

Article

Catalytic Systems Based on Cp_2ZrX_2 ($\text{X} = \text{Cl}, \text{H}$), Organoaluminum Compounds and Perfluorophenylboranes: Role of Zr,Zr- and Zr,Al-Hydride Intermediates in Alkene Dimerization and Oligomerization

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Abstract: The activity and chemoselectivity of the $\text{Cp}_2\text{ZrCl}_2\text{-XAlBu}^i_2$ ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$ catalytic systems activated by $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ were studied in reactions with 1-hexene. The activation of the systems by $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in the selective formation of head-to-tail alkene dimers in up to 93% yields. NMR studies of the reactions of Zr complexes with organoaluminum compounds (OACs) and boron activators showed the formation of Zr,Zr- and Zr,Al-hydride intermediates, for which diffusion coefficients, hydrodynamic radii, and volumes were estimated using the diffusion ordered spectroscopy DOSY. Bis-zirconium hydride clusters of type $x[\text{Cp}_2\text{ZrH}_2\text{-Cp}_2\text{ZrHCl}\text{-ClAlR}_2] \cdot y\text{R}_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$ were found to be the key intermediates of alkene dimerization, whereas cationic Zr,Al-hydrides led to the formation of oligomers.

Keywords: zirconocene; metal hydrides; alkene dimerization; nuclear magnetic resonance



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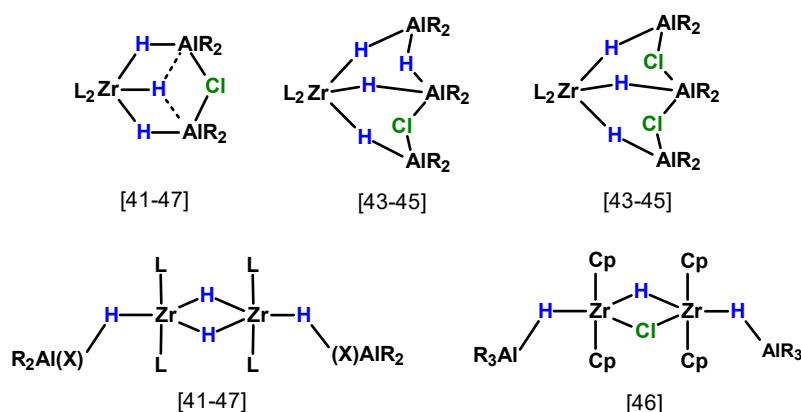
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1. Introduction

Among the catalytic methods for alkene di-, oligo-, and polymerization, approaches that use Ziegler–Natta-type catalytic systems, based on metallocenes or post-metallocenes, typically Group 4 transition metal complexes, in combination with organoaluminum or organoboron activators, have great potential for development [1–5]. Apart from the known action of alkyl cations $[(\text{L}_2\text{MAlk})^+\text{X}^-]$ as polymer chain growth centers, the idea of the participation of $[(\text{L}_2\text{MH})^+\text{X}^-]$ -type hydride complexes as catalytic active species in the reactions of alkene di-, oligo-, and polymerization has been repeatedly pointed out [2,4,6–15]. This assumption follows both from the structure of the reaction products (the presence of vinylidene terminal groups, arising upon chain termination via β -H elimination, which generates intermediates with M–H bond) and from the fact that the efficiency of catalytic systems increases upon the introduction of hydride-generating additives such as AlBu^i_3 [13,16–25]. Moreover, there are several studies on the synthesis and identification of catalytically active hydride Zr,B-complexes (Scheme 1). For example, complexes $[\text{Cp}'_2\text{ZrH}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{Cp}'_2\text{ZrH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ were found to be active in the ethylene and propylene polymerization [26,27]. Additionally, hydride complexes $[\text{Cp}'_4\text{Zr}_2\text{H}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{F}, \text{SiPr}^i_3$), highly active initiators for the isobutene homopolymerization and isobutene–isoprene copolymerization, were described [28].

A number of Zr borohydride complexes were prepared by Piers et al. by the reaction of alkylzirconocenes with $\text{HB}(\text{C}_6\text{F}_5)_2$ [29–31]. The complexes were found to be active in ethylene polymerization provided that additional alkylation with MAO takes place [30]. Zr,B-hydride complexes were also obtained in the reaction of rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium difluoride with HAlBu^i_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ [32,33]. The activation of hafnocenes with $\text{AlBu}^i_3/(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ yielded hydrido-bridged species of

(Scheme 2). Among the hydride complexes, novel Zr,Zr-structures were identified and their high affinity to MAO with the ability to give $x[\text{Cp}_2\text{ZrH}_2 \cdot \text{Cp}_2\text{ZrHCl} \cdot \text{ClAlR}_2] \cdot y\text{MAO}$ -type adducts was shown [46]. Moreover, the adducts were found to be reactive towards alkenes to specifically give dimerization products in high yields [47].



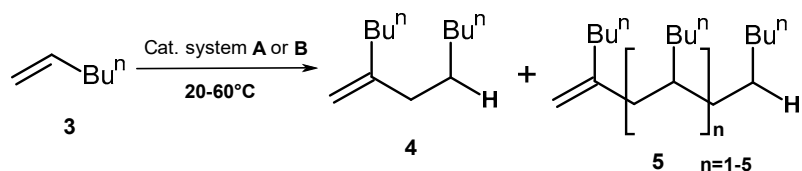
Scheme 2. Structures of Zr,Al-hydride complexes studied in Refs. [41–47].

In continuation of this research, we studied the activation of Zr,Zr- and Zr,Al-hydride complexes, formed in the Cp_2ZrCl_2 – XAlBu^i_2 ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2$ – ClAlEt_2 systems, by organoboron compounds $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ and the ability of the corresponding adducts to act as active intermediates in the alkene di- and oligomerization.

2. Results and Discussion

2.1. Study of 1-Hexene Transformations in Cp_2ZrCl_2 – XAlBu^i_2 ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2$ – ClAlEt_2 Catalytic Systems Modified with Boron Activators

The L_2ZrCl_2 – XAlBu^i_2 ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2$ – ClAlR_2 bimetallic systems perform alkene hydrometalation providing zirconium and aluminum alkyls [48,49]. The addition of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ to the Cp_2ZrCl_2 – XAlBu^i_2 system ($\text{X} = \text{H}, \text{Bu}^i$) ($\text{X} = \text{H}, \text{Bu}^i$) (catalytic system A) gives alkene dimers (4) and oligomers (5) (Scheme 3, Table 1). The product yield and chemoselectivity markedly depend on the reagent ratio and reaction temperature. For example, the reaction carried out at $[\text{Zr}]:[\text{Al}]:[\text{B}]:[1\text{-alkene}]$ ratio of 1:16:1:1000 and a temperature of 40 °C for 90 min results in 60% conversion of 1-hexene (Table 1, Entry 1). In the mixture of oligomeric products, dimer 4 predominates (41% yield). The increase of the reaction temperature to 60 °C leads to higher monomer conversion (at the level of 95%) and maximizes the percentage of oligomeric products (Table 1, Entry 2).



Cat. system A: Cp_2ZrCl_2 (1): HAlBu^i_2 : $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$:1-alkene = (1-4):(16-25):1:1000
 Cat. system B: $[\text{Cp}_2\text{ZrH}_2]_2$ (2): ClAlEt_2 : $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$:1-alkene = (1-4):(4-5):1:400

Scheme 3. 1-Hexene dimerization and oligomerization under the action of catalytic systems A or B.

Table 1. Catalytic activity and chemoselectivity of systems **A** and **B** in the reaction with 1-hexene.

Entry	Catalytic Systems A or B			[Zr]:[Al]:[B]:[1-alkene]	T, °C	Time, min	Alkene Conversion, %	Product Composition, %					
	Zr Complex	OAC ^a	Organoboron Activator					4	n = 1	n = 2	5 n = 3	n = 4	n = 5
1	Cp ₂ ZrCl ₂	HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	1:16:1:1000	40	90	60	41	10	4	2	2	1
2		HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	1:16:1:1000	60	90	95	29	16	15	13	12	9
3		HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	4:16:1:1000	40	90	90	67	10	5	3	2	2
4		HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]		60	90	97	52	14	13	8	7	3
5		AlBu ⁱ ₃	(Ph ₃ C)[B(C ₆ F ₅) ₄]		40	90	95	38	14	16	10	9	7
6		HAIBu ⁱ ₂	B(C ₆ F ₅) ₃		40	60	> 99	93	3	-	-	-	-
7		HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	4:25:1:1000	40	90	99	52	17	11	9	6	3
8		HAIBu ⁱ ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	4:16:1:400	40	90	>99	59	13	10	7	5	5
9	[Cp ₂ ZrH ₂] ₂	ClAlEt ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	1:3:1:400	60	150	30	28	-	-	-	-	-
10		ClAlEt ₂	(Ph ₃ C)[B(C ₆ F ₅) ₄]	4:8:1:400	40	150	81	81	-	-	-	-	-
11		ClAlEt ₂	B(C ₆ F ₅) ₃		40	90	91	86	-	-	-	-	-

^a OAC—organoaluminum compound.

An increase in Cp_2ZrCl_2 and HALBu^i_2 content up to $[\text{Zr}]:[\text{Al}]:[\text{B}]:[\text{alkene}] = 4:16:1:1000$ increases the conversion of the substrate to 90% and the yield of dimers up to 67% (Table 1, Entry 3). As in the previous case, the relative amount of oligomeric products grows with the rise of the reaction temperature (Table 1, Entry 4). The replacement of HALBu^i_2 with AlBu^i_3 (Table 1, Entry 5) or increase in the HALBu^i_2 concentration (Table 1, Entry 7) also leads to a higher oligomer yield. In all experiments, the yield of hydroalumination product (hexane) after the hydrolysis was no more than 1%. It should be noted that, in almost all cases, the dimerization product significantly prevailed, which may be a consequence of different pathways to dimers and oligomers in these catalytic systems.

The reaction pathway can be completely shifted towards the formation of dimers by using zirconocene hydride. Thus, in the course of studying the properties of catalytic system **B**, $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$, in the reaction with 1-hexene, it was found that the activity of the system significantly depends on the initial reagent ratio. For example, when $[\text{Zr}]:[\text{Al}]:[\text{B}]:[1\text{-alkene}] = 1:3:1:400$, the degree of alkene conversion is 30% in 150 min at 60 °C (Table 1, Entry 9). An increase in the $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ content to $[\text{Zr}]:[\text{B}] = 1:(3\text{--}10)$ leads to a complete loss of catalytic system activity. An increase in $[\text{Cp}_2\text{ZrH}_2]_2$ and ClAlEt_2 concentration in system **B** substantially elevates the conversion of the substrate. At the ratio $[\text{Zr}]:[\text{Al}]:[\text{B}]:[1\text{-alkene}] = 4:8:1:400$ and a temperature of 40 °C, 81% of dimers with vinylidene double bond are formed in 150 min of the reaction (Table 1, Entry 10).

The replacement of $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ by $\text{B(C}_6\text{F}_5)_3$ results in a more selective formation of dimerization products in up to 93% yield in the presence of either Cp_2ZrCl_2 or $[\text{Cp}_2\text{ZrH}_2]_2$ (Table 1, Entries 6,11).

In order to identify the intermediates responsible for alkene dimerization and oligomerization, we further studied the structure and activity of hydride complexes formed in the $\text{Cp}_2\text{ZrCl}_2\text{-HALBu}^i_2\text{-(Ph}_3\text{C)[B(PhF}_5)_4]$ ($\text{B(C}_6\text{F}_5)_3$) and $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ ($\text{B(C}_6\text{F}_5)_3$) systems by means of NMR spectroscopy.

2.2. NMR Study of Hydride Intermediate Structure in the Cp_2ZrY_2 ($\text{Y} = \text{H, Cl}$)-OAC Systems Activated by $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ or $\text{B(C}_6\text{F}_5)_3$

Our investigation of the reaction of Cp_2ZrCl_2 with HALBu^i_2 at low content of organoaluminum compound (OAC) and $[\text{Zr}]:[\text{Al}] = 1:(3\text{--}5)$ showed the existence of a Zr,Zr-hydride intermediate **7** [47], along with the well-known Zr,Al-hydride clusters **6** [41,44,50] and **8** [41,42] (Figure 1a, Scheme 4, Table 2). As we have previously demonstrated [46], an equilibrium mixture of complexes **6–8** is also formed upon the interaction of $[\text{Cp}_2\text{ZrH}_2]_2$ with ClAlEt_2 taken in 1: 3 ratio. In this case, a larger relative amount of complex **7** is observed (Figure 2a). This complex, in fact, is the product of replacing one hydride atom in the zirconocene dihydride dimer with chlorine. Therefore, it can be considered as a complex formed in the reaction of the Cp_2ZrH_2 monomer with Cp_2ZrHCl . The dialkylaluminum hydride, produced as a result of the chloride/hydride exchange, reacts with Cp_2ZrH_2 and ClAlEt_2 , providing trihydride complex **6**.

Table 2. ^1H and ^{13}C NMR (δ , ppm, 400.13 MHz (^1H), 100.62 (^{13}C), T = 298 K), diffusion coefficients, hydrodynamic radii, and volumes of complexes **6–10** obtained by the diffusion ordered spectroscopy DOSY.

Complex	$\delta_{\text{H}} \text{ Cp}$	$\delta_{\text{C}} \text{ Cp}$	$\delta_{\text{H}} \text{ Zr-H}$	$\delta_{\text{H}} \text{ AlR}$	$D_{\text{tr}}, 10^{-10} \text{ m}^2 \text{ s}^{-1}$	$R_{\text{h}}, \text{ \AA}$	$V_{\text{h}}, \text{ \AA}^3$
6a ^a	5.61 (s, 10H)	104.7	−1.09 (br.t, 6.3 Hz, 1H) −2.28 (br.d, 6.3 Hz, 2H)	0.32 (m) 1.25 (m)	9.3	4.2	319
7a ^a	5.48 (s, 20H)	107.6	−1.39 (d, 17.0 Hz, 2H) −6.53 (t, 17.0 Hz, 1H)	0.17 (q, 8.1 Hz, 4H) 1.35 (t, q, 8.1 Hz, 4H)	7.5	4.9	505
8a ^a	5.73 (s, 10H)	107.2	−1.66 (br.s, 1H) −2.63 (br.s, 1H)	0.32 (m) 1.25 (m)	8.3	4.6	403
9a ^b	5.30 (s, 20H)	107.7	−1.51 (d, 16.8 Hz, 2H) −6.62 (t, 16.8 Hz, 1H)	0.14 (q, 8.1 Hz, 4H) 1.33 (t, q, 8.1 Hz, 4H)	5.0	6.9	1344
10 ^b	5.06 (s, 20H)	107.5	−1.72 (br.d, 16.8 Hz, 2H) −6.87 (br.t, 16.8 Hz, 1H)	−0.11 (br.q, 7.2 Hz, 4H) 0.88–1.01 (m)	1.8	17.2	21236

^a Complexes are obtained in the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$, d_8 -toluene system. ^b Complexes are obtained in the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$, d_6 -benzene system.

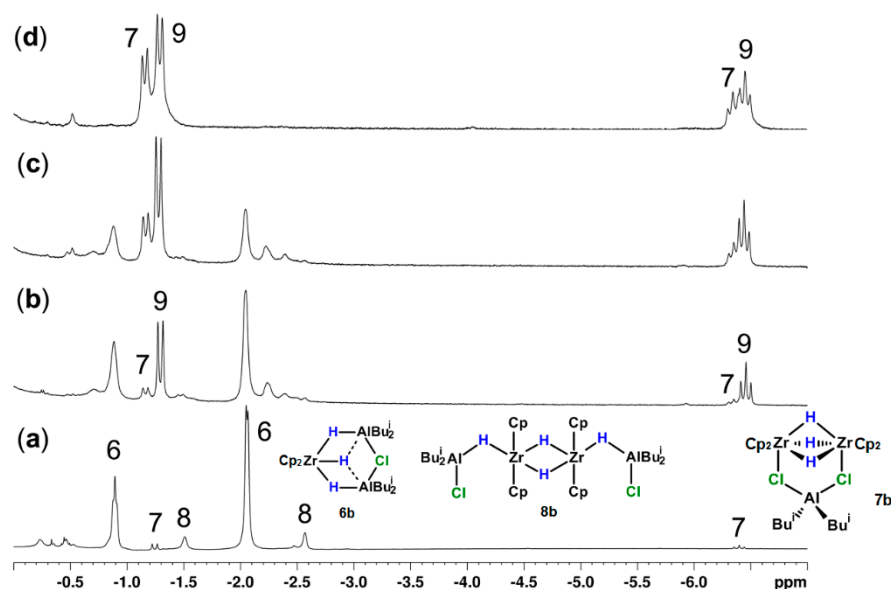
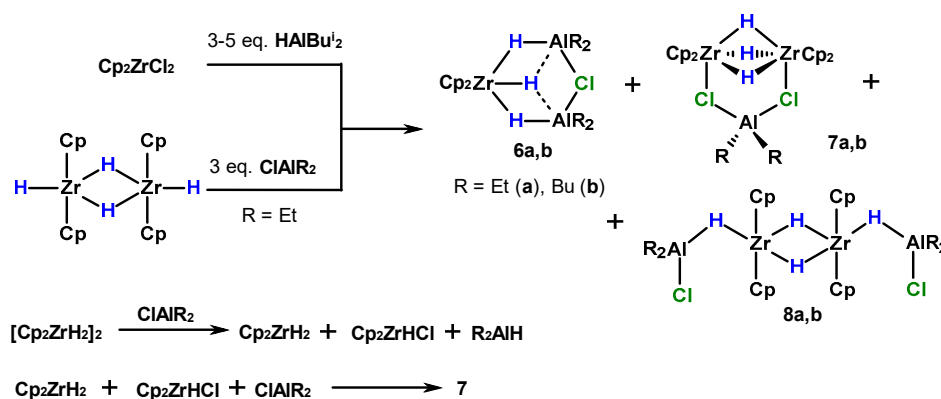


Figure 1. ^1H NMR of the Cp_2ZrCl_2 - HAlBu_2 - $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ system in C_6D_6 ($T = 299\text{ K}$): (a) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:5:0$; (b) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:3:0.25$; (c) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:3:0.45$; and (d) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:3:0.5$. The order of mixing the reagents in the experiments (b–d) is HAlBu_2 - $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ - Cp_2ZrCl_2 .



Scheme 4. Reaction of Cp_2ZrCl_2 and $[\text{Cp}_2\text{ZrH}_2]_2$ with organoaluminum compounds (OACs).

The ^1H NMR spectrum of complex **7a** exhibits a distinct triplet signal at $\delta_{\text{H}} -6.53$ ppm, which was assigned to the hydride atom of the Zr-H-Zr bridge. This signal correlates with a doublet at $\delta_{\text{H}} -1.39$ ppm in the COSY HH spectrum. The observed signals correspond to the AX_2 spin system, denoting a symmetrical arrangement of hydride ligands in the molecule. For these hydrides, the geminal constants $^2J = 17$ Hz of the hydrides in **7** were greater than that of analogous atoms in **6** or **8** ($^2J = 4-8$ Hz) [41,42,44,50]. The sharp multiplet signals of hydride atoms and the absence of their exchange in the exchange spectroscopy (EXSY) spectra in the case of **7** are consequences of higher stability of the structure, whereas complexes **6** and **8** could be involved in the dynamic processes [44]. The intensity ratio being 1 (Zr-H): 2 (Zr-H): 20 (Cp) indicates the presence of two ZrCp_2 moieties in the molecule. A study of the reaction of complex **7a** with $\text{B}(\text{C}_6\text{F}_5)_3$ (Figure S15, Supplementary Materials) shows that the adducts **9** and **10** contain one diethylaluminum chloride molecule. Indeed, the ^1H NMR spectrum exhibits quartet signals of CH_2 groups of ethyl substituents at Al in the range of -0.2 to -0.3 ppm, the intensity of which corresponds to one AlEt_2 moiety. The signals correlate both with high-field hydride signals and with a low-field signal of the cyclopentadienyl group in the NOESY spectra (Figure S13, Supplementary Materials). Moreover, HMBC spectra show cross-peaks between the doublet of hydrides at $\delta_{\text{H}} -1.39$ ppm and the signal of α -carbon atom of the AlCH_2 group at $\delta_{\text{C}} 3.3$ ppm

(Figure S16). Therefore, we can conclude that complexes **7**, **9**, and **10** contain one ClAlR_2 molecule per bis-zirconium core. This is in agreement with the structure of the adducts formed in the presence of methylaluminoxane (MAO) [47]. Thus, as follows from NMR data and our preliminary quantum-chemical calculations, complex **7** probably has a cyclic structure shown in Scheme 4.

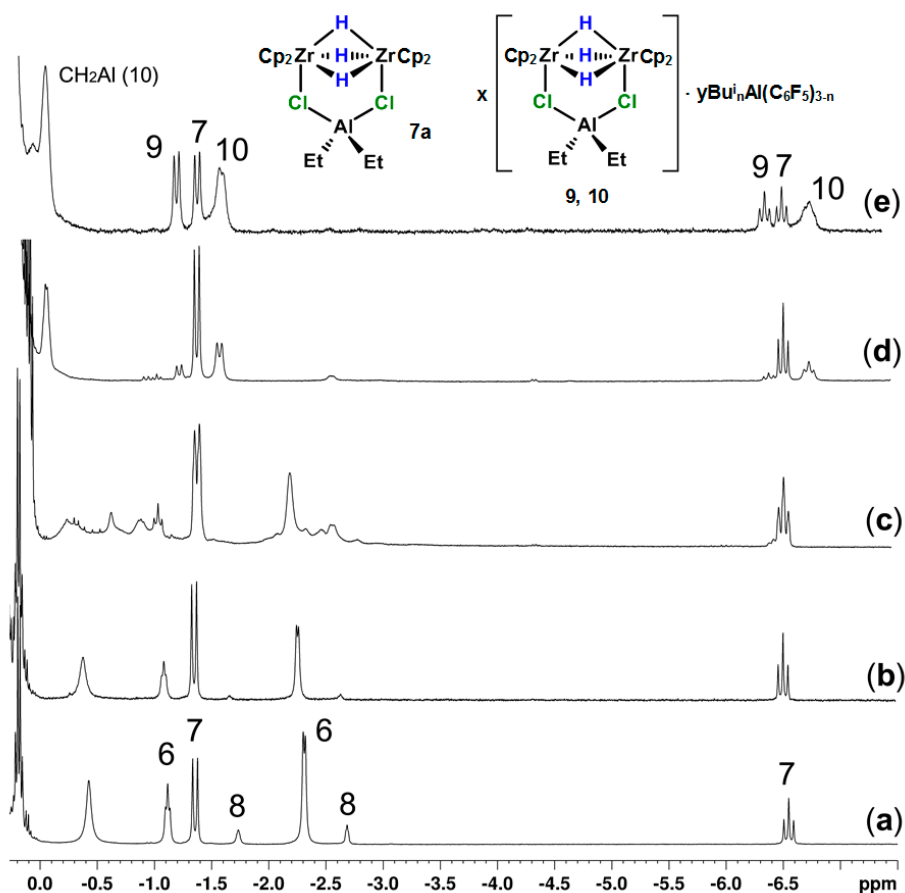


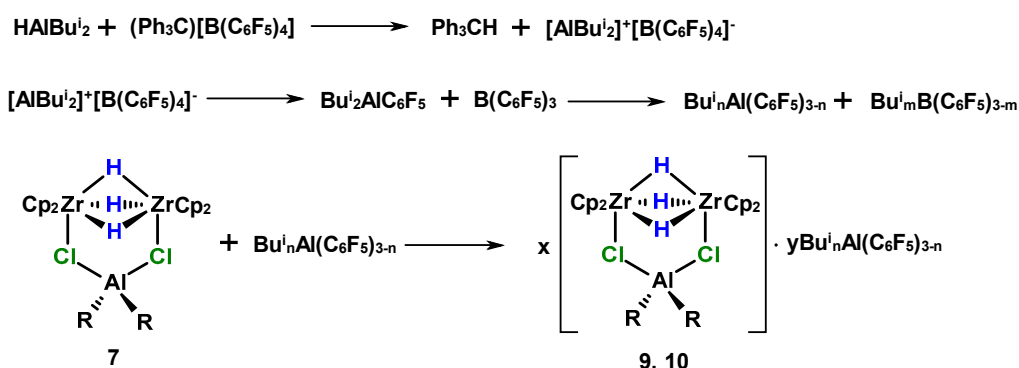
Figure 2. ^1H NMR of the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ system in C_6D_6 ($T = 299\text{ K}$): (a) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:4:0$; (b) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:4:0.15$; (c) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:4:0.2$, upper layer; (d) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:4:0.2$, heavy fraction; and (e) $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:3:0.5$. The order of mixing the reagents is $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]\text{-ClAlEt}_2\text{-[Cp}_2\text{ZrH}_2]_2$.

The addition of $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ to the $\text{Cp}_2\text{ZrCl}_2\text{-HAlBu}^i_2$ system brings about changes in the NMR spectra (Figure 1b–d). First, the signals of the dimeric complex **8** disappear. Second, the signals of the hydride atoms of complex **6** begin to split, which may be attributable to the formation of cationic species similar to those described previously [11,26,27,39]. Third, new high-field doublet and triplet signals corresponding to adducts **9** and **10** arise. A similar behavior of the complexes is observed in the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$ system upon the addition of $(\text{Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ or $\text{B(C}_6\text{F}_5)_3$ (Figure 2 and Figure S15). The diffusion coefficients of adducts **9** and **10** are much lower than those of complex **7** (Table 2, Figure 3). During the reaction, as in the case of methylaluminoxane [46,47], the formation of a heavy fraction is observed at the bottom of the NMR tube. The NOESY spectra of adduct **10** (Figure S13, Supplementary Materials) show a negative NOE effect inherent in large molecules [51,52]. Since the lineshape of the hydride atom signals of complexes **7**, **9**, and **10** does not change, it can be concluded that the bis-zirconium core in complex **7**, which is neutral, is preserved after the addition of a boron activator.



Figure 3. DOSY of the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2\text{-B}(\text{C}_6\text{F}_5)_3$ (1:3:0.5) system in C_6D_6 ($T = 297.1\text{ K}$), heavy phase.

We assume that **7** interacts with perfluorophenylaluminum (Scheme 5), which may be generated via the reaction of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ with dialkylaluminum hydride, formed in the $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$ system (Scheme 4). Indeed, NMR monitoring of the reaction of HAlBu^i_2 with $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ showed the appearance of Ph_3CH ($\delta_{\text{H}} 5.40\text{ ppm}$), $\text{Bu}^i_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$ and $\text{Bu}^i_n\text{B}(\text{C}_6\text{F}_5)_{3-n}$ within 5 min (Figures S5 and S6, Supplementary Materials). The latter ($\text{Bu}^i_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$ and $\text{Bu}^i_m\text{B}(\text{C}_6\text{F}_5)_{3-m}$) are generated as a result of $[\text{AlBu}^i_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ degradation (Scheme 5) [53,54]. The coordination of complex **7** with the organoaluminum compound $\text{Bu}^i_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$, which gives adducts **9** and **10**, follows from the cross-correlation of doublet signal of the hydride atom at -1.51 ppm with the signal of *o*-F atoms of the perfluorophenyl group in OAC at -120.78 ppm in the $^1\text{H}\text{-}^{19}\text{F}$ HMBC spectra (Figure S8, Supplementary Materials).



Scheme 5. Possible way for the formation of adducts **9** and **10**.

A change in the order of reagent mixing, namely, the addition of ClAlEt_2 and then $[\text{Cp}_2\text{ZrH}_2]_2$ to the activator, provides an increase in the content of Zr,Zr-hydride clusters **9** and **10** (Figure 2e and Figure S15). This fact can be explained as follows. Compound $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$, which is initially present in the system, quickly reacts with HAlR_2 , gener-

ated in the $[\text{Cp}_2\text{ZrH}_2]_2\text{--ClAlEt}_2$ system (Scheme 4), to give $\text{R}_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$ (Scheme 5). The latter is coordinated to complex 7, resulting from the reaction of Cp_2ZrH_2 with Cp_2ZrHCl and ClAlEt_2 . A low concentration of HAlR_2 does not allow complex 6 to be formed.

An estimation of the hydrodynamic radii and volumes of complexes 6–10 through the diffusion coefficients determined using the diffusion ordered spectroscopy (DOSY) is shown in Table 2. The hydrodynamic radii R_h were calculated using the modified Stokes–Einstein equation, Equation (1) [55,56], as follows:

$$D_t = \frac{kT \left[1 + 0.695 \left(\frac{R_{\text{solvent}}}{R_h} \right)^{2.234} \right]}{6\pi\eta R_h} \quad (1)$$

where R_h is the hydrodynamic radius of the solute, R_{solvent} is the hydrodynamic radius of the solvent (d_6 -benzene; the van der Waals radius is 2.7 Å), k is the Boltzmann constant, T is the temperature, D_t is the diffusion coefficient, and η is the viscosity of the solution.

The hydrodynamic volumes (V_h) of complexes as spherical particles were calculated according to Equation (2) as follows:

$$R_h = \sqrt[3]{\frac{3V_h}{4\pi}} \quad (2)$$

Adduct 10 reacts with 1-hexene to give dimer 4 (Figure 4, Scheme 6). It should be noted that complexes 7 and 9 were inactive towards the alkene. Thus, complex 7 activated by an organoboron compound is the intermediate that selectively affords dimers in the studied systems. The same activity towards the alkene was observed for the adducts of complex 7 with MAO [47].

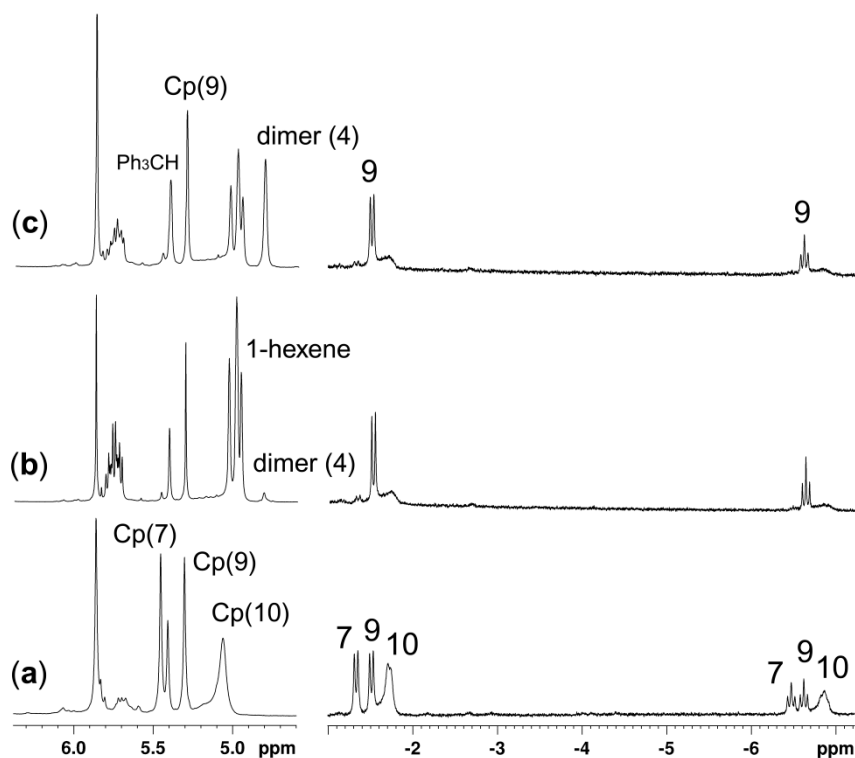
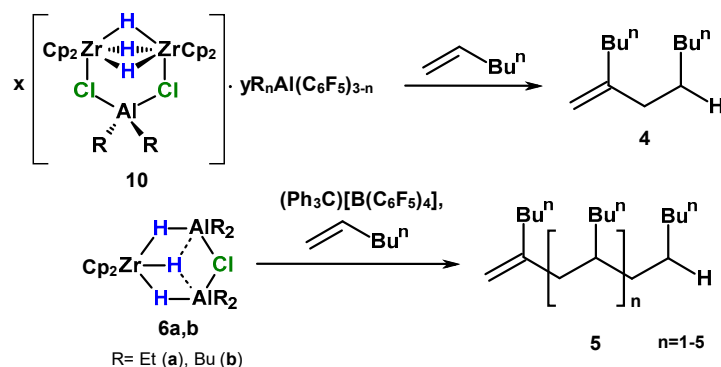


Figure 4. NMR monitoring of the reaction of complexes 7, 9, and 10 with 1-hexene in d_6 -benzene (intensity of upfield signals is increased): (a) $[\text{Cp}_2\text{ZrH}_2]_2\text{--ClAlEt}_2\text{--}(\text{Ph}_3\text{C})[\text{B}(\text{PhF}_5)_4]$ system, $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:3:0.5$; (b) $[\text{Zr}]:[\text{Al}]:[\text{B}]:[1\text{-alkene}] = 1:3:0.5:3.5$, 5 min; and (c) $[\text{Zr}]:[\text{Al}]:[\text{B}]:[1\text{-alkene}] = 1:3:0.5:3.5$, 10 min.



Scheme 6. Reaction of complex 6 and adduct 10 with 1-hexene.

The trihydride complex 6, mainly formed both in system **A** and in system **B** with an excess of OAC, reacts with $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ to give a mixture of intermediates, which give rise to signals in the -6.6 to -0.1 ppm range for hydride atoms (Figure 1a–c, Figures 2c and 5b) and which are in intermolecular exchange, as follows from the EXSY spectra (Figure S22, Supplementary Materials). The composition of the mixture depends on the $[\text{Zr}]:[\text{Al}]:[\text{B}]$ ratio and the order of reagent mixing. The observed ^1H NMR signal splitting is probably caused by the hydrogen atom removal with the formation of Ph_3CH and cationic complexes structurally similar to those described previously [11,26,27,39]. The addition of 1-hexene to this system leads to the appearance of oligomers as soon as in the 5th minute of the reaction (Figure 5c, Scheme 6).

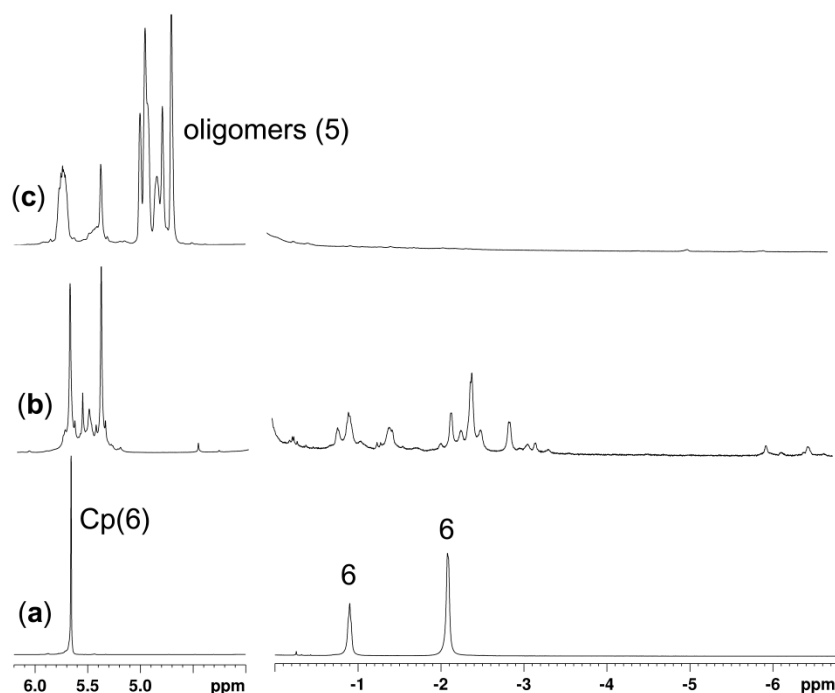
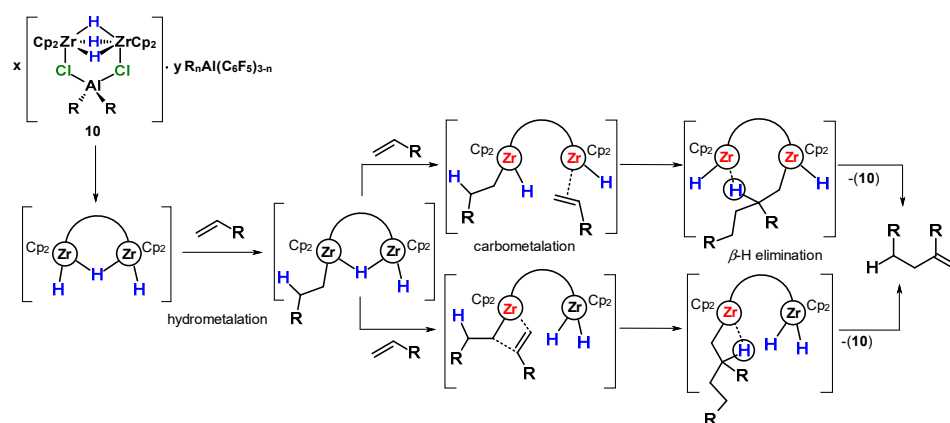


Figure 5. The formation of cationic complexes in the $\text{Cp}_2\text{ZrCl}_2\text{-HAlBu}^i_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ system and their reactivity towards 1-hexene (intensity of upfield signals is increased): (a) $\text{Cp}_2\text{ZrCl}_2\text{-HAlBu}^i_2$ system, $[\text{Zr}]:[\text{Al}] = 1:5$; (b) $\text{Cp}_2\text{ZrCl}_2\text{-HAlBu}^i_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ system, $[\text{Zr}]:[\text{Al}]:[\text{B}] = 1:5:0.5$; and (c) $\text{Cp}_2\text{ZrCl}_2\text{-HAlBu}^i_2\text{-(Ph}_3\text{C)[B(C}_6\text{F}_5)_4]$ system after the 1-hexene addition.

Thus, the $\text{Cp}_2\text{ZrCl}_2\text{-XAlBu}^i_2$ ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$ systems activated by $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ are able to accomplish selective dimerization and oligomerization of alkenes to give head-to-tail vinylidene products, similarly to systems based on Zr

complexes and MAO [3,6–8,13,57–59]. Among the post-metallocene Zr and Hf complexes with [ONNO]-type amino-bis(phenolate) ligands activated by neutral $B(C_6F_5)_3$, the best selectivity to 1-hexene dimers (up to 97%) was found to hafnium catalysts [60]. Nevertheless, data on the direct participation of metal hydrides in chemo- and regioselective dimerization of alkenes are limited and are mainly concerned with Sc [61], Y [62], Ta [63], and Ru [64] complexes.

The bis-zirconium hydride complexes we discovered, in combination with either an MAO activator [46,47] or organoboron compounds $((Ph_3C)[B(C_6F_5)_4]$ or $B(C_6F_5)_3$), provide the selective formation of dimers in reactions with alkenes. It is evident that the first step is hydrometalation of the alkene (Scheme 7). The addition of a second alkene molecule and subsequent β -H elimination to give dimers could occur with the involvement of one or two metal sites. Similar two-site catalysis is known for alkene polymerization in the presence of group 4 metal complexes [65]. Nevertheless, certain issues remain unanswered: how the bis-zirconium structures are activated; what is the principle of formation of the heavy fraction that is active towards alkenes; and how dimerization of alkenes with the participation of these adducts takes place. Further development of our study would be concerned with the determination of the structure of active sites and the mechanism of alkene dimerization under the action of bimetallic complexes.



Scheme 7. Proposed mechanism: one or two Zr reaction centers?

3. Materials and Methods

1D (1H , ^{13}C , and ^{19}F) and 2D (COSY HH, HSQC, HMBC, NOESY) NMR spectra were recorded on spectrometer Bruker AVANCE-400 (400.13 MHz (1H), 100.62 MHz (^{13}C), 376.44 (^{19}F)) (Bruker, Rheinstetten, Germany) using standard Bruker pulse sequences. Toluene- d_8 and benzene- d_6 were used as the solvents and the internal standards. ^{19}F spectra were referenced externally to $CFCl_3$. 1D and 2D DOSY spectra were obtained using the ledbpgp2s pulse sequence (LED with bipolar gradient pulse pair, 2 spoil gradients) with acquisition parameters $\delta = 1$ ms, $\Delta = 0.1$ – 0.2 s. The spectra were recorded at 296–298 K and temperature stabilization accuracy within 0.1 K. For the calibration of gradient strength the self-diffusion coefficient of HDO in D_2O was measured at 298 K ($1.902 \cdot 10^{-9}$ m²/s) [66,67]. The diffusion coefficients were defined using NMR relaxation Guide implemented into the Bruker TopSpin program v.3.2 following the known procedure (see, for example, Refs. [68,69]).

The product composition was determined using a gas chromatograph mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Tokyo, Japan) equipped with the GC-2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan). Details on the GC-MS analysis of dimers and oligomers are given in the Supplementary Materials.

3.1. General Procedures

All operations for organometallic compounds were carried out under argon according to the Schlenk technique. Complex **1** was synthesized from ZrCl_4 (99.5%, Merck, Darmstadt, Germany) according to a known procedure [70]. The zirconocene dihydride $[\text{Cp}_2\text{ZrH}_2]_2$ (**2**) was obtained from (**1**) as described previously [41,42,50]. Commercially available ClAlEt_2 (97%, Strem, Newburyport, MA, USA), HAlBu^i_2 (99%, Merck), AlBu^i_3 (95%, Strem), $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ (97%, Abcr, Karlsruhe, Germany), $\text{B}(\text{C}_6\text{F}_5)_3$ (95%, Merck), and terminal alkene 1-hexene (97%, Fisher Scientific, Pittsburgh, Pennsylvania, U.S.) were used. The solvents (toluene, benzene) were dried over AlBu^i_3 and distilled immediately prior to use.

CAUTION: The pyrophoric nature of aluminum hydrides and aluminum alkyls require special safety precautions in their handling.

3.2. Reaction of Cp_2ZrCl_2 with HAlBu^i_2 (AlBu^i_3), $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{B}(\text{C}_6\text{F}_5)_3$), and 1-hexene

A flask equipped with a magnetic stirrer and filled with argon was loaded with 0.022–0.088 mmol (6.3–25.7 mg) of Cp_2ZrCl_2 , 0.062–0.352 mmol (0.011–0.063 mL) of HAlBu^i_2 or 0.14 mmol (0.035 mL) of AlBu^i_3 , 0.022 mmol of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ (20 mg) or $\text{B}(\text{C}_6\text{F}_5)_3$ (11 mg), and 0.22–2.2 mmol (0.03–2.7 mL) of 1-hexene. The reaction was carried out with stirring at temperatures 40 or 60 °C. The samples (0.1 mL) were syringed into tubes under argon after 15, 30, 60, 90, 120, and 150 min of the reaction; then the samples were immediately decomposed with 10% HCl at 0 °C. Products were extracted with benzene, and the organic layer was dried over Na_2SO_4 . The yields of dimers and oligomers were determined by GC/MS.

3.3. Reaction of $[\text{Cp}_2\text{ZrH}_2]_2$ with ClAlEt_2 , $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{B}(\text{C}_6\text{F}_5)_3$), and 1-Hexene

A flask equipped with a magnetic stirrer and filled with argon was loaded with 0.088 mmol (20 mg) of $[\text{Cp}_2\text{ZrH}_2]_2$ (all ratios are given relative to monomer), 0.176 mmol (0.022 mL) of ClAlEt_2 , 0.022 mmol of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ (20 mg) or $\text{B}(\text{C}_6\text{F}_5)_3$ (11 mg), and 8.8 mmol (1.1 mL) of 1-hexene. The reaction was carried out with stirring at temperatures 40 or 60 °C. The samples (0.1 mL) were syringed into tubes under argon after 15, 20, 30, 60, 90, 120, and 150 min of the reaction; then the samples were immediately decomposed with 10% HCl at 0 °C. Products were extracted with benzene, and the organic layer was dried over Na_2SO_4 . The yields of dimers and oligomers were determined by GC/MS.

3.4. NMR Study of the Reaction of Cp_2ZrCl_2 with HAlBu^i_2 , $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$, and 1-Hexene

Method A. The NMR tube was filled with 0.05–0.1 mmol (14.6–29.2 mg) of Cp_2ZrCl_2 and 0.5 mL of benzene- d_6 under argon. Then 0.15–0.3 mmol (0.027–0.054 mL) of HAlBu^i_2 was added at room temperature. The mixture was stirred and the formation of complexes **6–8** was monitored by NMR. Further 0.025 mmol (22.8 mg) of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ was added, and the mixture was analyzed by NMR. **Method B.** The NMR tube was filled with 0.025 mmol (22.8 mg) of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$, 0.15–0.3 mmol (0.027–0.054 mL) of HAlBu^i_2 , and 0.5 mL of benzene- d_6 under argon at room temperature. The mixture was stirred and 0.05–0.1 mmol (14.6–29.2 mg) of Cp_2ZrCl_2 was added. The formation of complexes was monitored by NMR.

3.5. NMR study of the Reaction of $[\text{Cp}_2\text{ZrH}_2]_2$ with ClAlEt_2 and $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{B}(\text{C}_6\text{F}_5)_3$)

Method A. The NMR tube was filled with 0.05 mmol (11.2 mg) of $[\text{Cp}_2\text{ZrH}_2]_2$ (**2**) and 0.5 mL of benzene- d_6 under argon. Then 0.15 mmol (18.6 mg) of ClAlEt_2 was added dropwise at 0 °C. The mixture was stirred and the formation of complexes **6–8** was monitored by NMR at room temperature. After addition of 0.025 mmol (22.8 mg) of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ (12.8 mg) a division of the reaction media into two fractions was observed. **Method B.** The NMR tube was filled with 0.025 mmol (22.8 mg) of $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ (12.8 mg), 0.15 mmol (18.6 mg) of ClAlEt_2 , and 0.5 mL of benzene- d_6 under argon.

Further 0.05 mmol (11.2 mg) of $[\text{Cp}_2\text{ZrH}_2]_2$ were added at 0 °C. The mixture was stirred and studied by NMR at room temperature.

4. Conclusions

In summary, we found the conditions for the synthesis of alkene dimers or oligomers in the $\text{Cp}_2\text{ZrCl}_2\text{-XAlBu}^i_2$ ($\text{X} = \text{H}, \text{Bu}^i$) and $[\text{Cp}_2\text{ZrH}_2]_2\text{-ClAlEt}_2$ catalytic systems activated by $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$. NMR studies showed that adducts with the bis-zirconium core of type $x[\text{Cp}_2\text{ZrH}_2\cdot\text{Cp}_2\text{ZrHCl}\cdot\text{ClAlR}_2]\cdot y\text{R}_n\text{Al}(\text{C}_6\text{F}_5)_{3-n}$ are key intermediates of the alkene dimerization. The oligomerization pathway in these systems is realized due to the existence of cationic Zr,Al-hydride species formed in the reaction of the complex $\text{Cp}_2\text{Zr}(\mu\text{-H})_3(\text{AlBu}^i_2)_2(\mu\text{-Cl})$ with boron activators. Therefore, it is relevant to continue studies of the reaction mechanism in order to identify the activation principle of bis-zirconium complexes by organoboron compounds and understand the necessity of participation of bimetallic sites for selective dimerization of alkenes.

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