Organometallic Chemistry

Synthesis and transformations of metallocycles

16.* Synthesis of a novel class of acyclic organoaluminum compounds, *threo*-2,3-disubstituted 1,4-dialumobutanes, with the use of zirconium catalysts

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A novel regio- and stereoselective method for synthesizing *threo*-2,3-disubstituted 1,4-dialumobutanes from α-olefins and haloalanes (Et_2AlCl, $(Et_2N)_2AlCl$, $(EtO)_2AlCl$, $Bu^i{}_2AlCl$) with the participation of catalytic amounts of Cp_2ZrCl_2 or $ZrCl_4$ in the presence of magnesium metal was developed. The products of hydrolysis and deuterolysis of the dialuminum compounds obtained have a *threo*-configuration. The selective transformations of 1,4-dialumobutanes to *trans*-3,4-disubstituted tetrahydrothiophenes, *trans*-1,2-disubstituted cyclobutanes, and disubstituted α,ω-dienes were found to be possible.

Key words: organoaluminum compounds, zirconacyclopentanes, zirconium catalysts, cycloalkanes, tetrahydrothiophenes, magnesium, olefins, alkoxides, amides.

To continue the development[2—5] of nontraditional methods for the synthesis of cyclic and acyclic organoaluminum compounds (OAC) in the presence of complex zirconium catalysts, we studied the reactions of α-olefins with dialkylaluminum chlorides (R_2AlCl), aluminum chloroalkoxides, and aluminum chloramides [$(RO)_2AlCl$, $(R_2N)_2AlCl$] in the presence of catalytic amounts of Cp_2ZrCl_2 or $ZrCl_4$ and magnesium metal as an acceptor of chloride ions.

We suggested that transmetallation of zirconacyclopentane intermediates formed *in situ*[6,7] from α-olefins, Cp_2ZrCl_2, and magnesium using dialkylaluminum chlorides may give 1,4-dialumobutanes (DAB) according to Scheme 1.

To verify this suggestion, we studied the reactions of Et_2AlCl or $Bu^i{}_2AlCl$ with α-olefins (1-hexene, 1-octene, 5-methyl-1-hexene, and allylbenzene) in the presence of metallic magnesium and 5 mol. % of Cp_2ZrCl_2 or $ZrCl_4$. The reactions were carried out in THF in an argon atmosphere at ambient temperature and a Mg : R_2AlCl : $R'CH=CH_2$ molar ratio of 1 : 2 : 2. We obtained DAB in 64—84 % yields (Scheme 2).

Disubstituted dialuminum compounds contain two chiral centers (C-2 and C-3) and can form diastereomer pairs. We analyzed[8] the DAB synthesized and the products of their hydrolysis or deuterolysis using ^{13}C NMR spectroscopy. We found that hydrolysis of OAC **1a—e** yields only one stereoisomer. A comparison of the chemical shifts of carbon atoms in the hydrolysis products with the previously determined[9] corresponding values for *erythro*- and *threo*-isomers of *vic*-dimethylalkanes

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* For Part 15, see Ref. 1.

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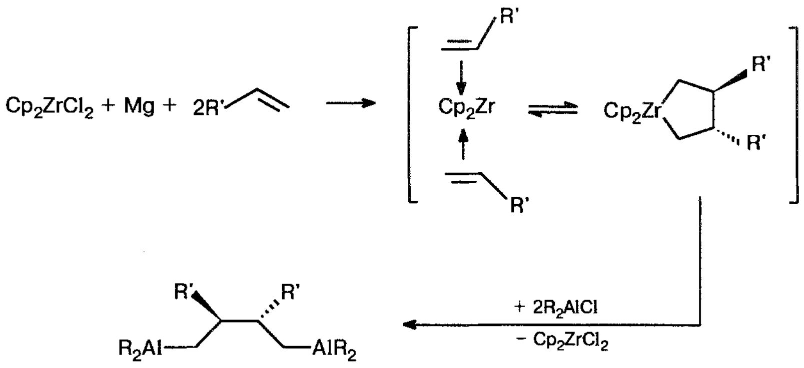
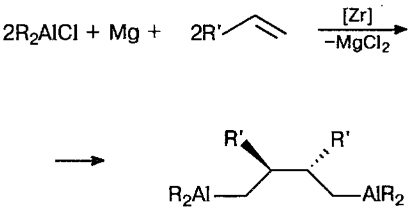
Scheme 1



Scheme 2



1a—e

a: R = Bu^i, R' = Bu^n
b: R = Et, R' = Am^i
c: R = Et, R' = Bu^n
d: R = Et, R' = Hex^n
e: R = Et, R' = PhCH$_2$

allowed us to unambiguously classify the DAB obtained as *threo*-stereoisomers.

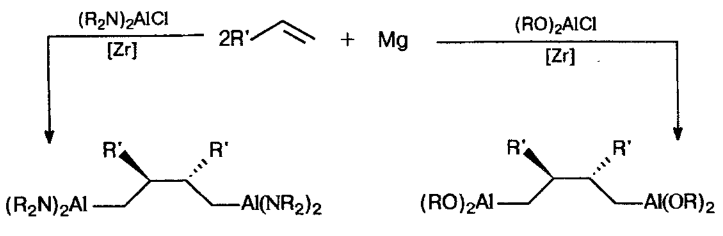
In addition to dialkylaluminum chlorides, we also reacted aluminum amides and alkoxides, prepared[10] *in situ* by the reaction of Et_2AlCl or $Bu^i{}_2AlCl$ with secondary amines or alcohols, with α-olefins. Under the optimal conditions chosen, the reactions gave the corresponding N- and O-containing DAB (**2** and **3**) in 60—78 % yields (Scheme 3). Along with Cp_2ZrCl_2, in this reaction we used the more readily available $ZrCl_4$.

In the absence of a zirconium catalyst, the above-mentioned reaction does not occur.

The reaction developed by us is general. We involved dialkylaluminum chlorides of various structures in it. As shown for dihexylaluminum chloride (Scheme 4), the latter can be synthesized by hydroalumination[11,12] of α-olefins by $Bu^i{}_2AlCl$ in the presence of Cp_2ZrCl_2 as a catalyst or by β-ethylation[13] of α-olefins using Et_2AlCl and catalytic amounts of $TiCl_4$.

To find the optimal conditions for preparing DAB, we studied the effects of the nature of the solvent, the concentration of the catalyst, the ratio between the starting monomers and reactants, and also the reaction conditions on the yield of OAC. We found that high yields of DAB are achieved when the reaction is conducted in THF. The replacement of THF by Et_2O results in a 20—30 % decrease in the yield of DAB. In hydrocarbon solvents this reaction does not occur. The highest selectivity of the formation of DAB is observed at a Zr : olefin : Mg ratio of

Scheme 3

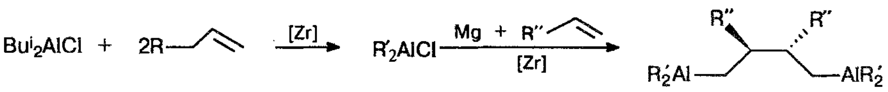


2a **3a—d**

a: R = Et, R' = Bu^n

a: R = R' = Bu^n
b: R = Bu^n, R' = Am^i
c: R = Bu^n, R' = Hex^n
d: R = Bu^n , R' = PhCH$_2$

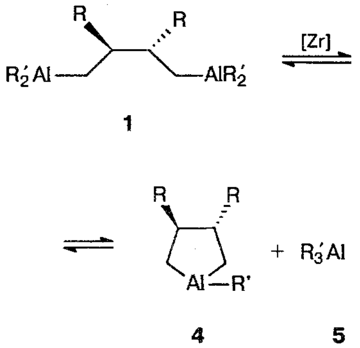
Scheme 4



1f

1f: R' = Hex, R'' = Bu^n

Scheme 5



3 : 200 : 100, when metallation is carried out at ~20 °C for 8 h.

Thus, the approach developed by us opens up a rather simple and effective one-step procedure for preparing a new class of dialuminum compounds directly from α-olefins and simple organoaluminum compounds with participation of available zirconium catalysts.

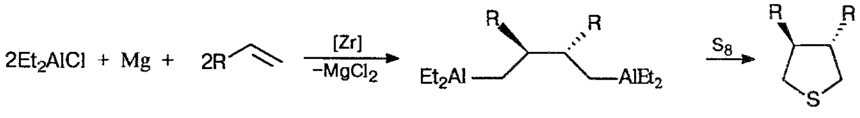
By analogy with substituted alumacyclopentanes,[14,15] we studied chemical transformations of the DAB obtained through the action of metal complex catalysts based on Cu, Zr, Ni, and Pd compounds. We have found that DAB react with elemental S (S_8) to give exclusively *trans*-3,4-disubstituted tetrahydrothiophenes, which is not typical of trialkylalanes. At the same time, trialkylalanes are known[8] to react with S_8 to give predominantly aluminum mercaptides. Therefore, we suppose that DAB **1** exist in an equilibrium with minor quantities of the corresponding alumacyclopentanes (**4**) and trialkylalanes (**5**) in the presence of zirconium complexes, according to Scheme 5.

Alumacyclopentanes **4** formed in this process react[15] with elemental sulfur (S_8) to give *trans*-3,4-disubstituted tetrahydrothiophenes. As the concentration of alumacyclopentanes **4** in the reaction mixture decreases, the equilibrium shifts to the right. Since DAB are involved in the reaction with elemental sulfur without their preliminary isolation from the reaction mixture, the general scheme of the formation of the molecules of tetrahydrothiophenes may be represented as follows (Scheme 6).

Like alumacyclopentanes, the DAB synthesized *in situ* are easily converted with high regio- and stereoselectivities into *trans*-1,2-disubstituted cyclobutanes (**7a—c**) through the action of allyl chloride (at an All—Cl : Al molar ratio of 3 : 1) and 5 mol. % of $Pd(acac)_2 + 2Ph_3P$ catalyst (Scheme 7).

When $Ni(acac)_2$ is used as the catalyst instead of the phosphine complex of palladium, the reaction occurs less selectively. In fact, the reaction of **1** with a threefold excess of allyl chloride or allyl acetate in the presence of a catalytic amount (3 mol. %) of freshly sublimated $Ni(acac)_2$ in Et_2O at 20 °C for 10 h followed by hydrolysis of the reaction mixture affords a mixture consisting of substituted cyclobutanes (**7a—c**) and alkenes (**8a—c**) in a ratio of (1 to 2.5) : 1 in 60—85 % overall yield (Scheme 8).

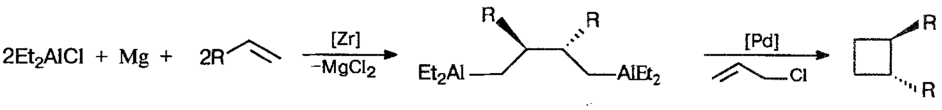
Scheme 6



6a—c

a: R = Bu^n (78 %); **b:** R = cyclohex-3-en-1-yl (70 %); **c:** R = $PhCH_2$ (62 %)

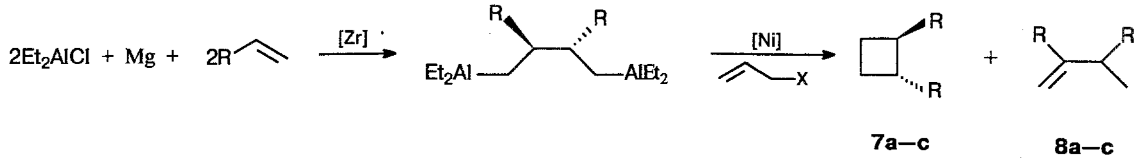
Scheme 7



7a—c

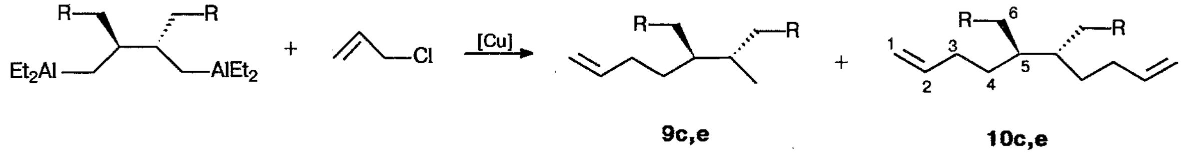
a: R = Bu^n (74 %); **b:** R = Am^i (71 %); **c:** R = $PhCH_2$ (65 %)

Scheme 8



a: R = Bu^n; **b:** R = Am^i; **c:** R = PhCH$_2$; X = Cl, OAc

Scheme 9



c: R = Pr^n; **e:** R = Ph

It may be assumed that methylenealkanes **8a—c** are formed through intramolecular β-hydride transfer of a hydrogen atom in the starting DAB with the participation of low-valent Ni complexes, similarly to the scheme that has been suggested for the transformation[16] of substituted alumacyclopentanes to 2-vinylalkanes.

The approach to the synthesis of *trans*-1,2-dialkyl substituted cyclobutanes from α-olefins and DAB in the presence of low-valent Ni or Pd complexes developed by us is now one of the most promising and effective techniques for preparing cyclobutanes of specified structures, along with the known methods of direct catalytic or photochemical 2π + 2π dimerization of olefins.

To elucidate the possibility of synthesizing α,ω-diolefins from OAC, we studied cross-coupling of DAB with allyl halides. Of the Fe, Co, Ni, Cu, Rh, and Pd based catalysts used, salts and complexes of copper (CuCl, CuBr, Cu(acac)$_2$ + 2Ph$_3$P) gave the best results. For example, the reaction of *threo*-2,3-dibutyl-1,4-bis-(diethylalumo)butane **1c** prepared *in situ* with a sixfold excess of allyl chloride in the presence of 3 mol. % CuCl at 25 °C affords a mixture of hydrocarbons that consists of *threo*-5,6-dibutylhept-1-ene (**9c**) and *threo*-5,6-dibutyldeca-1,9-diene (**10c**) in ~4 : 1 ratio in ~40 % overall yield (Scheme 9).

To increase the activity of OAC **1c,e** synthesized with respect to cross-coupling, we converted the latter into ate-complexes by mixing with BuLi at an Al : BuLi molar ratio of 1 : 1. In this case, the overall yield of cross-coupling products **9** and **10** was as high as 90 %. Allyl iodide reacts more selectively than allyl chloride under similar conditions and gives predominantly *threo*-5,6-dibutylhept-1-ene **9c**. We were not able to involve alkyl halides, for example Bu^{n}Cl, in the cross-coupling.

Thus, the study of the catalytic activation of the Al—C bond in cyclic and acyclic OAC in reactions with α-olefins with the aid of complex zirconium catalysts carried out in this work made it possible to develop a general method for the synthesis of *threo*-2,3-disubstituted 1,4-dialumobutanes. Based on the latter, nontraditional one-step procedures for preparing cyclobutanes, α,ω-dienes, or thiophanes in high yields have been suggested.

Experimental

The reactions were carried out in an atmosphere of dry argon. GLC analysis was carried out on a Khrom-41 chromatograph in an He flow using a 1200×3 mm column packed with 5 % SE-30 or 15 % PEG-6000 on Chromaton N-AW. Mixtures of compounds **7a—c** and **8a—c** were separated on a preparative-scale Perkin-Elmer F-21 chromatograph using a 5 m×8 mm column packed with 5 % SE-30 on Chromaton N-AW and He as the carrier gas (300 mL min^{-1}). IR spectra were recorded on a UR-20 spectrometer (film); mass spectra were obtained on an MKh-1306 spectrometer at 70 eV and 130 °C. The ^{1}H NMR spectra were run in CDCl$_3$ on a Tesla BS-567 spectrometer (100 MHz) using tetramethylsilane as the internal standard; ^{13}C NMR spectra were recorded in C$_6$D$_6$ on a Jeol FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance proton decoupling. The yields of alumacyclopentanes were determined by GLC analysis of the hydrolysis or deuterolysis products.

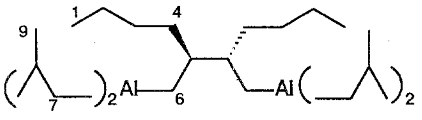
***threo*-2,3-Disubstituted 1,4-dialumobutanes.** *A.* At ~0 °C in a dry argon atmosphere, Cp$_2$ZrCl$_2$ (0.3 mmol), magnesium powder (10 mmol), α-olefin (20 mmol), THF (10 mL), and Et$_2$AlCl or Bu$^i_2$AlCl (20 mmol) were placed in a 50-mL glass reactor equipped with a magnetic stirrer. The temperature was increased to ~20 °C, and the mixture was stirred for 8 h.

B. THF (10 mL) and Et$_2$AlCl or Bu$^i_2$AlCl (20 mmol) were placed in a reactor under conditions similar to those used in procedure *A*. Diethylamine (40 mmol) was added with cooling, the temperature was increased to 35—40 °C, and the mixture was stirred for 1 h. Then Cp$_2$ZrCl$_2$ (0.3 mmol), magnesium powder (10 mmol), and the corresponding α-olefin (20 mmol) were added, and the mixture was stirred for 10 h.

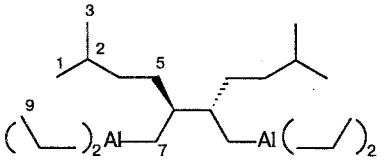
C. THF (10 mL) and Et_2AlCl or $Bu^i{}_2AlCl$ (20 mmol) were placed in a reactor under conditions similar to those used in procedure *A*. *n*-Butanol (40 mmol) was added dropwise with cooling, the temperature was increased to 35—40 °C, and the mixture was stirred for 1 h. Then the reactor was again cooled to ~20 °C, $ZrCl_4$ or Cp_2ZrCl_2 (0.3 mmol), magnesium powder (10 mmol), and the corresponding α-olefin (20 mmol) were added, and the mixture was stirred for 10 h. The ^{13}C NMR spectra of *threo*-2,3-disubstituted 1,4-dialumobutanes are presented in Table 1.

***trans*-3,4-Disubstituted tetrahydrothiophenes.** The DAB prepared in THF according to the above-described procedure were evacuated for 2 h, 35—40 mL of dry benzene was added under argon, and elemental sulfur (S_8 : Al—C = 3 : 1) was added in small portions. The temperature was brought to ~80 °C, and the mixture was stirred for 8 h, treated with 5 % HCl, and extracted with ether. The individual products were isolated by vacuum rectification. The isolated products **6a—c** were identified by comparison with authentic samples.[15]

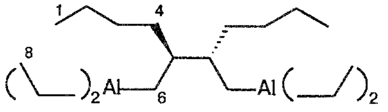
Table 1. ^{13}C NMR spectra of *threo*-2,3-disubstituted 1,4-dialumobutanes **1—4** (C_6D_6, tetramethylsilane as the internal standard)



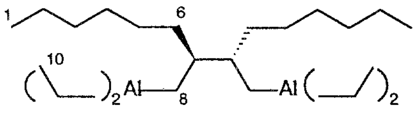
1a



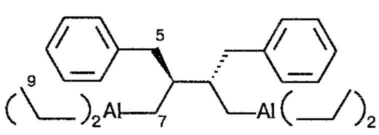
1b



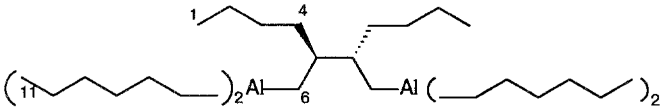
1c



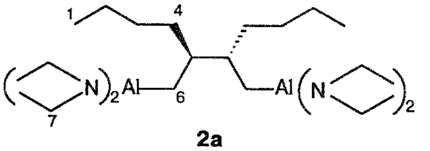
1d



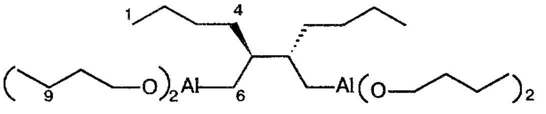
1e



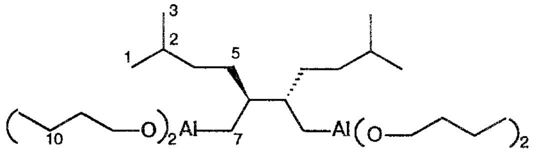
1f



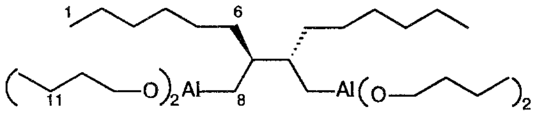
2a



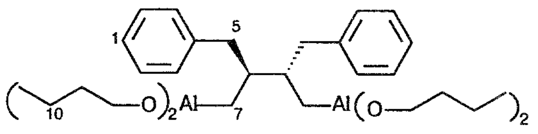
3a



3b



3c



3d

Com-	δ											
pound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
1a	14.48 q	23.28 t	31.22 t	36.97 t	38.63 d	9.15 t	19.54 t	25.18 d	26.10 q	26.22 q		
1b	23.39 q	29.48 d	23.53 q	36.82 t	38.21 t	46.36 d	11.60 t	1.70 t	10.53 q			
1c	14.35 q	23.36 t	33.07 t	36.76 t	38.66 d	9.06 t	1.30 t	9.88 q				
1d	14.39 q	23.30 t	32.78 t	30.61 t	28.35 t	38.80 t	45.83 d	11.50 t	1.65 t	10.04 q		
1e	125.82 d	128.91 d	129.37 d	144.41 s	45.91 t	47.97 d	1.22 t	10.46 q				
1f	15.18 q	23.82 t	31.12 t	38.90 t	46.30 d	12.26 t	10.17 t	25.92 t	37.06 t	32.95 t	23.57 t	15.04 q
2a	14.39 q	23.20 t	32.64 t	37.06 t	38.49 d	10.48 t	39.57 t	12.35 q				
3a	14.40 q	23.10 t	32.64 t	36.97 t	37.62 d	10.63 t	64.90 t	35.28 t	19.72 t	14.40 q		
3b	23.18 q	29.13 d	23.42 q	36.79 t	38.43 t	45.66 d	12.50 t	64.82 t	35.27 t	19.84 t	14.46 q	
3c	14.75 q	23.67 t	33.08 t	30.72 t	26.01 t	38.71 t	45.64 d	13.00 t	65.32 t	34.43 t	19.54 t	14.67 q
3d	126.04 d	127.84 d	129.78 d	143.34 s	44.97 t	46.90 d	12.50 t	64.90 t	35.13 t	19.40 t	14.23	

***trans*-3,4-Disubstituted cyclobutanes.** The DAB prepared in THF according to the above-described procedure were evacuated for 2 h and 35—40 mL of dry ether was added under argon. At −5 °C, allyl chloride in an All—Cl : Al—C = 3 : 1 ratio and then a two-component catalyst consisting of 0.5 mmol of $Pd(acac)_2$ and 1 mmol of Ph_3P were added. The temperature was brought to ~20 °C, and the mixture was stirred for 10 h. The reaction was accompanied by evolution of an equimolar amount of propylene. The reaction mixture was treated with 5 % HCl and extracted with ether. The individual products were isolated by vacuum rectification. The isolated products **7a—c** were identified by comparison with authentic samples.[14]

The use of $Ni(acac)_2$ instead of phosphine complex of palladium as a catalyst results in a mixture consisting of disubstituted cyclobutanes **7a—c** and methylenealkanes **8a—c**.

6-Methyl-5-methylenedecane (8a), yield 42 %, b.p. 72—74 °C (10 Torr). ^1H NMR, δ: 0.80—1.06 (m, 9 H, CH_3); 1.12—1.60 (m, 10 H, CH_2); 1.86—2.24 (m, 3 H, CH, CH_2); 4.70 (s, 2 H, $C=CH_2$). ^{13}C NMR, δ: 14.17 (q, C-1, C-10); 22.97 (t, C-2); 30.43 (t, C-3); 33.64 (t, C-4); 155.08 (s, C-5); 40.01 (d, C-6); 35.54 (t, C-7); 29.86 (t, C-8); 22.79 (t, C-9); 107.10 (t, C-11); 20.24 (q, C-12). MS, *m/z*: 168 $[M]^+$. Found (%): C, 85.68; H, 14.22. $C_{12}H_{24}$. Calculated (%): C, 85.71; H, 14.29.

2,6,9-Trimethyl-5-methylenedecane (8b), yield 35 %, b.p. 81—83 °C (2 Torr). ^1H NMR, δ: 0.86 (d, *J* = 6.6 Hz, 6 H, CH_3); 0.91 (d, *J* = 6.6 Hz, 6 H, CH_3); 1.05 (d, *J* = 7.6 Hz, 3 H, CH_3); 1.04—1.60 (m, 8 H, CH_2); 2.00—2.20 (m, 3 H, CH, CH_2); 4.70 (s, 2 H, $C=CH_2$). ^{13}C NMR, δ: 22.68 (q, C-1, C-10, C-11, C-14); 28.03 (d, C-2); 37.52 (t, C-3); 31.66 (t, C-4); 155.40 (s, C-5); 40.29 (d, C-6); 33.48 (t, C-7); 36.83 (t, C-8); 28.25 (d, C-9); 107.08 (t, C-12); 20.28 (q, C-13). IR, ν/cm^{-1}: 3070, 2945, 2920, 2860, 1630, 1470, 1385, 1360, 880. MS, *m/z*: 196 $[M]^+$. Found (%): C, 85.66; H, 14.23. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29.

2,3-Dibenzylbut-1-ene (8c), yield 24 %. ^1H NMR, δ: 1.04 (d, *J* = 6.7 Hz, 3 H, CH_3); 1.74—1.85 (m, *J* = 5.7 Hz, 2 H, CH_2); 2.30—2.50 (m, 1 H, CH); 2.81 (dd, *J* = 11.2 Hz, 2 H, CH_2); 4.78 (s, 1 H, $C=CH_2$); 4.99 (s, 1 H, $C=CH_2$); 7.12—7.40 (m, 10 H, Ph). ^{13}C NMR, δ: 110.67 (t, C-1); 153.66 (s, C-2); 40.56 (d, C-3); 19.51 (q, C-4); 42.06 (t, C-5); 141.14 (s, C-6); 129.10 (d, C-7, C-11); 128.15 (d, C-8, C-10); 125.63 (d, C-9); 42.61 (t, C-12); 139.93 (s, C-13); 129.16 (d, C-14, C-18); 129.19 (d, C-15, C-17); 125.86 (d, C-16). IR, ν/cm^{-1}: 3065, 2945, 2910, 2835, 1590, 1480, 1440, 900, 720, 690. MS, *m/z*: 236 $[M]^+$. Found (%): C, 91.42; H, 8.52. $C_{18}H_{20}$. Calculated (%): C, 91.53; H, 8.47.

Cross-coupling of 1,4-dialuminum compounds with allyl halides under the action of copper catalysts. An equimolar amount of BuLi (a hexane solution) was added to the DAB prepared by the above-described procedure. At −5 to 0 °C, the CuCl catalyst and allyl halide in an Al : Cu : All—Hal : R—All molar ratio of 20 : 0.3 : 60 : 20 were added. The reaction mixture was stirred for 6 h at ~20 °C. When the reaction was completed, the catalyzate was decomposed by 5 % HCl and extracted with ether, and the extract was dried with $MgSO_4$. After removal of the solvent the residue was distilled *in vacuo*.

***threo*-5,6-Di(*n*-butyl)hept-1-ene (9c),** yield 66 %. IR, ν/cm^{-1}: 3080, 2930, 2855, 1640, 1460, 1375, 990, 910. ^1H NMR, δ: 0.74—0.95 (m, 9 H, CH_3); 1.24 (m, 16 H, CH, CH_2); 1.88—2.18 (m, 2 H, CH_2); 4.88—5.08 (m, 3 H, $CH=CH_2$). ^{13}C NMR, δ: 113.9 (t, C-1); 139.6 (d, C-2); 30.9 (t, C-3); 32.4 (t, C-4); 41.8 (d, C-5); 34.3 (d, C-6); 15.5 (q, C-7); 34.3 (t, C-8); 30.2 (t, C-9); 23.1 (t, C-10); 14.2 (q, C-11); 33.7 (t, C-12); 29.3 (t, C-13); 23.1 (t, C-14); 14.2 (q, C-15). MS, *m/z*: 210 $[M]^+$. Found (%): C, 85.78; H, 14.21. $C_{15}H_{30}$. Calculated (%): C, 85.71; H, 14.29.

***threo*-5,6-Dibenzylhept-1-ene (9e),** yield 54 %. IR, ν/cm^{-1}: 3090, 3045, 2945, 2875, 1650, 1615, 1510, 1470, 1395, 1090, 1055, 1020, 935, 765. ^1H NMR, δ: 0.79—0.86 (m, 3 H, CH_3); 1.21—2.09 (m, 8 H, CH, CH_2); 2.52—2.58 (m, 2 H, $CH_2—C=$); 4.87—5.04 (m, 3 H, $CH=CH_2$); 7.03—7.17 (m, 10 H, Ph). ^{13}C NMR, δ: 114.3 (t, C-1); 138.7 (d, C-2); 31.9 (t, C-3); 37.5 (t, C-4); 40.20 (d, C-5); 43.7 (d, C-6); 14.5 (q, C-7); 42.7 (t, C-8); 141.4 (s, C-9); 128.9 (d, C-10); 128.0 (d, C-11); 125.5 (d, C-12); 128.0 (d, C-13); 128.9 (d, C-14); 40.3 (t, C-15); 141.4 (s, C-16); 128.9 (d, C-17); 128.0 (d, C-18); 125.5 (d, C-19); 128.0 (d, C-20); 128.9 (d, C-21). MS, *m/z*: 278 $[M]^+$. Found (%): C, 90.57; H, 9.21. $C_{21}H_{26}$. Calculated (%): C, 90.65; H, 9.35.

***threo*-5,6-Di(*n*-butyl)deca-1,9-diene (10c),** yield 20 %. IR, ν/cm^{-1}: 3095, 2985, 2940, 2870, 1640, 1470, 1010, 930. ^1H NMR, δ: 0.89 (t, 6 H, CH_3); 1.23 (m, 18 H, CH, CH_2); 1.84—2.18 (m, 4 H, CH_2); 4.88—6.02 (m, 6 H, $CH=CH_2$). ^{13}C NMR, δ: 114.08 (t, C-1); 139.48 (d, C-2); 32.37 (t, C-3); 30.38 (t, C-4); 38.96 (d, C-5); 30.21 (t, C-6); 30.08 (t, C-7); 23.14 (t, C-8); 14.17 (q, C-9). MS, *m/z*: 250 $[M]^+$. Found (%): C, 86.32; H, 13.58. $C_{18}H_{34}$. Calculated (%): C, 86.40; H, 13.60.

***threo*-5,6-Dibenzyldeca-1,9-diene (10e),** yield 18 %. IR, ν/cm^{-1}: 3090, 3045, 2945, 2875, 1650, 1610, 1510, 1465, 1390, 1090, 1055, 1020, 935, 765, 725. ^{13}C NMR, δ: 114.3 (t, C-1); 138.7 (d, C-2); 31.9 (t, C-3); 35.5 (t, C-4); 40.7 (d, C-5); 43.6 (t, C-6); 141.4 (s, C-7); 128.9 (d, C-8, C-11); 128.0 (d, C-9, C-12); 125.5 (d, C-10). MS, *m/z*: 318 $[M]^+$. Found (%): C, 90.48; H, 9.36. $C_{24}H_{30}$. Calculated (%): C, 90.57; H, 9.43.

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