Synthesis and transformations of metallacycles 29.* Direct alumination of olefins, conjugated dienes, and acetylenes with alkylhaloalanes catalyzed by Zr and Ti complexes

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Catalytic methods were developed for the synthesis of acyclic 1,2- and 1,4-dialuminum compounds by the reactions of olefins, dienes, or acetylenes with R₂AlCl (R = Et, Et_2N , (*cyclo*-C₆H₁₁)₂N, BuⁿO, or *n*-C₆H₁₃O) in the presence of Ti- or Zr-containing complex catalysts and magnesium metal as an acceptor of chloride ions.

Key words: organoaluminum compounds, titanium- and zirconium-containing catalysts, metallacycles, olefins, dienes, acetylenes, [60]fullerene, alumination.

Cyclic organoaluminum compounds (OAC) containing simultaneously two Al atoms at positions 1,1, 1,4, or 1,5 of the carbon chain are generally prepared^{2,3} by thermal hydroalumination of acetylenes and 1,3- or 1,4-dienes with diisobutylaluminum hydride (DIBAH).

These reactions are characterized by rather low selectivity and are very sensitive to the structure of the starting acetylene or diene as well as to the nature of the functional groups involved in the starting unsaturated compound. As a consequence, this method shows little promise from the preparative standpoint.

With the aim of developing an efficient procedure for the synthesis of difficultly accessible 1,2- or 1,4-dialuminum compounds, we studied the reactions of α -olefins, acetylenes, 1,3-dienes, and [60]fullerene with R₂AlCl in the presence of catalysts based on Ti or Zr salts and complexes.

When choosing the procedure for the synthesis of 1,2- and 1,4-dialuminum compounds, we started from the assumption that cycloalumination of olefins and acety-lenes^{4,5} with alkylhaloalanes in the presence of Ti or Zr complexes proceeds through the intermediate formation of titanium- or zirconium-containing three- and five-membered metallacycles, which can be transmetallated under the reaction conditions with the starting alkylhaloalanes to give the corresponding 1,2-dialuminio-ethanes, 1,2-dialuminioethenes, 1,4-dialuminiobutanes, and 1,4-dialuminiobuta-1,3-dienes (Scheme 1).

In the above-mentioned reactions, we used the Cp_2ZrCl_2 and Cp_2TiCl_2 complexes (hereinafter, [Zr] and

* For Part 28, see Ref. 1.

[Ti], respectively) as catalysts, which are most active in cycloalumination of olefins and acetylenes with alkyl derivatives of Mg and Al giving rise to the corresponding three- and five-membered metallacycles of main-group metals.^{4,5}

We succeeded in performing the reactions shown in Scheme 1 under catalytic conditions starting from α -olefins, 1,3-dienes, or acetylenes and Et₂AlCl under the conditions developed earlier^{4,5} for the synthesis of aluminacyclopropanes and aluminacyclopentanes. These reactions require the use of an acceptor of chloride ions, *viz.*, magnesium metal, which simultaneously reduces Ti and Zr complexes.

We studied the reactions of styrene and its derivatives, 1,2- and 1,3-dienes, [60]fullerene, and mono- and disubstituted acetylenes.

Results and Discussion

The reaction of styrene with Et₂AlCl in the presence of Mg and Cp₂TiCl₂ (the molar ratio styrene : Al : Mg : Ti = 10 : 22 : 12 : 0.5) in THF (~20 °C, 8 h) afforded a mixture of OAC 5–7 in ~85% yield. These compounds were identified based on the results of analysis of deuterolysis products **8**, **9**, and **10** obtained in a ratio of ~6 : 1 : 3 (Scheme 2).

In the reactions in benzene or toluene, the yields of OAC 5–7 decreased to 5–8%. The reactions did not proceed in aliphatic solvents (hexane, cyclohexane) virtually at all. In the reactions with the use of $Ti(OPr^i)_4$, $Ti(OBu^n)_4$, or $TiCl_4$ as the catalyst, the total yield of OAC 5–7 decreased to 50, 45, or 25%, respectively, the ratio

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8: **9**: **10** being $\sim 5: 2: 4$. In the presence of the catalyst Cp₂ZrCl₂ or ZrCl₄, the yield of OAC **6** increased to 35–40% with a simultaneous decrease in the yield of 1,2-bis(diethylaluminio)-1-phenylethane (**5**) to 20–25%.

Based on our earlier results⁴⁻⁶ and the data published in the literature,^{7,8} the most probable scheme can be proposed for the formation of 1,2- and 1,4-dialuminum compounds 5 and 6 from styrene in the presence of Cp₂TiCl₂. In this process, powdered magnesium (activated with the starting Et₂AlCl) reduces Cp₂TiCl₂ to "Cp₂Ti." Titanacene, which is generated *in situ*, coordinates a styrene molecule to form titanacyclopropane intermediate **11**, whose transmetallation with Et₂AlCl affords compound 5. Under the reaction conditions, the second styrene molecule adds at the Ti—C bond complex 11, which facilitates the formation of 1,1-dicyclopentadienyl-2,5diphenyltitanacyclopentane (12). Transmetallation of the latter with the starting Et_2AICI gives rise to minor product 6 (Scheme 3).

Hydroalumination product 7 is formed by hydrometallation of a styrene molecule with Ti hydride complexes, which are generated⁹ upon dehydrogenation of THF molecules with low-valence titanium complexes according to the scheme reported earlier.¹⁰

Alumination of substituted styrenes (α -phenylstyrene and *o*-, *p*-, and α -methylstyrenes) with Et₂AlCl in the



presence of Cp2TiCl2 and an activated magnesium powder under the chosen optimum conditions gave rise to 1-arylsubstituted 1,2-dialuminioethanes 13-16 (55-60%) and hydroalumination by-products (25-30%) (Scheme 4). Deuterolysis of OAC 13-16 afforded 1,2-dideuterio-

ethanes 17-20, respectively. In these experiments, 1,4-dialuminio-1,4-diarylbutanes were generated virtually not all. Conceivably, in the step of formation of the titanacyclopropane intermediates of type 11, the bulky aryl substituents hinder the addition of a new arylethylene mol-



ecule at the Ti–C bond to form 2,5-diaryltitanacyclopentanes, which are precursors of 1,4-dialuminio-1,4diarylbutanes.

To elucidate the possibility of the use of monohaloalanes other than Et₂AlCl, bis(dialkylamino)- and dialkoxychloroalanes were subjected to Cp₂TiCl₂-catalyzed alumination. The reactions were carried out in the presence of 5 mol.% of Cp₂TiCl₂ in THF at 20–21 °C for 8 h to prepare N- and O-containing 1,2-dialuminio-1phenylethanes **21a**–**d** in 50–60% yields and hydroalumination products in 30–35% yields (Scheme 5).

Scheme 5



21: R = BuⁿO (**a**), n-C₆H₁₃O (**b**), Et₂N (**c**), (cyclo-C₆H₁₁)₂N (**d**)

Alumination of styrene with the use of halogen-containing amides and aluminum alkoxides produced virtually no regioisomeric 1,4-dialuminio-1,4-diphenylbutanes. Apparently, the starting aluminum amides and alkoxides containing the N and O heteroatoms with the lone electron pair form complexes with titanacyclopropane intermediate **11** thus hindering the incorporation of a new styrene molecule at the Ti—C bond and the formation of 1,4-dialuminum compounds.

Unlike arylolefins, aliphatic α -olefins were subjected to hydroalumination with Et₂AlCl in the presence of the [Cp₂TiCl₂ + Mg] catalyst to give diethylalkylalanes **22**.¹⁰ In the presence of the Cp₂ZrCl₂ catalyst, these reactions afforded 2,3-dialkyl-1,4-dialuminiobutanes **23**¹¹ with high selectivity (Scheme 6).





Et₂AlCl.

the central atom of the catalyst, facilitates stabilization of titanacyclopropane intermediates, which react with Et_2AIC1 to give the corresponding dialuminum compounds 24 (~60%) (Scheme 7).

We failed to carry out Cp₂TiCl₂-catalyzed alumination

of disubstituted olefins, for example, of cyclohexene, cyclooctene, or 2-octene. Apparently, the above-men-

tioned olefins form unstable titanacyclopropane interme-

diates, which cannot be transmetallated with the starting

Of the 1,3-dienes under study, viz., 1,4-diphenylbuta-

Scheme 7



Hydrocarbons with cumulated double bonds (for example, allenes) react with Et_2AlCl in THF in the presence of 5 mol.% of Cp_2TiCl_2 as the catalyst and Mg to produce unsaturated 1,2- and 1,4-dialuminum compounds **26** and **27** in a ratio of ~5 : 4 in a total yield of 75–80% ¹² (Scheme 8).

Scheme 8



R = Alk, Ph

In deuterolysis products of the reaction mixture, we found 1,2- and 1,4-dideuterated as well as monodeute-rated olefins (10-15%), which indicates that under the

R = Alk



m = 60—120, *n* = 1—6

reaction conditions used the process was accompanied by the side hydroalumination reaction. 10

The electron density distribution in the [60]fullerene molecule imparts properties¹³ typical of olefins. This gave promise that C_{60} could be successfully subjected to Cp_2TiCl_2 -catalyzed dialumination with Et_2AlCl . Actually, the reaction of [60]fullerene with an excess of Et_2AlCl (the molar ratio C_{60} : Al = 1 : (60-120), 5 mol.% of Cp_2TiCl_2 , a toluene—THF mixture as the solvent) in the presence of Mg as the acceptor of chloride ions afforded a mixture of bis(diethylaluminio)fullerenes (**28**) in 70–85% yields. Hydrolysis and deuterolysis of the reaction mixture revealed polyhydrofullerenes $C_{60}H_{2n}$ (**29**) and $C_{60}D_{2n}$ (**30**) (n = 1-6) (Scheme 9).

To examine the possibility of alumination of acetylenic hydrocarbons and to prepare previously unknown unsaturated 1,2-dialuminum compounds, we carried out the Cp₂TiCl₂-catalyzed reactions of Et₂AlCl with acetylenes. Using the reaction of diphenylacetylene with Et₂AlCl as an example, it was shown that the reaction in the presence of activated Mg and Cp₂TiCl₂ (the molar ratio PhC=CPh : Al : Mg : Ti = 10 : 20 : 12 : 0.5) in THF (8 h, ~20 °C) produced 1,2-bis(diethylaluminio)-1,2-diphenylethene (31a) in ~70% yield. Alumination involving dialkyl-substituted acetylenes (oct-4-yne, dec-5-yne) proceeded less selectively to give 1,2-dialkyl-1,2-bis(diethylaluminio)ethenes 31b,c, 1,2,3,4-tetraalkyl-1,4-bis(diethylaluminio)buta-1,3-dienes 32b,c, and hexasubstituted benzenes 33b,c in a ratio of ~6:1:3 in a total yield of 70-85% (Scheme 10).

The formation of compounds **32b,c** and **33b,c** can be accounted for by the most probable scheme involving the generation of "Cp₂Ti" from Cp₂TiCl₂ under the reaction conditions in the presence of activated magnesium (Scheme 11). The "Cp₂Ti" compound is coordinatively unsaturated, which facilitates the incorporation of a molecule of dialkyl-substituted acetylene into the coordination sphere of the titanium atom to give the titanacyclopropene intermediate.^{14–17} Transmetallation of the latter with the starting Et_2AlCl affords the target product 31. Unlike the bulky phenyl substituent, the alkyl substituents (Prⁿ, Buⁿ) do not hinder the addition of a new molecule of dialkyl-substituted acetylene at the Ti-C bond to form titanacyclopentadiene 36. The latter is transmetallated with the starting Et₂AlCl to give 1,4-dialuminiobuta-1,3-diene 32. Under the reaction conditions, titanacyclopentadiene 36 can involve one more molecule of dialkyl-substituted acetylene to yield hexasubstituted benzene 33 with elimination of reactive "Cp₂Ti."

With the aim of searching for the starting OAC, which are less pyrophoric than Et₂AlCl, to perform alumination of disubstituted acetylenes as well as for the purpose of synthesizing new types of N- and O-containing 1,2-dialuminioethenes, we studied the reactions of diphenylacetylene with bis(diethylamino)aluminum chloride and di(*n*-butoxy)aluminum chloride^{18,19} in the presence of Cp₂TiCl₂ and magnesium metal (THF as the solvent, 8 h, ~20 °C, the molar ratio R₂AlCl : PhC=CPh : Cp₂TiCl₂ = 25 : 10 : 0.5). Alumination of diphenylacetylene with the above-mentioned aluminum compounds afforded N- and



R = Prⁿ, Buⁿ

O-containing dialuminioethenes 37 and 38 in 65-70% yields (Scheme 12).

The results of our study demonstrated that 1,2-dialuminioethenes are formed by transmetallation of titanacyclopropene intermediates, which are generated *in situ*, with R_2AICl .¹⁴⁻¹⁷ We attempted to add an ethylene molecule at the active Ti-C bond of titanacyclopropenes with the aim of expanding the three-membered metallacycle and preparing *in situ* titanacyclopentene intermediates **39** under the reaction conditions. Transmetallation



of the latter with R₂AlCl could afford previously unknown substituted 1,4-dialuminiobut-1-enes **40** (Scheme 13). We chose ethylene because of its high coordinating ability and the fact that it can be easily generated²⁰ from 1,2-dichloroethane and dosed in an equimolar amount with respect to the starting acetylene.

We studied the reaction of Et_2AlCl with PhC=CPh in the presence of an excess of Mg and catalytic amounts (5 mol.%) of Cp₂TiCl₂ as the model process. 1,2-Dichloroethane was supplied to the reaction zone in THF in a mixture with an equimolar amount of acetylene during 6 h. Activated magnesium served as the acceptor of chloride ions thus facilitating the transformation of dichloroethane into ethylene. Under these conditions, 1,4-bis(diethyl-aluminio)-1,2-diphenylbut-1-ene (**41**) and 1,2-bis(diethylaluminio)-1,2-diphenylethylene (**31a**) were prepared in ~60 and ~10% yields, respectively (Scheme 14).

These results demonstrated that the controlled incorporation of ethylene at the Ti–C bond in the step of formation of titanacyclopropene intermediates provides a simple route for the synthesis of a new class of unsaturated aliphatic OAC, *viz.*, 1,2-dialkyl(phenyl)-1,4-dialuminiobut-1-enes, from disubstituted acetylenes and dialkylhaloalanes.







Experimental

The reactions with organometallic compounds were carried out under dry argon. The solvents were dried according to standard procedures and distilled immediately before use. The starting catalysts Cp₂ZrCl₂ and Cp₂TiCl₂ were prepared according to a known procedure.²¹ Commercially available 86% Et₂AlCl was purchased from the Redkinskii pilot-production plant (Russia). The deuterolysis products were analyzed by GLC on a Chrom-5 chromatograph (1200×3-mm column with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW, He as the carrier gas). The IR spectra were measured on an IR-75 spectrometer (films). The mass spectra were obtained on an MX-1306 mass spectrometer (70 eV, 200 °C). The ¹H and ¹³C NMR spectra were recorded on JEOL FX-90Q (90 and 22.5 MHz) and Bruker AM-300 (300 and 75 MHz) spectrometers in CDCl₃ with Me₄Si as the internal standard. The atomic numbering scheme used for the description of the ¹³C NMR spectra is shown in Scheme 15. The ¹³C NMR spectra of OAC were recorded on a JEOL FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance proton decoupling. Dilute solutions of OAC in THF with the addition of C₆D₁₂ for internal stabilization of the magnetic field were used. Solutions of OAC were placed in sealed tubes under dry argon. The yields of OAC were determined by GLC of hydrolysis products. The starting aluminum amides and alkoxides were prepared according to known procedures.^{18,19} Compounds 8, 9, 18, 25, 29, 30, 34a,b, 35b, and 42 were identified by comparing them with authentic samples.^{6,22–25}

Reactions of olefins with Et₂AlCl—Mg—[Ti, Zr] (general procedure). A magnesium powder (12 mmol), $Cp_2TiCl_2 (Cp_2ZrCl_2)$ (0.5 mmol), THF (10 mL), olefin (10 mmol), and Et₂AlCl (22 mmol) were placed in a glass reactor under a dry argon atmosphere at -5 °C. The reaction solution was warmed to 21-22 °C and stirred for 8 h. The reaction mixture was treated with a 10% DCl solution in D₂O. The products were extracted with Et₂O or hexane and isolated by distillation.

Reactions of acetylenes with $Et_2AlCl-Mg-[Ti, Zr]$ (general procedure). Under the conditions used in the reactions of olefins, acetylene (10 mmol) and Et_2AlCl (22 mmol) were added to a mixture of Cp_2TiCl_2 (Cp_2ZrCl_2) (0.5 mmol),

Mg (powder) (12 mmol), and THF (10 mL). The reaction solution was warmed to 21-22 °C and stirred for 8 h. Then the reaction mixture was treated with a 10% DCl solution in D₂O. The products were extracted with Et₂O or hexane and isolated by distillation.

Reaction of [60]fullerene with Et₂AlCl-Mg-[Ti, Zr] (general procedure). A solution of fullerene (0.025 mmol) in toluene (30 mL) was placed in a glass reactor under dry argon and the reaction mixture was stirred until C_{60} was completely dissolved. Then Cp₂TiCl₂ (0.0025 mmol) and Et₂AlCl (0.75 mmol) were added. The reaction mixture was stirred for 12 h, treated with 5% HCl or DCl, and passed through a column (silica gel L, 40/100 µm). The products were isolated by successive elution with toluene and MeOH.

1,2-Bis(diethylaluminio)-1-phenylethane (5). 13 C NMR, δ : 1.1 (t, C(7), C(9)); 8.7 (t, C(2)); 9.5 (q, C(8), C(10)); 18.3 (d, C(1)); 126.2 (d, C(6)); 128.0 (d, C(5)); 128.5 (d, C(4)); 137.0 (s, C(3)).

1,2-Bis(diethylaluminio)-*o*-tolylethane (13). ¹³C NMR, δ: 0.9 (br.t, C(10), C(12)); 8.9 (q, C(11), C(13)); 9.9 (br.t, C(2)); 18.2 (br.d, C(1)); 21.8 (q, C(9)); 126.5 (d, C(6)); 126.7 (d, C(7)); 128.3 (d, C(5)); 128.9 (d, C(8)); 138.1 (s, C(4)); 143.3 (s, C(3)).

1,2-Bis(diethylaluminio)-*p*-tolylethane (14). 13 C NMR, δ : 1.6 (br.t, C(8), C(10)); 9.1 (q, C(9), C(11)); 9.8 (br.t, C(2)); 18.5 (br.d, C(1)); 20.9 (q, C(7)); 128.0 (q, C(5)); 129.8 (d, C(4)); 133.4 (s, C(6)); 138.8 (s, C(3)).

1,2-Bis(diethylaluminio)-2-phenylpropane (15). ¹³C NMR, δ : 0.9 (br.t, C(8), C(10)); 9.0 (q, C(9), C(11)); 11.3 (br.t, C(2)); 21.0 (q, C(7)); 23.2 (s, C(1)); 126.6 (d, C(6)); 127.3 (d, C(4)); 128.3 (d, C(5)); 137.3 (s, C(3)).

1,2-Bis(diethylaluminio)-1,1-diphenylethane (16). ¹³C NMR, δ: 1.3 (br.t, C(7), C(9)); 9.1 (q, C(8), C(10)); 14.7 (br.t, C(2)); 45.6 (br.s, C(1)); 126.9 (d, C(6)); 127.3 (d, C(4)); 128.2 (d, C(5)); 145.2 (s, C(3)).

o-(1,2-Dideuterioethyl)toluene (17). B.p. $151-152 \, ^{\circ}C$, $n^{20}{}_{D}$ 1.5046. IR, v/cm⁻¹: 685, 745, 880, 1010, 1060, 1310, 1370, 1420, 1580, 2170, 2870, 3010, 3050. ¹H NMR, δ : 1.14 (d, 2 H, CH₂D, $J_{C,D}$ = 7.2 Hz); 2.24 (s, 3 H, Tol); 2.65 (t, 1 H, CHD, $J_{C,D}$ = 7.2 Hz); 7.02-7.24 (m, 5 H, CH arom.). ¹³C NMR, δ : 15.8 (t, C(9), $J_{C,D}$ = 19.5 Hz); 21.6 (q, C(7)); 31.2 (d, C(8), $J_{C,D}$ = 19.5 Hz); 126.5 (d, C(4)); 127.3 (d, C(5)); 128.9 (d, C(6)); 129.2 (d, C(3)); 136.7 (s, C(2)); 142.5 (s, C(1)).

(1,2-Dideuterioisopropyl)benzene (19). B.p. 64–65 °C (20 Torr), n^{20} _D 1.4926. IR, v/cm⁻¹: 700, 745, 880, 1010, 1450, 1490, 1590, 1610, 2165 (v_{C,D}), 2950, 3010, 3050. ¹H NMR, δ : 0.97 (m, 5 H, CDH₂, Me); 6.79–7.19 (m, 5 H, Ph). ¹³C NMR, δ : 23.8 (t, C(6), $J_{C,D}$ = 18.8 Hz); 24.1 (q, C(7)); 34.1 (s, C(5), $J_{C,D}$ = 18.8 Hz); 125.6 (d, C(4)); 127.5 (d, C(2)); 128.3 (d, C(3)); 141.3 (s, C(1)).

1,2-Dideuterio-1,1-diphenylethane (20). B.p. 139–140 °C (10 Torr), $n^{20}_{\rm D}$ 1.5756. IR, v/cm⁻¹: 700, 745, 880, 1010, 1450, 1490, 1590, 2165 (v_{C,D}), 2950, 3000. ¹³C NMR, δ : 21.0 (t, C(2), $J_{\rm C,D}$ = 19.1 Hz); 28.9 (s, C(1), $J_{\rm C,D}$ = 19.1 Hz); 125.9 (d, C(6)); 128.6 (d, C(4)); 129.0 (d, C(5)); 145.9 (s, C(3)).

1,2-Bis(*n***-butoxyaluminio)-1-phenylethane (21a).** ¹³C NMR, δ: 8.9 (br.t, C(2)); 13.9 (q, C(10), C(14)); 18.2 (br.d, C(1)); 19.1 (t, C(9), C(13)); 34.8 (t, C(8), C(12)); 64.8 (t, C(7), C(11)); 126.4 (d, C(6)); 127.0 (d, C(4)); 128.7 (d, C(5)); 137.1 (s, C(3)).

1,2-Bis(n-hexyloxyaluminio)-1-phenylethane (21b). ¹³C NMR, δ: 8.9 (br.t, C(2)); 14.1 (q, C(12), C(18)); 18.9



(br.d, C(1)); 22.9 (t, C(11), C(17)); 25.3 (t, C(9), C(15)); 31.8 (t, C(10), C(16)); 32.7 (t, C(8), C(14)); 64.9 (t, C(7), C(13)); 125.9 (d, C(6)); 126.3 (d, C(4)); 128.7 (d, C(5)); 137.1 (s, C(3)).

1,2-Bis[(diethylamino)alumino]-1-phenylethane (21c). ¹³C NMR, δ : 9.3 (br.t, C(2)); 15.0 (q, C(8), C(10)); 18.4 (br.d, C(1)); 43.8 (t, C(7), C(9)); 125.9 (d, C(6)); 127.0 (d, C(4)); 128.5 (d, C(5)); 137.2 (s, C(3)).

1,2-Bis[(dicyclohexylamino)aluminio]-1-phenylethane (21d). 13 C NMR, δ : 9.5 (br.t, C(2)); 19.0 (br.d, C(1)); 25.6 (t, C(9), C(13)); 26.9 (t, C(10), C(14)); 38.3 (t, C(8), C(12)); 54.3 (d, C(7), C(11)); 126.0 (d, C(6)); 127.3 (d, C(4)); 128.8 (d, C(5)); 137.1 (s, C(3)).

3,4-Bis(diethylaluminio)-1,4-diphenylbut-1-ene (24). ¹³C NMR, δ : 0.9 (br.t, C(13), C(15)); 8.9 (q, C(14), C(16)); 18.4 (br.d, C(1)); 24.1 (br.d, C(2)); 125.8 (d, C(12)); 126.2 (d, C(8)); 128.4 (d, C(7), C(11)); 128.2 (d, C(10)); 128.8 (d, C(6)); 128.9 (d, C(4)); 130.3 (d, C(3)); 137.7 (s, C(5)); 140.5 (s, C(9)).

1,2-Dideuterio[60]fullerene (30). MS of negative ions (325 °C, $E_e = 0 \text{ eV}$), $m/z (I_{rel} (\%))$: 720 [C₆₀] (100); 724 [C₆₀D₂] (8); 728 [C₆₀D₄] (14); 732 [C₆₀D₆] (28); 736 [C₆₀D₈] (16); 740 [C₆₀D₁₀] (12); 744 [C₆₀D₁₂] (24).

1,2-Bis(diethylaluminio)-1,2-diphenylethene (31a). ¹³C NMR, $\delta^*: 0.8$ (t, C(7)); 8.9 (q, C(1)); 127.0 (d, C(6)); 128.5 (d, C(4)); 128.7 (d, C(5)); 137.9 (s, C(3)).

Hexa(*n*-propyl)benzene (33b). B.p. 160 °C (1 Torr). IR, v/cm⁻¹: 710, 880, 1080, 1370, 1450, 1605, 2850, 2880, 2915, 2940. ¹H NMR, δ : 0.99 (t, 18 H, Me, J = 7.0 Hz); 1.25–1.70 (m, 12 H, CH₂); 2.30–2.53 (m, 12 H, CH₂). ¹³C NMR, δ : 13.8 (q, C(9)); 22.7 (t, C(8)); 29.1 (t, C(7)); 139.5 (s, C(1)–C(6)).

Hexa(*n*-butyl)benzene (33c). B.p. 185 °C (1 Torr). ¹H NMR, δ : 1.08 (t, 18 H, Me, J = 7.0 Hz); 1.23–1.75 (m, 24 H, CH₂); 2.39–2.57 (m, 12 H, CH₂–Ph). ¹³C NMR, δ : 14.1 (q, C(10)); 22.4 (t, C(9)); 32.5 (t, C(8)); 28.9 (t, C(7)); 139.5 (s, C(1)–C(6)).

cis-5,6-Dideuteriodec-5-ene (34c). B.p. 173 °C, n^{20}_{D} 1.4276. ¹H NMR, δ : 0.81 (t, 6 H, Me, J = 7.0 Hz); 1.25–1.40 (m, 8 H, CH₂); 1.98–2.09 (m, 4 H, CH₂C=). ¹³C NMR, δ : 14.1 (q, C(1)); 22.5 (t, C(2)); 26.9 (t, C(4)); 32.1 (t, C(3)); 129.6 (s, C(5), $J_{C,D}$ = 23.6 Hz).

5,8-Dideuterio-6,7-di(*n*-butyl)dodeca-5*E*,7*E*-diene (35c). B.p. 153 °C (8 Torr), n^{25}_{D} 1.4486. ¹H NMR, δ : 0.90 (m, 12 H, Me); 1.13–1.44 (m, 16 H, CH₂); 2.48–2.68 (m, 8 H, CH₂C=). ¹³C NMR, δ : 14.0 (q, C(1)); 14.2 (q, C(10)); 22.3 (t, C(2)); 23.2 (t, C(9)); 26.96 (t, C(4)); 27.02 (t, C(7)); 31.3 (t, C(3)); 32.2 (t, C(8)); 126.1 (d, C(5), J_{C,D} = 23.0 Hz); 141.4 (s, C(6)).

1,2-Bis[(diethylamino)aluminio]-1,2-diphenylethene (37). ¹³C NMR, δ:* 13.0 (q, C(8)); 41.9 (d, C(7)); 125.5 (d, C(6)); 126.6 (d, C(4)); 128.5 (d, C(5)); 137.7 (s, C(3)).

1,2-Bis[di(*n*-butoxy)aluminio]-1,2-diphenylethene (38). ¹³C NMR, δ :* 13.2 (q, C(10)); 22.8 (t, C(9)); 34.2 (t, C(8)); 64.6 (t, C(7)); 126.1 (d, C(6)); 127.8 (d, C(4)); 128.3 (d, C(5)); 137.9 (s, C(3)). This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-97903a and 02-03-97904a).

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^{*} The signals of C(1) and C(2) were not observed because of the quadrupole broadening of the carbon signals due to coupling with the ²⁷Al nuclei (I = 5/2).

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