



On study of chemoselectivity of reaction of trialkylalanes with alkenes, catalyzed with Zr π -complexes

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ABSTRACT

The influence of the organoaluminium compound nature, Zr π -ligand environment, solvent type and reagent ratio on the chemoselectivity of reactions of trialkylalanes (AlMe_3 , AlEt_3) with alkenes, catalyzed with L_2ZrCl_2 [$\text{L} = \text{Cp}$, Cp' ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$), Cp^* ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$), Ind (indenyl), Flu (fluorenyl)] has been studied. It is shown that in the case of AlMe_3 , the hydro- and carboalumination products, and alkene dimers are formed. The catalytic reaction of AlEt_3 with the olefins yields aluminacyclopentanes altogether with the hydro- and carboalumination products, and the dimers. A probable reaction mechanism has been proposed.

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1. Introduction

The reactions of trialkylalanes with olefins and acetylenes, catalyzed with Zr complexes, are widely applied in organic and organometallic chemistry. It was shown that the process chemoselectivity significantly depends on the type of organoaluminium compounds (OACs). For example, in several works by Negishi [1], the reaction of AlMe_3 with acetylenes, in the presence of Cp_2ZrCl_2 catalyst, follows predominantly the carbometallation pathway. The authors proposed the Zr,Al-complexes as being the key reaction intermediates, which are formed as a result of a ligand exchange between AlMe_3 and Cp_2ZrCl_2 (Scheme 1) [1b–e].

Later, the authors showed that a similar reaction of AlMe_3 with olefin (octene-1), in the presence of 8 mol% Cp_2ZrCl_2 , provides both 2-methylalkene (2) and dimerization product (3), instead of expected 2-methylalkylalane (1) (Scheme 2) [2a].

It was shown that the application of Zr complexes with the sterically hindered π -ligands, for example, Erker's catalyst – bis(1-neomenthylindenyl)zirconium dichloride ($\text{Ind}_2^*\text{ZrCl}_2$), is the only way which allows carbometallation of olefins at high chemo- and stereoselectivity [2a,b].

It should be also mentioned that asymmetric methylalumination of monosubstituted alkenes, catalyzed with $\text{Ind}_2^*\text{ZrCl}_2$, can be significantly accelerated by the action of either water or MAO [3].

Earlier in Dzhemilev's works [4a–c], it was shown that the use of AlEt_3 in the reactions with alkenes and acetylenes, in the pres-

ence of Cp_2ZrCl_2 catalyst, in hexane, provides cyclic OACs (4 and 5) (Scheme 3).

A mechanistic study of these reactions pointed out the fact of key Zr,Al-complex 14 generation; this complex readily interacts with olefins [1d,4d,e]. The complex was first described by Kaminsky during his NMR study of $\text{AlEt}_3\text{-Cp}_2\text{ZrCl}_2$ system [5].

AlBu_3^i in these reactions exclusively yields the alkene hydroalumination products [6]. In this case a fast process of $\beta\text{-C-H}$ activation in $[\text{Cp}_2\text{ZrBu}^i]$ species occurs and results in the formation of Zr,Al-hydride complexes, which hydrometallates olefins [7].

In summary, the information in literature which concerns chemoselectivity of reactions of trialkylalanes (AlMe_3 and AlEt_3) with olefins, in the presence of zirconocene catalysts, appears to be fragmentary and inconsistent, despite the fact of being important in mechanistic research. Therefore, the purpose of this work is a systematic study of the influence of various factors on the chemoselectivity of the reactions. Among the major factors we have considered the following: the type of the OAC, Zr π -ligand environment, initial reagent ratios and the solvent nature.

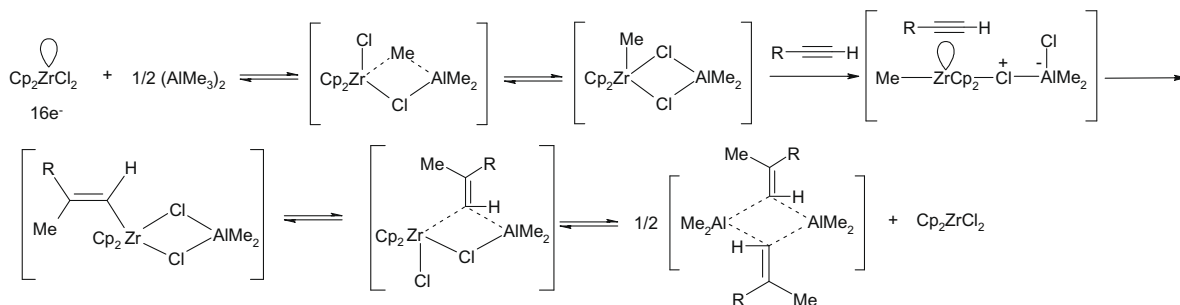
2. Results and discussion

2.1. Chemoselectivity of the reaction of hexene-1 with AlMe_3 , catalyzed with L_2ZrCl_2

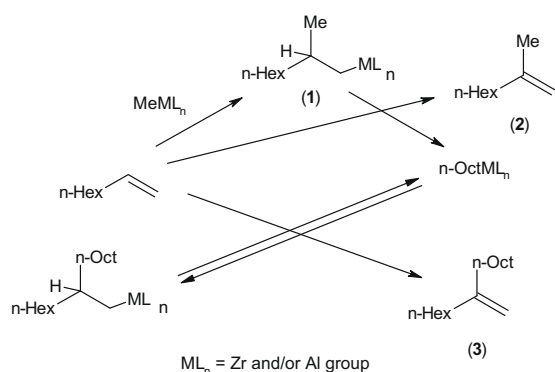
The reaction of hexene-1 with AlMe_3 , in the presence of 2 mol% of L_2ZrCl_2 ($\text{L} = \text{Cp}$, Cp' , Cp^* , Ind, Flu), at mole ratio $\text{Me}_3\text{Al}:\text{alkene}:\text{L}_2\text{ZrCl}_2 = 60:50:1$, and room temperature, proceeds with the

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Scheme 1.



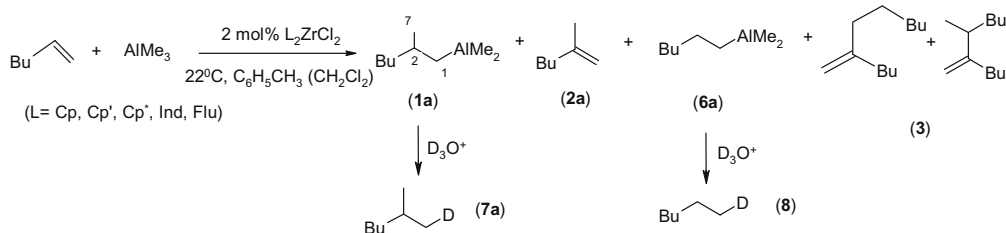
Scheme 2.

formation of carbo- (**1a**, **2a**), hydroalumination (**6a**) products and dimers (**3**) with the total yield of up to 92% (Scheme 4).

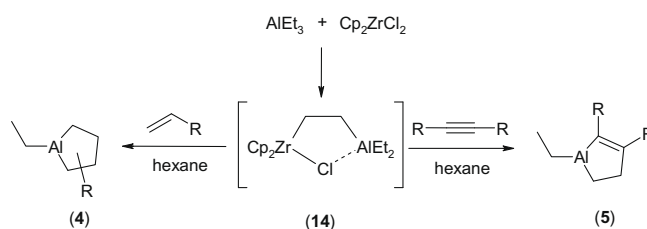
According to the data presented in Table 1, the conversion of hexene-1 and chemoselectivity of the reaction significantly depend on the structure of π -ligand in the zirconium complex and on the solvent nature. Thus, the reaction, which runs in the presence of Zr complexes with Cp and Cp' ligands, yields mainly dimers (**3**); an essential part of those consists of "head-to-tail" dimerization product (mole ratio ht:tt \sim 7:1). Formation of α -olefin dimers in the systems OAC – transition metal complex was repeatedly discussed in literature (see, for example, [8]). In the case of Cp_2ZrCl_2 and $\text{Cp}'_2\text{ZrCl}_2$ the aromatic solvent replacement with CH_2Cl_2 does not change the ratio between products **1a**, **2a**, and **6a**, but substantially increases the yield of dimerization products **3**.

In the reaction of AlMe_3 with hexene-1, in the presence of Zr π -complexes with sterically hindered ligands ($L = \text{Cp}^*$, Ind or Flu), a predominance of the carboalumination process (products **1a** + **2a**) was observed. Application of CH_2Cl_2 as the solvent, and $\text{Cp}'_2\text{ZrCl}_2$ or $\text{Flu}_2\text{ZrCl}_2$ as the catalysts, selectively gives **1a** with the yield of over 50%; in this case the yield of dimers **3** decreases with the growth of Zr π -ligand size.

The NMR ^{13}C spectrum of **1a** exhibits characteristic broadened signal of α -carbon atom attached to Al [9a] at 20.9 ppm; this signal correlates with proton resonance lines of AB system in ^1H spectra



Scheme 4.



Scheme 3.

at high field in the range of 0–0.2 ppm. These protons are diastereotopic due to the neighboring chiral center at β -carbon atom. The chemical shift of 155.9 ppm in ^{27}Al NMR spectrum confirms the dimeric structure of **1a** [9b].

Further, we studied OAC, $\text{Cp}'_2\text{ZrCl}_2$, and alkene concentration influence on the reaction product yields. As shown in Table 2, the increase in the catalyst concentration accelerates the carboalumination process (products **1a** + **2a**). At stoichiometric conditions, when the mole ratio $\text{Me}_3\text{Al} : \text{alkene} : \text{Cp}'_2\text{ZrCl}_2$ is 2:2:1, almost selective formation of **1a** with yield of 65% was observed.

Taking into account reaction mechanisms proposed in Refs. [2a,8b,c], and also considering the experimental data concerning interligand change between AlR_3 and zirconocenes [5,10], we suggested Scheme 5.

In the first stage of the process, AlMe_3 alkylates the zirconocene, thus, providing complex **9**, which then carbometallates alkenes with the formation of intermediate **10**. Further, the transmetalation of **10** by trialkylalane gives carboalumination product **1** and, thus, finishes the small catalytic cycle **A**. In parallel to the transmetalation, intermediate **10** can undergo β -C–H-activation that results in disubstituted alkene **2** and hydride complex **11**, which initiates subsequent catalytic cycle **B**. This cycle runs via intermediate **12**, which appears to be the source of dimers **3** and hydroalumination products **6**. The observation of alkylalanes **6** indicates the contribution of the large catalytic cycle **C** into the whole process. Therefore, we can suggest that complex **9** is the key intermediate of reaction of AlMe_3 with alkenes, and this is the complex which drives the process through catalytic cycles **A–C**.

Table 1The product yields of the reaction of hexene-1 with AlMe₃, catalyzed with L₂ZrCl₂ (mole ratio AlMe₃:alkene:L₂ZrCl₂ = 60:50:1, reaction time 24 h, 22 °C).

L ₂ ZrCl ₂	Solvent	Hexene-1 conversion, %	Yield, %			
			1a (7a)	2a	6a (8)	3
Cp ₂ ZrCl ₂	CH ₂ Cl ₂	92	3	14	7	68
	C ₆ H ₅ CH ₃	69	3	21	7	38
Cp ₂ ⁺ ZrCl ₂	CH ₂ Cl ₂	84	11	14	7	52
	C ₆ H ₅ CH ₃	39	9	9	9	12
Cp ₂ ⁺ ZrCl ₂	CH ₂ Cl ₂	68	53	8	7	–
	C ₆ H ₅ CH ₃	44	15	14	14	1
Ind ₂ ZrCl ₂	CH ₂ Cl ₂	87	28	18	8	33
	C ₆ H ₅ CH ₃	70	38	14	10	8
Flu ₂ ZrCl ₂	CH ₂ Cl ₂	64	51	4	3	6
	C ₆ H ₅ CH ₃	22	16	3	<1	3

Table 2Influence of mole ratio AlMe₃:hexene-1:Cp₂⁺ZrCl₂ on the product yields (reaction time 24 h, 22 °C, CH₂Cl₂).

Mole ratio	Hexene-1 conversion, %	Yield, %			
		1a (7a)	2a	6a (8)	3
AlMe ₃ :alkene:Cp ₂ ⁺ ZrCl ₂					
60:50:1	68	53	8	7	–
60:50:2	71	59	5	6	1
2:2:1	67	65	2	–	1

It should be noted that the long reaction time of 24 h, during which we observed only 70% of the alkene conversion (e.g. in system Me₃Al–alkene–Cp₂⁺ZrCl₂), testifies a slow rate of the alkene introduction into complex **9**, which is the result of electronic and steric ligand effects [10]. The decrease in dimer **3** yield altogether with the growth of π-ligand size can also be affected by the same electronic and steric factors, which disturb the introduction of the second alkene molecule into intermediate **12**. Moreover, the influence of a solvent on the yield of carboalumination products and dimers probably is connected with the stability of the complexes **9** and **12** and also with the ratio of the reaction rates, which run through the cycles **A**, **B** and **C**.

Thus, the proposed scheme adequately describes the experimental data obtained; however, the mechanism is still questionable, since both the structure of the catalytically active centers and the mechanism of alkenes introduction into bimetallic systems are unclear. These problems have been discussed in numerous works, e.g. [11, and ref. cited herein], and, of course, the scheme proposed by us requires additional experimental and theoretical verification.

According to Scheme 5, one can assume that zirconocene hydrides of type **11** should be capable to catalyze not only the hydro-metalation reactions, but also the alkene carbometallation and dimerization reactions. Indeed we found that reaction of hexene-1 with AlMe₃ in the presence of either L₂ZrH₂ or L₂ZrHCl (L = Cp, Cp') both under the catalytic and stoichiometric conditions results in the same products as in the case of L₂ZrCl₂ (Table 3).

2.2. Chemoselectivity of the reaction of hexene-1 with AlEt₃, catalyzed with L₂ZrCl₂

The reaction of hexene-1 with AlEt₃, in the presence of 2 mol% of L₂ZrCl₂ (Scheme 6), at room temperature, yields the products of cyclo- (**4**), carbo- (**1b**, **2b**) and hydroalumination (**6a**). Moreover, in some reactions we identified dimers **3**.

As follows from Table 4, alkene conversion in the reaction with AlEt₃ mainly does not depend on the catalyst type and the solvent

nature, and the total yield of products is more than 90%. The conversion decreased to 71–88% only in the case of Flu₂ZrCl₂.

We observed the maximal yields of aluminacyclopentane **4** (>63%) in the reaction that run in benzene and in the presence of Zr complexes substituted with Cp, Cp⁺, Cp⁺ and Ind ligands. The use of CH₂Cl₂ as the solvent altogether with Zr catalysts, which contain bulky ligands (Cp⁺, Ind), increases the yield of carbometallation product **1b** to 48%. The formation of dimers **3** was found in the reaction of hexene-1 with AlEt₃, catalyzed with Flu₂ZrCl₂. Noteworthy, the maximal yield of **3** of up to 49% was achieved in CH₂Cl₂, as in the case of AlMe₃. The unusual behavior of fluorenyl complex can be caused by the tendency of π-ligands toward η³-coordination [12].

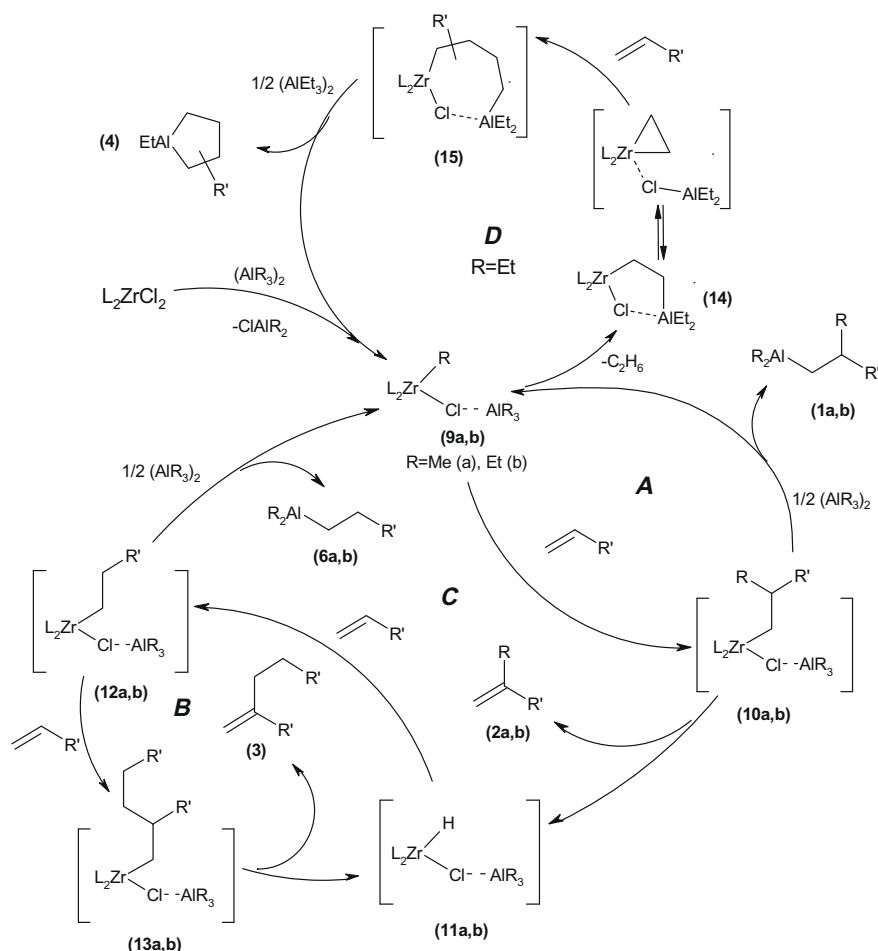
Further we studied the influence of initial reagents mole ratio on the product yields (Table 5).

As shown in Table 5, the raising of OAC, alkene or catalyst concentration under the catalytic conditions reduces both the hexene-1 conversion and the yield of ethylaluminum products (**1b** and **2b**), and increases the yield of hydroalumination product (**6b**) and aluminacyclopentane (**4**). At stoichiometric conditions we observed the high alkene conversion, while the ratio **1b**:**4** remained the same ~2:1.

The 1-diethylalumina-2-butylhexane (**1b**) was identified by both the analysis of deuterolysis product and the means of ¹H, ¹³C, ²⁷Al NMR spectroscopy using one- and two-dimensional procedures. Thus, the NMR ¹³C spectrum of **1b**, also as spectrum of **1a**, exhibits broadened signal of α-carbon atom bonded with Al at 18.5 ppm. The signal corresponds to the multiplet at 0.48 ppm in ¹H spectra, which shape is not change in the temperature range of 220–300 K. This fact and also the ²⁷Al chemical shift of **1b** at 166.9 ppm prove the dimeric structure of **1b**. In contrast to **1a** the protons of AlCH₂ group at 0.48 ppm of **1b** are not diastereotopic, probably, due to the reducing of chirality degree at β-carbon atom, which occurs as a result of replacement of methyl in **1a** with ethyl group in **1b** [13, p. 65].

Thus, summarizing experimental results we suppose that reactions in catalytic system L₂ZrCl₂–AlEt₃–alkene run by the same pathways, which are shown in Scheme 5, however, one additional catalytic cycle **D**, which provides cyclometallation products, is added.

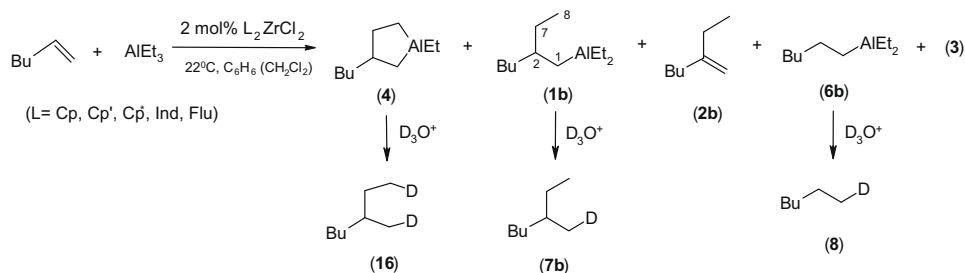
The increasing of carbometallation product (**1** and **2**) yield with the use of chlorine-containing solvent (CH₂Cl₂) and Zr complexes substituted with bulky ligands (Cp⁺, Ind) could be caused by the raising of complex **9** living time due to the decreasing of rates of both interligand exchange and β-C–H activation processes. The lower yield of dimers **3** in the case of AlEt₃ comparably with AlMe₃ could be caused by rapid transmetalation of complex **12** into complex **6**.



Scheme 5.

Table 3
Influence of mole ratio and Zr π -ligand environment on the product yields in the reaction of hexene-1 with AlMe_3 in the presence of zirconocene hydrides L_2ZrH_2 or L_2ZrHCl [$\text{L} = \text{Cp}, \text{Cp}'$] (reaction time 24 h, 22°C , toluene).

L_2ZrH_2	Mole ratio AlMe_3 :alkene:[Zr]	Hexene-1 conversion, %	Yield, %			
			1a (7a)	2a	6a (8)	3
Cp_2ZrHCl	60:50:1	69	2	10	11	46
	2:1:1	88	4	13	38	33
	2:2:1	97	14	4	37	42
Cp_2ZrH_2	60:50:1	40	8	–	3	29
	2:1:1	62	11	–	5	46
	2:2:1	58	13	7	9	38
$\text{Cp}'_2\text{ZrH}_2$	60:50:1	70	29	21	7	13
	2:1:1	54	40	–	11	3
	2:2:1	72	37	4	6	25



Scheme 6.

Table 4The product yields of the reaction of hexene-1 with AlEt₃, catalyzed with L₂ZrCl₂ (mole ratio AlEt₃:alkene:L₂ZrCl₂ = 60:50:1, reaction time 24 h, 22 °C).

L ₂ ZrCl ₂	Solvent	Hexene-1 conversion, %	Yield, %				
			1b (7b)	2b	4 (16)	6b (8)	3
Cp ₂ ZrCl ₂	CH ₂ Cl ₂	96	16	16	51	13	<1
	C ₆ H ₆	91	24	2	63	2	–
Cp' ₂ ZrCl ₂	CH ₂ Cl ₂	98	16	9	62	10	–
	C ₆ H ₆	97	6	10	69	12	–
Cp' ₂ ZrCl ₂	CH ₂ Cl ₂	99	48	13	21	10	7
	C ₆ H ₆	96	15	2	74	5	–
Ind ₂ ZrCl ₂	CH ₂ Cl ₂	93	36	3	45	7	2
	C ₆ H ₆	99	25	–	74	<1	<1
Flu ₂ ZrCl ₂	CH ₂ Cl ₂	88	6	19	6	14	49
	C ₆ H ₆	71	8	13	31	12	10

Table 5Influence of mole ratio AlEt₃:hexene-1:Cp'₂ZrCl₂ on the product yields (reaction time 24 h, 22 °C, CH₂Cl₂).

Mole ratio AlEt ₃ :alkene:Cp' ₂ ZrCl ₂	Hexene-1 conversion, %	Yield, %				
		1b (7b)	2b	4 (16)	6b (8)	3
60:50:1	~99	48	13	21	10	7
60:50:2	76	43	4	20	7	2
120:50:1	74	16	9	36	12	1
60:100:1	80	19	9	35	14	3
2:2:1	98	60	1	33	4	1

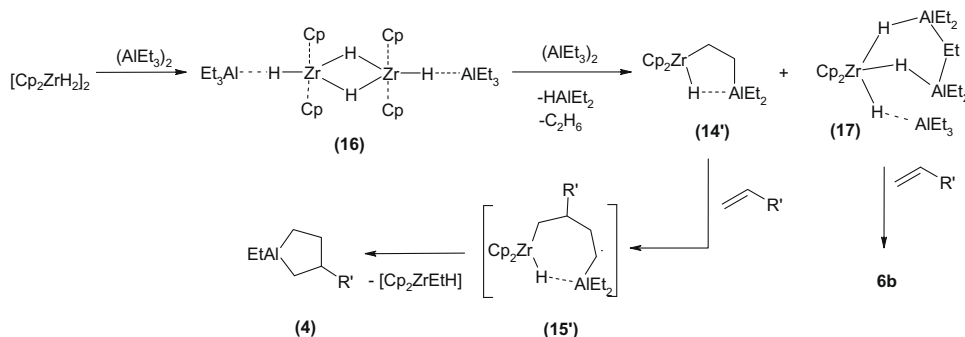
We found that as in the case of AlMe₃ zirconocene hydrides (L₂ZrH₂ or L₂ZrHCl [L = Cp, Cp']) catalyze the reaction of AlEt₃ with hexene-1, which provides the same hydro-, carbo-, cyclometallation products and dimers (Table 6). Therefore, the zirconocene hy-

drides of type **11** (Scheme 5) could be the possible intermediates of the reaction.

Interestingly that the reaction of AlEt₃ with hexene-1 in the presence of 2 mol% of L₂ZrH₂ (L = Cp, Cp') gave aluminacyclopentane **4** with high yield of 75–83%. According to Scheme 5, formation of aluminacyclopentane is possible through the five-membered intermediate **14**, which contains Zr–Cl–Al bridge. Probably, zirconocene dihydrides generate the intermediate **14'** similar to **14**, which also cyclometallate alkenes (Scheme 7). The NMR study of Cp₂ZrH₂ and AlEt₃ interaction (1:2) confirmed the generation of complex **14'** through the known hydride complex **16** [7a]. Complex **14'** is formed altogether with intermediate of preliminary structure **17**, which contains [Cp₂ZrH₃] fragment with three different hydrides. The fast interaction of **17** with hexene-1 gave the hydrometallation product **6b**, whereas complex **14'** slowly reacted with alkene providing aluminacyclopentane **4**.

Table 6Influence of mole ratio and Zr π-ligand environment on the product yields in the reaction of hexene-1 with AlEt₃ in the presence of zirconocene hydrides L₂ZrH₂ or L₂ZrHCl [L = Cp, Cp'] (reaction time 24 h, 22 °C, benzene).

L ₂ ZrH ₂	Mole ratio AlEt ₃ :alkene:[Zr]	Hexene-1 conversion, %	Yield, %				
			1b (7b)	2b	4 (16)	6b (8)	3
Cp ₂ ZrHCl	60:50:1	96	5	6	62	22	<1
	2:1:1	94	–	–	38	–	–
	2:2:1	96	9	1	42	43	<1
Cp ₂ ZrH ₂	60:50:1	99	6	1	75	17	–
	2:1:1	85	24	2	54	5	–
	2:2:1	66	32	3	30	<1	–
Cp' ₂ ZrH ₂	60:50:1	99	3	<1	83	12	<1
	2:1:1	98	38	5	–	47	8
	2:2:1	98	16	8	29	38	7



3. Conclusion

The influence of the organoaluminium compound nature, Zr π -ligand environment, solvent type and reagent ratio on the chemoselectivity of reactions of trialkylalanes (AlMe₃, AlEt₃) with alkenes, catalyzed with L₂ZrCl₂ has been studied. In the case of AlMe₃, the hydro- and carboalumination products, and alkene dimers are formed. The catalytic reaction of AlEt₃ with the olefins yields aluminacyclopentanes altogether with the hydro- and carboalumination products, and the dimers. It was shown that the OAC nature and Zr π -complex structure exhibit the most effect on the reactions pathway.

The reaction of alkenes with AlMe₃, which runs in chlorinated solvents (CH₂Cl₂) in the presence of Zr complexes with small π -ligands (Cp and Cp'), yields mainly dimers. The use of Zr complexes substituted with more bulky π -ligands (Cp*, Ind) and chlorine-containing solvents (CH₂Cl₂) increases the carboalumination products yield. The chlorinated solvent replacement with hydrocarbons in reaction with AlEt₃ substantially increases the yield of aluminacyclopentanes.

We found that reaction of hexene-1 with AlMe₃ in the presence of either L₂ZrH₂ or L₂ZrHCl (L = Cp, Cp') both under the catalytic and stoichiometric conditions results in the same products as in the case of L₂ZrCl₂. This fact implies participation of zirconocene hydrides as intermediates in the reaction of alkenes with AlR₃, catalyzed with L₂ZrCl₂.

The probable reaction mechanism is proposed. The mechanism includes four catalytic cycles **A–D**, where the complex [L₂ZrRCl·AlR₃] is the key intermediate of the whole process.

4. Experimental

4.1. General

All operations with organometallic compounds were carried out under argon using Schlenk techniques. Solvents (benzene and toluene) were dried by refluxing over *i*-Bu₂AlH and freshly distilled prior to use. Methylene chloride was dried over P₂O₅. Commercially available 98% AlEt₃ and 97% AlMe₃ (Aldrich) were involved into the reactions. The catalysts L₂ZrCl₂ were prepared using the standard techniques from ZrCl₄ (99.5%, Aldrich) (L = Cp [14a], Cp' [14b], Ind [14c], Flu [14d]). Cp₂ZrCl₂ (97%) was purchased from Aldrich. The Schwartz reagents Cp₂ZrHCl and Cp₂ZrH₂ were prepared as described previously in Refs. [15,7a].

The NMR spectra ¹H, ¹³C and ²⁷Al were recorded on spectrometer Bruker AVANCE-400 (400.13 MHz (¹H), 100.62 MHz (¹³C) and 104.23 MHz (²⁷Al)). *d*₆-Benzene, *d*₈-toluene and *d*-chloroform were used as solvents and internal standards. The samples were prepared in standard tubes of 5 mm diameter. Chemical shifts are internally referenced to the TMS signal. ²⁷Al chemical shifts are referenced to the Al(H₂O)₆Cl₃ signal. One- and two-dimensional NMR spectra (COSY HH, HSQC, HMBC) were measured with standard pulse sequences.

The yields of hydro-, carbo- and cycloalumination products were determined from the yields of hydrolysis products, which were calculated relative to amount of the initial olefin. The hydrolysis products of reaction mixture were analyzed on chromatograph Carlo Erba (He, column 50,000 × 0.32 mm, fixed phase "Ultra-1", flame-ionizing detector). Mass spectra were obtained on spectrometer MD 800, TRIO 1000 VG Masslab (Great Britain).

4.2. Reaction of hexene-1 with AlR₃ (R = Me, Et) in the presence of L₂ZrCl₂ (L = Cp, Cp', Cp*, Ind, Flu)

A 10 ml flask equipped with a magnetic stirrer and filled with argon was loaded with 1–2 mmol of L₂ZrCl₂, 1.0 ml of methylene

chloride or toluene (benzene), 2–100 mmol of hexene-1 and 2–120 mmol of AlR₃. The reaction mixture was stirred for 24 h at 22 °C. Then the mixture was decomposed with 10% HCl or DCl at 0 °C. The products were extracted with benzene; further, the organic layer was dried over Na₂SO₄ and analyzed by GC or GC–MS.

4.2.1. 1-Dimethylalumina-2-methylhexane (**2a**)

¹H NMR (C₇D₈) δ 0.09, 0.11 (AB, dd, ²J_{HH} = 14.2 Hz, 2H, AlCH₂); 1.60–1.72 (m, 1H, CH); 0.96 (d, ³J_{HH} = 6.8 Hz, 3H, CH₃); 1.18–1.41 (m, 6H, CH₂); 0.92 (t, ³J_{HH} = 6.9 Hz, 3H, CH₃); –0.27 (s, 6H, MeAl). ¹³C NMR (C₆D₆) δ 20.89 (br, C₁), 30.54 (C₂), 41.79 (C₃), 29.88 (C₄), 23.02 (C₅), 14.02 (C₆), 24.52 (C₇), –7.40 (MeAl). ²⁷Al NMR (C₆D₆) δ 155.9.

4.2.2. 1-Diethylalumina-2-ethylhexane (**3a**)

¹H NMR (C₇D₈) δ 0.48 (m, 2H, AlCH₂CH), 1.59–1.62 (m, 1H, CH), 1.21–1.49 (m, 8H, CH₂), 0.90–0.95 (m, 6H, CH₃), 0.24–0.31 (m, 4H, AlCH₂CH₃), 1.14 (t, ³J_{HH} = 8.0 Hz, 6H, AlCH₂CH₃). ¹³C NMR (C₆D₆) δ 18.56 (br, C₁), 36.58 (C₂), 38.51 (C₃), 31.21 (C₄), 23.09 (C₅), 13.95 (C₆), 29.52 (C₇), 11.23 (C₈), 7.59 (CH₃CH₂Al), 2.40 (br., CH₂Al). ²⁷Al NMR (C₆D₆) δ 166.9.

4.2.3. 1-Deuterio-2-methylhexane (**7a**)

¹H NMR (CDCl₃) δ 0.90–0.93 (m, 2H, CH₂D), 0.94 (d, ³J_{HH} = 6.8 Hz, 3H, CH₃CH), 0.96 (t, ³J_{HH} = 6.0 Hz, 3H, CH₃), 1.48–1.52 (m, 1H, CH), 1.18–1.21 (m, 4H, CH₂), 1.32–1.36 (m, 2H, CH₂CH₃). ¹³C NMR (CDCl₃) δ 22.53 (t, C₁, J_{C–D} = 18.9 Hz), 29.90 (C₂), 38.95 (C₃), 31.46 (C₄), 23.19 (C₅), 14.35 (C₆), 22.83 (C₇). MS *m/z*: 101 [M⁺].

4.2.4. Deuterio-2-ethylhexane (**7b**)

¹H NMR (CDCl₃) δ 0.82–0.95 (m, 8H, CH₃, CH₂D); 1.22–1.39 (m, 5H, CH, CH₂); 1.04–1.15, 1.26–1.35 (AB, m, 1H, CHCH₂); 1.10–1.18, 1.24–1.35 (AB, m, 1H, CHCH₂). ¹³C NMR (CDCl₃) δ 18.88 (t, C₁, J_{C–D} = 19.0 Hz), 34.30 (C₂), 36.46 (C₃), 29.50 (C₄), 23.03 (C₅), 14.22 (C₆), 29.47 (C₇), 11.36 (C₈). MS *m/z*: 115 [M⁺].

Spectral data of products were identical to those of authentic sample **2a** [17], **2b** [16], **3** [8], and **16** [4a].

4.3. Reaction of hexene-1 with AlR₃ in the presence of L₂ZrH₂ (L = Cp, Cp')

A 10 ml flask equipped with a magnetic stirrer and filled with argon was loaded with 1 mmol of L₂ZrH₂, 1.0 ml of toluene (benzene), 2–60 mmol of AlR₃ and 1–50 mmol of hexene-1. The reaction mixture was stirred for 24 h at 22 °C. Then the mixture was decomposed with 10% HCl or DCl at 0 °C. The products were extracted with benzene; further, the organic layer was dried over Na₂SO₄ and analyzed by GC–MS.

4.4. Reaction of hexene-1 with AlR₃ in the presence of Cp₂ZrHCl

A 10 ml flask equipped with a magnetic stirrer and filled with argon was loaded with 1 mmol of Cp₂ZrHCl, 1.0 ml of toluene (benzene), 2–60 mmol AlR₃ and 2–50 mmol of hexene-1. The mixture was stirred for 24 h at 22 °C. The mixture was decomposed with 10% HCl or DCl at 0 °C. The products were extracted with benzene; further, the organic layer was dried over Na₂SO₄ and analyzed by GC–MS.

4.5. NMR study of the interaction of [Cp₂ZrH₂]₂ with AlEt₃

An NMR tube filled with argon was loaded with 0.6 mmol (134 mg) of Cp₂ZrH₂ and 0.4 ml of *d*₈-toluene. AlEt₃ (0.6 mmol, 0.11 ml) was added dropwise until the precipitate was dissolved. Finally the formation of complex **16** was observed [7a]. The mix-

ture was cooled to 0 °C, then 0.6 mmol of AlEt₃ were added. The formation of complexes **14'** and **17** was observed after 20 min by NMR.

Complex **14** (300 K). ¹H NMR (C₇D₈) δ –3.33 (s, 1H, ZrHAl), –0.81 (dd, AB, ²J_{HH} = 10.0 Hz, 2H, AlCH₂), 1.30 (m, 2H, ZrCH₂), 0.25–0.29 (m, 4H, AlCH₂CH₃), 1.26 (t, ³J_{HH} = 8.0 Hz, 6H, AlCH₂CH₃), 5.19 (s, 10H, Cp). ¹³C NMR (C₆D₆) δ –8.94 (t, J_{C–H} = 126 Hz, AlCH₂), 31.46 (t, J_{C–H} = 147 Hz, ZrCH₂), 2.44 (AlCH₂CH₃), 9.41 (AlCH₂CH₃), 102.28 (Cp).

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