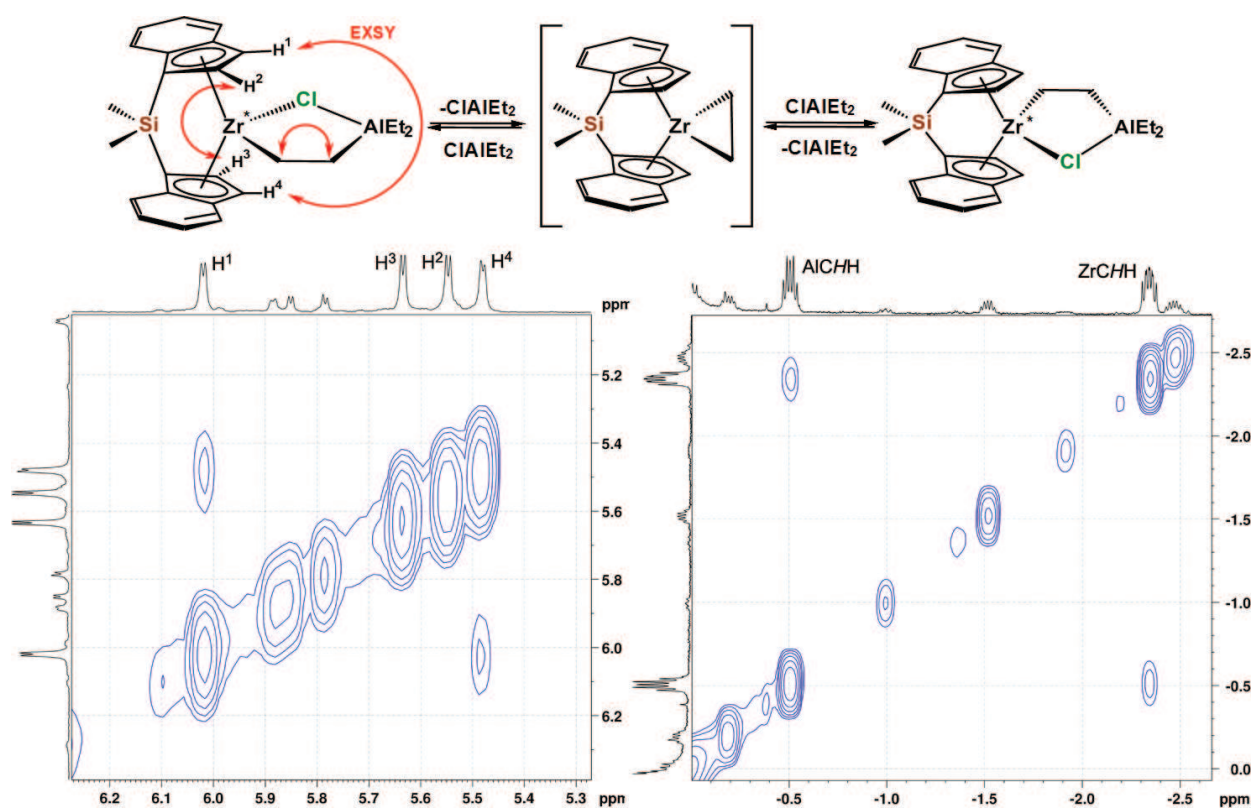
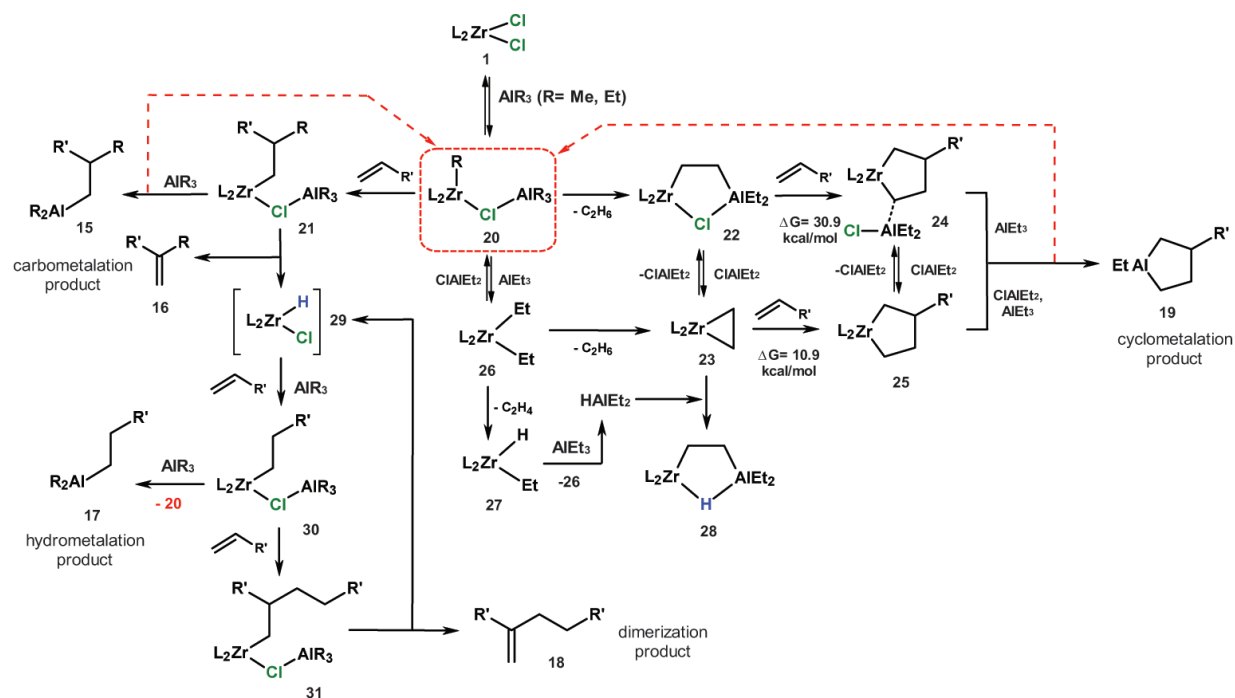


Figure 4. EXSY spectra of system $Me_2SiInd_2ZrCl_2-(AlEt_2)_3$ in d_8 -toluene at 305 K ($\tau = 0.3$ s).



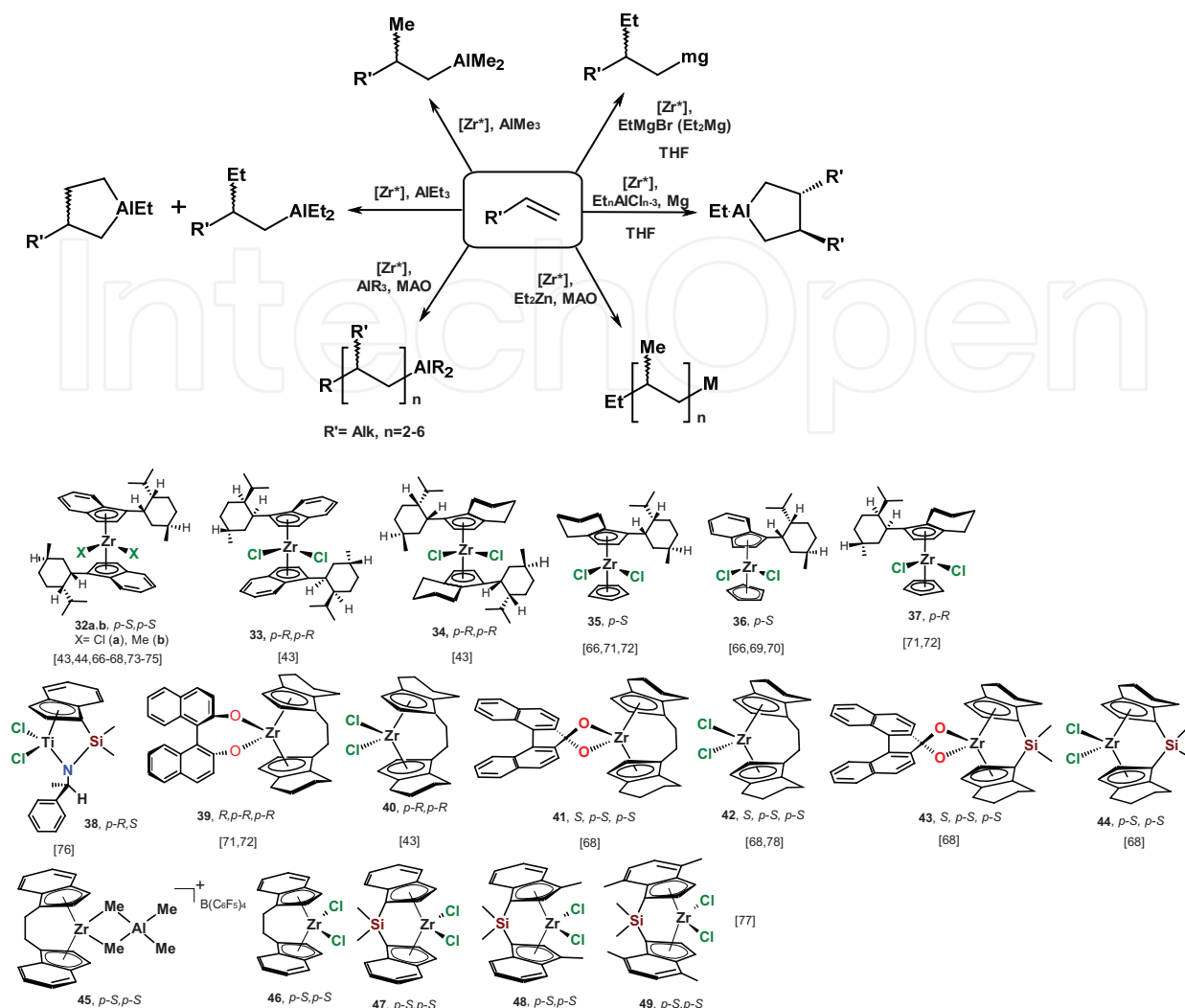
Scheme 7. Mechanisms of reactions of alkenes with AlR_3 ($\text{R} = \text{Me, Et}$), catalyzed with $\text{Zr } \eta^5$ -complexes.

by OACs goes via several stages and gives alumolanes. The probability of this process was shown experimentally using low temperature NMR spectroscopy [56].

3. Asymmetric alkene carbo- and cycloalumination, catalyzed by enantiomerically pure Group IV metallocenes

The development of stereoselective catalytic methods for the synthesis of cyclic and acyclic OAC using chiral transition metal η^5 -complexes is an actual field of chemistry. Among these, chiral Ti and Zr complexes found application in the enantioselective functionalization of alkenes with organomagnesium and -aluminum compounds [7–11, 34, 64, 65].

Thus, in the reaction of alkenes with organoaluminum compounds C_2 - and C_1 -symmetric conformationally labile (32–37) and rigid (38–49) enantiomerically pure complexes were used as catalysts (**Scheme 8**). Thus, the high enantioselectivity (up to 95%*ee*) of alkene carbometalation by AlR_3 ($\text{R} = \text{Me, Et}$) was achieved in the reactions, catalyzed by conformationally labile complex **32a** in chlorinated solvents [43, 44]. Later, it was demonstrated that the replacement of AlMe_3 by AlEt_3 in the reaction catalyzed by complex **32a** results in the *R* to *S* change of the absolute configuration of the β -stereogenic center in the carboalumination products [66–68]. Furthermore, the cycloalumination of terminal alkenes gives aluminacyclopentanes with 24–57%*ee* [44, 66, 67, 69]; the maximum enantioselectivity (~57%*ee*) in cycloalumination was found in the reaction of vinyl-substituted hydrocarbons with AlEt_3 conducted in CH_2Cl_2 [67].



Scheme 8. Enantiomerically pure Zr and Ti complexes as catalysts in the reactions of alkenes with AlR_3 ($R = Me, Et$) [43, 44, 66–78].

Study on the olefin carboalumination with $AlMe_3$ in the presence of conformationally rigid *ansa*-zirconocenes **45–49** showed that the highest enantioselectivity (about 80%*ee*) was achieved in the styrene methylalumination, catalyzed by the $[Ph_3C][B(C_6F_5)_4]$ -activated complex **45** [71]. The reaction of alkenes with $AlMe_3$ catalyzed by **44** in the presence of MAO gave methylalumination products in 66% yield and with enantiomeric purity of 65%*ee* [68]. Using of complexes **42, 44** in the alkene carboalumination with $AlEt_3$ afforded 2-ethyl-substituted derivatives with enantiomeric excess of 50–51%*ee*. The reaction provided optically active diastereomerically pure functionally substituted alkylated alkene dimers as well [68]. The strategy of all-syn deoxypropionate motif construction, found in a number of natural products, by the asymmetric oligomerization of propylene in the presence of **42** with both stereoselectivity and chain-end functionalizability has been presented in Ref. [72].

Thus, the chemo- and enantioselectivity of these reactions are substantially affected by the catalyst and alkene structures, OAC nature and reaction conditions (temperature, reactant ratio

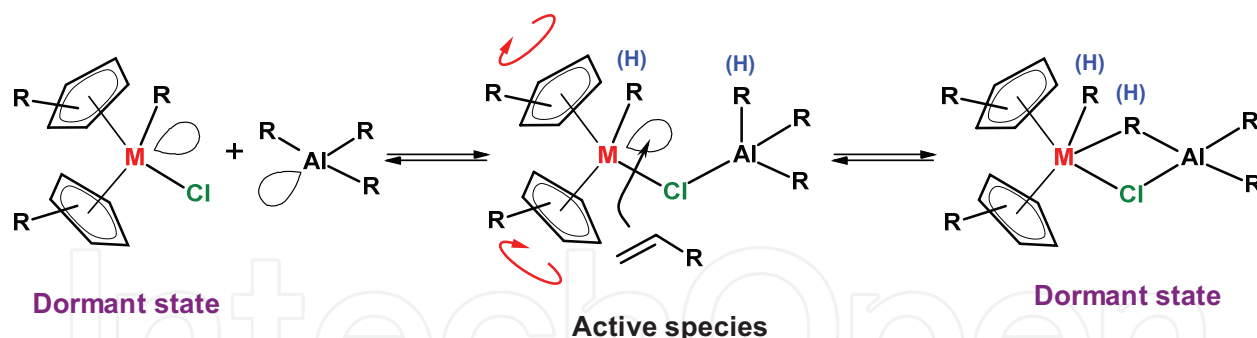
and solvent). Presumably, the key factor determining the dependence of enantioselectivity on the solvent nature and OAC structure is the conformational behavior of the η^5 -ligands in bimetallic Zr, Al-intermediates, which control the reaction pathways. The effect of a solvent nature on the rate of intramolecular exchange between conformers of neomenthyl-substituted zirconocenes **32a**, **35** and **36**, which are formed as a result of the rotation of the indenyl fragments relative to $[\text{ZrCl}_2]$, has been shown by the means of dynamic nuclear magnetic resonance (DNMR) spectroscopy [68]. Comparison of the conformer composition and dynamics of the complexes with their activity and stereoselectivity in the reactions of OACs with alkenes led to the conclusion that the enantioselectivity of the reactions is determined by the kinetic factor, namely, by the rate of interaction in a pair: conformer of catalytically active center-substrate. Thus, in order to achieve high enantioselectivity in the studied reactions, the catalyst molecule should have a specific conformational mobility for the formation of a suitable rotamer, which lifetime will be sufficient for the alkene insertion.

In this connection, further optimization of the ligand environment, namely the search for appropriate conformers that could be formed via either introduction of suitable substituents into the indenyl ligand or upon binding of ligands could advance these studies toward the design of more efficient catalysts for alkene functionalization by organomagnesium and -aluminum reagents.

4. Conclusions

Thus, the catalytic alkene hydro-, carbo- and cycloalumination are complex multi-step processes, in which a large number of intermediate bimetallic Zr, Al-complexes are involved. Studies of the reaction mechanisms allow to understand the chemistry of the processes on a deeper level and to narrow the search for new catalytic systems.

Finally, the next remarks should be sound. First, the initial OACs exist as self-associated structures in the solutions, where the exchange between hydride atoms or alkyl groups could run via dissociation on monomers, which represents the Lewis acids and which effective concentration influences on the stages of key intermediates formation. Second, since the catalyst (IV group transition metals) is a Lewis acid too due to a free nonbonding orbital, then it disturbs the above balance, making the system more dynamic. Thus, one of the important roles of the catalyst besides the formation of active species is to accelerate the exchange through the dissociation with the release of the active OAC monomer. Third, the interaction of alkyl or hydride complex with the monomer gives active species—bimetallic intermediates, which reactivity depends on the availability of the free nonbonding orbital (**Scheme 9**). The active species should be coordinatively unsaturated, where at least one of the bridge bond is broken. In the case of bimetallic hydride complexes, there is the tendency to form inactive bridge bonds, whereas bimetallic alkyl substituted intermediates are inclined to the dissociation. Therefore, the activity of intermediates depends on the living time of active species, in which the electrophilicity of the metal center could be increased via η^5 -ligand, thereby accelerating the process of alkene introduction. However, there is a danger of another process—C—H activation in the products, which could be prevented by using more bulky ligands or more polar solvents.



Scheme 9. Exchange processes in bimetallic intermediates as factors that determine the properties of catalytic systems.

Fourth, the activity of catalytic systems and the degree of asymmetric induction in catalytic alkene functionalization by OACs is substantially affected by the intramolecular ligand mobility and conformational composition of the bimetallic intermediates.

Thus, the regulation of activity, chemo- and stereoselectivity of the studied systems is the problem of fine tuning of the catalytically active center, in which should be a balance between electronic and steric factors of the catalyst, OAC and the substrate.

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References

- [1] Woodward S, Dagorne S, editors. Modern Organoaluminum Reagents. Preparation, Structure, Reactivity and Use. Berlin Heidelberg: Springer-Verlag; 2013. p. 312. DOI: 10.1007/978-3-642-33672-0
- [2] Tolstikov GA, Dzhemilev UM, Tolstikov AG. Aluminiyorganicheskie soedineniya v organicheskom sinteze (Organoaluminum compounds in organic synthesis). Novosibirsk: Akad. izd. GEO; 2009. p. 645. ISBN 978-5-9747-0147-4

- [3] Ibragimov AG, Dzhemilev UM. Metal complex catalysis in the synthesis of organo-aluminium compounds. *Russian Chemical Reviews*. 2000;**69**(2):121-135. DOI: 10.1070/RC2000v069n02ABEH000519
- [4] Dzhemilev UM, Ibragimov AG. Hydrometallation of unsaturated compounds. In: Andersson PG, Munslow IJ, editors. *Modern Reduction Methods*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2008. pp. 447-490. Chapter 18. DOI: 10.1002/9783527622115.ch18
- [5] Dzhemilev UM, Ibragimov AG. Catalytic cyclometalation reaction of unsaturated compounds in synthesis of magna- and aluminacarbocycles. *Journal of Organometallic Chemistry*. 2010;**695**(8):1085-1110. DOI: 10.1016/j.jorganchem.2010.01.002
- [6] D'yakonov VA. *Dzhemilev Reaction in Organic and Organometallic Synthesis*. Chemistry Research and Applications Series. New York: Nova Science Publishers; 2010. p. 96. ISBN: 978-1-60876-683-3
- [7] Negishi E. Asymmetric carbometallations. In: Ojima I, editor. *Catalytic Asymmetric Synthesis*. 2nd ed. New York, USA: John Wiley & Sons, Inc.; 2005. pp. 165-190. Chapter 4. DOI: 10.1002/0471721506.ch5
- [8] Negishi E, Huo S. Zirconium-catalyzed enantioselective carboalumination of "unactivated" alkenes as a new synthetic tool for asymmetric carbon-carbon bond formation. *Pure and Applied Chemistry*. 2002;**74**(1):151-157. DOI: 10.1351/pac200274010151
- [9] Negishi E. Transition metal-catalyzed organometallic reactions that have revolutionized organic synthesis. *Bulletin of the Chemical Society of Japan*. 2007;**80**(2):233-257. DOI: 10.1246/bcsj.80.233
- [10] Negishi E. Bimetallic catalytic systems containing Ti, Zr, Ni, and Pd. Their applications to selective organic syntheses. *Pure and Applied Chemistry*. 1981;**53**(12):2333-2356. DOI: 10.1351/pac198153122333
- [11] Xu S, Negishi E. Zirconium-catalyzed asymmetric carboalumination of unactivated terminal alkenes. *Accounts of Chemical Research*. 2016;**49**(10):2158-2168. DOI: 10.1021/acs.accounts.6b00338
- [12] Ziegler K, Krupp F, Zosel K. Eine einfache synthese primärer Alkohole aus Olefinen. *Angewandte Chemie*. 1955;**67**:425-426. DOI: 10.1002/ange.19550671609
- [13] Guiry PJ, Coyne AG, Carroll AM. 10.19 – C–E bond formation through hydroboration and hydroalumination. In: Crabtree RH, Mingos DMP, editors. *Comprehensive Organometallic Chemistry III*. Elsevier Ltd.; Oxford. 2007. pp. 839-869. DOI: 10.1016/B0-08-045047-4/00141-2
- [14] Zaidlewicz M, Wolan A, Budny M. 8.24 Hydrometallation of C=C and C≡C bonds. Group 3. In: Knochel P, Molander GA, editors. *Comprehensive Organic Synthesis II*. 2nd ed. Elsevier Ltd.; Amsterdam. 2014. pp. 877-963. DOI: 10.1016/B978-0-08-097742-300826-0
- [15] Joseph J, Jaroschik F, Harakat D, Radhakrishnan KV, Vasse JL, Szymoniak J. Titanium-catalyzed hydroalumination of conjugated dienes: Access to fulvene-derived allylaluminium

reagents and their diastereoselective reactions with carbonyl compounds. *Chemistry—A European Journal*. 2014;**20**(18):5433-5438. DOI: 10.1002/chem.201304775

- [16] Sato F, Sato S, Sato M. Addition of lithium aluminium hydride to olefins catalyzed by zirconium tetrachloride: A convenient route to alkanes and 1-haloalkanes from 1-alkenes. *Journal of Organometallic Chemistry*. 1976;**122**(2):C25-C27. DOI: 10.1016/S0022-328X(00)80622-1
- [17] Sato F, Sato S, Kodama H, Sato M. Reactions of lithium aluminum hydride or alane with olefins catalyzed by titanium tetrachloride or zirconium tetrachloride. A convenient route to alkanes, 1-haloalkanes and terminal alcohols from alkenes. *Journal of Organometallic Chemistry*. 1977;**142**(1):71-79. DOI: 10.1016/S0022-328X(00)91817-5
- [18] Ashby EC, Noding SA. Hydrometalation. 3. Hydroalumination of alkenes and dienes catalyzed by transition metal halides. *Journal of Organic Chemistry*. 1979;**44**(24):4364-4371. DOI: 10.1021/jo01338a025
- [19] Ashby EC, Noding SA. Hydrometalation. 5. Hydroalumination of alkenes and alkynes with complex metal hydrides of aluminum in the presence of bis(cyclopentadienyl) dichlorotitanium. *Journal of Organic Chemistry*. 1980;**45**(6):1035-1041. DOI: 10.1021/jo01294a023
- [20] Negishi E, Yoshida T. A novel zirconium-catalyzed hydroalumination of olefins. *Tetrahedron Letters*. 1980;**21**(16):1501-1504. DOI: 10.1016/S0040-4039(00)92757-6
- [21] Weliange NM, McGuinness DS, Gardinera MG, Patel J. Cobalt-bis(imino)pyridine complexes as catalysts for hydroalumination–isomerisation of internal olefins. *Dalton Transactions*. 2016;**45**:10842-10849. DOI: 10.1039/c6dt01113f
- [22] Parfenova LV, Pechatkina SV, Khalilov LM, Dzhemilev UM. Mechanism of Cp₂ZrCl₂-catalyzed olefin hydroalumination by alkylalanes. *Russian Chemical Bulletin, International Edition*. 2005;**54**:316-327. DOI: 10.1007/s11172-005-0254-z
- [23] Parfenova LV, Kovyazin PV, Nifant'ev IE, Khalilov LM, Dzhemilev UM. Role of Zr, Al-hydride intermediate structure and dynamics in alkene hydroalumination by XAlBui₂ (X= H, Cl, Bui), catalyzed with Zr η^5 -Complexes. *Organometallics*. 2015;**34**(14):3559-3570. DOI: 10.1021/acs.organomet.5b003
- [24] Parfenova LV, Khalilov LM, Dzhemilev UM. Mechanisms of reactions of organoaluminum compounds with alkenes and alkynes catalyzed by Zr complexes. *Russian Chemical Reviews*. 2012;**81**(6):524-548. DOI: 10.1070/RC2012v081n06ABEH004225
- [25] Butler MJ, Crimmin MR. Magnesium, zinc, aluminium and gallium hydride complexes of the transition metals. *Chemical Communications*. 2017;**53**:1348-1365. DOI: 10.1039/c6cc05702k
- [26] Wailes PC, Weigold H, Bell AP. Reaction of dicyclopentadieny zirconium dihydride with trimethylaluminum. Formation of a novel hydride containing both Zr-H-Zr and Zr-H-Al. *Journal of Organometallic Chemistry*. 1972;**43**:C29-C31. DOI: 10.1016/S0022-328X(00)81589-2

- [27] Shoer LI, Gell KI, Schwartz G. Mixed-metal hydride complexes containing Zr-H-Al bridges. Synthesis and relation to transition-metal-catalyzed reactions of aluminum hydrides. *Journal of Organometallic Chemistry*. 1977;**136**:c19-c22. DOI: 10.1016/S0022-328X(00)82126-9
- [28] Baldwin SM, Bercaw JE, Brintzinger HH. Alkylaluminum-complexed zirconocene hydrides: Identification of hydride-bridged species by NMR Spectroscopy. *Journal of the American Chemical Society*. 2008;**130**:17423-17433. DOI: 10.1021/ja8054723
- [29] Parfenova LV, Vildanova RF, Pechatkina SV, Khalilov LM, Dzhemilev UM. New effective reagent $[\text{Cp}_2\text{ZrH}_2\cdot\text{ClAlEt}_2]_2$ for alkene hydrometallation. *Journal of Organometallic Chemistry*. 2007;**692**:3424-3429. DOI: 10.1016/j.jorganchem.2007.04.007
- [30] Welianje NM, McGuinness DS, Gardinera MG, Patel J. Insertion and isomerisation of internal olefins at alkylaluminium hydride: Catalysis with zirconocene dichloride. *Dalton Transactions*. 2015;**44**:20098-20107. DOI: 10.1039/c5dt03257a
- [31] Pankratyev EY, Tyumkina TV, Parfenova LV, Khalilov LM, Khursan SL, Dzhemilev UM. DFT study on mechanism of olefin hydroalumination by XAlBui_2 in the presence of Cp_2ZrCl_2 catalyst. I. Simulation of intermediate formation in reaction of HAlBui_2 with Cp_2ZrCl_2 . *Organometallics*. 2009;**28**:968-977. DOI: 10.1021/om800393j
- [32] Pankratyev EY, Tyumkina TV, Parfenova LV, Khalilov LM, Khursan SL, Dzhemilev UM. DFT and ab initio study on mechanism of olefin hydroalumination by XAlBui_2 , in the presence Cp_2ZrCl_2 catalyst. II. Olefin interaction with catalytically active centers. *Organometallics*. 2011;**30**:6078-6089. DOI: 10.1021/om200518h
- [33] Parfenova LV, Balaev AV, Gubaidullin IM, Pechatkina SV, Abzalilova LR, Spivak SI, Khalilov LM, Dzhemilev UM. Kinetic model of olefin hydroalumination by HAlBui_2 and AlBui_3 in presence of Cp_2ZrCl_2 catalyst. *International Journal of Chemical Kinetics*. 2007;**39**(6):333-339. DOI: 10.1002/kin.20238
- [34] Negishi E. Discovery of ZACA reaction – Zr-catalyzed asymmetric carboalumination of alkenes. *Archive for Organic Chemistry*. 2011;**(8)**:34-53. DOI: 10.3998/ark.5550190.0012.803
- [35] Sinn H, Kaminsky W, Vollmer HJ, Woldt R. Lebende Polymere bei Ziegler-Katalysatoren extremer Produktivität. *Angewandte Chemie*. 1980;**92**(5):396-402. DOI: 10.1002/ange.19800920517
- [36] Sinn H, Kaminsky W, Vollmer HJ, Woldt R. "Living polymers" on polymerization with extremely productive ziegler catalysts. *Angewandte Chemie International Edition*. 1980;**19**(5):390-392. DOI: 10.1002/anie.198003901
- [37] Sinn H, Kaminsky W. Ziegler-Natta catalysis. *Advances in Organometallic Chemistry*. 1980;**18**:99-149. DOI: 10.1016/S0065-3055(08)60307-X
- [38] Kaminsky W, editor. Polyolefins: 50 years after Ziegler and Natta II. Polyolefins by Metallocenes and Other Single-Site Catalysts. Berlin Heidelberg: Springer-Verlag; 2013. p. 366. DOI: 10.1007/978-3-642-40805-2

- [39] Chen EY-X, Marks TJ. Cocatalysts for metal-catalyzed olefin polymerization: Activators, activation processes, and structure–activity relationships. *Chemical Reviews*. 2000; **100**(4):1391-1434. DOI: 10.1021/cr980462j
- [40] Dzhemilev UM, Vostrikova OS, Tolstikov GA, Ibragimov AG. New method for inserting ethyl group in β -position of higher α -olefins using diethylaluminum chloride. *Russian Chemical Bulletin*. 1979;**28**:2441-2442. DOI: 10.1007/BF00951739
- [41] Dzhemilev UM, Ibragimov AG, Vostrikova OS, Tolstikov GA, Zelenova LM. New method of β -alkylation of α -olefins using dialkylaluminum chlorides with catalytic amounts of Ti, Zr, and Hf complexes. *Russian Chemical Bulletin*. 1981;**30**:281-284. DOI: 10.1007/BF00953581
- [42] Dzhemilev UM, Ibragimov AG, Vostrikova OS, Tolstikov GA. Carbalumination of higher α -olefins catalyzed by titanium and zirconium complexes. *Russian Chemical Bulletin*. 1985;**34**:196-197. DOI: 10.1007/BF01157356
- [43] Kondakov DY, Negishi E. Zirconium-catalyzed enantioselective methylalumination of monosubstituted alkenes. *Journal of the American Chemical Society*. 1995;**117**:10771-10772. DOI: 10.1021/ja00148a031
- [44] Kondakov DY, Negishi E. Zirconium-catalyzed enantioselective alkylalumination of monosubstituted alkenes proceeding via noncyclic mechanism. *Journal of the American Chemical Society*. 1996;**118**:1577-1578. DOI: 10.1021/ja953655m
- [45] Christoffers J, Bergman RG. Zirconocene-alumoxane (1:1) – a catalyst for the selective dimerization of α -olefins. *Inorganica Chimica Acta*. 1998;**270**:20-27. DOI: 10.1016/S0020-1693(97)05819-2
- [46] Parfenova LV, Gabdrakhmanov VZ, Khalilov LM, Dzhemilev UM. On study of chemoselectivity of reaction of trialkylalanes with alkenes, catalyzed with Zr π -complexes. *Journal of Organometallic Chemistry*. 2009;**694**:3725-3731. DOI: 10.1016/j.jorganchem.2009.07.037
- [47] Kaminsky W, Sinn H. Mehrfach durch Metalle Substituierte Athane. *Liebigs Annalen der Chemie*. 1975;(3):424-437. DOI: 10.1002/jlac.197519750307
- [48] Kaminsky W, Vollmer HJ. Kernresonanzspektroskopische Untersuchungen an den Systemen Dicyclopentadienyl zircon (IV) und Organoaluminium. *Liebigs Annalen der Chemie*. 1975;(3):438-448. DOI: 10.1002/jlac.197519750308
- [49] Yoshida T, Negishi E. Mechanism of the zirconium-catalyzed carboalumination of alkynes. Evidence for direct carboalumination. *Journal of the American Chemical Society*. 1981;**103**:4985-4987. DOI: 10.1021/ja00406a071
- [50] Negishi E, Kondakov DY, Choueiri D, Kasai K, Takahashi T. Multiple mechanistic pathways for zirconium-catalyzed carboalumination of alkynes. Requirements for cyclic carbometallation processes involving C-H activation. *Journal of the American Chemical Society*. 1996;**118**:9577-9588. DOI: 10.1021/ja9538039

- [51] Beck S, Brintzinger HH. Alkyl exchange between aluminium trialkyls and zirconocene dichloride complexes—a measure of electron densities at the Zr center. *Inorganica Chimica Acta*. 1998;**270**:376-381. DOI: 10.1016/S0020-1693(97)05871-4
- [52] Tritto I, Zucchi D, Destro M, Sacchi MC, Dall'Occo T, Galimberti M. NMR investigations of the reactivity between zirconocenes and β -alkyl-substituted aluminoxanes. *Journal of Molecular Catalysis A Chemical*. 2000;**160**:107-114. DOI: 10.1016/S1381-1169(00)00237-5
- [53] Tebbe FN, Parshall GW, Reddy GS. Olefin homologation with titanium methylene compounds. *Journal of the American Chemical Society*. 1978;**100**:3611-3613. DOI: 10.1021/ja00479a061
- [54] Bochmann M, Lancaster SJ. Cationic group IV metal alkyl complexes and their role as olefin polymerization catalysts: The formation of ethyl-bridged dinuclear and heterodinuclear zirconium and hafnium complexes. *Journal of Organometallic Chemistry*. 1995;**497**:55-59. DOI: 10.1016/0022-328X(95)00109-4
- [55] Rocchigiani L, Busico V, Pastore A, Macchioni A. Comparative NMR study on the reactions of Hf(IV) organometallic complexes with Al/Zn alkyls. *Organometallics*. 2016;**35**:1241-1250. DOI: 10.1021/acs.organomet.6b00088
- [56] Khalilov LM, Parfenova LV, Rusakov SV, Ibragimov AG, Dzhemilev UM. Synthesis and conversions of metallocycles. 22. NMR studies of the mechanism of Cp₂ZrCl₂-catalyzed cycloalumination of olefins with triethylaluminum to form aluminacyclopentanes. *Russian Chemical Bulletin*. 2000;**49**:2051-2058. DOI: 10.1023/A:1009536328369
- [57] Balaev AV, Parfenova LV, Gubaidullin IM, Rusakov SV, Spivak SI, Khalilov LM, Dzhemilev UM. The mechanism of Cp₂ZrCl₂-Catalyzed alkene cycloalumination with triethylaluminum to give aluminacyclopentanes. *Doklady Physical Chemistry*. 2001;**381**:279-282. DOI: 10.1023/A:1012900227841
- [58] Gabdrakhmanov VZ. Mechanism of catalytic olefin carboalumination by trialkylalanes in the presence of Zr n⁵-complexes [dissertation]. Ufa; 2010. p. 112
- [59] Kovyazin PV, Permyakov VK, Parfenova LV, Nifant'ev IE, Khalilov LM, Dzhemilev UM. Zirconium ansa-complexes as catalysts in reactions of trialkylalanes with alkenes. In: *Book of Abstracts of International Symposium «Modern trends in Organometallic Chemistry and Catalysis»* (devoted to 90th Anniversary of Academician M.E. Volpin); June 3-7; Moscow. 2013. p. P48
- [60] Parfenova LV, Berestova TV, Molchankina IV, Khalilov LM, Whitby RJ, Dzhemilev UM. Stereocontrolled monoalkylation of mixed-ring complex CpCp'ZrCl₂ (Cp' = 1-neomenthyl-4,5,6,7-tetrahydroindenyl) by lithium, magnesium and aluminum alkyls. *Journal of Organometallic Chemistry*. 2013;**726**:37-45. DOI: 10.1016/j.jorganchem.2012.12.004
- [61] Tyumkina TV, Islamov DN, Parfenova LV, Whitby RJ, Khalilov LM, Dzhemilev UM. Mechanistic aspects of chemo- and regioselectivity in Cp₂ZrCl₂-catalyzed alkene cycloalumination by AlEt₃. *Journal of Organometallic Chemistry*. 2016;**822**:135-143. DOI: 10.1016/j.jorganchem.2016.08.019

- [62] Dzhemilev UM, Ibragimov AG. Regio- and stereoselective synthesis for a novel class of organoaluminium compounds — substituted aluminacyclopentanes and alumina-cyclopentenones assis. *Journal of Organometallic Chemistry*. 1994;**466**:1-4. DOI: 10.1016/0022-328X(94)88022-0
- [63] Dzhemilev UM. Catalytic replacement of transition metal atoms in metallocarborocycles by the atoms of nontransition metals. *Mendeleev Communications*. 2008;**18**:1-5. DOI: 10.1016/j.mencom.2008.01.001
- [64] Hoveyda AH, Morken JP. Enantioselective C-C and C-H bond formation mediated or catalyzed by chiral ebthi complexes of titanium and zirconium. *Angewandte Chemie International Edition*. 1996;**35**:1263-1284. DOI: 10.1002/anie.199612621
- [65] Hoveyda AH. Chiral zirconium catalysts for enantioselective synthesis. In: Marek I, editor. *Titanium and Zirconium in Organic Synthesis*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2002. pp. 180-229. Chapter 6. DOI: 10.1002/3527600671.ch6
- [66] Parfenova LV, Berestova TV, Tyumkina TV, Kovyazin PV, Khalilov LM, Whitby RJ, Dzhemilev UM. Enantioselectivity of chiral zirconocenes as catalysts in alkene hydro-, carbo- and cycloalumination reactions. *Tetrahedron Asymmetry*. 2010;**21**:299-310. DOI: 10.1016/j.tetasy.2010.01.001
- [67] Parfenova LV, Kovyazin PV, Tyumkina TV, Makrushina AV, Khalilov LM, Dzhemilev UM. Catalytic enantioselective ethylalumination of terminal alkenes: Substrate effect and absolute configuration assignment. *Tetrahedron Asymmetry*. 2015;**26**:124-135. DOI: 10.1016/j.tetasy.2014.11.019
- [68] Parfenova LV, Zakirova IV, Kovyazin PV, Karchevsky SG, Istomina GP, Khalilov LM, Dzhemilev UM. Intramolecular mobility of η^5 -ligands in chiral zirconocene complexes and enantioselectivity of alkene functionalization by organoaluminum compounds. *Dalton Transactions*. 2016;**45**:12814-12826. DOI: 10.1039/c6dt01366j
- [69] Parfenova LV, Kovyazin PV, Tyumkina TV, Berestova TV, Khalilov LM, Dzhemilev UM. Asymmetric alkene cycloalumination by AlEt_3 , catalyzed with neomenthylindenyl zirconium η^5 -complexes. *Journal of Organometallic Chemistry*. 2013;**723**:19-25. DOI: 10.1016/j.jorganchem.2012.10.021
- [70] Parfenova LV, Berestova TV, Kovyazin PV, Yakupov AR, Mesheryakova ES, Khalilov LM, Dzhemilev UM. Catalytic cyclometallation of allylbenzenes by EtAlCl_2 and Mg as new route to synthesis of dibenzyl butane lignans. *Journal of Organometallic Chemistry*. 2014;**772-773**:292-298. DOI: 10.1016/j.jorganchem.2014.09.033
- [71] Bell L, Whitby RJ, Jones RVH, Standen MCH. Catalytic asymmetric carbomagnesiation of unactivated alkenes. A new, effective, active, cheap and recoverable chiral zirconocene. *Tetrahedron Letters*. 1996;**37**:7139-7142. DOI: 10.1016/0040-4039(96)01561-4
- [72] Bell L, Brookings DC, Dawson GJ, Whitby RJ, Jones RVH, Standen MCH. Asymmetric ethylmagnesiation of alkenes using a novel zirconium catalyst. *Tetrahedron*. 1998;**54**:14617-14634. DOI: 10.1016/S0040-4020(98)00920-X

- [73] Shaughnessy H, Waymouth RM. Enantio- and diastereoselective catalytic carboalumination of 1-Alkenes and α , ω -dienes with cationic zirconocenes: Scope and mechanism. *Organometallics*. 1998;**17**:5728-5745. DOI: 10.1021/om9807811
- [74] Wipf P, Ribe S. Water/MAO acceleration of the zirconocene-catalyzed asymmetric methylalumination of α -olefins. *Organic Letters*. 2000;**2**:1713-1716. DOI: 10.1021/ol005865w
- [75] Wipf P, Ribe S. Water-accelerated tandem Claisen rearrangement-catalytic asymmetric carboalumination. *Organic Letters*. 2001;**3**:1503-1505. DOI: 10.1021/ol015816z
- [76] Millward DB, Cole AP, Waymouth RM. Catalytic carboalumination of olefins with cyclopentadienyl amidotitanium dichloride complexes. *Organometallics*. 2000;**19**:1870-1878. DOI: 10.1021/om990707y
- [77] Petros RA, Camara JM, Norton JR. Enantioselective methylalumination of α -olefins. *Journal of Organometallic Chemistry*. 2007;**692**:4768-4773. DOI: 0.1016/j.jorganchem.2007.06.028
- [78] Ota Y, Murayama T, Nozaki K. One-step catalytic asymmetric synthesis of all-syn deoxypropionate motif from propylene: Total synthesis of (2R,4R,6R,8R)-2,4,6,8-tetramethyl-decanoic acid. *Proceedings of the National Academy of Sciences*. 2016;**113**:2857-2861. DOI: 10.1073/pnas.1518898113

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