316 *Russian Chemical Bulletin, International Edition, Vol. 54, No. 2, pp. 316—327, February, 2005*

Mechanism of Cp_2ZrCl_2-catalyzed olefin hydroalumination by alkylalanes

L. V. Parfenova,* S. V. Pechatkina, L. M. Khalilov, and U. M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

The composition of intermediates of the Cp_2ZrCl_2-catalyzed hydroalumination of α-olefins by isobutylalanes ($HAlBu^i_2$, $AlBu^i_3$, $ClAlBu^i_2$) was studied by dynamic ^1H and ^{13}C NMR spectroscopy. The reaction of Cp_2ZrCl_2 with isobutylalanes affords the complex $(Cp_2ZrHCl \cdot HAlBu^i_2)_2$ responsible for α-olefin hydroalumination.

Key words: reaction mechanism, hydroalumination, dynamic NMR spectroscopy, olefins, organozirconium compounds, organoaluminum compounds.

The direct hydroalumination of olefins by activated aluminum and hydrogen producing mixed trialkylalanes has first been performed by Ziegler.[1] Further, methods for direct thermal hydroalumination of alkenes by simplest organoaluminum compounds (OAC) were developed to synthesize higher representatives of this class.[2—4]

The first attempts to extend the scope of this reaction by metal complex catalysts are related, in particular, to the use of titanium and zirconium compounds in olefin hydroalumination followed by the oxidation of higher OAC produced to primary alcohols.[5] Among considerable achievements in this area is the development of olefin hydroalumination with $LiAlH_4$ in the presence of $ZrCl_4$;[6,7] mono- and β,β′-disubstituted α-olefins do selectively react to form the corresponding lithium tetraalkylalanates.

The authors of the known work[8] postulate that hydroalumination proceeds through intermediate zirconium hydride complexes, which would hydrozirconate the starting olefins to form active alkylzirconium intermediates. Their subsequent transmetallation results in the regeneration of the starting hydrides (Scheme 1).

Scheme 1

$$LiAlH_4 \xrightarrow{ZrCl_4} L_nZrH \xrightarrow{CH_2=CH—R}$$

$$\longrightarrow L_nZrCH_2—CH_2—R \xrightarrow{LiAlH_4} L_nZrH + al—CH_2—CH_2R$$

al = LiAl/4; L_n are ligands at Zr atom

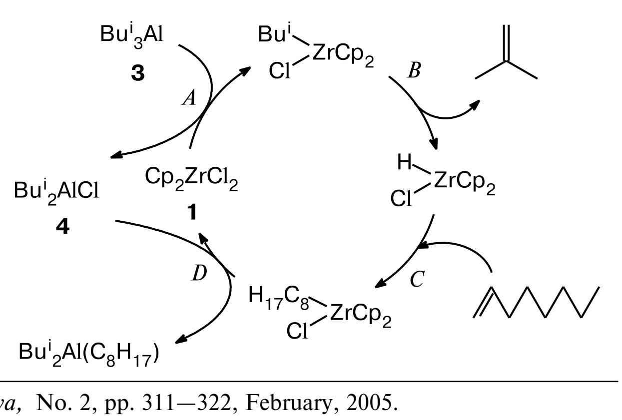
According to available data,[6] Cp_2ZrCl_2 (**1**), VCl_4, Cp_2TiCl_2, and $TiCl_4$ can be used along with $ZrCl_4$ as hydroalumination catalysts. However, the use of the zirconium catalysts is preferential in the most cases.

The hydroalumination of linear and cyclic olefins by $HAlBu^i_2$ (**2**) has previously[9,10] been found to occur more efficiently when $(RO)_nZrCl_{4-n}$ (n = 1—4) are used as catalysts.

It is found[11] that Cp_2ZrCl_2 (**1**) catalyzes the hydroalumination of linear α-olefins by $AlBu^i_3$ (**3**). It is also shown[12—14] that $ClAlBu^i_2$ (**4**) hydroaluminates mono- and disubstituted linear and cyclic olefins in the presence of Cp_2ZrCl_2. The yields of products of olefin hydroalumination are 85—99% and decrease to 50% when Cp_2ZrCl_2 is replaced by $ZrCl_4$. This reaction occurs under very mild conditions (0—20 °C) and can be applied to di- and triolefins, including cyclic and functionally substituted olefins,[15] in particular, containing electron-donor substituents,[16,17] whose hydroalumination with aluminum hydrides cannot be performed.

Based on these results, the authors[11] proposed the mechanism of catalytic olefin hydroalumination by trialkylalanes, including steps of alkylation (*A*), elimination of isobutylene (*B*), hydrozirconation (*C*), and transmetallation (*D*) (Scheme 2).

Scheme 2



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 311—322, February, 2005.

The authors of the above-considered works postulate that zirconium hydrides are formed in these reactions as intermediates and, as it has been shown,[18—20] can hydrozirconate olefins. This was not experimentally proved before the beginning of our studies.

In the present work, we studied olefin hydroalumination by alkylalanes, *viz.*, $HAlBu^i_2$ (**2**), $AlBu^i_3$ (**3**), and $ClAlBu^i_2$ (**4**), in the presence of Cp_2ZrCl_2 (**1**) as the catalyst and identified intermediate complexes and key intermediates of the process.

Results and Discussion

Based on the present studies and published[11] and our data obtained previously,[12,16,21,22] we determined the conditions (OAC, reagent ratio, solvent, and temperature) under which olefin hydroalumination occurs almost completely. When studying the hydroalumination of such alk-1-enes as hex-1-ene (**5a**), hept-1-ene (**5b**), oct-1-ene (**5c**), non-1-ene (**5d**), dec-1-ene (**5e**), we found that the yield of products increases with the elongation of the hydrocarbon chain (Table 1), although this increase is insignificant.

Benzene turned out to be an optimum solvent. For instance, when $AlBu^i_3$ was used as the hydroaluminating agent, the yields of the products exceed 90%, while in THF they are lower than 15%. Among the OAC used, $AlBu^i_3$ (**3**) provides the highest rate of hydroalumination of α-olefins (Fig. 1; molar ratio Cp_2ZrCl_2 : OAC : olefin = 1 : 60 : 50). The reaction of catalyst **1** with $ClAlBu^i_2$ (**4**) has a long induction period (up to 3 h). Among the studied OAC, the lowest hydroalumination activity belongs to $HAlBu^i_2$ (**2**), although the highest reaction rate should be expected in this case, taking into account the aforesaid. An increase in the catalyst concentration increases the reaction rate. For example, for the reaction with $ClAlBu^i_2$ (**4**), a fivefold increase in the catalyst concentration substantially shortens the induction period (Fig. 2). The temperature plot of the yield of the hydroalumination product for $AlBu^i_3$ (**3**) is shown in Fig. 3. For all OAC, yields of the hydroalumination products increase with temperature.

Table 1. Yields (%) of the hydroalumination products of olefins **5a—e** (5 h, 20 °C, C_6H_6, molar ratio Cp_2ZrCl_2 : OAC : olefin = 1 : 60 : 50)

OAC	Olefin				
	5a	**5b**	**5c**	**5d**	**5e**
2	17	18	17	19	18
3	91	93	94	95	96
4	75	76	78	81	82

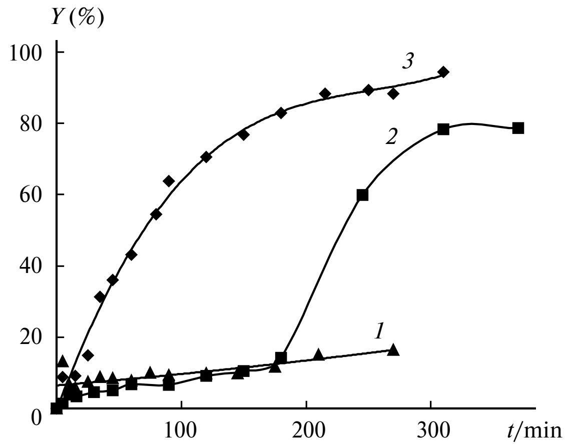


Fig. 1. Influence of the OAC type on the yield of product of oct-1-ene hydroalumination (*Y*): $HAlBu^i_2$ (*1*), $ClAlBu^i_2$ (*2*), and $AlBu^i_3$ (*3*) (molar ratio Cp_2ZrCl_2 : OAC : olefin = 1 : 60 : 50, C_6H_6, 20 °C).

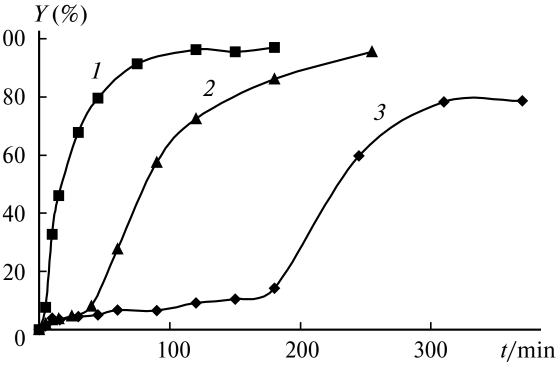


Fig. 2. Influence of the catalyst concentration on the yield of the product of oct-1-ene hydroalumination (*Y*) by diisobutylaluminum chloride (**4**) (C_6H_6, 20 °C): molar ratio Cp_2ZrCl_2 : **4** : olefin = 1 : 12 : 10 (*1*), 0.3 : 12 : 10 (*2*), and 0.2 : 12 : 10 (*3*).

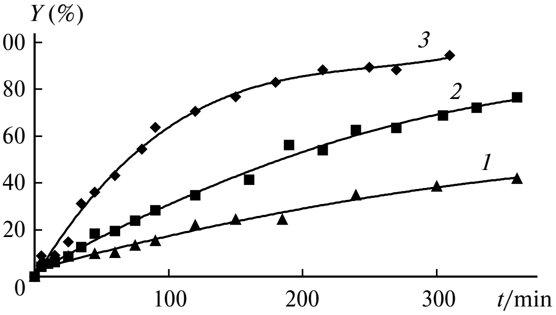
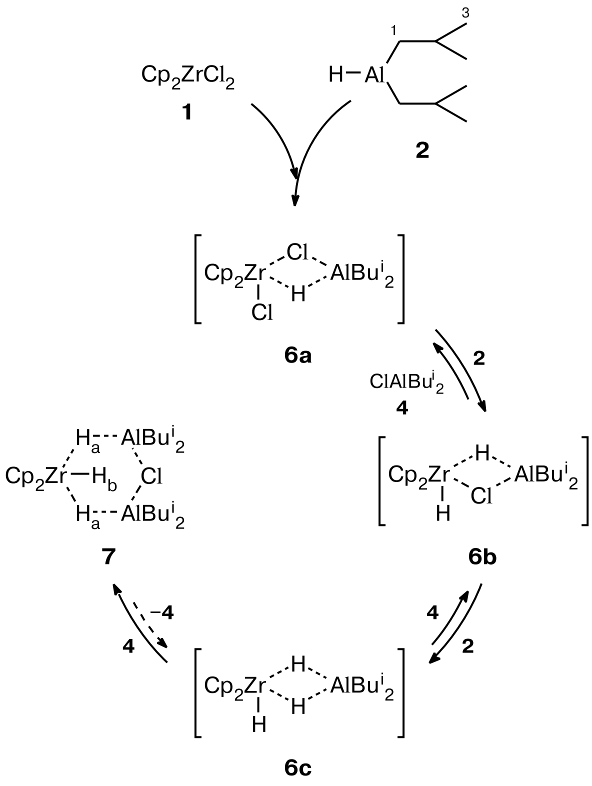


Fig. 3. Temperature effect on the yield of the product of oct-1-ene hydroalumination (*Y*) by triisobutylaluminum (**3**): *T* = 0 (*1*), 10 (*2*), and 20 °C (*3*) (molar ratio Cp_2ZrCl_2 : **3** : olefin = 1 : 60 : 50, C_6H_6).

We chose dynamic ^1H and ^{13}C NMR spectroscopy as the main technique for studying intermediate complexes of the reaction involving Cp_2ZrCl_2 (**1**). Complexes of the Cp_2ZrRR' type contain ten equivalent protons and ten carbon atoms of the Cp fragment, whose chemical shifts depend on the ligand environment of the central Zr atom and can be used as characteristic labels. For instance, the replacement of one Cl atom in the starting complex **1** (δ_H 6.02 and δ_C 116.02) by Et group to form the $Cp_2ZrEtCl \cdot AlEt_3$ complex[23] results in the the upfield shift of the signal of the Cp rings (δ_H 5.91 and δ_C 113.28). The replacement of the Cl atom by the H atom in a hydride complex, *e.g.*, $Cp_2ZrH_2 \cdot HAlBu^i_2 \cdot ClAlBu^i_2$,[8,18,24,25] results in a stronger upfield shift of the signals of the Cp rings (δ_H 5.71 and δ_C 104.30).

To establish the structure of intermediate complexes involved in hydroalumination, we studied the systems consisting of Cp_2ZrCl_2 (**1**) and three types of OAC ($HAlBu^i_2$, $AlBu^i_3$, and $ClAlBu^i_2$). Complex **1** was completely dissolved in benzene-d_6 at 20 °C and the ratio **1** : OAC = 1 : 3. The Cp_2ZrCl_2—$HAlBu^i_2$ system turned out to be the simplest for the description of the results of the reaction. The monitoring of the reaction at −90—−70 °C revealed the formation of an unstable complex with the low-intensity signal of the Cp rings in the ^{13}C NMR spectra (δ 108.50). When the temperature increases to −10 °C, the complex irreversibly transforms into stable structure **7** with the signal of the Cp rings at δ 105.16 (Scheme 3). An increase in the $HAlBu^i_2$ concentration to the molar ratio Cp_2ZrCl_2 : OAC = 1 : 15 results in the upfield shift of the signal of the Cp rings of complex **7** to δ 104.53.

Scheme 3



Complex **7** was described in literature[8,18,24,25] and identified by us on the basis of the ^1H NMR spectra. It was shown by the 2D HH—COSY spectra that the system of three hydride atoms is spin-bound. The geminal spin-spin coupling constant (SSCC), being 6.1 Hz, was found from the 1D ^1H NMR spectrum (Table 2).

The formation of complex **7** involves three $HAlBu^i_2$ molecules *via* the successive interligand exchange of the Cl atoms in the starting Cp_2ZrCl_2 by the H atoms in molecule **2**. This process proceeds, probably, through reversible intermediate steps in which the formation of bridged structures **6a—c** can be assumed (see Scheme 3). The signal observed at low temperature (δ_C 108.50) can belong to the carbon atoms of the Cp rings of one of these complexes.

Complex **7** is known to reduce carbonyl compounds to alcohols[18] and hydrogenate acetylenes.[25] However, the activity of this complex toward olefins was not studied. All our attempts to involve complex **7** in the reaction with alkenes were unsuccessful. These results suggest that one of the intermediate complexes, *viz.*, **6a**, **6b**, or **6c**, is responsible for alkene hydroalumination.

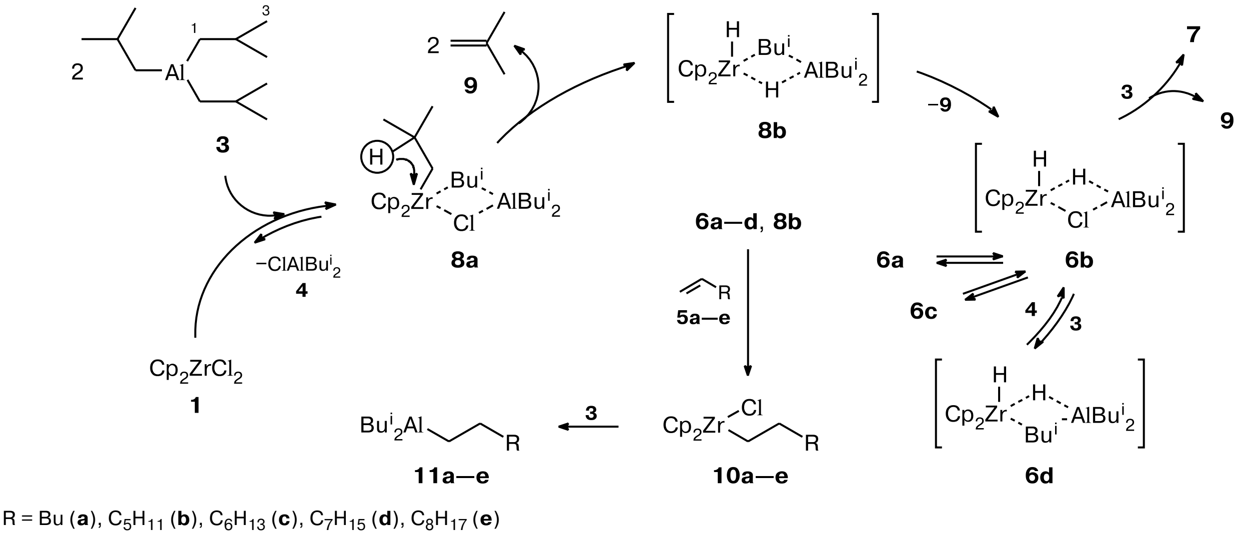
Monitoring the reaction of Cp_2ZrCl_2 with $AlBu^i_3$ (1 : 3) in benzene-d_6 at 20 °C, we found one more resonance line of the Cp rings in the ^{13}C NMR spectra at δ 113.24. Along with the latter, the spectrum contains lines characteristic of one of the hypothetical complexes **6a**, **6b**, or **6c** (δ_{Cp} 108.50) and complex **7** (δ_{Cp} 105.16). The signal at δ_{Cp} 113.24 is always accompanied by that at δ 81.70, which is a triplet with the SSCC $^1J_{C,H}$ = 117.2 Hz characteristic of organozirconium compounds.[26] Based on the chemical shift and SSCC values, we can assign this signal to the C atom of the isobutyl group bound to the Zr atom in alkyl complex **8a** (Scheme 4).

By analogy to the $Cp_2ZrClEt \cdot AlEt_3$ complex, whose structure was discussed in detail,[23,27,28] a binuclear structure can be assigned to complex **8a**. With an increase in the $AlBu^i_3$ concentration to the molar ratio **1** : **3** = 1 : 15, the content of alkyl complex **8a** decreases, and the concentration of complex **7** increases simultaneously. In parallel (according to the ^1H and ^{13}C NMR spectra), isobutylene (**9**) is formed, most likely, due to the β-hydride transfer in complex **8a**. Trihydride complex **7** appears due to the interligand exchange in complex **8a** through hypothetical complexes **8b** and **6b** (see Scheme 4). This process directly involves $AlBu^i_3$ and, therefore, an increase in the concentration of the latter increases the rate of transition **8a** → **7**. When olefin **5** is introduced into this system to the molar ratio **1** : **3** : **5** = 1 : 3 : 1, two signals at δ_{Cp} 113.24 and 108.50 disappear gradually. A new signal of the Cp rings appears instead them at δ_{Cp} 113.43, which is accompanied by a signal at δ_C 64.92—65.44 as a triplet with the SSCC $^1J_{C,H}$ = 119.2 Hz. We assigned the latter signal to the C atom of the alkyl substituent bound to the Zr atom in complexes **10a—e**. In excess $AlBu^i_3$, these

Table 2. ^{13}C NMR spectra with some direct spin-spin coupling constants ($^1J_{C,H}$) for compounds **1—4**, **5a**, **7**, **8a**, **9**, **10a—e**, **11a—e**, **13a—e**, **15**, **16**, and **17b,c** (benzene-d$_6$ as internal standard and solvent)

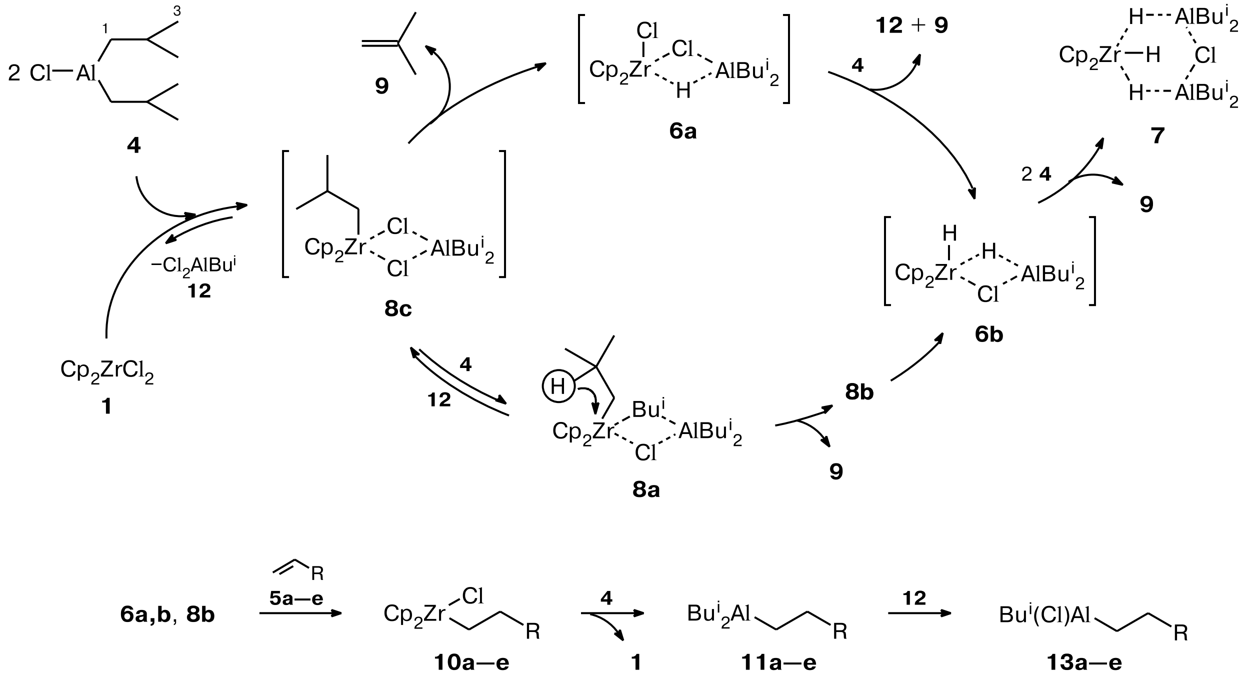
Compound	δ ($^1J_{C,H}$/Hz)													
	Cp	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
1	116.02	—	—	—	—	—	—	—	—	—	—	—	—	—
2	—	23.17	26.62	28.12	—	—	—	—	—	—	—	—	—	—
3	—	25.51	26.29	28.38	—	—	—	—	—	—	—	—	—	—
4	—	28.25	25.97	27.92	—	—	—	—	—	—	—	—	—	—
5a	—	113.86	137.28	33.55	31.08	22.24	13.65	—	—	—	—	—	—	—
7	105.16	22.72	26.62	28.18	—	—	—	—	—	—	—	—	—	—
8a	113.24	25.62	26.53	28.35	81.70	35.18	28.85	—	—	—	—	—	—	—
	(174.4)				(117.2)	—	—	—	—	—	—	—	—	—
9	—	111.03	142.31	24.21	—	—	—	—	—	—	—	—	—	—
10a	113.43	—	—	—	65.18	34.62	29.74	32.54	23.24	14.46	—	—	—	—
	(174.4)				(119.2)									
10b	113.49	—	—	—	64.79	34.62	25.97	29.42	32.54	23.11	14.46	—	—	—
10c	113.43	—	—	—	65.25	34.55	26.03	30.00	29.68	32.54	23.17	14.46	—	—
10d	113.43	—	—	—	65.44	34.55	25.90	30.20	29.94	29.94	32.41	23.17	14.46	—
10e	113.49	—	—	—	64.92	34.62	26.03	30.33	29.74	29.74	30.33	32.47	23.24	14.46
11a	—	25.25	27.92	28.25	11.30	24.99	35.79	32.21	23.17	14.46	—	—	—	—
11b	—	25.88	27.83	28.16	11.51	25.23	36.03	29.59	32.39	23.22	14.37	—	—	—
11c	—	25.56	26.44	28.26	11.76	23.90	35.95	29.66	29.50	32.33	23.05	14.33	—	—
11d	—	25.63	26.37	28.23	11.98	24.26	36.01	29.79	29.96	29.60	32.30	23.05	14.29	—
11e	—	25.59	26.34	28.20	11.95	24.26	35.95	29.72	30.02	30.02	29.56	32.27	23.02	14.26
13a	—	28.16	25.88	27.83	12.81	24.97	33.95	31.41	22.50	14.44	—	—	—	—
13b	—	28.16	25.88	27.83	12.55	24.84	35.57	29.59	32.39	23.22	14.37	—	—	—
13c	—	28.10	25.76	27.74	12.67	24.65	35.49	29.76	29.76	32.40	23.09	14.33	—	—
13d	—	28.10	25.69	27.68	12.76	24.65	35.49	29.83	29.99	29.83	32.33	23.05	14.29	—
13e	—	28.13	25.85	27.74	12.37	24.7	35.56	29.86	30.15	30.15	29.86	32.33	23.12	14.29
15	101.08	24.08	26.62	27.92	—	—	—	—	—	—	—	—	—	—
16	106.10	28.16	26.99	28.48	—	—	—	—	—	—	—	—	—	—
17b	106.05	2.67	10.62	—	—	—	—	—	—	—	—	—	—	—
17c	106.15	26.42	27.73	29.09	—	—	—	—	—	—	—	—	—	—

Scheme 4



R = Bu (**a**), C$_5$H$_{11}$ (**b**), C$_6$H$_{13}$ (**c**), C$_7$H$_{15}$ (**d**), C$_8$H$_{17}$ (**e**)

Scheme 5



R = Bu (**a**), C_5H_{11} (**b**), C_6H_{13} (**c**), C_7H_{15} (**d**), C_8H_{17} (**e**)

complexes undergo transmetallation to form diisobutylalkylalanes **11a—e** with signals of the C atoms in the ^{13}C NMR spectra, which are characteristic of these compounds and similar to those described in the literature.[29]

For the reaction of Cp_2ZrCl_2 (**1**) with $ClAlBu^i_2$ (**4**) (1 : 3), as in the case of the OAC studied above, the NMR spectra contain signals characteristic of complex **7** and the signal at δ_{Cp} 108.50. However, under the experimental conditions, the complex with the signals at δ_{Cp} 108.50 is rather stable and detectable at room temperature, unlike the Cp_2ZrCl_2—$HAlBu^i_2$ system. This complex is transformed into compound **7** only with an increase in the $ClAlBu^i_2$ concentration to a ratio of 1 : 15. It is most likely that in this system complex **7** is formed *via* several successive steps (Scheme 5) through the intermediate formation of hydride complexes **6a,b** and **8b**, which can be responsible for olefin hydroalumination.

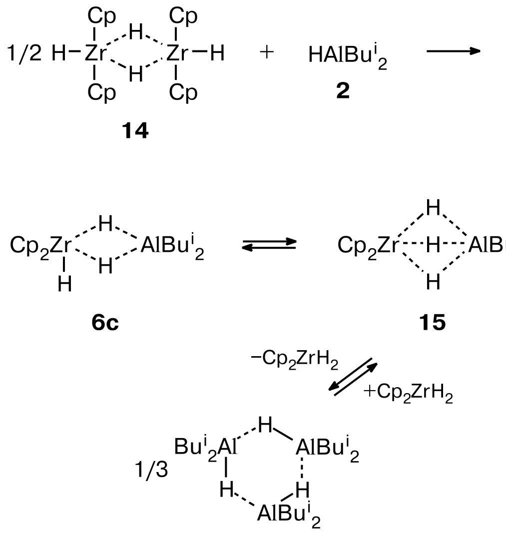
When reagents **1**, **4**, and **5** are mixed in a molar ratio of 1 : 3 : 1, alkyl complexes **10a—e** can be detected, which are transformed into alkylchloroalanes **13a—e** upon the addition of $ClAlBu^i_2$. During this reaction we observed the regeneration of the starting Cp_2ZrCl_2 (**1**) and, hence, assumed that the reaction of complexes **10** with OAC **4** first affords alkylalanes **11**, which then react with Cl_2AlBu^i (**12**) formed in the initial steps of the process. As a result, olefin hydroalumination products are formed: alkylchloroalanes **13a—e**.

Thus, these studies did not allow us to establish the structure of the Zr,Al-containing complexes responsible for olefin hydroalumination: at the reagent ratios approaching that of the catalytic variant, the content of stable trihydride complex **7** increases, and the latter is not involved in olefin hydroalumination.

To establish the structure of true intermediate zirconium complexes, we attempted to perform the encounter synthesis of hypothetical hydride complexes **6a—d** and **8b**. For this purpose, we specially studied the interaction of OAC **2—4** with Cp_2ZrH_2, which was synthesized according to a described procedure.[8]

The reaction of Cp_2ZrH_2 with $HAlBu^i_2$ (Scheme 6) affords the known[8] dark blue complex **15** with the pentacoordinate Al atom instead of complex **6c**. The ^{1}H NMR spectra of this complex exhibit one broadened signal of the hydride atoms ($\Delta W_{1/2} \approx 33$ Hz), whose surface area corresponds to the resonance line of the Cp rings as 3 : 10. The position of the broadened signal of the hydride atoms in the ^{1}H NMR spectrum of complex **15** depends on the $HAlBu^i_2$ concentration. At the molar ratio Cp_2ZrH_2 : $HAlBu^i_2$ = 1 : 1, the signal of the hydride atoms of complex **15** lies at δ –1.94. The further addition of OAC **2** to a ratio of 1 : 3 results in the downfield shift of the signal to δ –0.62. The shift of this signal can be explained by the existence of an intermolecular exchange between $HAlBu^i_2$ and complex **15** (see Scheme 6). With an increase in the $HAlBu^i_2$ concentration, the signal of the Cp rings in the ^{13}C NMR spectra also shifts from 100.00 to 102.20 ppm. The temperature variation from –90 to +40 °C does not almost change the position of the broadened signal of the hydride atoms. Thus, structure **15** is more probable than structure **6c**.

Scheme 6



To prove additionally the structure of complex **15**, we determined its molecular weight by the cryoscopic method.[8] The experimental value of the molecular weight was 326 g mol^{-1}, which is close to the theoretical value for structure **15** (366 g mol^{-1}).

As shown by experiments, complex **15** reacts with olefins to form hydroalumination products **11a—e**.

To synthesize complex **6b**, we studied the reaction of Cp$_2$ZrH$_2$ with ClAlBu$^i_2$ (1 : 1). However, instead of the expected compound **6b** we observed the formation of previously undescribed complex **16** (Scheme 7), whose ^{1}H NMR spectrum contains broadened signals of the hydride H atoms at δ −0.65—−1.35 of the Zr—H—Al (H$_a$) bond and at δ −2.80—−2.56 of the Zr—H—Zr (H$_b$) bond with an intensity ratio of 1 : 1. At the same time, toward the signals of the H atoms of the Cp rings, this ratio is 1 : 10. It follows from the 2D HH—COSY NMR spectra that the system of hydride atoms in complex **16** is strongly bound.

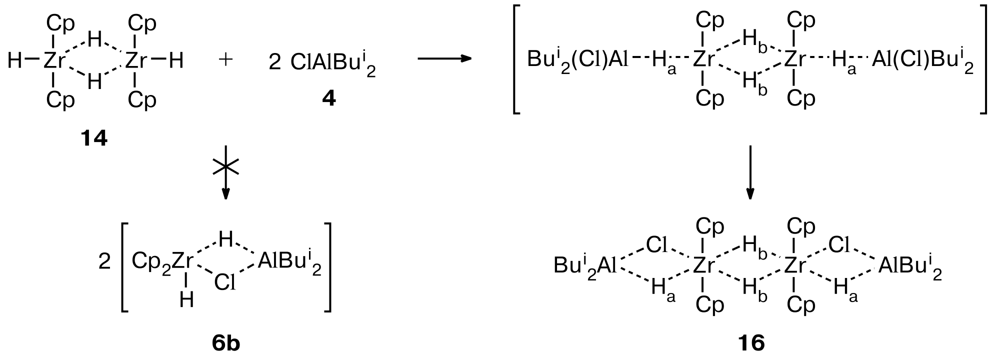
The study of the molecular weight of complex **16** by cryoscopy in benzene confirmed the dimeric structure of this compound. The experimental value of the molecular weight was 788 g mol^{-1}, while the theoretical weight is equal to 800 g mol^{-1}. The signals of the Cp ring in the ^{13}C NMR spectrum of this complex appear at δ 106.10—108.50. It should be mentioned that the chemical shift depends on the ClAlBu$^i_2$ concentration: an increase in the content of OAC **4** in the system results in the descreening of the C atoms of the Cp rings.

There are published assumptions on the existence of such dimeric complexes with the composition (Cp$_2$ZrH$_2$·AlR′$_3$)$_2$ (R′ = Me (**17a**)[8], Et (**17b**)[30]), which are formed in the reaction of Cp$_2$ZrH$_2$ with AlR′$_3$. The ^{1}H NMR spectra of complex **17a** exhibit triplet signals of the bridging hydride atoms of the Zr—H—Zr bond at δ −2.92 and protons of the Zr—H—Al bond at δ −0.92. By analogy to complexes **17a,b**, we assumed the formation of a bridged bimetallic zirconium complex in the case of the reaction of Cp$_2$ZrH$_2$ with AlBu$^i_3$ (Scheme 8).

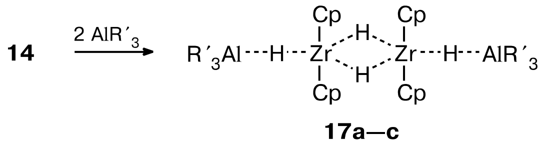
In our experiments, the reaction of Cp$_2$ZrH$_2$ with AlBu$^i_3$ afforded complex **17c** instead of the expected **6d**. For complex **17c**, the set of signals of the hydride atoms in the ^{1}H NMR spectrum is identical to signals in the spectra of complexes **17a,b**.

It should be noted that the appearance of an OAC molecule in the composition of complexes **17a—c** does not distort the dimeric structure of the starting [Cp$_2$ZrH$_2$]$_2$, whose structure has previously[31] been discussed in detail. The formation of complexes **17a—c** shifts the triplet signals of the bridging hydride atoms from δ −3.45 in the starting [Cp$_2$ZrH$_2$]$_2$ to δ −2.92, and the signal of the terminal proton shifts substantially: from δ 3.85 to δ −0.92. The study of the temperature dependence of the spectra of the starting [Cp$_2$ZrH$_2$]$_2$ showed[31] that two triplets of the hydride atoms are transformed into broadened singlets on heating the sample to +60 °C, while at +70 °C the intensities of signals from the terminal hydride in-

Scheme 7



Scheme 8



R′ = Me (**a**), Et (**b**), Buⁱ (**c**)

crease relatively. These facts were explained by two processes: the fast exchange between the bridging and terminal hydrides at low temperatures and the dimer—monomer equilibrium.

The association of the $[Cp_2ZrH_2]_2$ complex and OAC to form complexes **17a—c** induces the same effects in the NMR spectra as the temperature increase in the case of nonassociated $[Cp_2ZrH_2]_2$. The geminal SSCC of the hydride atoms decreases from 7.3 to 4.9 Hz compared to the starting $[Cp_2ZrH_2]_2$ but the triplet structure of the signals remains unchanged. The heating of complexes **17a—c** to +40 °C induces their decomposition. Thus, the appearance of OAC both accelerates processes of the intramolecular exchange between the bridging and terminal hydrides and shifts the dimer—monomer equilibrium.

In the 1D ^{1}H NMR spectra of complex **16**, the signal of the H_b proton at δ –2.56 is a broadened triplet with the SSCC ^2J = 4.2 Hz and belongs to the bridging H atom of the Zr—H—Zr bond. The signal of the H_a proton bound to the Zr and Al atoms (Zr—H—Al bond) is broader than the signal of the bridging H_b atom and does not split into a multiplet. The resonance line width of the H_a proton at the half-height is $\Delta W_{1/2} \approx 14.2$ Hz. The broadened signals of the hydride atoms in complex **16** can be due to both an increase in the rate of the aforementioned exchange between the H_a and H_b protons and the symmetry loss in the molecule preceding the formation of this complex (see Scheme 7) by the additional coordination of the Al and Zr atoms through the Cl atom in structure **16**. The temperature plot of the chemical shifts of the H_a and H_b protons is presented in Fig. 4.

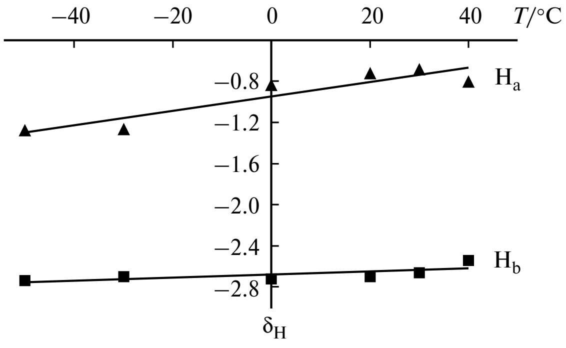


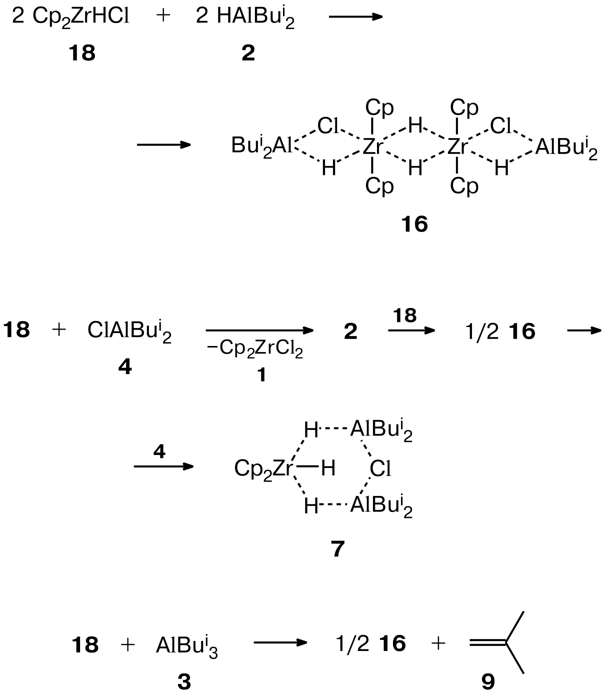
Fig. 4. Temperature plot of the chemical shifts of hydride atoms in complex **16**.

When the temperature of a solution containing complex **16** in toluene-d_8 increases from –60 to +40 °C, the position of the H_b signal remains virtually unchanged, whereas the resonance line of H_a undergoes a downfield shift by 0.5 ppm. At temperatures higher than 40 °C complex **16** would decompose with gas evolution and formation of paramagnetic dark cherry-colored species.

To synthesize complexes **6a** and **8b**, which also can be key intermediates in olefin hydroalumination, we studied the reaction of the Schwartz reagent Cp_2ZrHCl (**18**)[32,33] with OAC **2—4** (reagent **18** was synthesized by the reaction of Cp_2ZrH_2 with $CHCl_3$).

The reaction of Cp_2ZrHCl with OAC **2** affords the same complex **16** (Scheme 9) as the reaction of Cp_2ZrH_2 with OAC **4**.

Scheme 9

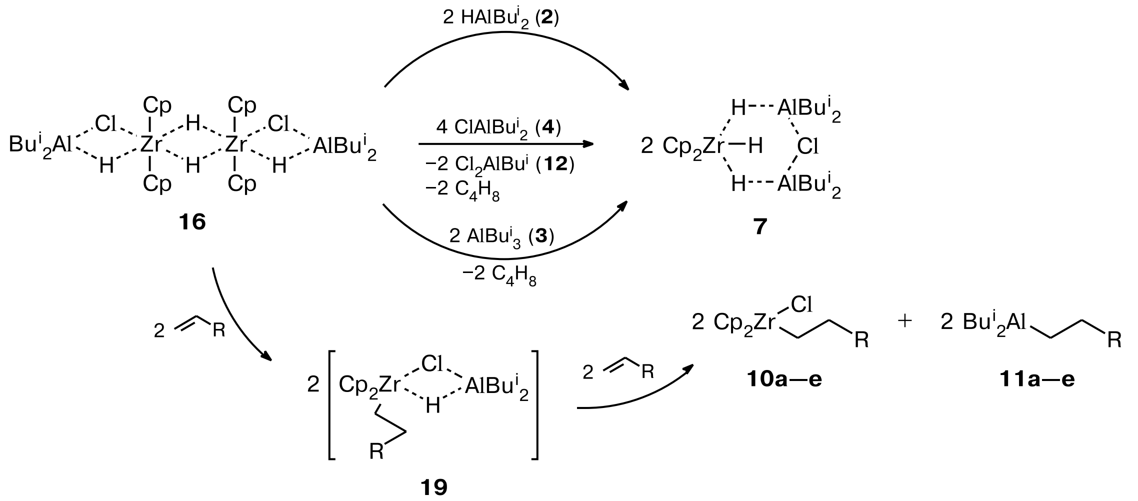


The reaction of Cp_2ZrHCl with $ClAlBu^i_2$ (**4**) even at low temperatures (below –90 °C) affords Cp_2ZrCl_2 and complexes **16** and **7** instead of complex **6a**. It is most likely that $HAlBu^i_2$ (**2**) appears primarily along with Cp_2ZrCl_2. In turn, compound **2** reacts with still unconsumed Cp_2ZrHCl to transform into complex **16**, which reacts with the remaining OAC **4** to yield complex **7**.

Attempts to detect complex **8b** in the reaction of Cp_2ZrHCl with $AlBu^i_3$ were unsuccessful: the formation of complex **16** and isobutylene (**9**) was observed at different temperatures, including –90 °C.

Summarizing the aforesaid, we may conclude that complexes **6a—d** and **8b** are unstable. Instead of them, we

Scheme 10



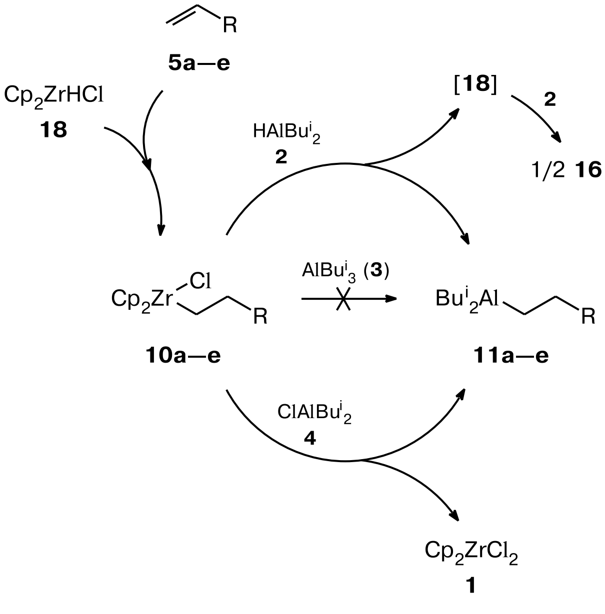
R = Bu (**a**), C_5H_{11} (**b**), C_6H_{13} (**c**), C_7H_{15} (**d**), C_8H_{17} (**e**)

obtained complexes **15**, **16**, and **17a—c** by the encounter synthesis and showed that all of them react with olefins to form alkylalanes **11**. However, only complex **16** obeys the logical scheme of the hydroalumination mechanism. First, as already mentioned, complex **16** reacts with olefins to form alkylzirconium complexes **10a—e** and hydrometallation products **11a—e** (Scheme 10). Second, complex **16** reacts with OAC **2—4** to form the known trihydride complex **7** (see Scheme 10). Third, the chemical shift of the Cp ring in the ^{13}C NMR spectrum of complex **16** at δ 108.50 is similar to the signal of the Cp rings observed for the reaction of Cp_2ZrCl_2 with OAC **2—4**. Therefore, it seems more reasonable to assume that dimeric structure **16** is involved in the first steps of hydroalumination instead of monomeric complex **6b**. All these facts favor complex **16** as the key intermediate responsible for alkene hydroalumination. It is most likely that the threefold excess of OAC necessary for the complete dissolution of Cp_2ZrCl_2 does not allow the direct observation of complex **16** during studies of the Cp_2ZrCl_2—OAC systems, because this complex is unstable under the reaction conditions.

We assumed first that the reaction of complex **16** with olefin should involve the formation of intermediate complex **19** (see Scheme 10). However, attempts to detect this complex in the reaction of Cp_2ZrCl_2 with OAC or prepare it by the encounter synthesis from $Cp_2Zr(CH_2)_2RCl$ [20] and $HAlBu^i_2$ failed. The reaction of complex **16** with olefin affords stable complexes **10** and alkylalanes **11**. The formation of the latter can be explained by the transmetallation of complexes **10**.

To study the transmetallation step, *i.e.*, transition of the alkyl fragment from the Zr atom in complexes **10a—e** to the Al atom to form complexes **11a—e**, we studied the reactions of compounds **10a—e** with different OAC (Scheme 11).

Scheme 11



The reaction of complexes **10** with OAC **2** affords alkylalanes **11** and complex **16**. The latter is formed due to the fast reaction of Cp_2ZrHCl formed *in situ* with $HAlBu^i_2$. The reaction of complexes **10** with OAC **4** affords Cp_2ZrCl_2 (**1**) and alkylalanes **11**. It should be emphasized that compounds **10** do not react with $AlBu^i_3$. However, as we already mentioned, the formation of alkyl complexes **10** was reliably proved during the studying the

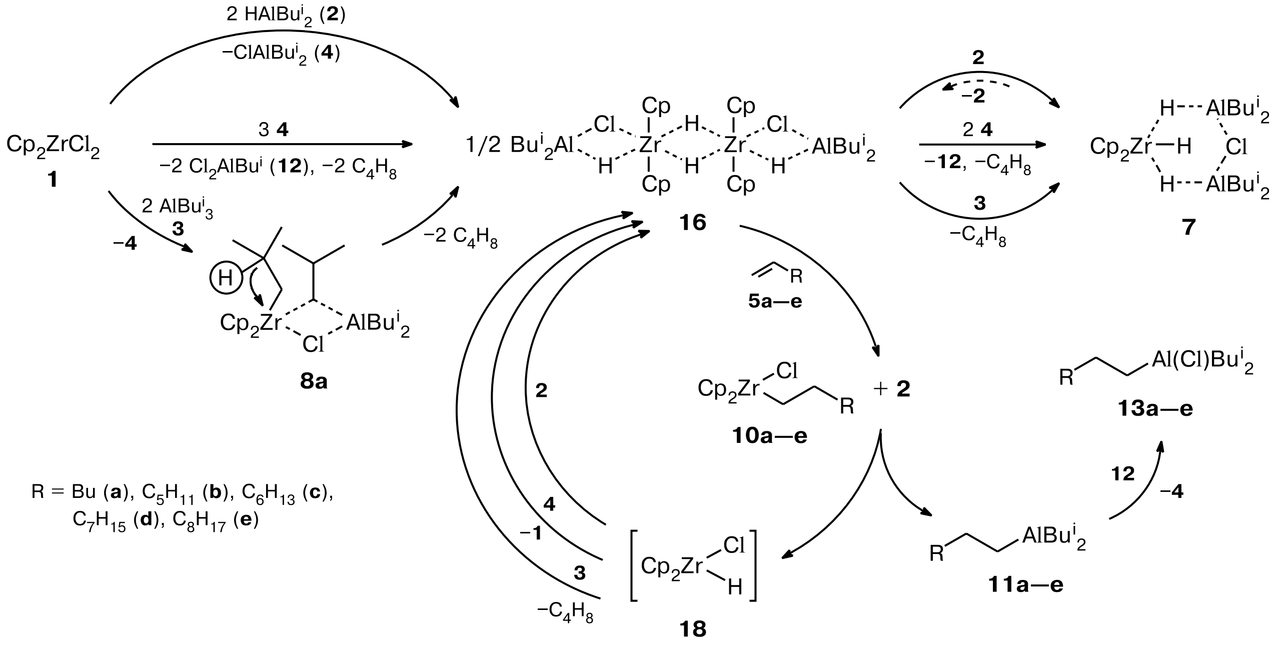
Cp_2ZrCl_2—$AlBu^i_3$ system. When reacting with excess $AlBu^i_3$, complexes **10** are transformed into alkylalanes **11**. Evidently, the action of complex **10** in hydroalumination is not isolated. The presence of $HAlBu^i_2$ is basically important: in the Cp_2ZrCl_2—$ClAlBu^i_2$ and Cp_2ZrCl_2—$AlBu^i_3$ systems, $HAlBu^i_2$ can be formed only in the reaction step of complex **16** with olefins (see Scheme 10). Thus, the fast transmetallation process occurs in the *in situ* formed reaction pair $Cp_2Zr(CH_2)_2RCl$—$HAlBu^i_2$ (complex **19** in Scheme 10 or the reaction of $Cp_2Zr(CH_2)_2RCl$ with $HAlBu^i_2$ in Scheme 11), *i.e.*, migration of the alkyl fragment from Zr to the Al atom resulting in the formation of alkylalanes **11** and Cp_2ZrHCl. The latter interacts, according to Scheme 9, with any of the OAC studied to form the key complex **16** and complete the catalytic cycle.

Thus, based on the experimental data obtained, we propose the generalized mechanism of olefin hydroalumination by diisobutylaluminum hydride, diisobutylaluminum chloride, and triisobutylaluminum (Scheme 12). In all systems studied, *viz.*, Cp_2ZrCl_2—$ClAlBu^i_2$, Cp_2ZrCl_2—$HAlBu^i_2$, and Cp_2ZrCl_2—$AlBu^i_3$, the mixed Zr,Al-containing hydride complexes are primarily formed, and among the latter only the complex $(Cp_2ZrH_2 \cdot ClAlBu^i_2)_2$ (**16**) is an active species of the catalyst, which hydroaluminates olefins. Depending on the nature of the starting OAC, complex **16** is formed *via* different routes. The reaction of Cp_2ZrCl_2 (**1**) with $HAlBu^i_2$ (**2**) through the step of ligand exchange of the Cl atom in molecule **1** and H atom in molecule **2** produces complex **16** and $ClAlBu^i_2$ (**4**). In the reaction **1** + **4**, complex **16** is formed due to the exchange of the Cl atom in molecule **1** by the Bu^i group of the starting OAC **4**. This involves the β-hydride transfer followed by isobutylene elimination. In the case of compounds **1** and **3**, alkyl complex **8a** is primarily formed and transformed into the key complex **16** due to the β-hydride transfer.

Intermediate **16** can further transform into trihydride complex **7**, which does not react with olefin. In the case of OAC **2**, this reaction can be reversible, and the low hydroalumination rate is explained by the low concentration of complex **16** in the reaction mixture due to the predomination of the forward reaction of complex **16** with $HAlBu^i_2$ over the backward reaction. In the case of OAC **3** and **4**, the transition **16** → **7** is irreversible. Molecules **3** and **4** contain no hydride atoms and, therefore, the formation of complex **16** is impeded by steps of Cl atom exchange by the Bu^i group, β-hydride transfer, and isobutylene elimination. Probably, the total rate in these steps is lower than the reaction rate of complex **16** with olefin, providing fast hydroalumination in the Cp_2ZrCl_2—$ClAlBu^i_2$ and Cp_2ZrCl_2—$AlBu^i_3$ systems.

Complex **16** coordinates olefins to form alkyl complexes **10** and $HAlBu^i_2$ (**2**), which then participates in transmetallation. This process generates alkylalanes **11** and Cp_2ZrHCl (**18**). In the case of OAC **4**, alkylalanes **11** react with Cl_2AlBu^i (**12**) formed in the initial reaction steps to yield products of olefin hydroalumination: alkylchloroalanes **13a—e**. The Cp_2ZrHCl that formed is transformed into complex **16** almost instantly and regardless of the nature of the starting OAC, thus completing the catalytic cycle.

Scheme 12



R = Bu (**a**), C_5H_{11} (**b**), C_6H_{13} (**c**), C_7H_{15} (**d**), C_8H_{17} (**e**)

Experimental

All procedures with organometallic compounds were carried out under argon. Prior to use benzene and toluene were distilled above $HAlBu^i_2$, and THF and ether were distilled above $LiAlH_4$. A 73% solution of $HAlBu^i_2$, a 97% solution of $ClAlBu^i_2$, and a 91% solution of $AlBu^i_3$ were used. Complex Cp_2ZrCl_2 was synthesized from $ZrCl_4$ according to a previously described procedure.[34]

Spectroscopic studies were carried out by dynamic ^1H and ^{13}C NMR spectroscopy with complete and partial proton decoupling in the temperature interval from −90 to +25 °C on Jeol FX-90Q and Bruker AM-300 spectrometers. Benzene-d_6 and toluene-d_8 were used as internal standards. Tubes with $d = 5$ mm were used.

The yield of hydroalumination products was determined from the yield of hydrolysis products of a reaction mixture, namely, saturated hydrocarbon relatively to the starting olefin. GLC analysis of the hydrolysis products was carried out on a Chrom-5 chromatograph (column 1200×3 mm, 5% SE-30 or 15% PEG-6000 on Chromaton N-AW, helium as a carrier gas).

Cryoscopic studies were carried out in benzene according to a standard procedure[35] in a glass cell with three necks: for argon, a stirrer, and a Beckman thermometer (the accuracy of determination of the melting point was 0.005 °C).

Study of the influence of the OAC type ($HAlBu^i_2$, $ClAlBu^i_2$, and $AlBu^i_3$), temperature of the reaction, and concentration of the Cp_2ZrCl_2 catalyst on the yield of olefin hydroalumination products. A flask with a magnetic stirrer was filled under argon with Cp_2ZrCl_2 (**1**) (0.20 mmol, 52.4 mg), olefins **5a—e** (10 mmol), and OAC (12 mmol, 2.3 mL of 73% solution of $HAlBu^i_2$ (**2**), 2.2 mL of 95% solution of $ClAlBu^i_2$ (**4**), or 2.9 mL of 82% solution of $AlBu^i_3$ (**3**)). The mixture was diluted with benzene to 5.9 mL. The reaction was carried out with stirring at three different temperatures (0, 10, and 20 °C). In the case of OAC **2** and **4**, the process was carried out at different concentrations of Cp_2ZrCl_2 (0.20, 0.30, 0.50, and 1.0 mmol). After 5, 10, 15, 20, 30, 60, 90, 120, 150, 180, 240, 300, and 360 min, samples (0.4 mL) were syringed into tubes filled with argon, and the samples were decomposed with 10% HCl at 0 °C. Products were extracted with benzene, and the organic layer was dried above $CaCl_2$. The yield of alkylalanes **11a—e** was determined by GLC (see Table 1). The NMR data for alkylalanes **11a—e** are presented in Table 2.

Study of the structure of intermediate complexes in the reactions of OAC 2—4 with Cp_2ZrCl_2 (1) by dynamic ^1H and ^{13}C NMR spectroscopy. ***A.*** Studies were carried out directly in the cell of an NMR spectrometer at ~20 °C. An NMR tube filled with argon was loaded with Cp_2ZrCl_2 (**1**) (0.3 mmol, 87.7 mg), benzene-d_6 (0.2 mL), and OAC (0.9 mmol, 0.17 mL of 73% solution of $HAlBu^i_2$ (**2**), 0.17 mL of 95% solution of $ClAlBu^i_2$ (**4**), or 0.20 mL of 91% solution $AlBu^i_3$ (**3**)) (molar ratio OAC : **1** = 3 : 1). ^1H and ^{13}C NMR spectra were recorded. The concentration of OAC was gradually increased to the molar ratio OAC : **1** = 15 : 1.

B. An NMR tube filled with argon was loaded with Cp_2ZrCl_2 (0.3 mmol, 87.7 mg) (**1**) and toluene-d_8 (0.2 mL). The tube was cooled to −90 °C, then OAC (0.3 mmol, 0.06 mL of 73% solution of $HAlBu^i_2$ (**2**), 0.06 mL of 95% solution of $ClAlBu^i_2$ (**4**), or 0.06 mL of 91% solution of $AlBu^i_3$ (**3**)) was added, and the mixture was transferred to the spectrometer cell to record spectra in the temperature interval from −90 to +25 °C.

Study of the structure of intermediate complexes in the reactions of OAC 2—4 with olefins 5a—e in the presence of Cp_2ZrCl_2 (1) by dynamic ^1H and ^{13}C NMR spectroscopy. Studies were carried out directly in the cell of an NMR spectrometer at ~20 °C. An NMR tube filled with argon was loaded with Cp_2ZrCl_2 (**1**) (0.3 mmol, 87.7 mg), benzene-d_6 (0.2 mL), OAC (0.9 mmol, 0.17 mL of 73% solution of $HAlBu^i_2$ (**2**), 0.17 mL of 95% solution of $ClAlBu^i_2$ (**4**), or 0.19 mL of 91% solution of $AlBu^i_3$ (**3**)), and olefin **5a—e** (0.3 mmol, molar ratio OAC : **1** : **5** = 3 : 1 : 1). The olefin concentration was increased until the molar ratio was OAC : **1** : **5** = 3 : 1 : 3; and the ^1H and ^{13}C NMR spectra were detected in parallel.

Complex Cp_2ZrH_2. The synthesis was based on a described procedure.[8] A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp_2ZrCl_2 (**1**) (1.2 mmol, 349.5 mg), benzene (0.3 mL), and $HAlBu^i_2$ (**2**) (3.6 mmol, 0.7 mL, 73% solution in hexane). After the complete dissolution of complex **1**, Et_3N (3.6 mmol, 0.50 mL) or Et_2NH (3.6 mmol, 0.42 mL) was added dropwise to the mixture. In the case of using Et_2NH, the yield of Cp_2ZrH_2 was 95%. The Cp_2ZrH_2 complex formed a white precipitate, and the solution became dark violet. The vigorous gas evolution was observed. The precipitate was centrifuged, washed with hexane (4×2 mL), and dried *in vacuo*. To check the structure, a small amount of the Cp_2ZrH_2 sample was placed in an NMR tube in C_6D_6 and treated with acetone. The ratio of signals of the Cp rings and Me groups showed the predominant formation of diisopropoxyzirconocene (>95%).

Reaction of Cp_2ZrH_2 with OAC 2. An NMR tube filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene-d_6 (0.5 mL), and then $HAlBu^i_2$ (**2**) (0.6 mmol, 0.17 mL, 50% solution in hexane) was added dropwise until the precipitate dissolved completely. A dark blue solution of complex **15** was obtained. The tube was transferred to the spectrometer cell to record spectra. The assignment of signals in the ^1H and ^{13}C NMR spectra of the synthesized complex are presented in Tables 2 and 3.

Reaction of Cp_2ZrH_2 with OAC 4. An NMR tube filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene-d_6 (0.5 mL), and then $ClAlBu^i_2$ (**4**) (0.6 mmol, 0.11 mL, 95% solution in hexane) was added drowise until the precipitate dissolved. The formation of complex **16** was observed. The assignment of signals in the ^1H and ^{13}C NMR spectra of the reaction products is presented in Tables 2 and 3.

Reaction of Cp_2ZrH_2 with $AlBu^i_3$ (3) and $AlEt_3$. An NMR tube filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene-d_6 (0.5 mL), and then OAC (0.6 mmol, 0.13 mL of 91% solution of $AlBu^i_3$ (**3**) and 0.07 mL of 94% solution of $AlEt_3$) was added dropwise until the precipitate dissolved. The formation of complexes **17b** and **17c** was observed. The assignment of signals in the ^1H and ^{13}C NMR spectra of the reaction products is presented in Tables 2 and 3.

Complex 16. A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene (1.5 mL), and $ClAlBu^i_2$ (**4**) (0.6 mmol, 0.14 mL, 76% solution in hexane) was added dropwise until the complete dissolution of Cp_2ZrH_2. The solvent was evaporated *in vacuo*. A viscous Vaseline-like pinkish-brown mixture was obtained. The assignment of signals in the ^1H and ^{13}C NMR of complex **16** is presented in Tables 2 and 3. IR (Nujol), ν/cm^{-1}: 1780

Table 3. ^{1}H NMR spectra with some spin-spin coupling constants ($^2J_{H,H}$) for compounds **7**, **14—16**, and **17a—c** (benzene-d$_6$ as internal standard and solvent)

Compound	δ ($^2J_{H,H}$/Hz)					
	Cp	H$_a$	H$_b$	CH$_2$	CH	Me
7	5.75 (10 H)	−2.04 (d, 2 H, $^2J_{H,H}$ = 7.5)	−0.87 (t, 1 H, $^2J_{H,H}$ = 7.5)	0.51 (d, 8 H, $^2J_{H,H}$ = 6.8)	2.15 (m, 4 H)	1.18 (d, 24 H, $^2J_{H,H}$ = 6.4)
14[31]	5.50 (20 H)	3.85 (t, 2 H, $^2J_{H,H}$ = 7.3)	−3.45 (t, 2 H, $^2J_{H,H}$ = 7.3)	—	—	—
15	5.64 (10 H)	−0.62—−1.94 (br.s, 3 H, $\Delta W_{1/2}$ = 33)	—	0.43 (d, 4 H, $^2J_{H,H}$ = 7.3)	2.14 (m, 2 H)	1.21 (d, 12 H, $^2J_{H,H}$ = 6.4)
16	5.81 (20 H)	−0.65—−1.35 (s, 2 H)	−2.56—−2.80 (br.t, 2 H, $^2J_{H,H}$ = 4.2)	0.43 (d, 8 H, $^2J_{H,H}$ = 5.4)	2.2 (m, 4 H)	1.34 (d, 24 H, $^2J_{H,H}$ = 6.3)
17a[8]	5.50 (20 H)	−0.92 (t, 2 H)	−2.92 (t, 2 H)	—	—	−0.41 (s, 18 H)
17b	5.72 (20 H)	−1.23 (t, 2 H, $^2J_{H,H}$ = 5.4)	−2.78 (t, 2 H, $^2J_{H,H}$ = 5.4)	0.32 (q, 12 H, $^2J_{H,H}$ = 8.0)	—	1.50 (t, 18 H, $^2J_{H,H}$ = 8.0)
17c	5.79 (20 H)	−1.05 (t, 2 H, $^2J_{H,H}$ = 4.9)	−2.74 (t, 2 H, $^2J_{H,H}$ = 4.9)	0.36 (d, 12 H, $^2J_{H,H}$ = 6.8)	2.21 (m, 6 H)	1.35 (d, 36 H, $^2J_{H,H}$ = 6.3)

(Zr—H—Al), 1450 (Zr—H—Zr). Molecular weight/g mol^{-1}, found: 788. Calculated: 800.

Reaction of complex 16 with OAC 2—4. An NMR tube filled with argon was loaded with Cp$_2$ZrH$_2$ (0.6 mmol, 134 mg) and benzene-d$_6$ (0.5 mL), and then ClAlBu$^i_2$ (**4**) (0.6 mmol, 0.11 mL, 95% solution in hexane) was added dropwise to the complete dissolution of the precipitate. Complex **16** was obtained, which was identified by the ^{1}H and ^{13}C NMR spectra. The tube was cooled to −60 °C, then OAC **2—4** (0.6 mmol, 0.17 mL of 50% solution of HAlBu$^i_2$ (**2**), 0.11 mL of 95% solution of ClAlBu$^i_2$ (**4**), or 0.13 mL of 91% solution of AlBu$^i_3$ (**3**)) was added, and the mixture was transferred to the cell of an NMR spectrometer to record spectra in the temperature interval from −60 to 0 °C. When the temperature increased to 0 °C, complex **16** transformed into trihydride complex **7**.

Reaction of complex 16 with olefins 5a—e. Complex **16** was synthesized as described above. Then the tube was cooled to 0 °C, olefin **5a—e** (0.6 mmol) was added, and the mixture was transferred to the cell of an NMR spectrometer to record spectra in the temperature interval from 0 to 20 °C. The formation of complexes **10a—e** and **11a—e** was observed with the temperature increase.

Complex Cp$_2$ZrHCl (18). A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp$_2$ZrH$_2$ (0.6 mmol, 134 mg) and benzene (0.5 mL). Chloroform (0.6 mmol, 0.05 mL) was added to the resulting suspension with stirring. The precipitate of Cp$_2$ZrHCl (**18**) was centrifuged and washed with benzene (2×2 mL). To verify the structure of complex **18**, a small amount of the sample was treated with acetone, dissolved in C$_6$D$_6$, and placed in an NMR tube. The ratio of surface areas of signals of the Cp rings and Me groups showed the predominant formation of monoisopropoxyzirconocene (>95%).

Reaction of Cp$_2$ZrHCl (18) with OAC 2. An NMR tube filled with argon was loaded with complex **18** synthesized from Cp$_2$ZrH$_2$ (0.6 mmol) in toluene-d$_8$, and HAlBu$^i_2$ (**2**) (0.6 mmol, 0.17 mL, 73% solution in hexane) until the precipitate dissolved completely. The formation of complex **16** was observed in solution.

Reaction of Cp$_2$ZrHCl (18) with OAC 4. An NMR tube filled with argon was loaded with complex **18**, which was prepared from 0.6 mmoles of Cp$_2$ZrH$_2$, in toluene-d$_8$, and ClAlBu$^i_2$ (**4**) (0.6 mmol, 0.11 mL, 95% solution in hexane) was added dropwise. The formation of complexes **1**, **16**, and **7** was observed in solution. The assignment of signals of the reaction products in the ^{1}H and ^{13}C NMR spectra is presented in Tables 2 and 3.

Reaction of Cp$_2$ZrHCl (18) with OAC 3. An NMR tube filled with argon was loaded with complex **18**, which was synthesized from 0.6 mmoles of Cp$_2$ZrH$_2$, in toluene-d$_8$, and AlBu$^i_3$ (**3**) (0.6 mmol, 0.13 mL, 91% solution in hexane) was added dropwise. The formation of complex **16** and evolution of isobutylene (**9**) were observed in solution.

Complexes Cp$_2$Zr(CH$_2$)$_2$RCl 10a—e. A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp$_2$ZrHCl (**18**) (prepared from 0.6 mmoles of Cp$_2$ZrH$_2$), benzene (0.5 mL), and olefins **5a—e** (0.6 mmol). The mixture was stirred for 24 h at 20 °C. Yellow solutions of alkylzirconium chlorides **10a—e** in benzene were obtained.

Reactions of compounds 10a—e with OAC 2—4. An NMR tube filled with argon was loaded with complexes **10a—e** (obtained from 0.6 mmoles of Cp$_2$ZrH$_2$) in toluene-d$_8$, and OAC **2—4** (0.11 mL of 73% solution HAlBu$^i_2$ (**2**), 0.11 mL of 95% solution of ClAlBu$^i_2$ (**4**), or 0.13 mL of 91% solution of AlBu$^i_3$ (**3**)) was added dropwise. In the case of HAlBu$^i_2$ (**2**), the formation of the reaction products, *viz.*, alkylalanes **11a—e** and complex **16**, was observed in solution. In the reaction with ClAlBu$^i_2$ (**4**), we observed the formation of alkylalanes **11a—e** and regeneration of the starting Cp$_2$ZrCl$_2$ (**1**). Compounds **10a—e** did not react with AlBu$^i_3$ (**3**).

This work was financially supported by the Foundation of the President of the Russian Federation (Program for Support of Young Candidates of Science (Grant

MK-2647.2003.03) and Leading Scientific Schools (Grant NSh-2189.2003.3)) and the Russian Foundation for Basic Research (Project No. 00-03-40132 (TsKP REGUTs)).

References

1. K. Ziegler, *Angew. Chem.*, 1956, **68**, 721.
2. A. Meisters and T. Mole, *J. Chem. Soc., Chem. Commun.*, 1972, 525.
3. L. I. Zakharkin, L. P. Sorokin, and I. M. Khorkina, *Zh. Org. Khim.*, 1961, **31**, 3311 [*J. Org. Chem. USSR*, 1961, **31** (Engl. Transl.)].
4. K. Ziegler and H. Lehmkuhl, in *Houben-Weyl, Metoden der organishen Chemie*, Thieme-Verlag, Stuttgard, 1970, **XIII/4**, 182.
5. F. Asinger, B. Fell, and R. Janssen, *Chem. Ber.*, 1964, **B97**, 2515.
6. F. Sato, S. Sato, and M. Sato, *J. Organomet. Chem.*, 1976, **122**, 25.
7. F. Sato, S. Sato, and M. Sato, *J. Organomet. Chem.*, 1977, **131**, 26.
8. L. I. Shoer, K. I. Gell, and J. Schwartz, *J. Organomet. Chem.*, 1977, **136**, 19.
9. G. A. Tolstikov, U. M. Dzhemilev, O. S. Vostrikova, and A. G. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 669 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 596 (Engl. Transl.)].
10. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2134 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
11. E. Negishi and T. Yoshida, *Tetrahedron Lett.*, 1980, **21**, 1501.
12. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, and L. M. Zelenova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 476 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 281 (Engl. Transl.)].
13. U. M. Dzhemilev, A. G. Ibragimov, O. S. Vostrikova, E. V. Vasil´eva, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1089 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1004 (Engl. Transl.)].
14. A. G. Ibragimov, Ph. D. (Chem.) Thesis, Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa, 1989, 127 pp. (in Russian).
15. E. Negishi, *Pure Appl. Chem.*, 1981, **53**, 2333.
16. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, and L. M. Zelenova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 361 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 281 (Engl. Transl.)].
17. O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, R. M. Sultanov, and U. M. Dzhemilev, *Tez. dokl. II Vsesoyuz. konf. po metalloorganicheskoi khimii* [*Proc. II All-Union Conf. on Organometallic Chemistry*], Gorkii, 1982, 58 (in Russian).
18. L. I. Shoer and J. Schwartz, *J. Am. Chem. Soc.*, 1977, **99**, 5831.
19. J. Schwartz and J. Latinger, *Angew. Chem.*, *Int. Ed. Engl.*, 1976, **15**, 333.
20. D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, 1974, **96**, 8115.
21. U. M. Dzhemilev, D. L. Minsker, A. A. Berg, O. V. Shitikov, S. I. Lomakina, and A. G. Ibragimov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2791 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2223 (Engl. Transl.)].
22. A.c. USSR 687076; *Byul. Izobret.* [*Invention Bulletin*], 1979, (35) 108 (in Russian).
23. L. M. Khalilov, L. V. Parfenova, S. V. Rusakov, A. G. Ibragimov, and U. M. Dzhemilev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 2086 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 2058].
24. A. R. Siedle, R. A. Newmark, J. N. Schroepfer, and P. A. Lyon, *Organometallics*, 1991, **10**, 400.
25. B. D. Carr and J. Schwartz, *J. Am. Chem. Soc.*, 1979, **101**, 3521.
26. E. Samuel and M. D. Rausch, *J. Am. Chem. Soc.*, 1973, **95**, 6263.
27. W. Kaminsky and H.-J. Vollmer, *Liebigs Ann. Chem.*, 1975, 438.
28. W. Kaminsky and H. Sinn, *Liebigs Ann. Chem.*, 1975, 424.
29. A. A. Panasenko, L. M. Khalilov, A. V. Kuchin, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1980, 2652 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
30. P. C. Wailes, H. Welgold, and A. P. Bell, *J. Organomet. Chem.*, 1972, **43**, 29.
31. P. G. Bickley, N. Hao, P. Bougeard, B. G. Sayrr, R. Burns, M. Burns, and M. J. McGlinchey, *J. Organomet. Chem.*, 1983, **246**, 257.
32. B. Kautzner, P. S. Wailes, and H. Weigold, *Chem. Commun.*, 1969, 1105.
33. S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, and S. M. King, *Tetrahedron Lett.*, 1987, **28**, 3895.
34. R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1969, **138**, 1369 [*Dokl. Chem.*, 1969 (Engl. Transl.)].
35. B. M. Rybak, *Analiz nefti i nefteproduktov* [*Analysis of Oil and Petroleum Products*], Gostoptekhizdat, Moscow, 1962, 888 pp. (in Russian).

Received June 15, 2004;
in revised form October 6, 2004