Ti Group Metallocene-Catalyzed Synthesis of 1-Hexene Dimers and Tetramers

Pavel V. Kovazin, Almira Kh. Bikmeeeva, Denis N. Islamov, Vasilii M. Yanybin, Tatyana V. Tyumkina and Lyudmila V. Parfenova *  

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, Prospekt Oktyabrya, 141, 450075 Ufa, Russia; kpv38@mail.ru (P.V.K.); almira.bikmeeva@gmail.com (A.K.B.); islamov19@gmail.com (D.N.I.); vyanybin@gmail.com (V.M.Y.); ttvnmr@gmail.com (T.V.T.)  
* Correspondence: luda_parfenova@ipc-ras.ru; Tel.: +7-347-284-3527

Abstract: 1-Hexene transformations in the catalytic systems $L_2MCl_2$–$XAlBu_i^2$ ($L = Cp$, $M = Ti$, $Zr$, $Hf$; $L = Ind$, rac-$H_4C_2[THInd]_2$, $M = Zr$; $X = H$, Bu$^t$) and $[Cp_2ZrH_2]_2$-MMAO-12, $[Cp_2ZrCl_2]$–B(C$_6$F$_5$)$_3$, or (Ph$_3$C)$[B(C_6F_5)_4]$ in chlorinated solvents (CH$_2Cl_2$, CHCl$_3$, o-Cl$_2$C$_6$H$_4$, ClCH$_2$CH$_2$Cl) were studied. The systems $[Cp_2ZrH_2]_2$–MMAO-12, $[Cp_2ZrCl_2]$–ClAlBu$_i^2$–MMAO-12, or $Cp_2ZrCl_2$–HAlBu$_i^2$–MMAO-12 ($B(C_6F_5)_3$) in CH$_2Cl_2$ showed the highest activity and selectivity towards the formation of vinylidene head-to-tail alkene dimers. The use of chloroform as a solvent provides further in situ dimer dimerization to give a tetramer yield of up to 89%. A study of the reaction of $[Cp_2ZrH_2]_2$ or $Cp_2ZrCl_2$ with organoaluminum compounds and MMAO-12 by NMR spectroscopy confirmed the formation of Zr,Zr-hydride clusters as key intermediates of the alkene dimerization. The probable structure of the Zr,Zr-hydride clusters and ways of their generation in the catalytic systems were analyzed using a quantum chemical approach (DFT).

Keywords: metallocenes; metal hydrides; dimerization; nuclear magnetic resonance; density functional theory

1. Introduction

Alkene dimers and oligomers represent a large class of compounds that are used as comonomers in ethylene polymerization and as raw materials for the production of adhesives, surfactants, fragrances, synthetic lubricating fuel additives, etc. [1–6]. The following industrial processes have been successfully developed and implemented for the production of olefin oligomers: (i) oligomerization of ethylene in the presence of triethylaluminum with subsequent oxidation to higher alcohols (Ziegler–Alfol process), (ii) Philips process of ethylene oligo— and polymerization on chromium catalysts, (iii) Ni-catalyzed synthesis of linear $\alpha$-olefins via ethylene oligomerization (shell higher olefin process (SHOP)), (iv) oligomerization of ethylene to linear C4–C10 olefins by $\alpha$-select technology (Axens) or $\alpha$-SABLIN technology (Sabic and Linde) [7]. Currently, some research groups are developing strategies for the production of highly efficient jet and diesel fuels via oligomerization of alkenes (1-butene, 1-hexene) synthesized from renewable plant raw materials [2,8].

Among the catalysts, Ti group metalloocene complexes showed high efficiency in alkene di-, oligo-, and polymerization [9–12]. In this way, the process of zirconocene-catalyzed dimerization of terminal alkenes to give products with a vinylidene moiety >C=CH$_2$ is well-known (Scheme 1) [5,6,13–20].
Despite significant progress in this area, the mechanism of the dimerization reaction is not fully understood. Earlier, the hypothesis on the key role of the hydride cation [Cp₂ZrH]⁺ was put forward [14]. Subsequently, it was postulated that bimetallic hydride complexes L₂Zr(μ-H)₂AlBu₂ can act as catalytically active species in the alkene dimerization [21,22]. Recently, we studied the systems Cp₂ZrCl₂-XAlBu₂ (X = H, Bu i) and [Cp₂ZrH₂]₂-ClAlR₂ (R = Me, Et, Bu i) activated by MMAO-12 (modified methylaluminoxane) or organoboron compounds and found new biszirconium hydride intermediates (Cp₂ZrH₂)₂-ClAlR₂ activated by MMAO-12, which provide selective formation of head-to-tail dimerization products [19,20,23]. However, the questions on the possible structure of the key intermediates and their formation in the catalytic systems remain open.

Thus, our work was aimed at investigating the effect of transition metal η⁵-complexes and solvents (chlorine-containing solvents) on the activity, chemo- and regioselectivity of the systems L₂MCl₂-XAlBu₂ (L = Cp, M = Ti, Zr, Hf; L = Ind, rac-H₄C₂[THInd]₂, M = Zr; X = H, Bu i) and [Cp₂ZrH₂]₂-ClAlR₂ activated by MMAO-12, B(C₆F₅)₃, or (Ph₃C)[B(C₆F₅)₄] in alkene oligomerization. NMR studies and quantum chemical calculations were applied to establish the possible structure of the hydride intermediates formed in these systems. The results showed that the M,M-type bimetallic hydrides and their action mechanisms are unique for the dimerization reaction.

2. Results and Discussion

2.1. Transformations of 1-Hexene with Cp₂MY₂ (M = Ti, Zr, Hf; Y = H, Cl)-XAlBu₂ (X = H, Bu i)

Catalytic Systems Activated by MMAO-12, B(C₆F₅)₃, or (Ph₃C)[B(C₆F₅)₄]

The conditions for the selective synthesis of vinylidene dimers in the presence of catalytic systems Cp₂ZrY₂ (Y = H, Cl)-XAlBu₂ (X = H, Bu i)-activator (Scheme 2, catalytic systems A and B), developed in our previous study, were taken as the starting point for the experiment (Table 1, entry 1) [19,20].

The reaction proceeds in toluene or benzene at 20–60 °C to give the target products in 81–98% yields within 5 to 150 min, depending on the type of activator (Table 1, entries 1, 15, 21, 27, and 43). The use of chlorine-containing solvents in these systems was found to accelerate the reaction. For example, the system [Cp₂ZrH₂]₂-ClAlBu₂-MMAO-12 with a molar ratio [Zr]:[Al]:[MMAO-12]:[1-hexene] = 1:3:30:400 at a temperature of 40 °C in CH₂Cl₂ gives 1-hexene dimer in a yield of more than 98% by the 15th minute of the reaction (Table 1, entry 2). When the reaction is carried out in chloroform, the relative content of dimers decreases to 92% (entry 4). Under the same conditions, the dimers produced in the first minutes of the reaction serve as substrates for the subsequent dimerization to afford dimers of dimer 7 in 75–79% yields in 180 min (entries 7, 8, Figures S26 and S27). According to ¹H and ¹³C NMR data, the structures of these products correspond to those proposed earlier [16,22,24–26]. Dimerization of 5 occurs probably via participation of cationic species formed upon the reaction of CH₂Cl₂ with ClAlR₂ or MMAO-12.

Scheme 1. Zirconocene-catalyzed dimerization of terminal alkenes.

**Table 1.** Catalytic activity and chemoselectivity of systems

| Alkene         | Catalytic systems I or II | Cat. systems: |
|----------------|---------------------------|---------------|
| 1-Hexene       | (I) Cp₂ZrCl₂ / MAO / 1-alkene (1:1:(90-500)) | (I) Cp₂ZrCl₂ / MAO / 1-alkene (1:1:(90-500)) |
|                | (II) L₂ZrCl₂ / AlBu₃ / MAO / 1-alkene (1:20:10:(100-2000)) | (II) L₂ZrCl₂ / AlBu₃ / MAO / 1-alkene (1:20:10:(100-2000)) |

### Results and Discussion

2.1. Transformations of 1-Hexene with Cp₂MY₂ (M = Ti, Zr, Hf; Y = H, Cl)-XAlBu₂ (X = H, Bu i)

Catalytic Systems Activated by MMAO-12, B(C₆F₅)₃, or (Ph₃C)[B(C₆F₅)₄]

The conditions for the selective synthesis of vinylidene dimers in the presence of catalytic systems Cp₂ZrY₂ (Y = H, Cl)-XAlBu₂ (X = H, Bu i)-activator (Scheme 2, catalytic systems A and B), developed in our previous study, were taken as the starting point for the experiment (Table 1, entry 1) [19,20].

The reaction proceeds in toluene or benzene at 20–60 °C to give the target products in 81–98% yields within 5 to 150 min, depending on the type of activator (Table 1, entries 1, 15, 21, 27, and 43). The use of chlorine-containing solvents in these systems was found to accelerate the reaction. For example, the system [Cp₂ZrH₂]₂-ClAlBu₂-MMAO-12 with a molar ratio [Zr]:[Al]:[MMAO-12]:[1-hexene] = 1:3:30:400 at a temperature of 40 °C in CH₂Cl₂ gives 1-hexene dimer in a yield of more than 98% by the 15th minute of the reaction (Table 1, entry 2). When the reaction is carried out in chloroform, the relative content of dimers decreases to 92% (entry 4). Under the same conditions, the dimers produced in the first minutes of the reaction serve as substrates for the subsequent dimerization to afford dimers of dimer 7 in 75–79% yields in 180 min (entries 7, 8, Figures S26 and S27). According to ¹H and ¹³C NMR data, the structures of these products correspond to those proposed earlier [16,22,24–26]. Dimerization of 5 occurs probably via participation of cationic species formed upon the reaction of CH₂Cl₂ with ClAlR₂ or MMAO-12.

Scheme 1. Zirconocene-catalyzed dimerization of terminal alkenes.

**Table 1.** Catalytic activity and chemoselectivity of systems

| Alkene         | Catalytic systems I or II | Cat. systems: |
|----------------|---------------------------|---------------|
| 1-Hexene       | (I) Cp₂ZrCl₂ / MAO / 1-alkene (1:1:(90-500)) | (I) Cp₂ZrCl₂ / MAO / 1-alkene (1:1:(90-500)) |
|                | (II) L₂ZrCl₂ / AlBu₃ / MAO / 1-alkene (1:20:10:(100-2000)) | (II) L₂ZrCl₂ / AlBu₃ / MAO / 1-alkene (1:20:10:(100-2000)) |
The replacement of MMAO-12 by [B(C₆F₅)₃] as activator leads to a significant reduction in substrate conversion. The reaction occurs only in chloroform, and the conversion of 1-hexene in 16 h is 75% with a 71% content of dimers in the product mixture (entries 18, 19). Unlike [B(C₆F₅)₃], compound (Ph₃C)[B(C₆F₅)₄] can activate the system [Cp₂ZrCl₂]-MMAO-12. Under these conditions, the conversion of 1-hexene in 3 h was higher in CH₂Cl₂ (99%, entry 26), and the reaction predominantly gave tetramer 7 in 69% yield. In contrast, in chloroform, the 1-hexene conversion was 81% in 16 h, and oligomeric products 6, including compound 7, prevailed in the product mixture (entries 24, 25).

The use of chlorine-containing solvents CH₂Cl₂ and CHCl₃ in the case of the system [Cp₂ZrCl₂]-MMAO-12 at the ratio [Zr]:[MMAO-12]:[1-hexene] = 1:30:400 allows the reaction to be carried out in the absence of ClAlBu₂ with a >99% conversion of 1-hexene and up to 89–91% yield of dimer 5 (entries 9, 10). In o-dichlorobenzene and 1,2-dichloroethane, the reaction proceeds to a lower substrate conversion and a lower yield of the dimeric product (entries 11–14). The composition of the reaction products formed in the system [Cp₂ZrCl₂]-MMAO-12-1-hexene for 16 h in any of the solvents (CH₂Cl₂, CHCl₃, o-C₆H₄Cl, CICH₂CH₂Cl) did not change significantly. Attempts to activate [Cp₂ZrCl₂] with boron-containing activators in the absence of ClAlR₂ were unsuccessful (entries 16, 17, 22, 23).

Thus, vinylidene dimer 5 is formed in a high yield and with high selectivity under the action of [Cp₂ZrCl₂]-MMAO-12 or [Cp₂ZrCl₂]-MMAO-12 in CH₂Cl₂. Chloroform facilitates the formation of a non-classical tetramer of 1-hexene (7), which could be used as a component of lubricants [16,24–26].

The catalytic system based on Cp₂ZrCl₂, HAlBu₂ and MMAO-12 also provides vinylidene dimers 5 in chlorinated solvents. In CH₂Cl₂ and CHCl₃, the reaction proceeds in 30 min with the conversion of 1-hexene above 99% and the yield of dimers of 98% (entries 28, 34). Increasing 1-hexene initial concentration to 1000 equivalents leads to decreased alkene conversion to 82% and the yield of dimeric product to 80% in CH₂Cl₂. Under these conditions, the conversion and the yield of dimers are higher in CHCl₃ than in CH₂Cl₂ and amount to >99% and 90–98% in 30 min, respectively (entries 32, 35).
Table 1. Catalytic activity and chemoselectivity of systems A and B in the reaction with 1-hexene.

| Entry | Catalytic Systems | [Zr]: [Al]: [Activator]:[1-Hexene] | Solvent | T, °C | Time, min | Alkene Conversion, % | Product Composition, % h |
|-------|-------------------|------------------------------------|---------|-------|-----------|----------------------|--------------------------|
|       | Zr Complex        | OAC a                              |         |       |           |                      | n = 1          | n = 2          | n = 3          |                |               |
| 1 [19] | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:100 | C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3} | 40 | 15 | >99 \textsuperscript{b} | 86 |
| 2     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CH\textsubscript{2}Cl\textsubscript{2} | 40 | 15 | >99 | 98 | 1.3 |
| 3     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CH\textsubscript{2}Cl\textsubscript{2} | 40 | 180 | 92 | 98 | 1.8 |
| 4     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CH\textsubscript{2}Cl\textsubscript{2} | 40 | 60 | 92 | 92 | 1.8 |
| 5     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CH\textsubscript{2}Cl\textsubscript{2} | 40 | 105 | >99 | 97 | 1.3 |
| 6     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 180 | 12.6 | 1.4 | 75 |
| 7     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 960 | 1.4 | 1.4 | 2.6 |
| 8     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 17 | 1 | 1 |
| 9     | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 30 | 1 | 8 |
| 10    | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 60 | <1 | 1 | 10 |
| 11    | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 960 | 94 | 3 | 1 |
| 12    | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 960 | 94 | 3 | 1 |
| 13    | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 960 | 94 | 3 | 1 |
| 14    | ClAlBu\textsubscript{i2} | MMAO-12 | 1:3:30:400 | CHCl\textsubscript{3} | 40 | 960 | 94 | 3 | 1 |
| 15 [20] | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:8:1:400 | C\textsubscript{6}H\textsubscript{6} | 40 | 90 | 81 | 81 |
| 16    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 17    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 18    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 20    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 21 [20] | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 22    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 23    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 24    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 25    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| 26    | ClAlBu\textsubscript{i2} | B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} | 4:1:400 | CHCl\textsubscript{3} | 40 | 960 | 0 | 0 |
| Entry | Zr Complex | OAC \(^{a}\) | Activator | [Zr]: [Al]: [Activator]: [1-Hexene] | Solvent | T, °C | Time, min | Alkene Conversion, % | Product Composition, % \(^{h}\) |
|-------|------------|-------------|-----------|-----------------------------------|---------|--------|-------------|-------------------|------------------|
| 27 \(^{19}\) | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:100 | C\(_{6}\)H\(_{5}\)CH\(_{3}\) | 40 | 15 | >99 \(^{d}\) | 91 |
| 28 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:400 | CH\(_{2}\)Cl\(_{2}\) | 40 | 30 | 98 | 97 | 1 |
| 29 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:400 | CH\(_{2}\)Cl\(_{2}\) | 40 | 60 | 99 | 98 | 1 |
| 30 | - | MMAO-12 | 1:3:30:400 | CH\(_{2}\)Cl\(_{2}\) | 40 | 180 | 98 | 96 | - |
| 31 | - | MMAO-12 | 1:3:30:400 | CH\(_{2}\)Cl\(_{2}\) | 40 | 960 | 99 | 92 | 4 | <1 |
| 32 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:1000 | CH\(_{2}\)Cl\(_{2}\) | 40 | 30 | 82 | 80 | 2 |
| 33 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:1000 | CH\(_{2}\)Cl\(_{2}\) | 40 | 60 | 88 | 77 | 2 | 9 |
| 34 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 30 | >99 | 98 | 2 |
| 35 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 30 | >99 | 90 | 7 | 3 |
| 36 | HAIBu\(^{i}\) \(^{2}\) | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 180 | >99 | 97 | 2 |
| 37 | - | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 180 | >99 | 5 | 3 | 2 | 89 |
| 38 | - | MMAO-12 | 1:10:400 | CHCl\(_{3}\) | 40 | 960 | 91 | 91 | <1 |
| 39 | - | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 30 | 99 | 93 | 4 | - |
| 40 | - | MMAO-12 | 1:3:30:400 | Cl\(_{2}\)C\(_{6}\)H\(_{4}\) | 40 | 960 | 99 | 91 | 5 | 1 |
| 41 | - | MMAO-12 | 1:3:30:400 | CHCl\(_{3}\) | 40 | 960 | >99 | 96 | 2 |
| 42 | Cp\(_{2}\)ZrCl\(_{2}\) | - | MMAO-12 | 1:3:30:400 | (CH\(_{2}\)Cl\(_{2}\)) | 40 | 960 | >99 | 96 | 2 |
| 43 \(^{20}\) | HAIBu\(^{i}\) \(^{2}\) | B(C\(_{6}\)F\(_{5}\))\(_{3}\) | 4:16:1:1000 | C\(_{6}\)H\(_{6}\) | 40 | 60 | >99 \(^{e}\) | 93 |
| 44 | HAIBu\(^{i}\) \(^{2}\) | B(C\(_{6}\)F\(_{5}\))\(_{3}\) | 4:16:1:1000 | CH\(_{2}\)Cl\(_{2}\) | 40 | 60 | >99 | 99 | 1 |
| 45 | HAIBu\(^{i}\) \(^{2}\) | B(C\(_{6}\)F\(_{5}\))\(_{3}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 60 | 83 | 82 | 1 |
| 46 | - | B(C\(_{6}\)F\(_{5}\))\(_{3}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 960 | 0 | 96 | 2 |
| 47 | - | B(C\(_{6}\)F\(_{5}\))\(_{3}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 960 | 0 | 96 | 2 |
| 48 \(^{20}\) | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | C\(_{6}\)H\(_{6}\) | 60 | 90 | 97 \(^{f}\) | 67 |
| 49 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CH\(_{2}\)Cl\(_{2}\) | 20 | 180 | >99 | 92 | 6 | 2 |
| 50 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CH\(_{2}\)Cl\(_{2}\) | 20 | 960 | >99 | 92 | 6 | 2 |
| 51 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CH\(_{2}\)Cl\(_{2}\) | 40 | 960 | >99 | 1 | 55 | 8 | 3 | 33 |
| 52 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CH\(_{2}\)Cl\(_{2}\) | 40 | 960 | >99 | 1 | 55 | 8 | 3 | 33 |
| 53 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CHCl\(_{3}\) | 20 | 180 | >99 | 1 | 55 | 8 | 3 | 33 |
| 54 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 180 | >99 | 76 | 8 | 2 | 13 |
| 55 | HAIBu\(^{i}\) \(^{2}\) | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 960 | >99 | 76 | 8 | 2 | 13 |
| 56 | - | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 960 | 0 | 76 | 8 | 2 | 13 |
| 57 | - | (Ph\(_{3}\))\([B(C\(_{6}\)F\(_{5}\))]\(_{4}\) | 4:16:1:1000 | CHCl\(_{3}\) | 40 | 960 | 0 | 76 | 8 | 2 | 13 |

\(^{a}\) OAC—organoaluminum compound; \(^{b}\) hydrometallation product, 4%; saturated dimer, 2%; unsaturated methylalumination product, 8% \(^{19}\); \(^{c}\) hydrometallation product, 5% \(^{20}\); \(^{d}\) hydrometallation product, 5%; saturated dimer, 1%; unsaturated methylalumination product, 2%; \(^{e}\) hydrometallation product, 3%; trimers, 3%; \(^{f}\) oligomers, 23%; \(^{g}\) 6-mers (29%) are identified; \(^{h}\) wt % in the reaction mixture, determined by GC–MS of deuterolysis or hydrolysis products (the details of the GC–MS analysis is shown in Supporting Information, Figures S28 and S29).
The reaction carried out in the presence of Cp₂ZrCl₂ and MMAO-12 at the ratio [Zr]:[MMAO-12]:[1-hexene] = 1:30:400 in chlorinated solvents (CH₂Cl₂, o-Cl₂C₆H₄, ClCH₂CH₂Cl) at 40 °C results in 91–96% yield of dimers (entries 30, 31, 39–42). Carrying out the reaction in chloroform gives dimers of 7 in a yield of up to 89% (entry 37). A decrease in the relative amount of MMAO-12 in the system to [Zr]:[MMAO-12]:[1-hexene] = 1:10:400 provides the selective formation of dimerization products at the level of 91% within 16 h.

The highest yield of dimer 5 at the level of 99% is achieved by using a neutral boron-containing activator B(C₆F₅)₃ in the system Cp₂ZrCl₂-HAlBu¹₂ at the ratio [Zr]:[Al]:[B(C₆F₅)₃]:[1-hexene] = 4:16:1:1000 and in dichloromethane as a solvent (entry 44).

Activation of system Cp₂ZrCl₂-HAlBu¹₂ by (Ph₃C)[B(C₆F₅)₃] at a ratio [Zr]:[Al]:[(Ph₃C)B(C₆F₅)₃]:[1-hexene] = 4:16:1:1000 and a temperature 40 °C affords alkene oligomers in both CH₂Cl₂ and CHCl₃ (entries 50–52, 54, 55). Selective formation of a dimer (92%, entry 49) occurs in CH₂Cl₂ at 20 °C, with the reaction time being up to 180 min.

Subsequently, the content of dimers decreases to 55%, and the amount of tetramer 7 increases to 33% (entry 50). Using chloroform as a solvent raises the yield of 7 to 65–72% (entries 54, 55).

The activity of Cp₂TiCl₂ (1a) and Cp₂HfCl₂ (1c) in the studied systems was lower than that of Cp₂ZrCl₂ (1b). Indeed, the conversion of 1-hexene in CH₂Cl₂ at 40 °C was 80% in 60 min of the reaction in the case of the Ti complex (Table 2, entries 1) and 84% in 120 min for the Hf complex (entries 5). The use of chloroform as a solvent increases substrate conversion to 93% for Cp₂TiCl₂ and decreases the conversion to 60% for Cp₂HfCl₂ (entries 3, 8). Moreover, these catalysts are significantly inferior in chemo- and regioselectivity to zirconocene dichloride. Thus, in the presence of Cp₂TiCl₂, the yield of oligomeric products 6 and tetramer 7, which represent a mixture of regioisomers, increases in total to 89%. The use of Cp₂HfCl₂ in CH₂Cl₂ leads to increased the content of vinylidene oligomers up to 28–37%. In chloroform, the yield of regioisomeric oligomers also increases in the first 60 min of the reaction (entry 8). Further, the appearance of products of toluene mono-, di-, and trialkylation with 1-hexene was found (entries 9, 10). It should be noted that in the presence of HAlBu¹₂, upon replacing MMAO-12 with boron-containing activators, the systems based on Cp₂TiCl₂ and Cp₂HfCl₂ completely lost their activity (Table 2, entries 11–14).

The effect of the ligand structure of zirconocenes on the activity of catalytic systems and the reaction route was also studied. For this purpose, we tested Zr η⁵-complexes (C₅Me₅)₂ZrCl₂ (1d), Ind₂ZrCl₂ (1e), and rac-H₂C₂(THInd)₂ZrCl₂ (1f) (Scheme 2) as components of the systems L₂ZrCl₂-HAlBu¹₂-MMAO-12 at molar ratio [Zr]:[Al]:[MMAO-12]:[1-hexene] = 1:3:30:400 and temperature of 40 °C. It turned out that (C₅Me₅)₂ZrCl₂ does not lead to the formation of the target products either in CH₂Cl₂ or in CHCl₃ (Table 3, entries 1, 2). In this case, 1-hexene was consumed for toluene alkylation (toluene is present in the system as a solvent for MMAO-12). The complex Ind₂ZrCl₂ showed lower activity than Cp₂ZrCl₂ (Table 3, entries 3–7) and shifted the reaction route toward the oligomerization (up to 87%) both in CH₂Cl₂ and CHCl₃. Ansa-zirconocene rac-H₂C₂(THInd)₂ZrCl₂ was inactive in CHCl₃ (entry 9); however, it catalyzed alkene oligomerization in CH₂Cl₂ (1-hexene conversion of >99%, entry 8). Thus, the zirconocene ligand structure significantly affects the course of the reaction, and some tested complexes mainly provided the formation of oligomeric products.
Table 2. Catalytic activity and chemoselectivity of systems Cp₂MCl₂-HAlBu′₂-activator (M = Ti, Hf) in the reaction with 1-hexene.

| Entry | Zr Complex | OAC | Activator | [Zr: [Al]: [Activator]:[1-Alkene]] | Solvent | T, °C | Time, min | Alkene Conversion, % | Product Composition, %
|-------|------------|-----|-----------|-----------------------------------|---------|------|----------|----------------------|----------------------|
|       |            |     |           |                                   |         |      |          |                      |                      |
| 1     | Cp₂TiCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 60       | 90                   | 80                   |
| 2     | Cp₂TiCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 60       | 93                   | 88                   |
| 3     | Cp₂TiCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | >99      | 5        | 4                    |
| 4     | Cp₂TiCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | >99      | 5        | 4                    |
| 5     | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 120      | 84                   | 2                    |
| 6     | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 120      | 84                   | 2                    |
| 7     | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 8     | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 9     | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 10    | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 11    | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 12    | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 13    | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |
| 14    | Cp₂HfCl₂   |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 960      | 96                   | 5                    |

Table 3. Catalytic activity and chemoselectivity of systems L₂ZrCl₂-HAlBu′₂-activator in the reaction with 1-hexene.

| Entry | Zr Complex | OAC | Activator | [Zr]: [Al]: [Activator]:[1-Alkene] | Solvent | T, °C | Time, min | Alkene Conversion, % | Product Composition, %
|-------|------------|-----|-----------|-----------------------------------|---------|------|----------|----------------------|----------------------|
|       |            |     |           |                                   |         |      |          |                      |                      |
| 1     | (C₅Mes)₂ZrCl₂ |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 2     | (C₅Mes)₂ZrCl₂ |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 3     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 4     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 5     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 6     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 7     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 8     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |
| 9     | Ind-ZrCl₂  |     | HAlBu′₂   | MMAO-12 1:3:30:400               | CH₂Cl₂ | 40   | 30       | 30                   | >99                  |

2.2. NMR Study of Intermediate Structure in MMAO-12-Activated Systems Cp₂ZrY₂ (Y = H, Cl)-OAC in Chlorinated Solvents

The effect of chlorinated solvents (CD₂Cl₂ and CDCl₃) on the structure of the intermediaes responsible for the alkene dimerization in the catalytic systems [Cp₂ZrH₂]₂-MMAO-12 was studied by NMR. The addition of MMAO-12 to a solution of [Cp₂ZrH₂]₂ in CD₂Cl₂ gives rise to a triplet at −5.95 ppm (J = 17.0 Hz) in the ¹H NMR spectra (Figure 1c, Figures S21–S23). In the COSY HH spectrum, the triplet correlates with the signal at −0.47 ppm, which is superimposed with the region of resonance lines of methyl group protons of MMAO-12 (−0.82−0.32 ppm). The spectra also exhibited signals for the Cp rings at 6.16 ppm (108.4 ppm in ¹³C NMR spectra), 6.39 ppm (112.8 ppm in ¹³C NMR spectra), and 6.61 ppm (116.2 ppm in ¹³C NMR spectra). The NOESY spectra showed the cross-peaks of the Cp-ring signal at 6.16 ppm with the upfield signals at −5.95 ppm and −0.47 ppm. Relying on these results and the data from previous studies [19,20], these signals were assigned to the biszirconium trihydride complex 9. The signals at 6.61 ppm and 6.39 ppm correspond to the Cp rings of Cp₂ZrCl₂ and Cp₂ZrMeCl (11), respectively [27].
The reaction of Cp₂ZrHCl with the starting Cp₂ZrH₂ and ClAlMe₂ makes it possible to selectively obtain complex 9 and then high-molecular-weight associates with MMAO-12 (9·MAO), which are active in the alkene dimerization [19,20].

As shown in Scheme 3, the system [Cp₂ZrH₂]₂-MMAO-12 in CD₂Cl₂ produces complex 9 via in situ formation of Cp₂ZrHCl and Cp₂ZrCl₂ by the reaction of zirconocene dihydride with a chlorine-containing solvent [28]. Residual AlMe₃ present in the MMAO-12 solution reacts with Cp₂ZrCl₂ to give methyl chloride complex 11 and ClAlMe₂. The reaction of Cp₂ZrHCl with the starting Cp₂ZrH₂ and ClAlMe₂ makes it possible to sequentially obtain complex 9 and then high-molecular-weight associates with MMAO-12 (9·MAO), which are active in the alkene dimerization [19,20].

Scheme 3. The reaction of Cp₂ZrCl₂ and [Cp₂ZrH₂]₂ with OACs and MMAO-12.
The $^1$H and $^{13}$C NMR spectra of the system [Cp$_2$ZrH$_2$]$_2$-ClAlBu$_i$$_2$ (Figure 1a, Figures S14 and S15) in CD$_2$Cl$_2$ exhibited signals of previously described intermediates [19,23,28,29]: complex 8 (broadened signals of hydride atoms at $\delta_{H}1$ = 0.38 and 1.91 ppm), dimeric complex 10 (broadened signals of hydride atoms at $\delta_{H}1$ = −1.42 and −2.38 ppm), and biszirconium trihydride complex 9 (doublet signal at $\delta_{H}2$ = 0.70 ppm ($J = 17.0$ Hz) and triplet at −5.87 ppm). The addition of MMAO-12 to the equilibrium mixture of the complexes leads to the vanishing of signals of complex 10 from the $^1$H NMR spectrum and the appearance of an additional triplet at −6.01 ppm attributable to the adduct 9-MAO (Figure 1b, Figures S16–S18).

A similar picture is observed in the $^1$H and $^{13}$C NMR spectra of Cp$_2$ZrCl$_2$-HAlBu$_i$$_2$ in CD$_2$Cl$_2$ (Figures S5 and S6). When MMAO-12 is added to the system, the signals of the dimeric complex 10 also disappear, the intensity of the signals of the trihydride 8 decreases, and additional triplets of 9-MAO appear in the upfield region at −6.21 ÷ −5.92 ppm (Figures S7 and S8).

The reaction of [Cp$_2$ZrH$_2$]$_2$ with MMAO-12 in either CDCl$_3$ or CD$_2$Cl$_2$ gives complexes Cp$_2$ZrCl$_2$ (δ$_{Cp}$ 6.76 ppm) and Cp$_2$ZrMeCl (δ$_{Cp}$ 6.58 ppm) (Figure 2c, Figures S19 and S20). Moreover, the $^1$H NMR spectrum showed a significant broadening of the signals of the hydride atom at −6.12 ppm and Cp rings of the heavy adduct 9-MAO, which disappeared from the spectra due to the precipitation of the heavy fraction to the bottom of the NMR tube.

![Figure 2. $^1$H NMR spectrum of systems Cp$_2$ZrCl$_2$-HAlBu$_i$$_2$-MMAO-12 and [Cp$_2$ZrH$_2$]$_2$-MMAO-12 in CDCl$_3$ (T = 298 K): (a) [Cp$_2$ZrCl$_2$][HAlBu$_i$$_2$]:[MMAO-12] = 1:4:0; (b) [Cp$_2$ZrCl$_2$][HAlBu$_i$$_2$]:[MMAO-12] = 1:4:0; (c) [Cp$_2$ZrH$_2$]:[MMAO-12] = 1:12.](http://example.com/figure2)

In the reaction of Cp$_2$ZrCl$_2$ with HAlBu$_i$$_2$ (1:4) in CDCl$_3$, only the Zr,Al-trihydride complex 8 was identified (Figure 2a, Figures S1 and S2). The signals of complexes 9 and 9-MAO appeared in the $^1$H NMR spectra after the addition of MMAO-12 and 1-hexene to the system (Figure 2b, Figures S3 and S4). The formation of complexes 8–10 was observed in the reaction of zirconocene dihydride with ClAlBu$_i$$_2$ taken in a 1:2 ratio in CDCl$_3$ (Figure S9). The addition of MMAO-12 to this system results in the disappearance of signals of complex 10, broadening of complex 8 signals, and the appearance of an additional broadened multiplet at −6.03 ppm, corresponding to the heavy adduct 9-MAO (Figure S11). NMR monitoring of the system’s reaction with 1-hexene showed the consumption of 9-MAO adduct and the accumulation of the vinylidene dimer (Figures S24 and S25).
Thus, biszirconium complex 9 is readily formed in the systems Cp₂ZrCl₂-HAlBu₁₂, [Cp₂ZrH₂]₂-MMAO-i₂, and [Cp₂ZrH₂]₂-ClAlBu₁₂ both in CD₂Cl₂ and in CDCl₃. This intermediate reacts with methylaluminoxane to give a heavy adduct, which selectively provides vinylidene dimers of 1-hexene.

2.3. DFT Study of the Structure of Biszirconium Complex 9

To refine the structure of complex 9, probable structures of cyclic isomers 9a–9d were optimized using the PBE/3c quantum chemical method [30–32]. Their structure is in line with the obtained NMR spectral data on the ratio of the signal intensities of the constituent moieties and the symmetry of the complex (Scheme 4). As follows from Scheme 4, the structures of the complexes significantly differ from one another. For example, in complex 9c, all three hydrides are located between the zirconium atoms and form a trihydride bridge, while in molecule 9a, there is only one bridging H atom. If the optimized structures of the two most energetically favorable hydride complexes 9a and 9c (Figure 3) are considered in detail, the length of the Zr–H bond varies, which may cause differences in the reactivity of the studied complexes. Thus, the lengths of both Zr–H bonds in the Zr–H–Zr moiety of complex 9a is 2.09 Å, while the lengths of two terminal Zr–H bonds are \(d_{Zr1-H1} = d_{Zr2-H1} = 1.83 \text{ Å}\). It is comparable with the Zr–H bond length in Cp₂ZrHCl calculated by the same method (\(d_{Zr-H} = 1.84 \text{ Å}\)).

![Scheme 4. Theoretically calculated structures of isomers of complex 9.](image)

![Figure 3. Optimized structures of isomers 9a and 9c.](image)

In isomer 9c, all three hydrogen atoms are inside the biszirconium cage. Meanwhile, the lengths of bridging Zr–H bonds are also increased compared to those in Cp₂ZrHCl, but are not equivalent to each other: \(d_{Zr1-H1} = d_{Zr2-H1} = 2.01 \text{ Å}, d_{Zr1-H2} = d_{Zr2-H3} = 1.97 \text{ Å}, d_{Zr1-H3} = d_{Zr2-H2} = 1.99 \text{ Å}\). Thus, one hydrogen atom is equidistant from both zirconium atoms, while the other two H atoms, forming an “inner” bridge, are characterized by...
some displacement towards one of the zirconium atoms. It is quite obvious that structural differences also determine energy differences (Table 4, Table S1).

Table 4. Relative thermodynamic parameters of isomeric complexes 9.

| Complex | $\Delta E$, Hartree | $\Delta E_{ZPVE}$, Hartree | $\Delta H$, kcal/mol | $\Delta G$, kcal/mol | $\Delta S$, cal/mol | $T \Delta S$, cal/mol |
|---------|----------------------|-----------------------------|----------------------|----------------------|---------------------|----------------------|
| 9a      | 0.000000             | 0.000000                    | 0.0                  | 0.0                  | 2475.2              |
| 9b      | 0.013103             | 0.012948                    | 8.2                  | 9.6                  | 1139.2              |
| 9c      | 0.003022             | 0.003398                    | 2.4                  | 3.3                  | 1517.2              |
| 9d      | 0.022146             | 0.023111                    | 14.4                 | 16.9                 | 0.0                 |

The most thermodynamically stable complex is 9a, in which the chlorine atoms are part of the Zr–Cl–Al moieties. Isomer 9b is higher in energy by 3.3 kcal/mol. The presence of bulky Cl atoms in the inner bridge of the biszirconium cage of structure 9d makes this complex least thermodynamically stable relative to other compounds.

To identify the structure of the complex observed by NMR spectroscopy, we compared theoretical and experimental NMR chemical shifts of hydride atoms in each of them (Table 5). It was found that in complex 9a, the hydrogen atom of the Zr–H–Zr moiety is significantly shielded ($\delta H^1 = -4.2$ ppm), while two other hydride atoms experience a de-shielding effect ($\delta H^2 = \delta H^3 = 2.9$ ppm). Thus, the difference in chemical shifts between the considered hydrogen atoms is $\Delta \delta = 7.1$ ppm, which is in good agreement with the experimental data. A similar trend is also observed for complex 9c, in which one of the hydride atoms of the inner Zr–H–Zr bridge should be in the upfield region of the $^1$H NMR spectrum. As follows from Table 5, the calculated NMR data for complexes 9b and 9d are in poor agreement with the NMR spectral parameters observed. It should be noted for comparison that the calculated chemical shifts of the hydride atoms of the open structure 9e proposed earlier [23] also do not agree well with the NMR experiment. As a result of a comprehensive analysis of chemical shifts and relative Gibbs energy, the complex 9a was proposed as the most probable structure.

Table 5. Calculated and experimental chemical shifts of isomeric complexes 9a–d (numbering according to Scheme 4).

| Complex | $\delta$(H$^1$), ppm | $\delta$(H$^2$), ppm | $\delta$(H$^3$), ppm | $\delta$(Cp), ppm |
|---------|----------------------|----------------------|----------------------|-------------------|
| 9a      | -4.2                | 2.9                  | 2.9                  | 5.9               |
| 9b      | -2.3                | 1.8                  | 1.8                  | 6.2               |
| 9c      | -3.6                | 3.7                  | 3.7                  | 6.2               |
| 9d      | 0.7                 | 0.8                  | 0.8                  | 6.0               |
| 9e      | -1.6                | -0.4                 | -0.4                 | 6.1               |
| 9 (experimental) | -5.9 | -0.7 | -0.7 | 6.1 |

3. Materials and Methods

3.1. General Procedures

All operations for organometallic compounds were performed under argon according to the Schlenk technique. Zirconocene 1 was prepared from ZrCl$_4$ (99.5%, Merck, Darmstadt, Germany) using the standard procedure [33]. The synthesis of [Cp$_2$ZrH$_2$]$_2$ (2) from (1) was carried out as described previously [28,34]. The solvents (CHCl$_3$, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl) were distilled from P$_2$O$_5$ immediately before use. The solvent o-Cl$_2$C$_6$H$_4$ (anhydrous, 99%, Merck) was used without further purification. Commercially available Cp$_2$HfCl$_2$ (98%, Strem, Newburyport, MA, USA), Cp$_2$TiCl$_2$ (99%, Strem), (C$_5$Me$_5$)$_2$ZrCl$_2$ (97%, Acros), rac-C$_2$H$_4$(THHind)$_2$ZrCl$_2$ (97%, Merck), HALBu$_2$ (99%, Merck), ClAIBu$_2$ (97%, Strem), MMAO-12 (7% wt Al in toluene, Merck), (Ph$_3$C)[B(C$_6$F$_5$)$_4$] (97%, Abcr, Karlsruhe, Germany), B(C$_6$F$_5$)$_3$ (95%, Merck), and 1-hexene (97%, Fisher Scientific, Pittsburgh, Pennsylvania, USA) were used for the reactions.
CAUTION: pyrophoric nature of aluminum alkyl and hydride compounds requires special safety precautions in their handling.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE−400 spectrometer (400.13 MHz ($^1$H), 100.62 MHz ($^{13}$C)) (Bruker, Rheinstetten, Germany). As the solvents and the internal standards, CD$_2$Cl$_2$ and CDCl$_3$ were employed. 1D and 2D NMR spectra (COSY HH, HSQC, HMBC, NOESY) were recorded using standard Bruker pulse sequences. The products were analyzed using a GC−MS-QP2010 Ultra gas chromatograph−mass spectrometer (Shimadzu, Tokyo, Japan) equipped with the GC−2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan). Details on the GC−MS analysis of dimers and oligomers are given in the SI.

3.2. Reaction of $[\text{Cp}_2\text{ZrH}_2]_2$ with ClAlBu$_2$, Activators (MMAO-12, (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$] or B(\text{C}_6\text{F}_3)_{12}$) and 1-Hexene

A flask with a magnetic stirrer was filled under argon with 10 mg (0.045 mmol) $[\text{Cp}_2\text{ZrH}_2]_2$ (all ratios are given relative to the monomer), 0.026 mL (0.135 mmol) ClAlBu$_2$, 0.58 mL (1.35 mmol) MMAO-12, 2.24 mL or 5.63 mL (17.9 or 45 mmol) 1-hexene, and 2 mL solvents (CHCl$_3$ or CH$_2$Cl$_2$). For organoboron activators (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$] or B(\text{C}_6\text{F}_3)_{12}$ the following amounts were used: 10 mg (0.045 mmol) $[\text{Cp}_2\text{ZrH}_2]_2$, 0.018–0.036 mL (0.10–0.18 mmol) ClAlBu$_2$, 6 mg (0.011 mmol) B(\text{C}_6\text{F}_3)_{12}$ or 10 mg (0.011 mmol) (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$], 0.6 mL (4.5 mmol) 1-hexene, and 2 mL solvent (CHCl$_3$, CH$_2$Cl$_2$, o-Cl$_2$C$_6$H$_4$, CICH$_2$CH$_2$Cl). The reaction was carried out with stirring at a temperature of 40 °C. After 5, 10, 15, 30, 60, 90, 120, 180, and 960 min, samples (0.1 mL) were syringed into tubes filled with argon and decomposed with 10% HCl at 0 °C. The products were extracted with CH$_2$Cl$_2$, and the organic layer was dried over Na$_2$SO$_4$. The yield of dimers or oligomers was determined by GC/MS.

3.3. Reaction of $L_2\text{MCl}_2$ (1a–f) with HAIB $^{12}$, MMAO-12, (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$] or B(\text{C}_6\text{F}_3)_{12}$ and 1-Hexene

A flask with a magnetic stirrer was filled under argon with 0.034 mmol (9–15 mg) $L_2\text{MCl}_2$, 0.019 mL (0.108 mmol) HAIB$^{12}$, 0.44 mL (1.02 mmol) MMAO-12, 1.7 or 4.2 mL (13.6 or 34 mmol) 1-hexene, and 2 mL solvents (CHCl$_3$, CH$_2$Cl$_2$, o-Cl$_2$C$_6$H$_4$, CICH$_2$CH$_2$Cl). For organoboron activators (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$] or B(\text{C}_6\text{F}_3)_{12}$ the following amounts were used: 0.034 mmol (9–15 mg) $L_2\text{MCl}_2$, 0.018–0.036 mL (0.10–0.18 mmol) HAIB$^{12}$, 5 mg (0.0085 mmol) B(\text{C}_6\text{F}_3)_{12}$ or 10–16 mg (0.011–0.017 mmol) (Ph$_3$C)[$\text{B}(\text{C}_6\text{F}_3)_{12}$], 1 or 1.7 mL (8.5 or 13.6 mmol) 1-hexene, and 2 mL solvents (CHCl$_3$, CH$_2$Cl$_2$, o-Cl$_2$C$_6$H$_4$, CICH$_2$CH$_2$Cl). The reaction was carried out with stirring at a temperature of 40 °C. After 15, 20, 30, 60, 90, 120, 180, and 960 min, samples (0.1 mL) were syringed into tubes filled with argon and decomposed with 10% HCl or DCI at 0 °C. The products were extracted with CH$_2$Cl$_2$, and the organic layer was dried over Na$_2$SO$_4$. The yields of the products were determined by GC/MS.

3.4. NMR Study of the Reaction of $[\text{Cp}_2\text{ZrH}_2]_2$ with ClAlR$_2$ and MMAO-12

An NMR tube was charged with 0.045 mmol (10 mg) $[\text{Cp}_2\text{ZrH}_2]_2$ in an argon-filled glovebox. The tube was cooled to 0 °C, and 0.045–0.2 mmol (8–35.3 mg) ClAlBu$_2$ was added dropwise. Then CDCl$_3$ or CD$_2$Cl$_2$ was added. The mixture was stirred, and the formation of complexes 8–10 was monitored by NMR at room temperature. Then 0.135–0.9 mmol (60–300 mg) MMAO-12 was added, and the formation of intermediates was monitored by NMR at room temperature (Figures S9–S18).

In the case of the system $[\text{Cp}_2\text{ZrH}_2]_2$·MMAO-12, the number of components was the same as described above (Figures S19–S23). The deuterated solvent was added to the NMR tube as the last component.
3.5. NMR Study of the Reaction of Cp₂ZrCl₂ with HAlBu₂ and MMAO-12

An NMR tube was charged with 0.034 mmol (10 mg) Cp₂ZrCl₂ in an argon-filled glovebox. The tube was cooled to 0 °C, and 0.068–0.136 mmol (10–19.3 mg) HAlBu₂ was added dropwise. Then CDCl₃ or CD₂Cl₂ was added. The mixture was stirred, and the formation of complexes 8–10 was monitored by NMR at room temperature. Then 0.135–0.9 mmol (60–300 mg) MMAO-12 was added, and the formation of intermediates was monitored by NMR at room temperature (Figures S1–S8).

3.6. Computational Details

DFT calculations were carried out in Priroda-06 program [32,35]. Geometry optimization, vibrational frequency analysis, and calculation of absolute chemical shielding, entropy, and thermodynamic corrections to the total energy of the compounds were carried out using the Perdew–Burke–Ernzerhof (PBE) functional [30]. PBE functional was used in combination with a 3ζ basis set [31]. 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, (14s3p5d1f) for Al and Cl, and (22s5p5d4f4g) for Zr. No symmetry of internal coordinate constraints was applied during optimizations. Thermodynamic parameters were determined at 298.15. Normal-mode vibrational frequency analysis was performed to confirm minima structures. Computations of absolute chemical shielding, σ, were carried out in the GIAO approach [36,37]. Chemical shifts were calculated as δ = σ_TMS − σ, where σ_TMS was the calculated shielding constant of tetramethylsilane. For comparison, structural and energetic parameters of complexes 9a–e were calculated using Gaussian 09 [38] at the PBE0 level of theory [39] employing the def2-TZVP basis set [40,41] with and without Grimme’s D3(0) empirical dispersion correction (GD3) [42] (Tables S2 and S3). Moreover, the method was successfully employed to calculate chemical shifts of Au hydrides [43]. Calculated chemical shifts obtained for 9a by two methods was comparable (PBE0/def2-TZVP: 3.1 ppm, PBE/3ζ: 3.1 ppm). Therefore, the PBE/3ζ method was used for the calculation of the chemical shifts of other complexes. As follows from Table S3 (Supporting Information), using the GD3 correction does not lead to significant changes in the energy of the studied complexes. Furthermore, we carried out the study on the solvent effect (CH₂Cl₂ and CHCl₃) using the conductor-like polarizable continuum model (CPCM) [44,45]. The data indicated minor energy changes (Supporting Information, Tables S4 and S5).

The program ChemCraft [46] was used to visualize obtained quantum chemical data. The energy at 0 K, the ZPVE correction, the enthalpy, the Gibbs free energy in gas, the temperature multiplied by the entropy, and Cartesian coordinates for all optimized structures are given in the Supporting Information.

4. Conclusions

As a result of studying the catalytic transformations of 1-hexene under the action of Ti group metallocenes, organoaluminum compounds, and activators MMAO-12, B(C₆F₅)₃ or (Ph₃P)₂[B(C₆F₅)₃] in chlorinated solvents, it was found that systems based on Zr complexes [Cp₂ZrH₂]₂·ClAlBu₂-MMAO-12, Cp₂ZrCl₂·HAlBu₂-MMAO-12 in CH₂Cl₂ selectively afford dimeric products in high yields. The use of CHCl₃ as the solvent facilitates the formation of non-classical tetramers of 1-hexene, the products of dimerization.

NMR studies showed that systems Cp₂ZrCl₂·HAlBu₂-MMAO-12, [Cp₂ZrH₂]₂-MMAO-12, and [Cp₂ZrH₂]₂·ClAlBu₂-MMAO-12 provide the adduct of biszirconium complex (Cp₂ZrH₂·Cp₂ZrHCl·ClAlR₂) with an activator both in CD₂Cl₂ and CDCl₃. The adduct reacts with 1-hexene and produces a vinylidene dimer.

The probable structure of the key biszirconium hydride complex was proposed based on a comparison of experimental and theoretical NMR data and estimation of the thermo-
dynamical stability of the complexes. These studies are necessary to further understand the mechanism of key intermediate activation by methylaluminoxane or organoboron compounds for selective alkene dimerization.

Supplementary Materials: Supplementary Materials are available online. Figures S1–S27: NMR spectra of catalytic systems, Figures S28 and S29: Examples of GC-MS analysis of dimers and oligomers, Tables S1–S5: Calculated thermodynamic parameters of isomeric complexes 9a–d.

Author Contributions: Conceptualization, L.V.P.; methodology, P.V.K. and T.V.T; validation, L.V.P., P.V.K. and T.V.T.; formal analysis, P.V.K. and T.V.T.; investigation, P.V.K., A.K.B., D.N.I. and V.M.Y.; resources, P.V.K. and L.V.P.; data curation, P.V.K., T.V.T. and L.V.P.; writing—original draft preparation, P.V.K. and T.V.T.; writing—review and editing, L.V.P.; visualization, P.V.K. and D.N.I.; supervision, L.V.P.; project administration, P.V.K.; funding acquisition, P.V.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Russian Science Foundation, grant number 19-73-10122.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The structural studies of compounds were carried out at the Center for Collective Use “Agidel” at the Institute of Petrochemistry and Catalysis, Russian Academy of Sciences.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available from the authors.

References
1. Organometallic Reactions and Polymerization; Osakada, K. (Ed.) Springer-Verlag: Berlin/Heidelberg, Germany, 2014; p. 301. [CrossRef]
2. Nicholas, C.P. Applications of light olefin oligomerization to the production of fuels and chemicals. Appl. Cat. A Gen. 2017, 543, 82–97. [CrossRef]
3. de Klerk, A. Oligomerization. In Fischer-Tropsch Refining; de Klerk, A., Ed.; Wiley-VCH Verlag: Hoboken, NJ, USA, 2011; pp. 369–391. [CrossRef]
4. McGuinness, D.S. Olefin Oligomerization via Metallacycles: Dimerization, Trimerization, Tetramerization, and Beyond. Chem. Rev. 2011, 111, 2321–2341. [CrossRef]
5. Nifant’ev, I.; Ivenchenko, P.; Tavtorkin, A.; Vinogradov, A.; Vinogradov, A. Non-traditional Ziegler-Natta Catalysis in α-Olefin Transformations: Reaction Mechanisms and Product Design. Pure Appl. Chem. 2017, 89, 1017–1032. [CrossRef]
6. Janiak, C. Metallocene and Related Catalysts for Olefin, Alkyne and Silane Dimerization and Oligomerization. Coord. Chem. Rev. 2006, 250, 66–94. [CrossRef]
7. Comyns, A.E. Encyclopedic Dictionary of Named Processes in Chemical Technology, 4th ed.; CRC Press: Boca Raton, FL, USA, 2014; p. 416. [CrossRef]
8. Harvey, B.G.; Meylemans, H.A. 1-Hexene: A Renewable C6 Platform for Full-performance Jet and Diesel fuels. Green Chem. 2014, 16, 770–776. [CrossRef]
9. Chen, E.Y.-X.; Marks, T.J. Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure–Activity Relationships. Chem. Rev. 2000, 100, 1391–1434. [CrossRef]
10. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. Selectivity in Propene Polymerization with Metallocene Catalysts. Chem. Rev. 2000, 100, 1253–1346. [CrossRef] [PubMed]
11. Kaminsky, W. The Discovery of Metallocene Catalysts and Their Present State of the Art. J. Polym. Sci. A Polym. Chem. 2004, 42, 3911–3921. [CrossRef]
12. Collins, R.A.; Russell, A.F.; Mountford, P. Group 4 Metal Complexes for Homogeneous Olefin Polymerisation: A Short Tutorial Review. App. Petroch. Res. 2015, 5, 153–171. [CrossRef]
13. Christoffers, J.; Bergman, R.G. Catalytic Dimerization Reactions of α-Olefins and α,ω-Dienes with Cp2ZrCl2/Poly(methylalumoxane): Formation of Dimers, Carbocycles, and Oligomers. J. Am. Chem. Soc. 1996, 118, 4715–4716. [CrossRef]
14. Christoffers, J.; Bergman, R.G. Zirconocene-alumoxane (1:1)—A Catalyst for the Selective Dimerization of α-Olefins. Inorg. Chim. Acta 1998, 270, 20–27. [CrossRef]
15. Nifant’ev, I.E.; Vinogradov, A.A.; Vinogradov, A.A.; Ivenchenko, P.V. Zirconocene-Catalyzed Dimerization of 1-Hexene: Two-stage Activation and Structure–Catalytic Performance Relationship. Cat. Commun. 2016, 79, 6–10. [CrossRef]
16. Nifant’ev, I.E.; Vinogradov, A.A.; Vinogradov, A.A.; Sedov, I.V.; Dorokhov, V.G.; Lyadov, A.S.; Ivchenko, P.V. Structurally Uniform 1-Hexene, 1-Octene, and 1-Decene Oligomers: Zirconocene/MAO-Catalyzed Preparation, Characterization, and Prospects of Their Use as low-viscosity Low-Temperature Oil Base Stocks. *Appl. Cat. A Gen.* 2018, 549, 40–50. [CrossRef]

17. Nifant’ev, I.E.; Vinogradov, A.A.; Vinogradov, A.A.; Churakov, A.V.; Bagrov, V.V.; Kashulin, I.A.; Roznyatovskiy, V.A.; Grishin, Y.K.; Ivchenko, P.V. The Catalytic Behavior of Heterocenes Activated by TIBA and MMAO under a Low Al/Zr Ratios in 1-Octene Polymerization. *Appl. Cat. A Gen.* 2019, 571, 12–24. [CrossRef]

18. Nifant’ev, I.; Vinogradov, A.; Vinogradov, A.; Karchevsky, S.; Ivchenko, P. Experimental and Theoretical Study of Zirconocene-Catalyzed Oligomerization of 1-Octene. *Polymers* 2020, 12, 1590. [CrossRef] [PubMed]

19. Parfenova, L.V.; Kovyazin, P.V.; Bikmeeva, A.K. Bimetallic Zr,Zr-Hydride Complexes in Zirconocene Catalyzed Alkene Dimerization. *Molecules* 2020, 25, 2216. [CrossRef]

20. Parfenova, L.V.; Kovyazin, P.V.; Bikmeeva, A.K.; Palatov, E.R. Catalytic Systems Based on Cp2ZrX2 (X = Cl, H), Organoaluminum Compounds and Perfluorophenylboranes: Role of Zr,Zr- and Zr,Al-Hydride Intermediates in Alkene Dimerization and Oligomerization. *Catalysts* 2021, 11, 39. [CrossRef]

21. Nifant’ev, I.; Vinogradov, A.; Vinogradov, A.; Karchevsky, S.; Ivchenko, P. Zirconocene-Catalyzed Dimerization of α-Olefins: DFT Modeling of the Zr-Al Binuclear Reaction Mechanism. *Molecules* 2019, 24, 3565. [CrossRef]

22. Nifant’ev, I.; Ivchenko, P. Fair Look at Coordination Oligomerization of Higher α-Olefins. *Polymers* 2020, 12, 1082. [CrossRef]

23. Parfenova, L.V.; Kovyazin, P.V.; Tyumkina, T.V.; Islomov, D.N.; Lypina, A.R.; Karchevsky, S.G.; Ivchenko, P.V. Reactions of bimetallic Zr,Al-hydride complexes with methylaluminoxane: NMR and DFT study. *J. Organomet. Chem.* 2017, 851, 30–39. [CrossRef]

24. Dong, S.Q.; Mi, P.K.; Xu, S.; Zhang, J.; Zhao, R.D. Preparation and Characterization of Single-Component Poly-α-olefin Oil Base Stocks. *Energy Fuels* 2019, 33, 9796–9804. [CrossRef]

25. Zhao, R.; Mi, P.; Xu, S.; Dong, S. Structure and Properties of Poly-α-olefins Containing Quaternary Carbon Centers. *ACS Omega* 2020, 5, 9142–9150. [CrossRef] [PubMed]

26. Shao, H.; Gu, X.; Wang, R.; Wang, X.; Jang, T.; Guo, X. Preparation of Lubricant Base Stocks with High Viscosity Index through 1-Decene Oligomerization Catalyzed by Alkylaluminum Chloride Promoted by Metal Chloride. *Energy Fuels* 2020, 34, 2214–2220. [CrossRef]

27. Parfenova, L.V.; Kovyazin, P.V.; Gabdrakhanov, V.Z.; Istomina, G.P.; Ivchenko, P.V.; Nifant’ev, I.E.; Khalilov, L.M.; Dzhemilev, U.M. Ligand Exchange Processes in Zirconocene Dichloride-Trimethylaluminum Bimetallic Systems and Their Catalytic Properties in Reactions with Alkenes. *Dalton Trans.* 2018, 47, 16918–16937. [CrossRef] [PubMed]

28. Parfenova, L.V.; Fedotkina, S.V.; Khalilov, L.M.; Dzhemilev, U.M. Mechanism of Cp2ZrCl2-Catalyzed Olefin Hydroalumination by Alkylalanes. *Russ. Chem. Bull.* 2005, 54, 316–327. [CrossRef]

29. Parfenova, L.V.; Kovyazin, P.V.; Nifant’ev, I.E.; Khalilov, L.M.; Dzhemilev, U.M. Role of Zr,Al Hydride Intermediate Structure and Dynamics in Alkene Hydroalumination with XAlBu2 (X = H, Cl, Bu), Catalyzed by Zr η3-Complexes. *Organometallics* 2015, 34, 3559–3570. [CrossRef]

30. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef]

31. Laikov, D.N. Razvitiye ekonomnogo podkhoda k raschetu molekul metodom funktsionala plotnosti i yego primeneniye k resheniyu slozhnykh khimicheskikh zadach. Ph.D Thesis, Moscow State University, Moscow, Russia, 2000. (In Russian). [CrossRef]

32. Laikov, D.N. Fast Evaluation of Density Functional Exchange-Correlation Terms Using the Expansion of the Electron Density in Auxiliary Basis Sets. *Chem. Phys. Lett.* 1997, 281, 151–156. [CrossRef]

33. Freidлина, R.K.; Brainina, E.M.; Nesmeyanov, A.N. The Synthesis of Mixed Pincerlike Cyclopentadienyl Compounds of Zirconium. *Dokl. Acad. Nauk SSSR* 1961, 138, 1639–1372.

34. Shoer, L.I.; Gell, K.I.; Schwartz, J. Mixed-Metal Hydride Complexes Containing Zr-H-Al Bridges. Synthesis and Relation to Transition-Metal-Catalyzed Reactions of Aluminum Hydrides. *J. Organomet. Chem.* 1977, 136, c19–c22. [CrossRef]

35. Laikov, D.N.; Ustynyuk, Y.A. PRIRODA-04: A quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing. *Russ. Chem. Bull.* 2005, 54, 820–826. [CrossRef]

36. Ditchfield, R. Self-consistent Perturbation Theory of Diamagnetism. *Mol. Phys.* 1974, 27, 789–807. [CrossRef]

37. Wolinski, K.; Hinton, J.F.; Pulay, P. Efficient Implementation of the Gauge-independent Atomic Orbital Method for NMR Chemical Shift Calculations. *J. Am. Chem. Soc.* 1990, 112, 8251–8260. [CrossRef]

38. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09* Rev. D.01; Gaussian: Wallingford, CT, USA, 2009.

39. Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* 1999, 110, 6158–6170. [CrossRef]

40. Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Row: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305. [CrossRef] [PubMed]

41. Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Energy-adjustedab Initio Pseudopotentials for the Second and Third Row Transition Elements. *Theor. Chim. Acta* 1990, 77, 123–141. [CrossRef]

42. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* 2011, 32, 1456–1465. [CrossRef]
43. Rocchigiani, L.; Fernandez-Cestau, J.; Chambrier, I.; Hrobárik, P.; Bochmann, M. Unlocking Structural Diversity in Gold(III) Hydrides: Unexpected Interplay of cis/trans-Influence on Stability, Insertion Chemistry, and NMR Chemical Shifts. *J. Am. Chem. Soc.* **2018**, *140*, 8287–8302. [CrossRef]

44. Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102*, 1995–2001. [CrossRef]

45. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* **2003**, *24*, 669–681. [CrossRef]

46. Zhurko, G.A.; Zhurko, D.A. *ChemCraft 1.6*; Informer Technologies, Inc.: Roseau, Dominica, 2009.