Organometallic Chemistry

Synthesis and conversions of metallocycles
22.* NMR studies of the mechanism of Cp_2ZrCl_2-catalyzed cycloalumination of olefins with triethylaluminum to form aluminacyclopentanes

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The mechanism of cycloalumination of olefins under the action of $AlEt_3$ in the presence of Cp_2ZrCl_2 giving rise to aluminacyclopentanes was investigated by dynamic ^1H and ^{13}C NMR spectroscopy. The bimetallic complex $Cp_2ZrEtCl—AlEt_3$ is formed initially and is converted into the bridged complex $Cp_2Zr(Cl)CH_2CH_2AlEt_2$ as a result of β-hydride shift and elimination of the ethane molecule. The resulting complex adds a molecule of the initial olefin yielding aluminacyclopentanes. Under the action of Et_2AlCl in the presence of an excess of $AlEt_3$, zirconacyclopentanes give rise to intermediate bimetallic complexes stable at −70 °C. Under the reaction conditions, the latter compounds are converted into aluminacyclopentanes.

Key words: reaction mechanism, metal-complex catalysis, cyclometallation, aluminacyclopentanes, dynamic NMR spectroscopy.

Although hydro- and carboalumination of unsaturated compounds under the action of alkylhaloalanes are well-known reactions, which are widely used in synthesis, catalytic cyclometallation of alkenes[2] and alkynes[3] with the use of organoaluminum compounds (OAC) in the presence of Cp_2MCl_2 (M = Ti or Zr) has been discovered only recently. This reaction was used for the preparation of new classes of organoaluminum compounds, for example, aluminacyclopentanes,[2] aluminacyclopentenes,[3] aluminacyclopropanes,[4] and aluminacyclopropenes.[5] The formation of aluminacyclopentenes in the reactions of alkynes with alkylalanes under the action of Cp_2ZrCl_2 (**1**) was later confirmed.[6]

Data on identification of intermediates formed under the conditions of the above-mentioned cycloalumination of alkenes and alkynes with alkylalanes under the action of Ti and Zr complexes are virtually lacking in the literature. However, investigation of the structures of intermediates formed in the above-mentioned reaction would allow one to establish the mechanism of catalytic cycloalumination of unsaturated compounds and to determine the sequence of steps of the formation of cyclic organoaluminum compounds.

Previously,[2] the mechanism of synthesis of aluminacyclopentanes was postulated according to which direct

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* For Part 21, see Ref. 1.

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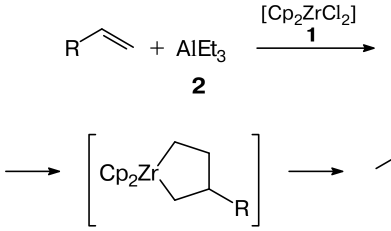
transmetallation of intermediate zirconacyclopentanes formed under the reaction conditions gives rise to aluminacyclopentanes[2] according to Scheme 1.

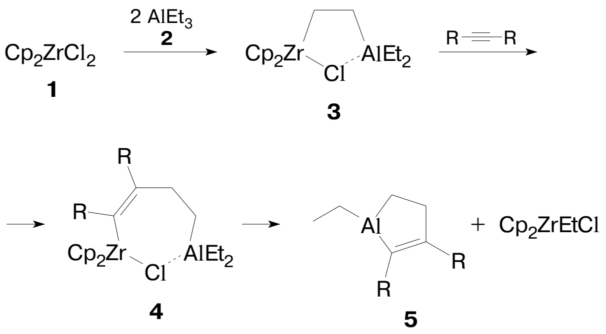
Scheme 1



Indeed, examples of the direct replacement of the zirconium atom in zirconacycles by a main-group metal atom with retention of the initial structure of the ring have been documented.[7,8]

An attempt[6] has been undertaken to explain the mechanism of cycloalumination of alkynes under the action of AlEt$_3$ (**2**) catalyzed by Cp$_2$ZrCl$_2$ (**1**) to form aluminacyclopentenes. The proposed scheme involved five-membered bimetallic complex **3** as the key intermediate, which added the alkyne molecule at the Zr—C bond giving rise to seven-membered bimetallic complex **4**. The latter decomposed to yield Cp$_2$ZrEtCl and the target aluminacyclopentene **5** (Scheme 2).

Scheme 2



The structure of five-membered bimetallic complex **3**, which was formed in the reaction of AlEt$_3$ (**2**) with Cp$_2$ZrCl$_2$ (**1**), has been discussed previously.[6,9,10] However, the structure of complex **4** has only been postulated and has not been supported by experimental data.

The present study was aimed at monitoring the course of catalytic cycloalumination of olefins with AlEt$_3$ (**2**) in the presence of Cp$_2$ZrCl$_2$ (**1**) by NMR spectroscopy, performing the experimental simulation of individual steps of the process, establishing the structures of the intermediates responsible for the formation of aluminacycles, and revealing the reaction mechanism based on the experimental data. We used hex-1-ene and styrene as olefins. In the former case, the reaction proceeded selectively to give 3-butylaluminacyclopentane,[2] whereas the reactions of styrene afforded aluminacyclopentane containing one (the major product) and two aryl substituents at different positions of the heterocycle along with aluminacyclopropane.[11] In the present study, we consider the mechanism of formation of the major reaction products, *viz.*, aluminacyclopentane containing one substituent in the aluminacycle.

In the forthcoming paper of this series, we will report the results of quantum-chemical calculations for the proposed experimental model of the reaction.

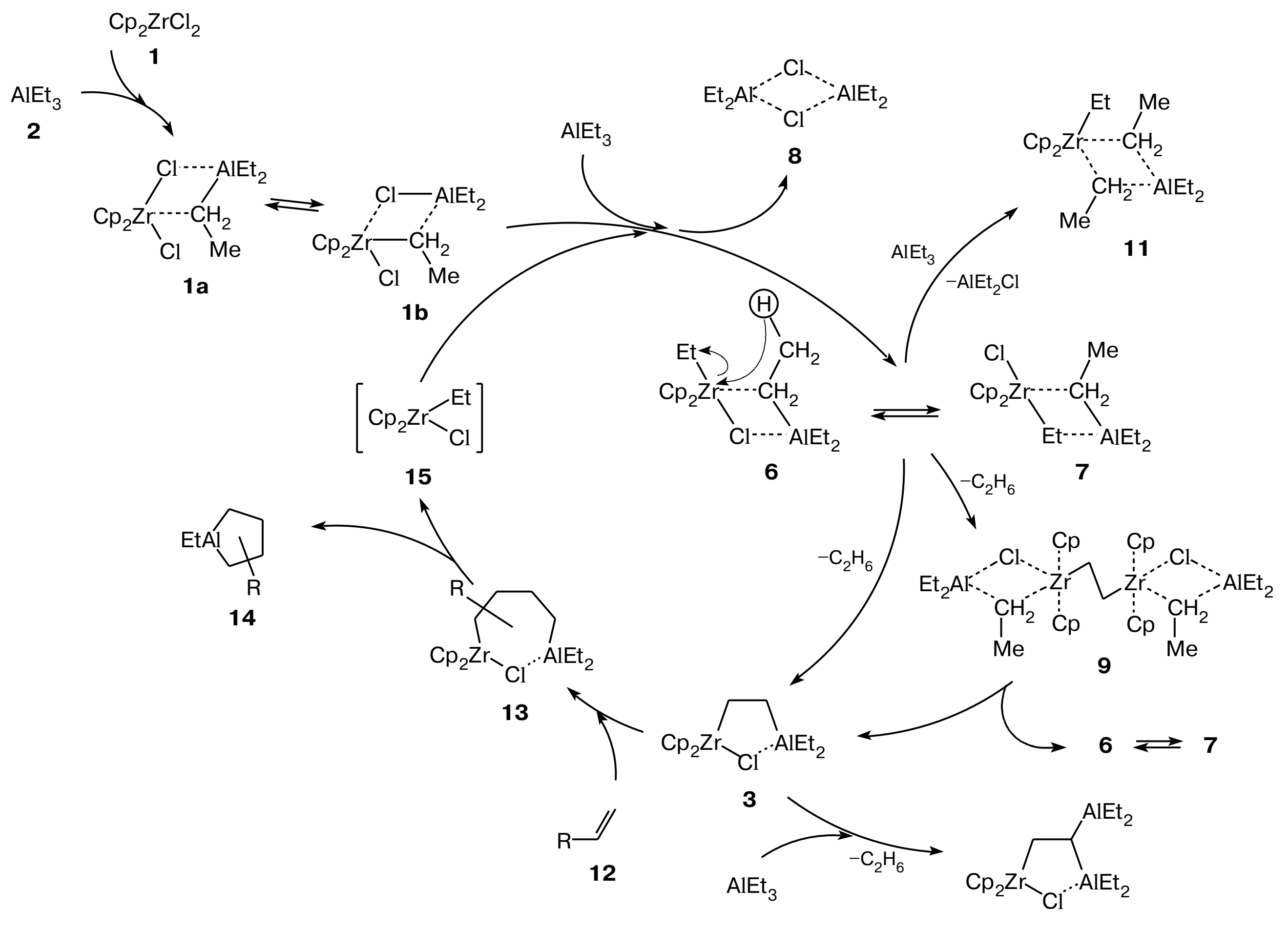
Results and Discussion

With the aim of establishing the structures of the key intermediates in cycloalumination of olefins, we studied the reaction of Cp$_2$ZrCl$_2$ (**1**) with AlEt$_3$ (**2**) using ^{1}H and ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of the initial triethylaluminum **2** recorded at −90 °C, the assignment of the signals of the bridging (C(1′) and C(2′)) and terminal (C(1) and C(2)) ethyl groups was made (Table 1). The ^{13}C NMR spectrum of Cp$_2$ZrCl$_2$ (**1**) has[12] the only signal for the carbon atoms of the Cp ring at δ 116.02.

According to the published data,[13] alkylalanes in solutions form four-center associates containing bridging alkyl groups. In this connection, it can be postulated that triethylaluminum molecules are coordinated to Cp$_2$ZrCl$_2$ through the bridging chlorine atoms and the carbon atoms of the methylene fragment of the ethyl group (transition states **1a** and **1b**) (Scheme 3). The ^{13}C NMR spectra of the Cp$_2$ZrCl$_2$—AlEt$_3$ system (1 : 1) at −70 °C have four broadened high-field signals for the C$_\alpha$ atoms of the bridging and terminal ethyl groups with the intensity ratios of 2 (δ 1.11) : 1 (δ 0.59) and 1 (δ −0.52) : 1 (δ −0.26), respectively. Pairs of these signals coalesce as the temperature increases to −45 °C resulting in two broadened signals at δ 1.04 and −0.32, which in turn coalesce into one signal (δ −0.19) at −20 °C. These phenomena of the intra- and intermolecular exchange (Scheme 4) as well as comparison of the intensities of the signals observed at high field and the resonance lines of the Cp rings located at low field are indicative of the formation of stable complexes **6** and **7** with composition Cp$_2$ZrEtCl—AlEt$_3$ (see Table 1) (a portion of the initial Cp$_2$ZrCl$_2$ remained unconsumed). It was found that the reaction of Cp$_2$ZrCl$_2$ with AlEt$_3$ also afforded a stoichiometric amount of Et$_2$AlCl (**8**) with respect to the initial AlEt$_3$.

In the ^{13}C NMR spectrum of the Cp$_2$ZrEtCl—AlEt$_3$ system, the resonance line of the C atom observed in the region of δ 51—56 is of considerable interest. The direct spin-spin coupling constant $J_{^{13}C-^{1}H}$ = 119.9 Hz[14] indicates that this signal belongs to the C atom of the methylene fragment of the terminal ethyl group bound to the Zr atom in complex **6**. This spectral line is shifted upfield, on the average, by 5 ppm as the temperature increases from −70 to 0 °C, which is indicative of the rapid (within the NMR time scale) exchange between

Scheme 3



12, 13, 14: R = Bu^n (**a**), Ph (**b**)

the terminal and bridging ethyl groups bound to the Zr atom under the reaction conditions. The addition of tetrahydrofuran to the reaction mixture caused destruction of dimeric structures **6** and **7** to form the solvated molecule $Cp_2ZrEtCl \cdot THF$ (**6a**).

Therefore, contrary to the data on the stability of the Cp_2ZrCl_2—$AlEt_3$ system (1 : 1) reported previously,[6] this system was unstable under the condition used in the present study and changed with time (Fig. 2). Initially, complexes **6** and **7** were formed, which were then converted into compounds **3** and **9**, respectively, through β-hydride shift and elimination of the ethane molecule, as has been mentioned previously.[9] In complex **9**, an additional β-hydride shift occurred from the methyl fragment of one of the bridging group to the dizirconium ethyl bridge giving rise to an equilibrium mixture of complexes **6** and **7** and five-membered bimetallic complex **3**. The latter reacted with an additional triethylaluminum molecule to give stable five-membered compound **10**. The assignment of the signals in the ^{13}C NMR spectra of the resulting complexes was made based on the ^1H NMR spectral data (see Ref. 10) and the 2D CHCORR spectra (Fig. 3). Thus the signal of the Cp rings (δ_H 5.77) of complex **9** corresponds to the signal at δ_C 110.55 in the ^{13}C NMR spectrum. In compound **10**, the hydrogen atoms of the Cp rings are sterically nonequivalent[9,10] due to the chiral center of the molecule, which is manifested in the anisochronism of the Cp-group signals (δ_H 5.57 and 5.64) although no analogous splitting was observed in the ^{13}C NMR spectra (δ_C 108.60). The resonance line of the protons of the Cp groups of complex **3** at δ_H 5.49 corresponds to the signal at δ_C 108.21. In addition, the spectra of the system under study have signals of ethane (at δ_H 0.78 and at δ_C 7.05) resulting from β-hydride shift in the course of formation of structures **3**, **9**, and **10**. The observed processes of β-hydride shift in alkyl groups are typical of Group IV transition metals.[15]

The formation of complexes **3** and **6—10** was also observed in the reactions with the use of triethylaluminum taken in ratios of 2 : 1, 5 : 1, 10 : 1, or 20 : 1 with respect to Cp_2ZrCl_2. Under these conditions, complex **11** was obtained along with compounds **3** and **6—10**. The structure of **11** was established by ^{13}C NMR spectroscopy. The assignment of the signal was made taking into account that the resonance lines of the carbon atoms of

Table 1. Characteristics of the ^{13}C NMR spectra and the values of selected direct spin-spin coupling constants $^1J_{^{13}\mathrm{C}-^1\mathrm{H}}$ for compounds **1—3**, **6—10**, **12a**, **14a**, **16—18**, and **20** (toluene-d$_8$ as the internal standard and the solvent)*

Compound	T/K	δ ($^1J_{^{13}\mathrm{C}-^1\mathrm{H}}$/Hz)												
		Cp	C(1)	C(2)	C(1′)	C(2′)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1	293	116.02 d (175.8)	—	—	—	—	—	—	—	—	—	—	—	—
2	183	—	−0.26 br.t	9.30 q	0.13 br.t	8.06 q	—	—	—	—	—	—	—	—
3	293	108.21 d	36.74 t	−0.74 br.t	—	—	3.71 br.t	9.56 q	—	—	—	—	—	—
6	203	113.28 d (174.4)	1.11 br.t	9.50 q	0.59 br.t	9.04 q	55.54 t (119.9)	18.79 q	—	—	—	—	—	—
6a	293	112.52 d	51.70 t	18.66 q	—	—	—	—	—	—	—	—	—	—
7	293	113.28 d (174.4)	−0.52 br.t	8.78 q	−0.26 br.t	9.37 q	—	—	—	—	—	—	—	—
8	293	—	2.86 br.t	9.76 q	—	—	—	—	—	—	—	—	—	—
9	293	110.55 d	13.52 t	0.91 br.t	—	—	8.84 q	—	—	—	—	—	—	—
10	293	108.60 d	43.01 t	−8.91 br.d	—	—	0.91 br.t	8.84 q	—	—	—	—	—	—
12a	293	—	113.86 t	137.28 d	—	—	33.55 t	31.08 t	22.24 t	13.65 q	—	—	—	—
14a	293	—	12.94 br.t	40.83 d	—	—	33.23 t	5.07 br.t	39.79 t	30.04 t	22.95 t	13.98 q	0.45 br.t	8.51 q
16	293	111.27 d	45.46 t	46.76 d	—	—	38.43 t	30.50 t	23.93 t	14.05 q	—	—	—	—
17	293	—	9.18 br.t	35.19 d	—	—	34.08 t	28.43 t	23.22 t	13.99 q	0.85 br.t	9.10 q	—	—
18	293	—	12.36 br.t	38.95 d	—	—	37.07 t	29.85 t	23.48 t	13.92 q	0.85 br.t	9.10 q	—	—
20	223	—	10.28 br.t	44.03 d	—	—	37.52 t	32.58 t	23.28 t	14.11 q	0.85 br.t	9.10 q	—	—

* The atomic numbering scheme is given in Fig. 1.

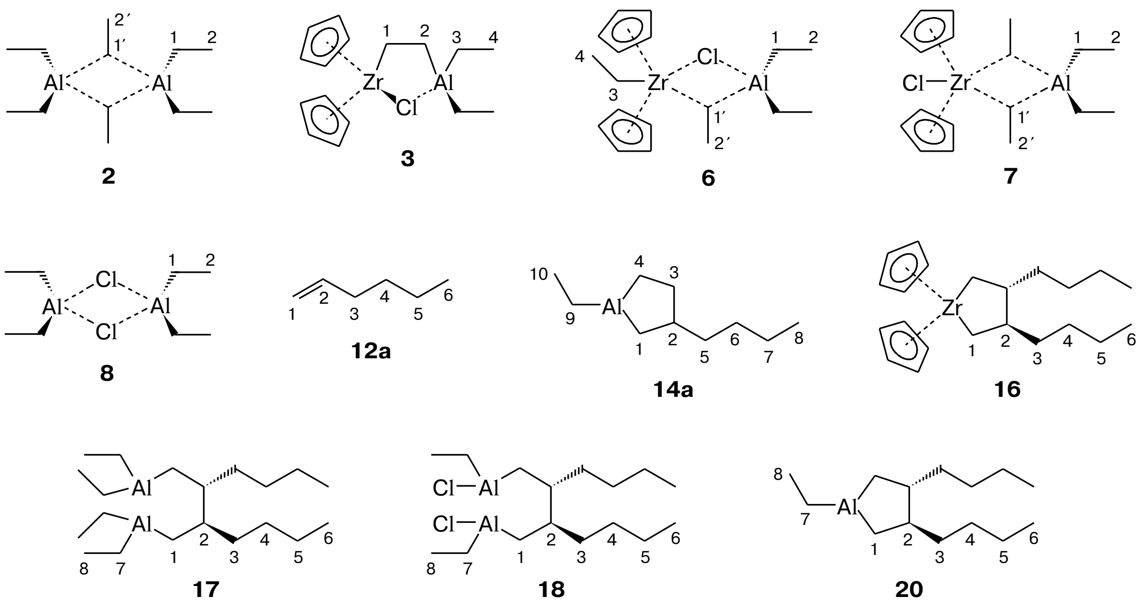
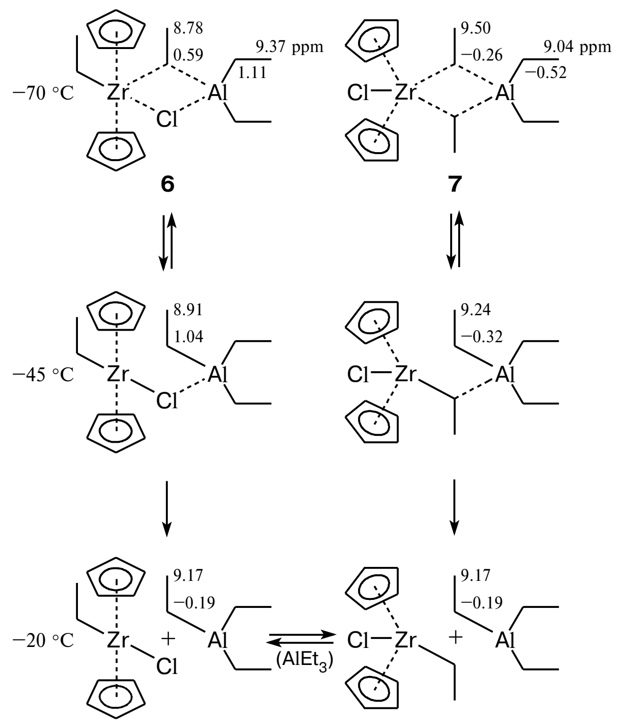


Fig. 1. Atomic numbering scheme for the C atoms in compounds **2**, **3**, **6—8**, **12a**, **14a**, **16—18**, and **20**.

Scheme 4



the Cp groups of rather unstable diethylzirconocene obtained from Cp_2ZrH_2 and ethylene are observed in the region of δ 102, whereas the addition of triethylaluminum leads to a slight downfield shift of this signal (δ_C 102.62), which is equal to the chemical shift of the Cp rings of bimetallic structure **10** formed in the Cp_2ZrCl_2—$AlEt_3$ system. Two-dimensional CHCORR spectroscopy (see Fig. 3) demonstrated that the resonance line of the protons of the Cp group of complex **11** in the ^1H NMR spectrum is observed at δ 5.28.

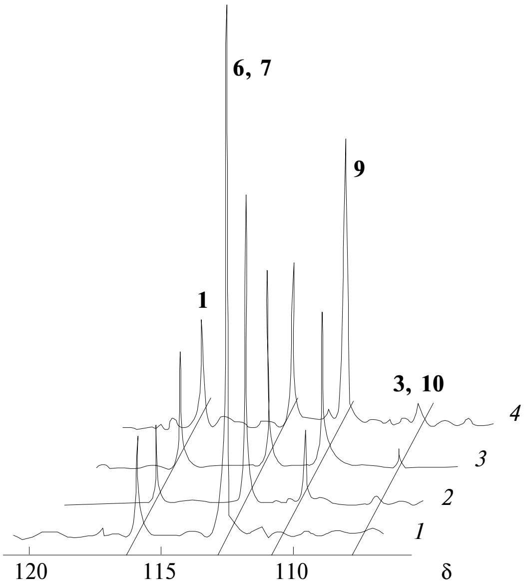


Fig. 2. Evolution of the Cp_2ZrCl_2—$AlEt_3$ system (1 : 1) with time: t = 15 (*1*), 95 (*2*), 225 (*3*), and 375 (*4*) min. The chemical shifts of the signals of the Cp rings in the ^{13}C NMR spectrum (22.50 MHz) are given.

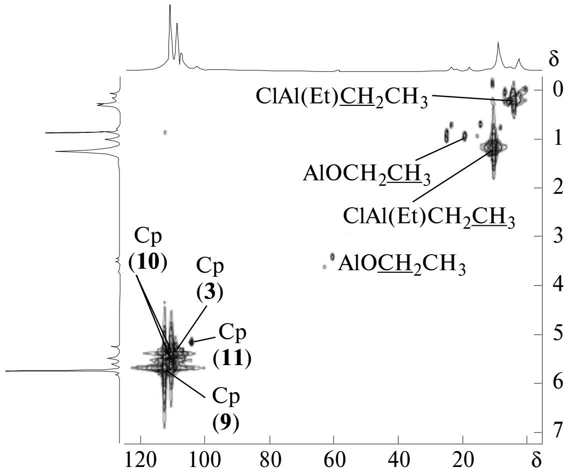


Fig. 3. 2D CHCORR spectrum of the 1 : 2 Cp_2ZrCl_2—$AlEt_3$ system (^{13}C, 75.46 MHz; ^1H, 300.13 MHz).

The addition of olefin **12** to the $AlEt_3$—Cp_2ZrCl_2 system afforded monosubstituted aluminacyclopentanes **14** both in the case of the Cp_2ZrCl_2-catalyzed process and in the case of mixing of all components in the stoichiometric ratio, but in the latter case the rate was lower and the yield was substantially smaller (in the case of the $AlEt_3$: Cp_2ZrCl_2 : styrene ratio of 1 : 1 : 1, the yield of the final aluminacyclopentane was ~0.5% after 24 h).

With the aim of elucidating the role of the Zr—Al complexes in the formation of aluminacycloalkanes, we prepared a solution of an equilibrium mixture of bimetallic complexes **3**, **9**, and **10** in toluene in the absence of Et_2AlCl. A decrease in the intensity of the resonance line of the Cp groups in the ^{13}C NMR spectra of five-membered bimetallic complex **3** simultaneously with the appearance of the signals for the C atoms of the corresponding aluminacyclopentanes **14** (Fig. 4) and complex **6**, which were observed upon the addition of hex-1-ene to the reaction mixture, indicate that compound **3** acts apparently as a catalytically active center responsible for the coordination of olefin, which eventually leads to the formation of cycloalumination products. Based on comparison of the spectral characteristics and the structures of the compounds prepared from dimethylzirconocene and alkylalanes,[16] it can be assumed that compound **3** is a σ-complex in which the zirconium and aluminum atoms are linked to each other not only through two carbon atoms but also through the bridging chlorine atom to form the bimetallic five-membered ring.

With the aim of revealing the role of zirconacyclopentane intermediates in cycloalumination of olefins, we studied the reactions of *trans*-3,4-dibutylbis(η^5-cyclopentadienyl)zirconacyclopentane (**16**) (see Ref. 17) with alkylhaloalanes using a model reaction as an example. It

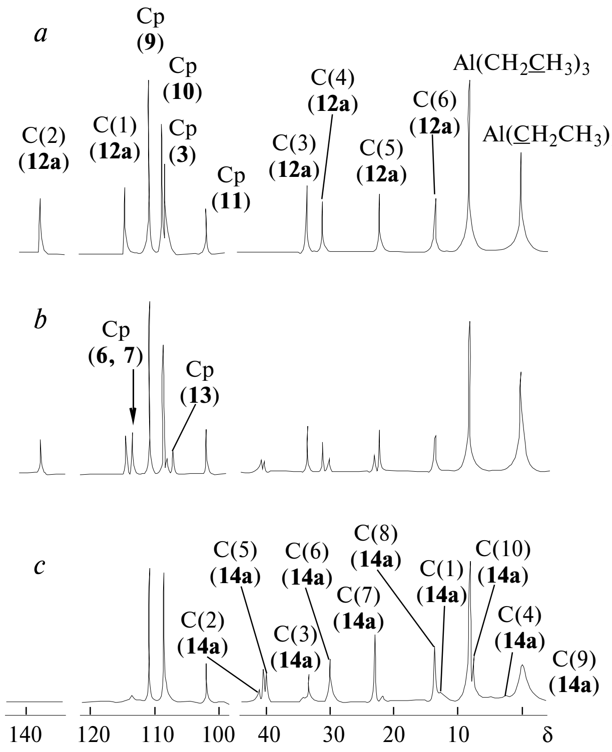


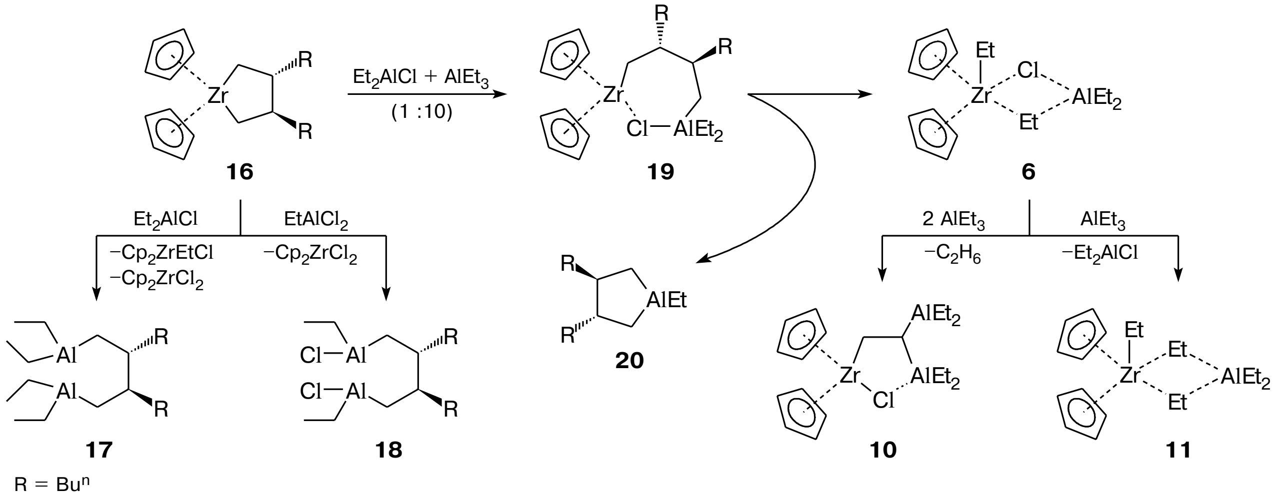
Fig. 4. Dynamic ^{13}C NMR spectrum (22.50 MHz; toluene-d$_8$ as the internal standard and the solvent) in studies of the participation of the Zr—Al-complexes in cyclometallation of olefins with triethylaluminum exemplified in hex-1-ene at the initial instant *t* = 0 min at −70 °C (*a*), at *t* = 20 min and −40 °C (*b*), and after completion of the reaction at 20 °C (*c*).

should be noted that zirconacyclopentane does not undergo transformations under the action of triethylaluminum. The addition of diethylaluminum chloride afforded compound **1** (δ_C(Cp) 116.35) along with Cp$_2$ZrEtCl (δ_C(Cp) 113.03) and 1,4-dialuminum compound **17**. Zirconacyclopentane was rather slowly converted into Cp$_2$ZrCl$_2$ and chlorine-containing 1,4-dialuminum compound **18** under the action of ethylaluminum dichloride. Hence, attempts to perform the stage of transmetallation of zirconacyclopentane with the use of individual trialkyl- or alklyhaloalanes were unsuccessful (Scheme 5). We demonstrated for the first time that the combined use of AlEt$_3$ and Et$_2$AlCl resulted in the desired transmetallation of zirconacyclopentane **16** to yield aluminacyclopentane **20**.

The model transmetallation reaction was carried out under the following reaction conditions: the tenfold excess of AlEt$_3$ (**2**) and the stoichiometric amount of Et$_2$AlCl were added to zirconacyclopentane **16**. An intermediate (δ_C(Cp) 107.56) (Fig. 5) was detected in the reaction performed at low temperature (−70 °C). Based on the published data,[18] this intermediate was identified as a seven-membered bimetallic complex (**19**). Complex **19** was very unstable and was transformed into 3,4-disubstituted aluminacyclopentane **20** and Cp$_2$ZrEtCl (**15**). The latter in turn was converted into complexes **10** and **11** (see Scheme 3). The ^{13}C NMR spectrum of aluminacyclopentane **20** has characteristic signals for the carbon atoms of the metallocycle at position 2 (according to Fig. 1) at δ 44.03.

The fact that the signal for the carbon atoms of the Cp rings of complex **19** corresponds to the signal at δ 107.43 observed in the course of the reaction of an equilibrium mixture of compounds **3**, **9**, and **10**, which has been prepared in the absence of Et$_2$AlCl, with hex-1-ene at −40 °C (see Fig. 4, *b*), suggests that seven-membered intermediate **13** is involved in cycloalumination of α-olefins. This assignment is supported by the fact that the resonance lines of the carbon nuclei of the Cp groups are shifted upfield by 5 ppm upon the ring expansion from the four-membered ring (in complex **6**) to the five-membered ring (in complex **3**). An analogous effect (up to 0.8 ppm) is observed when the number of

Scheme 5



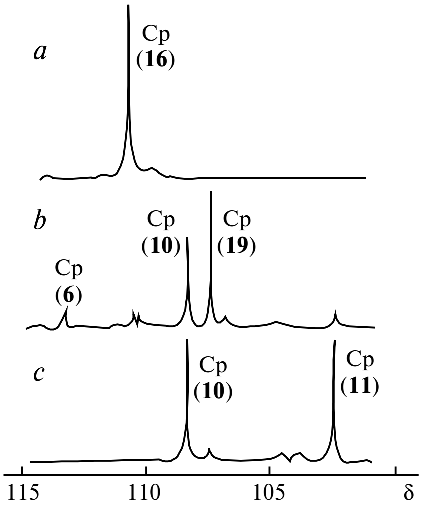


Fig. 5. Dynamic NMR spectrum in studies of the stage of transmetallation of zirconacyclopentane **16** with diethylaluminum chloride in the presence of an excess of $AlEt_3$ (the region of resonance lines of the Cp rings is given) (22.50 MHz; toluene-d_8 as the internal standard and the solvent): the initial sample at $T = 293$ K (*a*), the sample after cooling to 203 K (*b*), and the sample after subsequent heating to 293 K (*c*).

atoms is increased from five (in the initial metallocycle **3**) to seven (in the product of insertion of α-olefin at the Zr—C bond whose composition corresponds to complex **13**). The intensities of the signals for the C atoms of the cyclopentadienyl groups corresponding to this complex are small because of the instability of the complex under the reaction conditions in the presence of an excess of triethylaluminum. The assignment of the resonance line at δ 107.43 to structure **13** is confirmed by the published data on the spectral characteristics of the seven-membered Zr—Al complex, *viz.*, Al,Zr-μ-chloro-1-(dicyclopentadienylzirconio(IV))-4-(dichloroaluminio)but-2-ene.[18]

Taking into account the experimental data, the following general scheme of the reaction mechanism of cyclometallation of olefins can be assumed (see Scheme 3). In the first stage, molecules of triethylaluminum **2** and catalyst **1** form complexes **1a** and **1b** owing to the rapid interligand exchange. These complexes give intermediates **6** and **7**, respectively, under the action of another molecule of $AlEt_3$. Intramolecular β-hydride shift with the simultaneous elimination of ethane affords key intermediate **3**. The expansion of the five-membered ring of **3** through the insertion of the α-olefin molecule at the Zr—C bond is favorable for the formation of unstable complex **13**, which is transformed under conditions of cycloalumination to give aluminacyclopentane **14** and ethylzirconocene chloride **15**. Coordination of the latter to yet another molecule of $AlEt_3$ gives rise to active complex **6**, thus closing the catalytic cycle.

The structures of the resulting aluminacyclopentanes **14** and **20** were established by ^{1}H and ^{13}C NMR spectroscopy and by analysis of their deuterolysis products.

Experimental

All operations with the use of organometallic compounds were carried out under an atmosphere of argon. The solvents were distilled from triisobutylaluminum immediately before use. A 91.8% solution of triethylaluminum in hexane was used; Cp_2ZrCl_2 was synthesized from $ZrCl_4$ according to a procedure reported previously.[19] Glass vessels and NMR tubes were dried at 200 °C and stored in a desiccator under argon.

Spectral studies were carried out on Jeol FX-90Q and Bruker AM-300 spectrometers using fully or partially proton-decoupled dynamic ^{1}H and ^{13}C NMR spectroscopy in the temperature range from −90 to 25 °C. Toluene-d_8 was used as the internal standard and the solvent. The mass spectra were measured on a Finnigan 4021 GLC-mass spectrometer and analyzed using a data base.[20]

Reaction of $AlEt_3$ (2) with Cp_2ZrCl_2 (1). ***A.*** Toluene-d_8 (0.5 mL) and Cp_2ZrCl_2 (0.146 g, 0.5 mmol) were placed in an NMR tube ($d = 5$ mm) filled with argon. The tube was cooled to −63 °C. Then $AlEt_3$ (0.07 mL, 0.5 mmol) was added and the tube was transferred to a unit of the spectrometer for recording the spectrum in a specified temperature mode (from −70 to 25 °C).

B. Toluene-d_8 (2 mL), Cp_2ZrCl_2 (0.584 g, 2 mmol), and $AlEt_3$ (a 91.8% solution in hexane; 0.3 mL, 2 mmol) were placed in a three-neck flask equipped with a magnetic stirrer and filled with argon at 20 °C and the reaction mixture was stirred. Aliquots (0.4 mL) of the mixture were withdrawn with the use of a syringe, placed in NMR tubes after 15, 95, 225, and 375 min, and the spectra were recorded at −60 °C (see Fig. 1).

Reactions of $AlEt_3$ (2) with olefins in the presence of catalytic amounts of Cp_2ZrCl_2 (1). Toluene-d_8 (2 mL), Cp_2ZrCl_2 (58.4 mg, 0.2 mmol), α-olefin (10 mmol), and $AlEt_3$ (a 91.8% solution in hexane; 1.79 mL, 12 mmol) were placed in a three-neck flask equipped with a magnetic stirrer and filled with argon at 20 °C. The mixture was stirred for 8 h and then treated with a 20% D_2SO_4 solution in D_2O at 0 °C. The products were extracted with hexane and the organic layer was dried with $MgSO_4$. The yields of aluminacyclopentanes were determined based on GLC of the deuterolysis products.

Cyclometallation of hex-1-ene afforded 3-butyl-1-ethylaluminacyclopentane (**14a**) in 65.8% yield. The NMR spectral data for aluminacyclopentane **14a** and its deuterolysis product correspond to the published data.[2]

Cyclometallation of styrene gave rise to 1-ethyl-3-phenylaluminacyclopentane (62.6%), 1-ethyl-2-phenylaluminacyclopentane (15.9%), 1-ethyl-2,4-diphenylaluminacyclopentane (3.6%), and 1-ethyl-2,5-diphenylaluminacyclopentane (1.2%). The assignment of the signals in the ^{1}H and ^{13}C NMR spectra of the reaction products have been reported previously.[11]

Preparation of an equilibrium mixture of bimetallic Zr—Al complexes 3, 9, and 10. Toluene (0.1 mL), Cp_2ZrCl_2 (0.292 g, 1 mmol), and $AlEt_3$ (a 91.8% solution in hexane; 1 mmol, 0.14 mL) were placed in an NMR tube filled with argon. The mixture was stirred at 20 °C. Then the tube was immersed in liquid nitrogen for a few seconds. Ethane was evolved and 1,2-bis((μ,μ-dichloro)diethylaluminio(dicyclopentadienyl)zirconio(IV))ethane precipitated as the mixture was heated to ~20 °C.[9] The solution was decanted from the precipitate and the precipitate was washed twice with toluene. Toluene-d_8 (0.1 mL) and $AlEt_3$ (a 91.8% solution in hexane; 0.14 mL, 1 mmol) were added to the solid residue. As a result, a transparent orange solution of 1,2-bis(chloro(dicyclopentadienyl)zirconio(IV))ethane (**9**), Al,Zr-μ-chloro-1-(dicyclopentadienylzirconio(IV))-2-(diethylaluminio)ethane (**3**), and Al,Zr-μ-chloro-1-(dicyclopentadienylzirconio(IV))-2,2-bis(diethylaluminio)ethane (**10**) was obtained. The ^{1}H NMR spectra of complexes **3**, **9**, and **10** agree with the published data.[9]

Reaction of Al,Zr-μ-chloro-1-(dicyclopentadienylzirconio(IV))-2-(diethylaluminio)ethane (3) with styrene. Styrene (0.11 mL, 1 mmol) was added at 20 °C to a solution of complexes **3**, **9**, and **10** in toluene prepared in an NMR tube as described above. Evolution of ethane (δ_C 7.08) and ethylene (δ_C 122.25) and the formation of the complex with composition $Cp_2ZrEtCl—AlEt_3$ (**6** and **7**) (δ_C(Cp) 113.28) and a mixture of mono- and diphenyl-substituted aluminacyclopentanes were observed. The mixture was stirred for 1 h and then treated with a 20% D_2SO_4 solution in D_2O at 0 °C. The products were extracted with hexane and the organic layer was dried with $MgSO_4$ to obtain a mixture of 1-ethyl-2-phenylaluminacyclopentane (71.5%), 1-ethyl-3-phenylaluminacyclopentane (19.9%), 1-ethyl-2,4-diphenylaluminacyclopentane (0.9%), and 1-ethyl-2,5-diphenylaluminacyclopentane (0.8%), which were identified based on studies of the deuterolysis products by GLC-mass spectrometry and ^1H and ^{13}C NMR spectroscopy. The assignment of the signals in the ^1H and ^{13}C NMR spectra of the reaction products has been reported previously.[11]

Reaction of Al,Zr-μ-chloro-1-(dicyclopentadienylzirconium(IV))-2-(diethylalumina)ethane (3) with hex-1-ene. Hex-1-ene (0.06 mL, 0.5 mmol) was added to a solution of complexes **3**, **9**, and **10** in toluene prepared in an NMR tube. Ethane was evolved (δ_C 7.08). The mixture was stirred for 1 h and then treated with a 20% D_2SO_4 solution in D_2O at 0 °C. The deuterolysis product, *viz*., 2-methylheptane (the yield was 95%), was extracted with hexane. The NMR spectral data for organoaluminum compounds and the deuterolysis products have been published previously.[2]

3,4-Dibutylbis(η^5-cyclopentadienyl)zirconacyclopentane (16).[17] Toluene-d_8 (1 mL) and Cp_2ZrCl_2 (0.247 g, 0.85 mmol) were placed in a three-neck flask equipped with a magnetic stirrer and filled with argon. A 2 *M* solution of *n*-butyllithium (1.7 mmol, 0.85 mL) was added to the suspension at −63 °C. The mixture was warmed to 0 °C with continuous stirring for 1 h. The flask was cooled to −30 °C and then hex-1-ene (0.22 mL, 1.7 mmol) was added. The temperature of the mixture was increased to ~20 °C and the mixture was stirred for 2 h. A portion of the mixture was filtered through a glass filter under a pressure of argon and placed in an NMR tube. The residue of zirconacyclopentane in the flask was treated with 10% HCl. *threo*-5,6-Dimethyldecane[21] was obtained in 75% yield.

Reaction of 3,4-dibutyl-bis(η^5-cyclopentadienyl)zirconacyclopentane (16) with Et_2AlCl. Diethylaluminum chloride (0.85 mmol) was added to a solution of zirconacyclopentane **16** (0.85 mmol) in toluene-d_8 at −63 °C and *threo*-2,3-dibutyl-1,4-bis(diethylaluminio)butane (**17**) was obtained (see Table 1). Then the mixture was treated with a 20% D_2SO_4 solution in D_2O at 0 °C. Deuterolysis afforded *threo*-5,6-bis(deuteriomethyl)decane.[21]

Reaction of 3,4-dibutyl-bis(η^5-cyclopentadienyl)zirconacyclopentane (16) with $EtAlCl_2$. Ethylaluminum dichloride (0.85 mmol) was added to a solution of zirconacyclopentane **16** (0.85 mmol) in toluene-d_8 at −63 °C and *threo*-2,3-dibutyl-1,4-bis((chloro)ethylaluminio)butane (**18**) was obtained (see Table 1). Then the mixture was treated with a 20% D_2SO_4 solution in D_2O at 0 °C. Deuterolysis afforded *threo*-5,6-bis(deuteriomethyl)decane.[21]

Reaction of 3,4-dibutyl-bis(η^5-cyclopentadienyl)zirconacyclopentane (16) with Et_2AlCl in the presence of an excess of $AlEt_3$. Triethylaluminum (8.5 mmol) and Et_2AlCl (0.85 mmol) were successively added to a solution of zirconacyclopentane **16** (0.85 mmol) in toluene-d_8 at −63 °C. The spectral data of the resulting 3,4-dibutyl-1-ethylaluminacyclopentane (**20**) are given in Table 1. The mixture was treated with a 20% D_2SO_4 solution in D_2O at 0 °C. Deuterolysis afforded *threo*-5,6-bis(deuteriomethyl)decane.[21]

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