Mechanistic aspects of chemo- and regioselectivity in Cp_2ZrCl_2 – catalyzed alkene cycloalumination by $AlEt_3$

Tatyana V. Tyumkina,[a,·] Denis N. Islamov,[a] Lyudmila V. Parfenova,[a] Richard J. Whitby,[b]
Leonard M. Khalilov, [a] Usein M. Dzhemilev [a]

[a]*Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 141 Pr. Oktyabrya,*
Ufa 450075, Russian Federation
[b]*Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*
E-mail: ttvnmr@gmail.com

Abstract

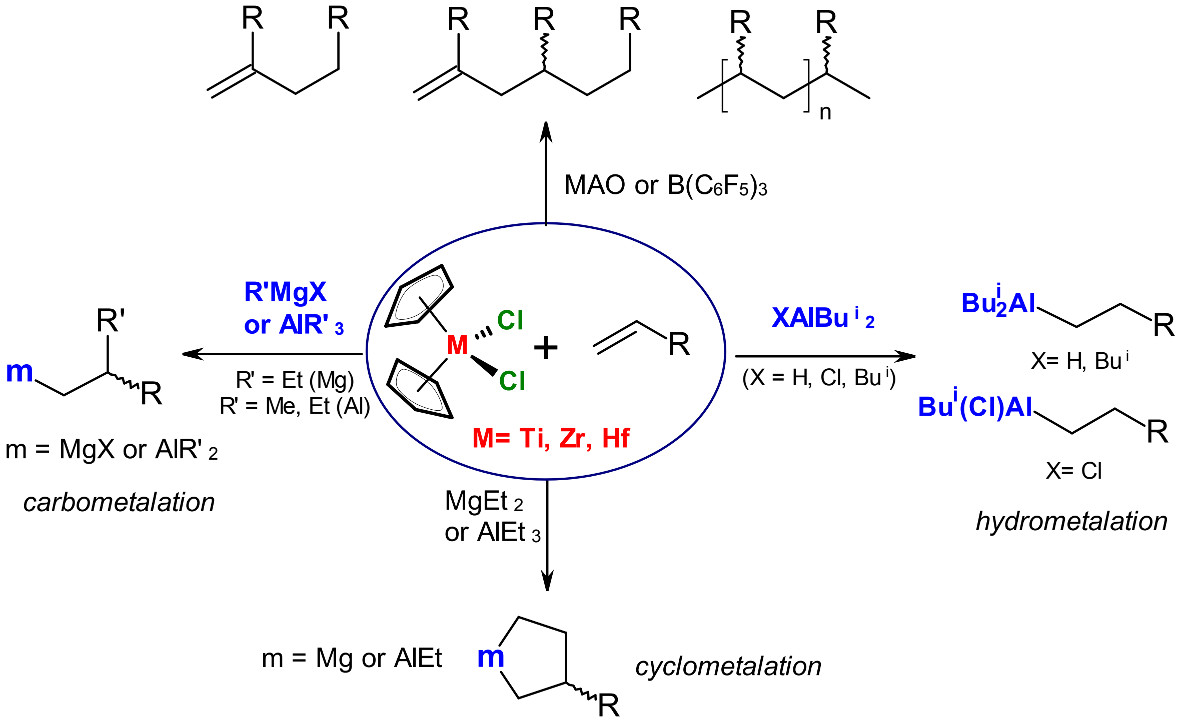
The reactions of styrene and 1-hexene with zirconacyclopropane and the bimetallic five-membered Zr,Al-complex [$Cp_2Zr(\mu\text{-}Cl)CH_2CH_2AlEt_2$] as catalytically active sites in Cp_2ZrCl_2-catalyzed cycloalumination of α-olefins with $AlEt_3$ have been studied by DFT quantum chemical methods (PBE/3ζ, B3LYP/VDZ, B3LYP(GD3)/VDZ, M06-2X/VDZ, M06-2X/VTZ//VDZ). It was shown that key intermediates can exist in dynamic equilibrium with each other, and with $ClAlEt_2$ adducts. Comparative analysis was carried out for the energy characteristics of alternative pathways in the reaction of styrene or 1-hexene with the intermediates, implying different orientations of the substrates towards the Zr-C bond. The obtained data were used to elucidate the reasons for the observed dependence of the reaction regioselectivity on the substrate structure and the minor by-products formation. The applicability of M06-2X/cc-pVTZ-PP//M06-2X/cc-pVDZ-PP and PBE/3ζ methods for the description of the available experimental data was shown.

Keywords: cycloalumination; DFT calculations; reaction mechanism; zirconacycle; regioselectivity

1. Introduction

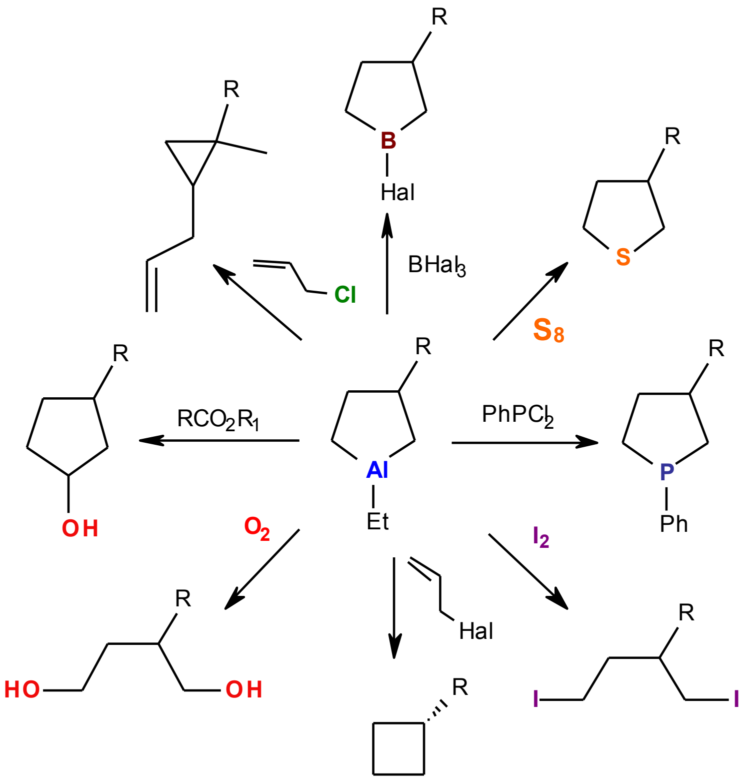
The discovery of metallocene compounds in the middle of the last century stimulated the development of numerous important trends in organometallic chemistry. One of these directions is homogeneous alkene polymerization, catalyzed by η^5- complexes of IV group transition metals in combination with MAO and organoboron compounds [1] (Scheme 1). Later it was shown that metallocenes can be used as catalysts in alkene or alkyne hydro- [2], carbo- [3] and cyclometalation [4]

[·] Corresponding author. E-mail: ttvnmr@gmail.com reactions, which provide both acyclic and cyclic organometallic compounds with high regio- and stereoselectivity.



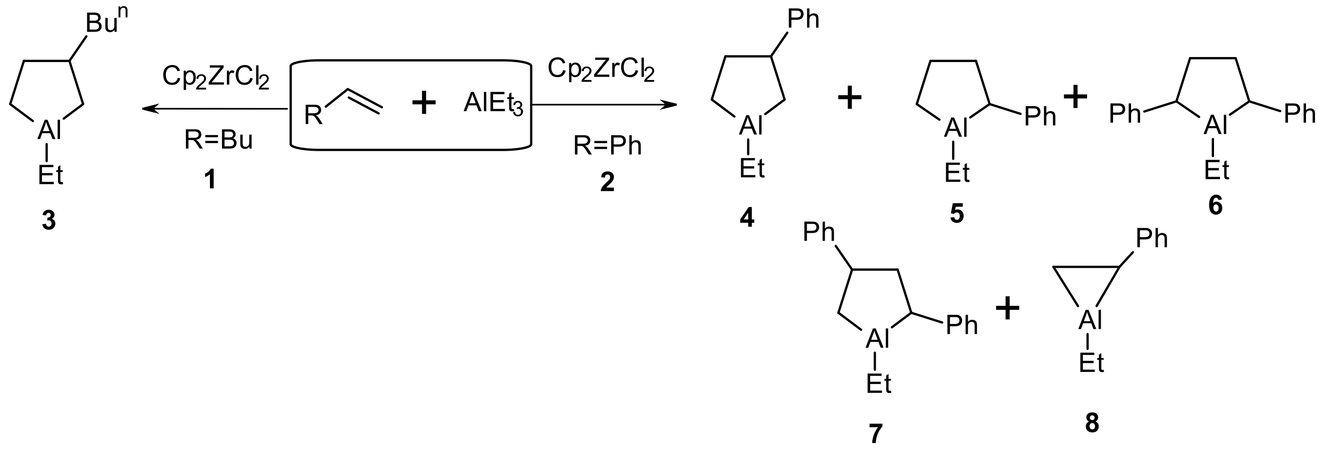
Scheme 1. η^5-Complexes of IV group transition metals in alkene polymerization and functionalization by organomagnesium and organoaluminum compounds

Catalytic alkene cycloalumination by $AlEt_3$ in the presence of Cp_2ZrCl_2 yields five-membered organoaluminum compounds (OAC) [4], aluminacarbocycles, which could be involved in the reactions with various electrophilic reagents to give a number of products: 1,4-butanediols, carbo- and heterocycles, etc. (Scheme 2) [5].



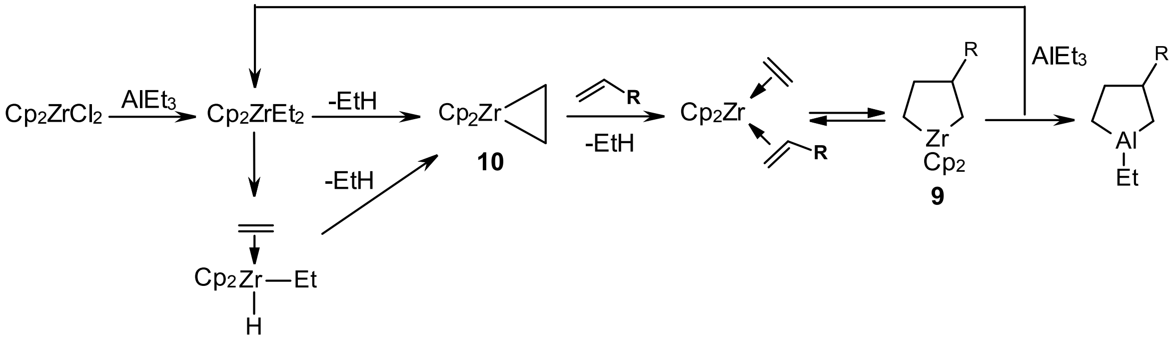
Scheme 2. Prospects of cyclic organoaluminum compounds in organic synthesis.

The cycloalumination regioselectivity was found to depend on the alkene structure [5]. Thus, cycloalumination of aliphatic terminal alkenes gives only the 3-substituted regioisomer of cyclic OAC [4], whereas styrene provides a mixture of 2- and 3-phenylalumolanes [6] (Scheme 3). Moreover, 2,4-diphenyl- (**6**, ~15%), 2,5-diphenylalumolane (**7**, ~3%), and 2-phenylaluminacyclopropane (**8**, ~7%) were identified as minor products. A similar regioselectivity dependence on the alkene structure was observed in the formation of zirconacyclopentane structures [7].



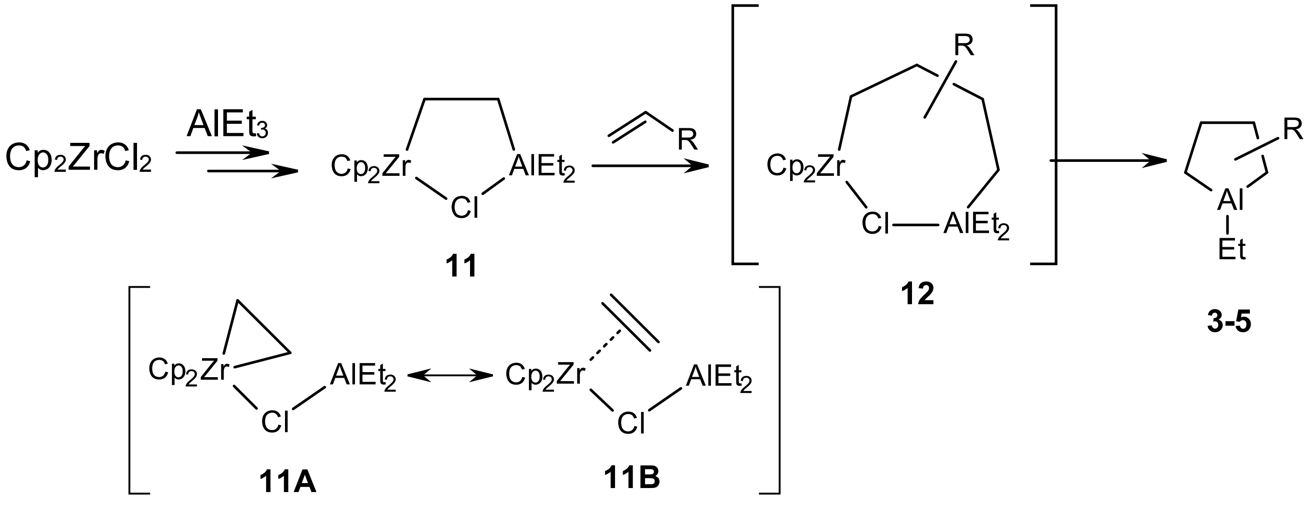
Scheme 3. Products of catalytic cycloalumination of 1-hexene and styrene.

Obviously, the reasons for these effects could be found in the reaction mechanism. Thus, Scheme 4 summarizes the ideas on the reaction flow, which are presented in Refs. [8], [9]. As follows from the scheme, zirconium complexes of various structures were proposed as the reaction intermediates. It is assumed that among these complexes zirconacyclopentane **9** forms via zirconium η^2- complexes [8]. Later the stage of hydride transfer in Cp_2ZrEt_2 followed by ethane elimination was ruled out in favour of the zirconacyclopropane **10** formation [9].



Scheme 4. Proposed mechanism of catalytic alkene cycloalumination [8], [9].

Experimental study on the mechanism of catalytic cycloalumination of alkynes [10] and alkenes [11] showed that the active site of the reaction is cyclic five-membered bimetallic Zr,Al-complex **11** (Scheme 5), which is fully converted to the target aluminacycles when treated with substrate. Earlier the intermediate **11** was found in the system Cp_2ZrCl_2 - $AlEt_3$ by W. Kaminsky [12]. The structure of the complex was identified by the means of ^1H and ^{13}C NMR spectroscopy.



Scheme 5. Experimental study on mechanism of catalytic alkene cycloalumination.

It was suggested that complex **11A** is the precursor of intermediate **11** [10] or they exist in dynamic equilibrium with each other [13]. The structure **11A** also can be represented as η^2- ethylene interaction with zirconium atom (complex **11B**, Scheme 5) analogous to known zirconocene-ethylene complex, stabilized by PMe_3 [14]. However, complexes **11A** and **11B** could be considered as mesomeric forms as shown in Scheme 5. It was postulated [11] that complex **11** transforms into 3-substituted aluminacyclopentanes *via* seven-membered bimetallic complex **12** (Scheme 5).

Thus, before our study there were no comprehensive answers on question how the probable key intermediates interact with the alkenes of various structures and regulate the reaction chemo- and regioselectivity. Therefore, the purpose of the work is quantum chemical study on the mechanism of the active site action in the alkene catalytic cycloalumination and elucidation of the fundamental factors that determine the reaction direction and position of alkyl(aryl) substitute in the products. For our theoretical studies we choose DFT PBE/3ζ method, because it satisfactorily describes the reactions catalyzed by IV group transition metal complexes [15]. The calculations were compared with the results obtained using the B3LYP method, which was widely applied for the theoretical study of the zirconocene systems as well [16] and the M06-2X functional as this has demonstrated excellent performance for zirconocene reactions in a recent benchmark study [17].

2. Experimental and Computational details

The DFT calculations with the Perdew-Burke-Ernzerhof (PBE) functional [18] in combination with a 3ζ basis set [19] were carried out using program Priroda-06 developed by Laikov [20]. The electronic configurations of the molecular systems were described by the orbital basis sets of contracted Gaussian-type functions of size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, (15s11p2d)/[10s6p2d] for Al and Cl, and (20s16p11d)/[14s11p7d] for Zr, which were used in combination with the density-fitting basis sets of uncontracted Gaussian-type functions of size (5s2p) for H, (10s3p3d1f) for C, (14s3p3d1f1g) for Al and Cl, and (22s5p5d4f4g) for Zr. DFT calculations with Gaussian 09 [21] used the M06-2X functional [22] with Dunnings correlation consistent cc-pVDZ and cc-pVTZ basis sets for H, C, Cl and Al [23], and the relativistically corrected effective core potential containing cc-pVDZ-PP and cc-pVTZ-PP basis sets for Zr [24] (as obtained from the EMSL Basis Set Exchange) [25]. Initial studies [Supplementary, Table S2] showed little benefit in optimizing structures using the larger basis set so we used singe point VTZ energy calculations at VDZ optimized structures. The VDZ calculations also provide the frequency data needed to correct electronic energies to Gibbs free energies. The ultrafine integration grid as implemented in Gaussian was used [26]. Initial studies on the effect of including solvent in the calculations through the Conductor – like Polarisable Continuum Model (CPCM) as implemented in Gaussian [27] (Supplementary, Table S3) showed generally small energy changes so were not used in the main work.

We also examined the use of the B3LYP functional [28] using the cc-pVDZ (H, C, Al, Cl) and cc-pVDZ-PP (Zr) basis sets, with and without Grimme's D3 empirical dispersion correction [29].

The geometry optimization of the complexes, vibrational frequency analysis, transition state (TS) search and calculation of entropy and thermodynamic corrections to the total energy of the compounds were carried out. The intrinsic reaction coordinates (IRC analysis) were also calculated to analyze the mechanism in detail for all the transition structures obtained at the same level of theory. No limitation was imposed on the changes in the geometric parameters of the subsystems studied. Thermodynamic parameters and activation energies were determined at 298.15 K. Both the minima and the transition states (TS, first order saddle point) were confirmed through calculation of the force constant (Hessian) matrix and analysis of the resulting frequencies. All minima were verified to have no negative frequencies and all the transition states were checked to have just one negative frequency.

Visualization of quantum chemical data was carried out using the programs QCC Front-End [30], ChemCraft [31] and GaussView 5 [32].

One- dimensional (BBO probe) ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument (400.13 MHz (^1H) and 100.62 MHz (^{13}C)) at temperatures 190 - 298 K in 5 mm ampules. The chemical shifts were internally referenced to d_8-toluene signals.

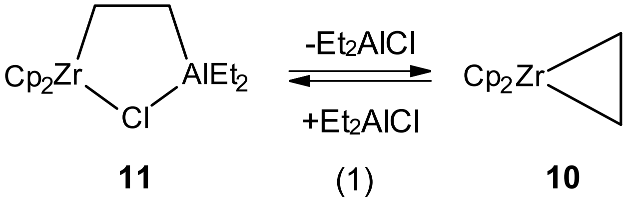
3. Results and discussion

3.1. Structure of the probable active sites in alkene cycloalumination reaction

The hypothetical structures of catalytically active complexes **11**, **11A**, and **11B** (Scheme 5) have been studied.

The structure of complex **11** was optimized on the PES of the molecule. In complex **11** the aluminum atom deviates from the plane of the four ring carbon atoms. Scanning of the Al-C bond dissociation in **11** was accompanied by energy increase only. The results indicate that there is no equilibrium between bimetallic Zr,Al-complexes **11** and **11A/11B**.

However, we suggested that due to rather low strength of the Zr-Cl bond [15] the organoaluminum moiety ($ClAlEt_2$) could be completely eliminated from the zirconium atom to give *in situ* the zirconacyclopropane **10** [33], which is extremely reactive towards alkene in the catalytic cycloalumination (Scheme 6). Metallacyclopropane structures are often represented as η^2-ethylene complexes. Nevertheless, sp^3 hybridization of carbon atoms that corresponds to the metallacyclopropane was established for $Cp^*_2Ti(C_2H_4)$, $Cp_2Zr(C_4H_6)$ and $Cp_2Zr(PMe_3)(C_2H_4)$ on the base of heteronuclear coupling constants ^1J (^{13}C-^1H) [34] and for $Cp_2Hf(PMe_3)(C_2H_4)$, $Cp_2Zr(AlkCH\text{-}CH_2)$, $Cp_2Zr(PhCH\text{-}CH_2)(PMe_3)$ on the base of NMR chemical shifts [35]. Moreover, the stronger coordination of olefin to the transition metal is accompanied by an increasing of C-C bond length to 1.449 Å (for example, in $Cp_2Zr(PMe_3)(C_2H_4)$ [34], [36]) comparing to 1.337 Å in ethylene molecule [37], whereas Zr-C bond lengths are 2.332 Å and 2.354 Å for the same example. Thus, the calculated values of d(Zr-C)= 2.31 Å and d(C-C)= 1.46 Å (PBE) and d(Zr-C)= 2.24 Å and d(C-C)= 1.48 Å (M06-2X) allows to attribute complex **10** to zirconacyclopropane structure.



Scheme 6. Probable equilibrium between the five-membered bimetallic complex **11** and zirconacyclopropane **10** (reaction 1).

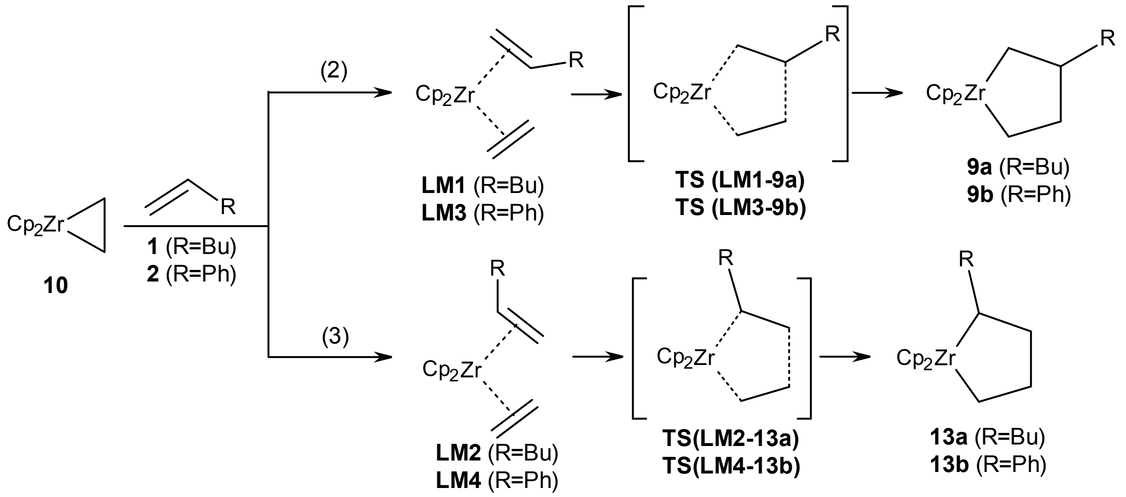
In order to determine the thermodynamic probability of zirconacyclopropane **10** formation under the reaction conditions, we studied the potential energy surface of bimetallic Zr,Al-complex **11** dissociation (reaction 1) towards three-membered metallacycle and Et_2AlCl. The relaxed scan of PES along the reaction coordinate showed that reaction (1) is endothermic (ΔG^{298} = 23.1 kcal/mol, M06-2X), nevertheless there is a theoretical probability of complex **11** dissociation, which confirms the idea of the possibility of dynamic processes involving elimination of OAC from the five-membered Zr,Al-complex [33]. Obviously, the equilibrium should be shifted toward complex **11**. Thus, the only bimetallic complex **11** in solution is detected in the ^{13}C NMR spectra in the temperature range of 190-298 K.

The obtained results give the conclusion that complexes **10** and **11** are in equilibrium, which provides more in-depth understanding of the mechanism of catalytic alkene cycloalumination. For example, the equilibrium explains the origin of the hydride five-membered Zr,Al-complex [$Cp_2Zr(\mu\text{-}H)CH_2CH_2AlEt_2$], detected in a previous study [38]. Therefore, complex **10** along with the known bimetallic complex **11** should be considered as an active site of catalytic alkene cycloalumination.

3.2. Reactions of olefins with zirconacyclopropane.

We simulated possible pathways of reactions between **10** and 1-hexene (**1**) or styrene (**2**) corresponding to two possible orientations of the substrate molecules relative to the Zr-C bond (Scheme 7, reactions (2) and (3)). The final addition products for each of these reactions are 3-

substituted (**9a**, **9b**) and 2-substituted (**13a, 13b**) zirconacyclopentanes. Relaxed potential energy surface scan along the reaction coordinate for reactions (2) and (3) involving two model olefins **1** and **2** demonstrated the existence of local minima (**LM1** – **LM4**) and transition states, which were optimized for the both pathways (Scheme 7). The existence of such prereaction complexes was proposed on the basis of the experimental data [4], while the theoretical studies has not been carried out.



Scheme 7. Possible ways of olefin coordination toward zirconacyclopropane **10**.

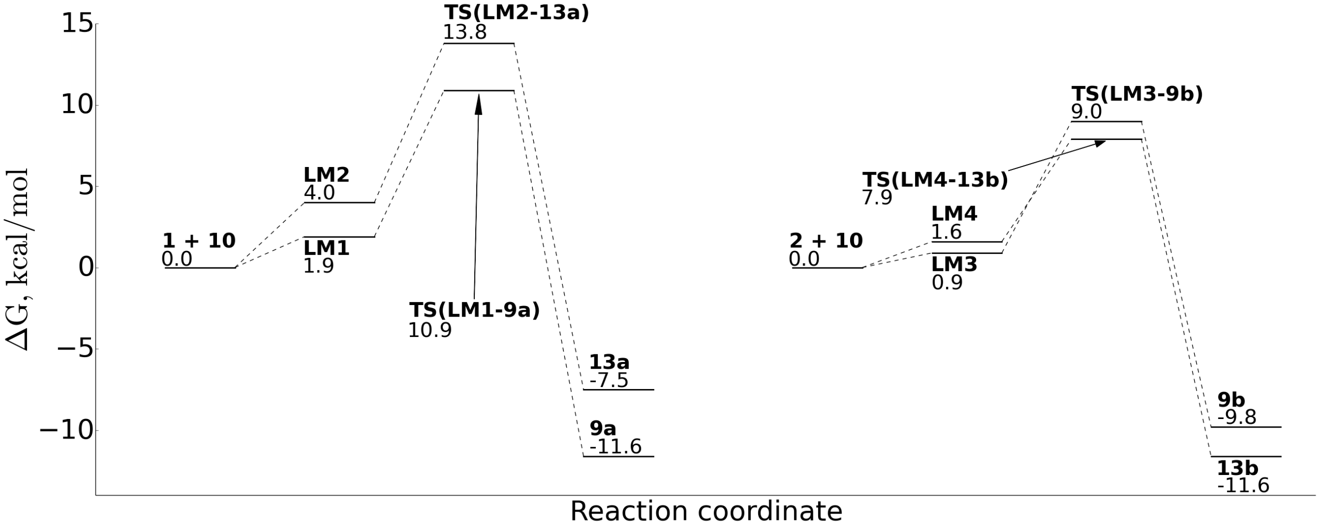


Fig. 1. Energy profile of reactions (2) and (3) for 1-hexene (left) and styrene (right) (M06-2X).

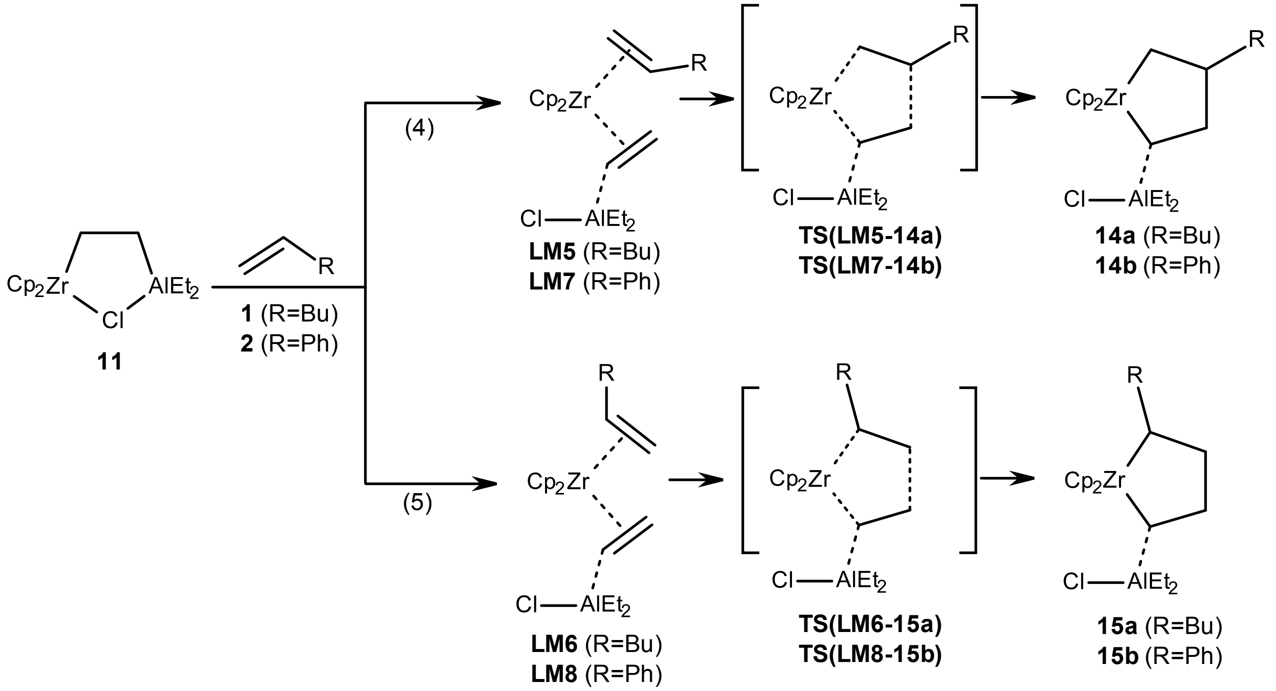
Comparative analysis of thermodynamic and activation parameters for reactions (2) and (3), which involve both aliphatic and aromatic olefins, revealed the distinctions that account for the observed dependence of the reaction regioselectivity on the alkene structure (Scheme 7, Fig 1). Comparison of the energy profiles involving 1-hexene and styrene indicates that for the former the 3-substitututed product (reaction 2) is favored both kinetically (10.9 cf 13.8 kCal/mol activation energy) and thermodynamically (4.1 kCal/mol more stable). For styrene reaction (3) leading to the 2-substituted product is favored (7.9 cf 9 kCal/mol activation energies; 1.8 kCal/mol more stable). The much smaller energy differences between the pathways for styrene are consistent with the observed mixture of 2- and 3-substituted products. The activation energy for the reverse reactions (18.8 - 22.5 kCal/mol) corresponding to a 1st order half life of minutes at room temperature, would suggest that under the catalytic conditions transmetallation of the product zirconacyclopentanes with aluminium is faster than the reverse reaction i.e. the reaction is probably under kinetic control.

It is noteworthy that the local minima **LM1-LM4**, which were found on the PES of the reaction **1** + **10** by a detailed scanning along the reaction coordinate, being higher in energy than the sum of the starting reagents (1-hexene + zirconacyclopropane) by ΔG^{298}_r = 1.9 - 4.0 kcal/mol (Fig. 1). Coordination of the styrene requires only ~ 1.0 kcal/mol (Fig. 1). The Gibbs free energy difference between local minima **LM4** and **LM3** is insignificant ($\Delta(G_{LM4}-G_{LM3})$ = 0.7 kcal/mol). Therefore, the orientation of the styrene molecule relative to the Zr-C bond is not crucial for the reaction pathway. However, the step of linear alkene bonding with **10** is expected to be more selective, because $\Delta(G_{LM2}-G_{LM1})$ = 2.1 kcal/mol. Energies of minima **LM1** and **LM2** are greater than that of zirconacyclopropane or styrene complexes **LM3** and **LM4**. Probably, the dependence of catalytic alkene carbo- and cycloalumination enantioselectivity *vs* alkene structure [39] is the consequence of differences in the local minima stabilities as well.

Local minima **LM1-LM4** can be considered as weak complexes, which are referred to bis-olefin structures discussed in the literature [40]. Indeed, the Zr-C and C-C bonds in the minima are longer than in the zirconacyclopentanes **9a**, **9b**, **13a** and **13b**. For example, in the optimized structure **LM1**, $d(\text{Zr-C}^1)$ = 2.44 Å, $d(\text{Zr-C}^2)$ = 2.40 Å (M06-2X), whereas in compound **9a** the corresponding covalent bonds are $d(\text{Zr-C}^1)$ = 2.28 Å, $d(\text{Zr-C}^2)$ = 2.28 Å (M06-2X). Formally, the inverse transformation from zirconacyclopentanes to **LM1-LM4** should be accompanied by cleavage of the $C^3 - C^4$ bond, i.e., the reaction should be characterized by an energy barrier. The possibility of this transformation depends not only on the barriers, but also on the thermodynamic stability of the minima with respect to zirconacyclopentanes. The energies of the stable species for 2-phenyl and 3-phenyl substituted - zirconacyclopentanes are close to each other in contrast with the alkyl substituted zirconacycles. Thus, the local minima **LM1-LM4** can be interpreted as pre-reaction complexes in the process of substituted zirconacyclopentane formation, which act as precursors for the cycloalumination products. The mechanism of the last transmetalation stage is the subject of our further studies.

*3.3. Reactions of olefins with bimetallic five-membered Zr,Al-complex **11**.*

In order to determine the possibility of intermediate **11** involvement in the cycloalumination reaction, we scanned the potential energy surface of the olefin insertion into the Zr-C bond of the bimetallic complex. The interaction between complex **11** and olefins (**1, 2**) can proceed along two alternative pathways (Scheme 8), which imply 1,2- or 2,1-orientations of the substrate relative to the Zr-C bond similarly to Scheme 7. The seven-membered complex **12**, which was proposed previously as intermediate in olefin cycloalumination [11] (Scheme 4), was not located on the PES of the reaction. In both ways the insertion of olefin into bimetallic Zr,Al-complex **11** is accompanied by removal of the $ClAlEt_2$ molecule from the zirconium coordination sphere. Obviously, this is due to relatively low strength of the Zr-Cl bond [15]. Thus, the first elementary step of the reactions (4) and (5) provides local minima **LM5** – **LM8** (Scheme 8). The elimination of $ClAlEt_2$ molecules from complexes **LM5** – **LM8** makes further transformations identical to reactions (2) and (3), which were described in the previous chapter. For comparison of the calculated thermodynamic parameters of these reactions with the parameters of reactions (4) and (5), we studied the PES of the formation of zirconacyclopentanes **14a**, **14b**, **15a**, and **15b** associated with OAC molecule (Scheme 8).



Scheme 8. Possible ways of olefin coordination toward complex **11**.

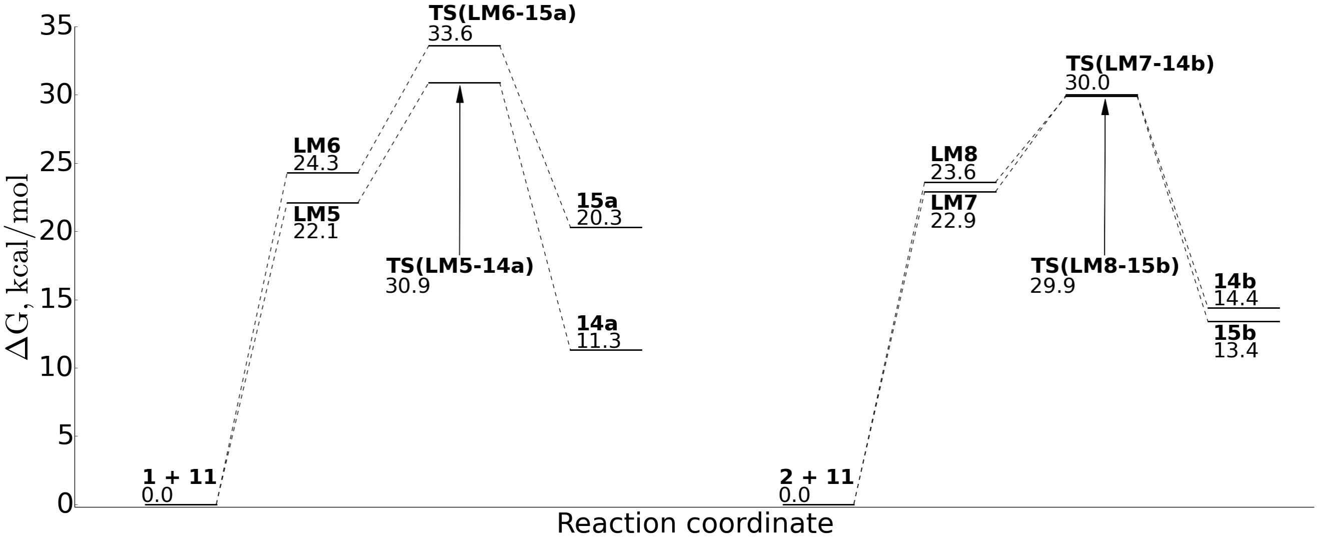


Fig. 2. Energy profile of reactions (4) and (5) for 1-hexene (left) and styrene (right) (M06-2X).

As follows from Figure 2, the processes of **LM5** – **LM8** formation from the alkene and **11** are energy consuming due to the process of OAC molecule displacement (Table 3). The $\Delta G^{298}{}_{r}$ values for this step vary in the range of 22.1-24.3 kcal/mol. These values are close to the energy parameters of the reactions (1) and (2). The relationships between the energies of **LM5** – **LM8** is comparable with **LM1** – **LM4**. As in the case of **LM2**, the formation of complex **LM6**, the precursor of 2-alkylzirconacyclopentane **15a**, is thermodynamically less probable. The interaction of the catalytically active five-membered complex **11** with styrene by the reactions 4 and 5 occurs with close activation parameters ($\Delta G^{\#}\sim$ 0.7 kcal/mol) and thermodynamic ($\Delta G\leq$ 1.0 kcal/mol), while the same parameters for reactions involving 1-hexene differ significantly ($\Delta G^{\#}\sim$ 2.0 kcal/mol, $\Delta G\sim$ 9.0 kcal/mol). This again displays the cause of differences in reaction regioselectivity for 1-hexene and styrene cycloalumination. It should be noted that elimination of the $ClAlEt_2$ molecule from the first local minimum requires $\Delta G_r =$ 2.9 kcal/mol.

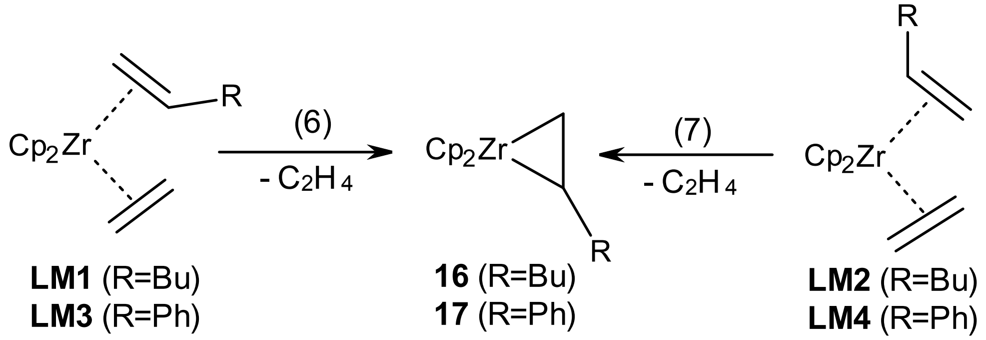
Thus, the obtained thermodynamic and activation parameters for reactions (4) and (5) indicate that complex **11** can be involved in the olefin cycloalumination through zirconacyclopropane generation. The rate-limiting step is insertion of the starting olefins into the Zr-C bond with simultaneous elimination of the $AlClEt_2$ molecule. Moreover, the comparative analysis of the processes of the direct alkene insertion into complex **10** and dissociation of **11** towards zirconacyclopropane are energetically close to each other. The activation energy for direct insertion into complex **11** is favoured by only 3 kCal/mol for insertion of 1-butene, and 1 or 2 kCal/mol (3- and 2-substituted zirconacycle) for styrene relative to that involving initial formation of free zirconocene(ethene) **10**.

3.4. Mechanism of by-products formation in the catalytic styrene cycloalumination.

As it was mentioned in the introduction, chemoselectivity of the reaction depends on the alkene structure. A specific feature of the styrene cycloalumination is the appearance of minor amounts of by-products **6**, **7**, **8** (Scheme 3), which formation mechanism remained unclear. Hypothetically, it can be assumed that compounds **6-8** originate from the corresponding zirconium intermediates **17-19** (Scheme 9 and 10), which arise from zirconocene "Cp_2Zr^{II}", analogously to Ti-based catalytic system [41].

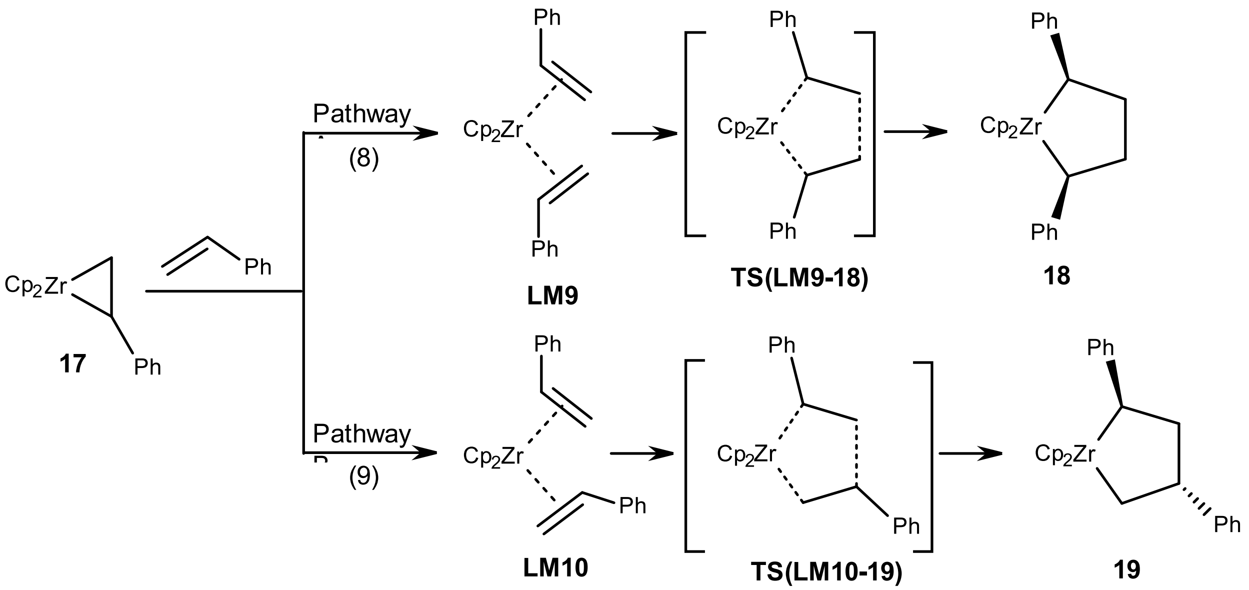
However, there are several problematic moments in the scheme. First, if "Cp_2Zr^{II}" is generated under the reaction conditions, why the same minor by-products are not observed in the case of linear alkenes? Second, unlike "Cp_2Ti^{II}" [42], "Cp_2Zr^{II}" was not experimentally identified, and it's involvement in the alkene (alkyne) transformation processes is being questioned [14], [43]. Third, according to our calculation the probability of "Cp_2Zr^{II}" formation at room temperature is low due to the high value of the Gibbs free energy for the dissociation **10** → "Cp_2Zr^{II}"+C_2H_4 (30.4 kcal/mol).

Thus, phenyl-substituted zirconacyclopropane could be considered as the precursor of disubstituted products. According to Scheme 9, complex **17** can be formed as a result of dissociation of the intermediates **LM3** and **LM4**. The estimation of the thermodynamic probability of the **LM1-LM4** dissociation to **16**, **17** with elimination of the ethylene molecule by reactions (6) and (7) (Scheme 9) showed that only low-energy complexes with styrene **LM3** and **LM4** can be converted to the zirconacyclopropane **17** (Table 1). According to the data obtained by both methods in the case of styrene derivatives ΔG_r^{298} is in the range of -3.3 ÷ 0.0 kcal/mol. Relatively small values of ΔG_r^{298} suggests the equilibrium on the stages (6) and (7). The same transformations for **LM1** and **LM2** are energetically unfavorable ($\Delta G_r^{298} \geq 0$). However, analysis of the calculation data for reactions (6) and (7) obtained by M06-2X method showed the possibility of the formation both phenyl- and alkylsubstituted zirconacyclopropanes. Moreover, among **LM1**-**LM4** local minima the ΔG^0_r of bisolefin complex **LM1** decomposition has the most negative value (-3.0 kcal/mol, Table 1). Probably, this most unstable complex is not realized in a real system, or its concentration is negligible to affect the cycloalumination reaction chemoselectivity.



Scheme 9. Dissociation of pre-reaction complexes towards zirconacyclopropanes **16, 17**.

The *in situ* generation of highly reactive compound **17** in the reaction mixture can start the second catalytic cycle with styrene (Scheme 10), which provides regioisomers **18** and **19**.



Scheme 10. Possible pathways of phenyl-substituted zirconacyclopropane transformation into disubstituted structures **18**, **19**.

The calculated data on thermodynamic and activation parameters by M06-2X for reactions (8) and (9) (Table1, Fig. 3) demonstrate the following: the energy barriers for the formation of compounds **18** and **19** are relatively low and both reactions are exothermic. As follows from Fig. 3, the formation of diphenyl substituted zirconacyclopentanes **18** and **19** needs only 9.1 and 10.7 kcal/mol, respectively. It should be noted that on scheme 10 we indicated stereochemistry of disubstituted zirconacycles as *trans* for **18** and *cis* for **19** on the base of their relatively greater stability (ΔG ~2.4 kcal/mol). The thermodynamic control of the reaction could be proposed as well, because the barriers of the reverse reactions from **18** or **19** to **LM9**/**LM10** are about 15.0 kcal/mol (see SI, Table S1). Compound **18** is formed with a lower barrier than compound **19**, which accounts for the predominant formation of the corresponding cyclic OAC among the reaction by-products.

Table 1

Calculated thermodynamic and activation parameters for reactions (8) and (9) (scheme 10) at T = 298.15 K ([ΔS] = cal/(mol·K); [ΔH] = [ΔG] = kcal/mol).

	PBE/3ζ						M06-2X/VTZ//VDZ					
Reaction	ΔH^0_r	ΔG^0_r	ΔS^0_r	$\Delta H^{\neq}_r$	$\Delta G^{\neq}_r$	$\Delta S^{\neq}_r$	ΔH^0_r	ΔG^0_r	ΔS^0_r	$\Delta H^{\neq}_r$	$\Delta G^{\neq}_r$	$\Delta S^{\neq}_r$
6	-	-	-				-	-	-			
LM1→16+C$_2$H$_4$	15.9	2.6	44.8				-16.6	-3.0	-45.4			

LM3→17+C_2H_4	13.7	0.0	46.0				-14.1	-0.9	-44.1			
7	-	-	-				-	-	-			
LM2→16+C_2H_4	14.2	1.2	43.6				-14.4	-1.0	-45.2			
LM4→17+C_2H_4	13.1	-0.2	44.5				-13.5	-0.3	-44.4			
8	-15.1	-0.6	-48.9				-28.1	-11.9	-54.2			
17+2→LM9	-8.8	6.2	-50.4				-10.8	3.4	-47.7			
LM9→18	-6.3	-6.7	1.5	7.2	8.1	-3.0	-17.3	-15.3	-6.5	3.5	5.7	-7.4
9	-13.3	-1.1	-40.7				-24.4	-9.8	-48.9			
17+2→LM10	-10.1	4.8	-50.1				-12.4	2.9	-51.5			
LM10→19	-3.2	-6.0	9.4	9.8	11.0	-3.9	-12.0	-12.7	2.5	6.9	7.8	-2.9

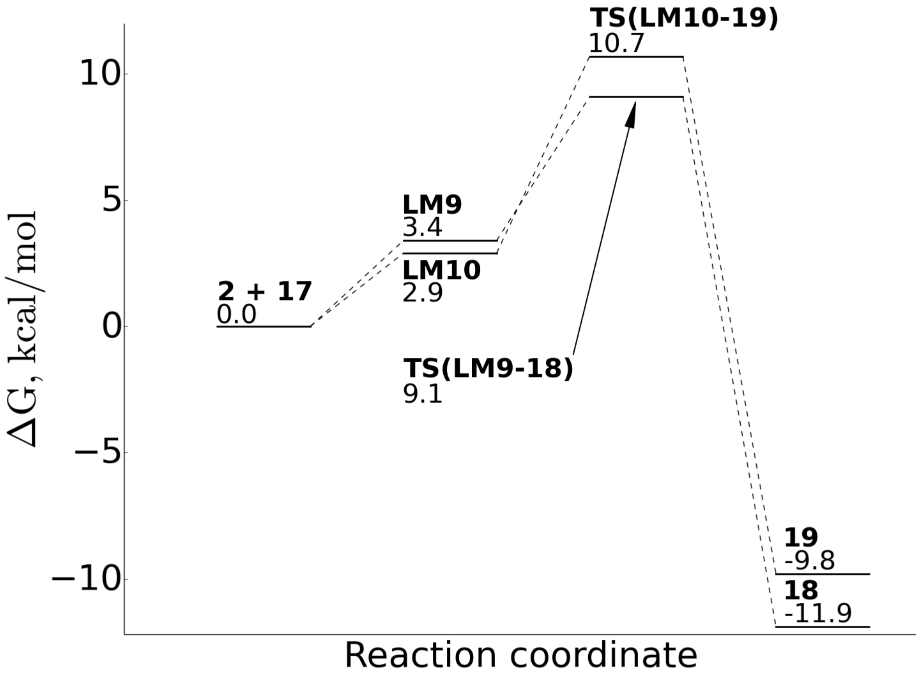
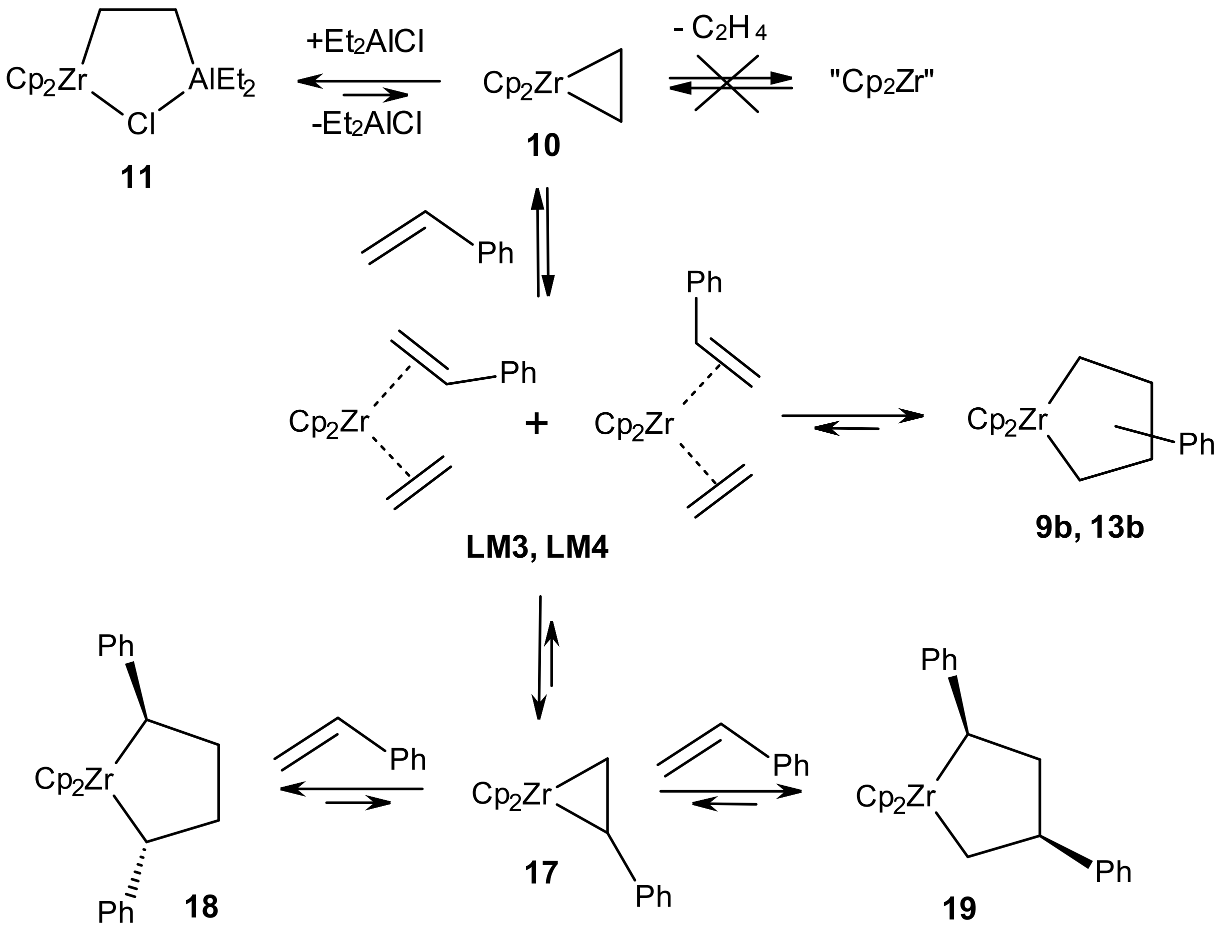


Fig. 3. Energy profile of reactions (8) and (9) (M06-2X).

Thus, the formation of by-products **6**, **7** and **8**, resulting from transmetalation of the corresponding zirconacyclopentanes, is caused by generation of phenyl-substituted zirconacyclopropane as a result of ethylene elimination from the low-energy pre-reaction zirconium complexes. However, the transformation channel of analogous complexes with 1-hexene proved to be thermodynamically unfavorable. As a result the probable mechanism of the by-products formation in the styrene cycloalumination can be presented as follows (Scheme 11).



Scheme 11. The probable mechanism of the by-products formation in the styrene cycloalumination reaction.

4.4. Comparison of calculation results obtained by various methods.

In order to compare the methods that were used in the present study we summarized the calculation data for series of reactions, which describe the mechanism of the interaction of the catalytically active sites with 1-hexene and styrene, in Table 2. We found that B3LYP method is less suitable for the description of the available experimental data on the reaction flow. It is noting that some of the geometries are distinctly different when going from B3LYP/VDZ to M06-2X/VTZ (or indeed B3LYP/VDZ with the Grimme's D3 dispersion correction). Method M06-2X in conjunction with a combined basis set VTZ@VDZ satisfactorily describes the experiment. It should be noted that the calculations using PBE/3ζ give results that are in good agreement with the experimental data, so it can be used as a method for a preliminary search of extrema on the PES of reaction, since it is less demanding of time and computer resources.

Table 2 Calculated thermodynamic and activation parameters (in parentheses) for all described reactions at T = 298.15 K at B3LYP, M06-2X, PBE DFT levels ([ΔS] = cal/(mol*K); [ΔH] = [ΔG] = kcal/mol) in combination with various basis sets.

Reaction	B3LYP/ VDZ	B3LYP(GD3)/ VDZ	M06-2X/ VDZ	M06-2X/ VTZ@VDZ	PBE/3ζ
10+Et_2AlCl → **11**	-11.9	-21.2	-25.2	-23.1	-7.2
1+10 → LM1	10.7	0.6	1.1	1.9	4.1
LM1 → 9a	-15.1 (9.9)	-13.3 (9.5)	-16.6 (8.1)	-13.4 (9.0)	-6.9 (10.2)
1+10 → LM2	12.9	2.6	3.1	4.0	5.4
LM2 → 13a	-13.3 (10.2)	-11.9 (9.3)	-14.7 (9.0)	-11.4 (9.9)	-5.4 (11.6)
1+10 → LM3	10.5	-1.2	0.1	0.9	3.2
LM3 → 9b	-12.7 (9.5)	-9.5 (10.4)	-13.7 (7.2)	-10.7 (8.1)	-4.1 (10.7)
2+10 → LM4	11.9	-0.3	0.6	1.6	3.4
LM4 → 13b	-14.5 (8.0)	-13.5 (7.1)	-16.4 (5.5)	-13.2 (6.4)	-5.8 (9.7)
1+11 → LM5	26.7	21.7	23.0	22.1	20.5
LM5 → 14a	-13.8 (9.6)	-14.6 (5.9)	-15.2 (7.4)	-10.8 (8.8)	-6.6 (8.9)
1+11 → LM6	29.1	22.1	25.1	24.3	23.1
LM6 → 15a	-12.1 (8.6)	-6.2 (6.6)	-8.3 (7.7)	-4.0 (9.3)	-2.1 (7.3)
2+11 → LM7	27.8	18.8	23.3	22.9	20.7
LM7 → 14b	-13.1 (8.9)	-9.1 (8.2)	-12.4 (5.7)	-8.5 (7.0)	-3.7 (9.5)
2+11 → LM8	28.6	20.7	24.2	23.6	21.9
LM8 → 15b	-12.6 (7.9)	-13.9 (6.9)	-13.9 (5.0)	-10.2 (6.3)	-3.9 (6.8)

4. Conclusions

The stages of 1-hexene or styrene interaction with the bimetallic five-membered Zr,Al-complex $[Cp_2Zr(\mu\text{-}Cl)CH_2CH_2AlEt_2]$ and zirconacyclopropane as possible key intermediates of α-olefin cycloalumination by $AlEt_3$, catalyzed with Cp_2ZrCl_2, has been studied using DFT. The existence of equilibrium between these key intermediates was shown to be thermodynamically probable. Analysis of the PES of the reaction steps between the complexes and olefins demonstrated that zirconacyclopropane has a similar reactivity with respect to the substrate than the bimetallic five-membered intermediate.

It was shown that the reactions of alkenes with zirconium complexes include the step of substrate coordination to the catalytically active site, resulting in the formation of low-energy pre-reaction complexes, which stability depends on the olefin structure. The step is barrierless and, therefore, reversible. The next stage is the formation of 2- and 3-substituted zirconacyclopentanes, the precursors of alumolanes, requiring barriers of ≤ 22 kcal/mol. Comparative analysis of two alternative pathways that imply different orientations of the styrene relative to the Zr-C bond showed similarity of the thermodynamic and activation parameters for the formation of 2- and 3-phenylzirconacyclopentanes, unlike analogous parameters for the reaction with terminal aliphatic alkene.

The high regioselectivity of the 1-hexene cycloalumination, which gives only 3-substituted aluminacyclopentane, is caused by relatively higher barriers and thermodynamic stability of corresponding zirconacyclopentane intermediate comparing with 2-substituted analog.

The probable mechanism of metallacyclic by-products formation in the catalytic cycloalumination of styrene has been proposed, which suggests the production of phenylzirconacyclopropane as the key intermediate upon ethylene elimination from low-energy pre-reaction zirconium complexes. The insertion of a second styrene molecule into phenylzirconacyclopropane affords 2,5- and 2,4-diphenylzirconacyclopentanes.

We showed that M06-2X/VDZ//VTZ and PBE/3ζ could be used for the explanation of the available experimental data, whereas B3LYP/VDZ is not suitable for this purpose, although much improved when the Grimme D3 empirical dispersion correction is applied.

Finally, the detailed study on the interaction of cycloalumination catalytically active site with olefins showed a significant role of energetics of bis-olefin complexes involved in the reaction, which control the chemo- and regioselectivity of the process. Further, the systematization of data on the features of olefin complexes of other metals will be a key to understanding the mechanism of the unsaturated compound cyclometalation and oligo/polymerization processes.

Acknowledgements

The authors thank the Russian Foundation of Basic Research (Grant No. 15-03-03227a) for financial support. RJW acknowledges the use of the IRIDIS High Performance Computing Facility, and associated support services at the University of Southampton.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

References

[1] (a) D.S. Breslow, N.R. Newburg, J. Amer. Chem Soc. 79 (1957) 5072;
(b) W. Kaminsky, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 3911.

[2] (a) K. Ziegler, H.G. Gellert, H. Lehmkuhl, W. Pfohl, K. Zosel, Lieb. Ann. Chem. 629 (1960) 1;
(b) F. Asinger, B. Fell, F. Theissen. Chem. Ber. 100 (1967) 937;
(c) F. Sato, S. Sato, M. Sato, J. Organomet. Chem., 122 (1976) 25;
(d) E.C. Ashby, S.A. Noding, J. Organomet. Chem. 177 (1979) 117;
(e) U.M. Dzhemilev, O.S. Vostrikova, A.G. Ibragimov, G.A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim. (1980) 2134;
(f) E. Negishi, T. Yoshida, Tetrahedron Lett., 21 (1980) 1501.

[3] (a) K. Ziegler, H. Gellert, H. Martin, K. Nagel, J. Schneider, Lieb. Ann. Chem. 91 (1954) 589;
(b) A.T. Menyailo, I.A. Kagan, Kchim. Prom.7 (1973) 491 (*in russian*);
(c) D.E. Van Horn, E. Negishi J. Am. Chem. Soc. 100 (1978) 2252;
(d) E. Negishi, N. Okukado, A.O. King, D.E. Van Horn, B.J. Spiegel, J. Am. Chem. Soc. 100 (1978) 2254;
(d) U.M. Dzhemilev, O.S. Vostrikova, G.A. Tolstikov, A.G. Ibragimov, Izv. Akad. Nauk SSSR, Ser. Khim. 2626 (1979) 2626.

[4] (a) U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, R.R. Muslukhov, G.A. Tolstikov, Russ. Chem. Bull. 38 (1989) 194;
(b) R.R. Muslukhov, L.M. Khalilov, A.P. Zolotarev, A.B. Morozov, A.G. Ibragimov, U.M. Dzhemilev, G.A. Tolstikov, Russ. Chem. Bull. 41 (1992) 1646.
(c) T.V. Tyumkina, D.N. Islamov, L.V. Parfenova, L.M. Khalilov, U.M. Dzhemilev, Magn. Reson. Chem. 54 (2016) 62

[5] U.M. Dzhemilev, V.A. Dyakonov, Topics in Organometallic Chem. 41 (2012) 215.

[6] A.G. Ibragimov, L.O. Khafizova, K.G. Satenov, L.M. Khalilov, L.G. Yakovleva, S.V. Rusakov, U.M. Dzhemilev, Russ. Chem. Bull. 48 (1999) 1574.

[7] S.Ren, Z. Qiu, Z. Xie, Organometallics 31 (2012) 4435.

[8] (a) U.M. Dzhemilev and A.G. Ibragimov, J. Organomet.Chem 466 (1994) 1.

[9] U.M. Dzhemilev Mendeleev Comm. 18 (2008) 1.

[10] E. Negishi, D.Y. Kondakov, D Chouiry, K. Kasai, T. Takahashi, J. Amer. Chem Soc. 118 (1996) 9577.

[11] (a) L.M. Khalilov, L.V. Parfenova, S.V. Rusakov, A.G. Ibragimov, U.M. Dzhemilev, Russ. Chem. Bull. 49 (2000) 2051;

(b) L.M. Khalilov, L.V. Parfenova, S.V. Rusakov, A.V. Balaev, U.M. Dzhemilev, in: M.A. Cato (Ed.), Trends in Organometallic Chemistry Research, Nova Science Publishers, New York, 2005, p. 55;

(c) A.V. Balaev, L.V. Parfenova, I.M. Gubaidullin, S.V. Rusakov, S.I. Spivak, L.M. Khalilov, U.M. Dzhemilev, Doklady Physical Chemistry (2001) 381: 279.

[12] W. Kaminsky, H. Sinn, Liebigs Ann. Chem. 3 (1975) 424.

[13] L.V. Parfenova, V.Z. Gabdrakhmanov, L.M. Khalilov, U.M. Dzhemilev, J. Organomet. Chem. 694 (2009), 3725.

[14] (a) E. Negishi, T. Takahashi, J. Amer. Chem Soc. 27 (1994) 124;

(b) H.G. Alt, L.E. Denner, J. Thewalt and M. D. Rausch, J. Organomet. Chem. 356 (1988) 85;

(c) M.D. Fryzuk, P.B. Duval, S.J. Rettig, 2001 Can. J. Chem. 79 (2001) 536.

[15] (a) E.Yu. Pankratyev, T.V. Tyumkina, L.V. Parfenova, L.M. Khalilov, S.L. Khursan, U.M. Dzhemilev, Organometallics 30 (2011) 6078;

(b) E.Yu. Pankratyev, T.V. Tyumkina, L.V. Parfenova, L.M. Khalilov, S.L. Khursan, U.M. Dzhemilev, Organometallics 28 (2009) 4, 968;

(c) I.E. Nifant′ev, L.Yu. Ustynyuk, D.N. Laikov, Organometallics 20 (2001), 25, 5375;

(d) L.Yu. Ustynyuk, E.A. Fushman, Mend Commun 19 (2009) 5, 182.

[16] (a) M.A. Bach, P. Parameswaran, E.D. Jemmis, U. Rosenthal, Organometallics 26 (2007) 2149;

(b) M. Linnolahti, P. Hirva, T.A. Pakkanen, Journal of Computational Chemistry 22 (2001) 51;

(c) T. Imabayashi, Y. Fujiwara, Y. Nakao, H. Sato, S. Sakaki, Organometallics 24 (2005) 2129;

(d) G. Liu, Y. Zhao, D. Cao, Journal of Organometallic Chemistry 693 (2008) 1020;

(e) F. Hasanayn, S. Gozem, Organometallics 27 (2008) 5426;

(f) P.J. Hay, Organometallics 26 (2007) 4424.

[17] Y. Sun, H. Chen J. Chem. Theor. Comput. 9 (2013) 4735.

[18] J.P. Perdew, K Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865

[19] D.N. Laikov, Ph.D. dissertation, Moscow State University, Russia, Moscow, 2000, in Russian.

[20] (a) D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151; (b) D.N. Laikov, Yu.A. Ustynyuk, Russ.

Chem. Bull. 54 (2005) 820.

[21] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[22] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* 120 (2008) 215

[23] (a) Dunning Jr., T. H. *J. Chem. Phys.* 90, (1989) 1007. (b) D. E. Woon and T. H. Dunning Jr., J. Chem. Phys., 98 (1993) 1358. (c) E. R. Davidson, Chem. Phys. Lett. 260 (1996) 514.

[24] K. A. Peterson, D. Figgen, M. Dolg, H. Stoll, J. Chem. Phys. 126 (2007) 124101

[25] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, J. Chem. Inf. Model., 47 (2007) 1045.

[26] E. R. Johnson, A. D. Becke, C. D. Sherrill, G. A. DiLabio, J. Chem. Phys. 131 (2009) 034111

[27] (a) V. Barone and M. Cossi, *J Phys Chem A,* 102 (1998), 1995. (b) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.,* 24 (2003) 669.

[28] A. D. Becke, *J. Chem. Phys.* 98 (1993) 5648 - 5652. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 37 (1988) 785-789. (c) P. J., Stephens, F. J.Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.

[29] S. Grimme, S. Ehrlich, L. Goerigk, J. Comp. Chem. 32 (2011) 1456.

[30] D.V. Besedin, QCC Front-End, version 2.09, 2005.

[31] G.A. Zhurko, D.A. Zhurko, ChemCraft, version 1.6, 2009.

[32] R. Dennington, T. Keith, J. Millam, GaussView 5, Semichem, Inc.: Shawnee Mission, KS, 2009.

[33] (a) L.V. Parfenova, P.V. Kovyazin, I.V. Zakirova, I.E. Nifant'ev, L.M. Khalilov, U.M. Dzhemilev, Book of abstracts of VI Russian Conference "New advances in NMR structural investigations", Kazan, Russia, April 6-9, 2015, P.62-63 (*in russian*);

(b) P.V. Kovyazin Ph.D. thesis. 2015, Institute of Petrochemistry and Catalysis of RAS (*in russian*).

[34] K. Mashima, A. Nakamura, J Orgamomet Chem, 428 (1992) 49.

[35] (a) T. Takahashi, M. Tamura, M. Saburt, Y. Uchida, E-i. Negishi, J. Chem. Soc., Chem Commun (1989) 852;

(b) V. K. Dioumaev, J.F. Harrod, Organometallics 16 (1997) 1452;

(c) T. Takahashi, M. Murakami, M. Kunishige, M. Saburt, Y. Uchida, K. Kozawa, T. Uchida, D.R. Swanson, E-i. Negishi, Chem. Lett (1989) 761.

[36] P. Binder, P. Muller, R. Benn, A. Rufinska, B. Gabor, C. Kruger, P. Betz, Chem. Ber., 112 (1989) 1035.

[37] L.S. Bartell, E.A. Roth, C.D. Hollowell, K. Kuchitzu, J.E. Young, J. Chem. Phys., 42 (1965) 2683.

[38] (a) E-i. Negishi, T. Nguyen, J.P. Maye, D. Chouiry, N. Suzuki, T. Takahashi, Chem. Lett, (1992) 2367.

(b) L.V. Parfenova, L.M. Khalilov, U.M. Dzhemilev, Russ. Chem. Rev. 81 (2012) 524.

[39] L.V. Parfenova, T.V. Berestova, I.V. Molchankina, L.M. Khalilov, R.J. Whitby, U.M. Dzhemilev, J. Organomet. Chem. 726 (2013) 37.

[40] (a) A. Stockis, R. Hoffmann, J. Amer. Chem Soc. 102 (1980) 2952;

(b) A. Nakamura Coordin Chem Rev, 109 (1991) 207.

[41] U.M. Dzhemilev, A.G. Ibragimov, L.O. Khafizova, S.V. Rusakov, L.M. Khalilov, Mend. Comm. (1997) 198.

[42] F. Sato, H. Urabe, S.Okamoto, Chem Rev. 100 (2000) 2835.

[43] S. Mansel, D. Thomas, C. Lefeber, D. Heller, R. Kempe, W. Baumann, U. Rosenthal, Organometallics 16 (1997) 2886.