Synthesis and transformations of metallacycles
38.* The Cp_2ZrCl_2-catalyzed cyclometallation of α,ω-diynes upon the action of RMgR´ or R_nAlCl_{3-n}

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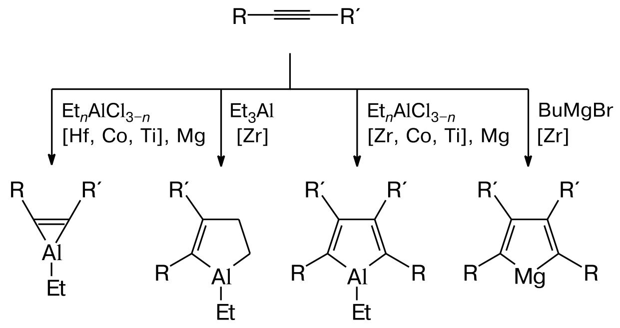
The Cp_2ZrCl_2-catalyzed cyclometallation of α,ω-alkadiynes upon the action of RMgR´ or R_nAlCl_{3-n} was accomplished to yield unsaturated di- and tricyclic (magnesa)aluminacarbocycles in up to 85% yield.

Key words: organoaluminum and -magnesium compounds, metallocomplex catalysis, aluminacyclopentadiene, magnesacyclopentadiene, diynes, cycloalumination, cyclomagnation.

It is known[2—6] that catalytic cyclometallation of alkynes with simple organoaluminum and -magnesium compounds in the presence of transition metal (Zr, Ti, Co, Hf) complexes is an efficient method for the synthesis of unsaturated three- and five-membered alumina- and magnesacarbocycles: aluminacyclopropenes, aluminacyclopent-2-enes, aluminacyclopenta-2,4-dienes, and magnesacyclopenta-2,4-dienes (Scheme 1).

Scheme 1



R = R´ = Me_3Si, Alk, Ar, $—(CH_2)_n—$;
R = H, Ph, Alk, Me_3Si, R´ = Ph, Alk; n = 0, 1;
[Zr] = Cp_2ZrCl_2, $(MeCp)_2ZrCl_2$, $ZrCl_4$; [Ti] = Cp_2TiCl_2;
[Hf] = Cp_2HfCl_2; [Co] = $CoCl_2$ + 2 Ph_3P, $Co(acac)_2$ + 2 Ph_3P

Despite the fact that cycloalumination of acetylenes was for the first time accomplished back in 1990 [2,7] and at the present time is widely used in the synthesis of carbo- and heterocyclic compounds,[8—12] as well as macrocyclic tetra- and polyketones,[13—15] until recently there was no literature information on catalytic cycloalumination or cyclomagnation of α,ω-diynes.

Meanwhile, accomplishment of these reactions, in our opinion, would have led to the development of efficient methods for the synthesis of new classes of bi-, tri-, or macrocyclic organoaluminum and -magnesium compounds, which are of practical interest in the development of one-pot methods for the synthesis of poorly available carbo- and heterocycles.

In continuation of the studies mentioned above, as well as for the study a possibility of running intra- and intermolecular cyclometallation of diacetylenes and synthesis of new classes of organoaluminum and -magnesium compounds, in the present work we for the first time attempted to accomplish catalytic cyclometallation of α,ω-diacetylenes using Cp_2ZrCl_2, as a catalyst precursor, which displays high catalytic activity and selectivity in cyclometallation of unsaturated compounds.[16—23]

We have chosen α,ω-bis(trimethylsilyl, methyl, phenyl)-diacetylenes as objects of our studies, as well as available Mg and Al alkyl and alkyl halide derivatives.

Initially, we studied a Cp_2ZrCl_2-catalyzed cycloalumination and cyclomagnation of α,ω-bis(trimethylsilyl)-diacetylenes, chosen as the model compounds, upon the action of alkylhaloalanes and Grignard reagents.

It was found that the reaction of 1,8-bis(trimethylsilyl)octa-1,7-diyne (**1b**) with $EtAlCl_2$ or $AlCl_3$ in the presence of 10 mol.% of Cp_2ZrCl_2 under developed conditions (diyne : $EtAlCl_2$: Mg : Cp_2ZrCl_2 = 10 : 40 : 80 : 1, 22 °C, THF, 24—72 h) results in the intramolecular cyclization at the two acetylene bonds of the alkadiyne molecule with the formation of 8-ethyl-7,9-bis(trimethylsilyl)-8-aluminabicyclo[4.3.$0^{1,6}$]nona-1(9),6(7)-diene (**2b´**) or 8-chloro-7,9-bis(trimethylsilyl)-8-aluminabicyclo-

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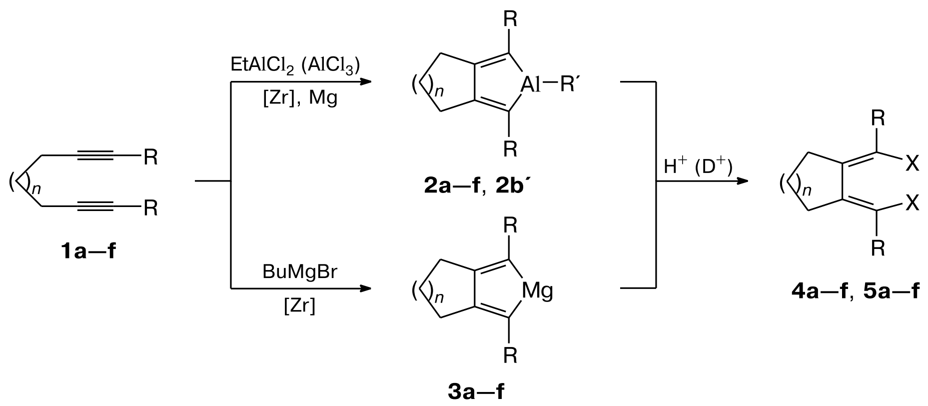
* For Part 37, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1607—1613, August, 2011.

Scheme 2



1—5	R	*n*	1—5	R	*n*	1—5	R	*n*
a	Me_3Si	1	**c**	Me_3Si	3	**e**	Me	2
b	Me_3Si	2	**d**	Me_3Si	4	**f**	Ph	2

R′ = Cl (**2a—f**), Et (**2b′**); X = H (**4a—f**), D (**5a—f**)

$[4.3.0^{1,6}]$nona-1(9),6(7)-diene (**2b**), respectively (Scheme 2). Subsequent acidic hydrolysis or deuterolysis of compounds **2b** and **2b′** furnished 1,2-bis(trimethylsilylmethylidene)cyclohexane (**4b**) and 1,2-bis(trimethylsilyldeuteromethylidene)cyclohexane (**5b**), respectively, in 79% yield.

Similar result was achieved in cycloalumination of 1,8-bis(trimethylsilyl)octa-1,7-diyne (**1b**) upon the action of Et_3Al in the presence of 5 mol.% of Cp_2ZrCl_2. Aluminacyclopentadiene **2b′** was formed in 34% yield instead of expected organoaluminum compound containing two aluminacyclopentene fragments in its structure (according to the results obtained earlier[2,3] on cycloalumination of disubstituted acetylenes).

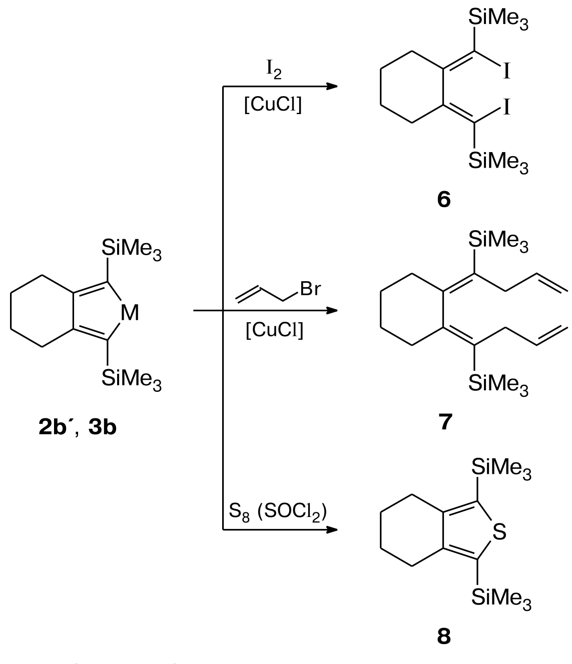
The reaction of diyne **1b** with RMgBr (R = Et, Bu) under conditions of catalytic cyclomagnation of disubstituted acetylenes[6] (diyne : RMgBr : Cp_2ZrCl_2 = 10 : 40 : 1, 22 °C, Et_2O) within 72 h led to 7,9-bis(trimethylsilyl)-8-magnesabicyclo$[4.3.0^{1,6}]$nona-1(9),6(7)-diene (**3b**) in 72% yield (see Scheme 2).

The structures of cyclic organometallic compounds (OMC) **2** and **3** were established based on one-dimensional (^{1}H, ^{13}C, Dept 135) and two-dimensional (HSQC, HMBC, and HH COSY) NMR spectra for the hydrolysis **4** and deuterolysis **5** products.

For example, the ^{13}C NMR spectrum of compound **4b** due to the symmetry of the molecule exhibits four signals at δ 161.57, 121.96, 34.51, and 26.66 corresponding to the molecular framework, as well as a high-field signal characteristic of the methyl groups at the Si atom (δ 0.13). For the partially deuterated compound **5b**, a triplet splitting of the signals for the carbon atoms of the double bond at δ 121.64 ($J_{C,D}$ = 23.0 Hz) was observed in the ^{13}C NMR spectrum, as well as disappearance of the downfield signal for the hydrogen atoms at the double bond in the ^{1}H NMR spectrum.

For more reliable confirmation of the structures of the synthesized metallacycles **2b** and **3b**, comparison of their relative reactivity in the cross-coupling and transmetallation reactions, as well as for the development of new one-pot methods for the synthesis of poorly available carbo- and heterocyclic compounds, we accomplished a number of transformations of compounds **2b** and **3b** involving I_2, allyl bromide and elementary sulfur (Scheme 3).

Scheme 3



M = AlEt (**2b′**), Mg (**3b**)

We showed that magnesacyclopentadiene **3b** quantitatively enter the iodonolysis reaction and cross-coupling with allyl bromide catalyzed with monovalent copper complexes to yield 1,2-bis(trimethylsilyliodomethylidene)cyclohexane (**6**) and 1,2-bis(trimethylsilylpropen-2-ylmethylidene)cyclohexane (**7**), respectively, whereas treatment of this compound with thionyl chloride at –40 °C or its reflux with S_8 in benzene according to procedures developed earlier[10] lead to 2,4-bis(trimethylsilyl)-3-thiabicyclo[4.3.$0^{1,5}$]nona-1(2),4(5)-diene (**8**) in 85 and 72% yields, respectively. It is possible that, due to the higher polarization of the Mg—C bond as compared to the Al—C bond, aluminacyclopentadiene **2b′** is considerably less active with respect to both I_2 (diiodine derivative **6** was obtained in 14% yield) and allyl bromide or elementary sulfur in the cross-coupling reactions (the yields of the corresponding compounds **7** and **8** were only 7 and 11%).

We also studied behavior of α,ω-bis(trimethylsilyl)diacetylenes **1a**,**c**,**d** with different distances between the triple bonds and diacetylenes **1e**,**f** with Me and Ph substituents at the triple bond in the cycloalumination and cyclomagnation reactions developed above. It was found that either decrease or increase in the number of methylene units binding the acetylene groups in the starting α,ω-diynes lead to a decrease in the yields of the target metallacycles **2** and **3** (Table 1).

Table 1. Catalytic cycloalumination and cyclomagnation of diacetylenes **1a**—**f**

Entry	Starting diacetylene	OMC	*t*/h	Yield of cyclic OMC* (%)
1	**1a**	$AlCl_3$	72	27 (**2a**)
2	**1a**	BuMgBr	72	14 (**3a**)
3	**1b**	$EtAlCl_2$	72	62 (**2b′**)
4	**1b**	Et_3Al	12	34 (**2b′**)
5	**1b**	$AlCl_3$	72	79 (**2b**)
6	**1b**	Bu_2Mg	72	53 (**3b**)
7	**1b**	BuMgBr	72	72 (**3b**)
8	**1b**	EtMgBr	72	44 (**3b**)
9	**1c**	$AlCl_3$	72	60 (**2c**)
10	**1c**	BuMgBr	72	39 (**3c**)
11	**1d**	$AlCl_3$	72	37 (**2d**)
12	**1d**	BuMgBr	72	25 (**3d**)
13	**1e**	$AlCl_3$	8	81 (**2e**)
14	**1e**	BuMgBr	72	42 (**3e**)
15	**1f**	$AlCl_3$	24	76 (**2f**)
16	**1f**	BuMgBr	72	10 (**3f**)

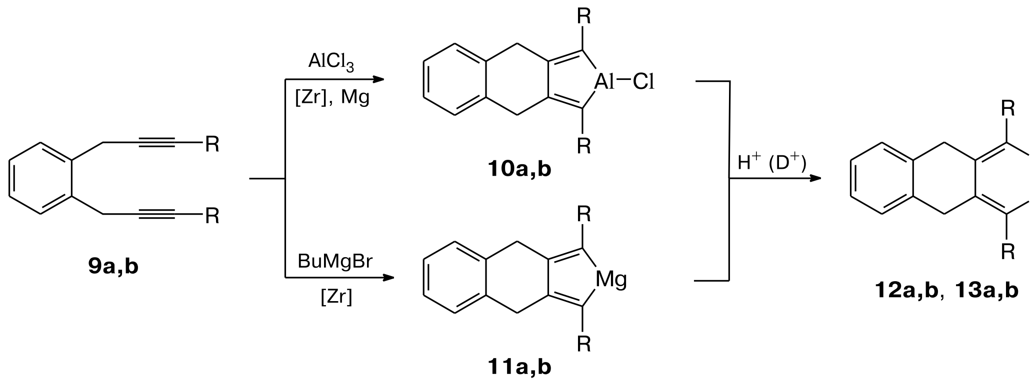
* Determined by GLC using products of acid hydrolysis.

Further, we found that under conditions developed above 1,2-(dihept-2-yn-1-yl)benzene (**9a**) and 1,2-bis(3-trimethylsilyl-2-propynyl)benzene (**9b**), like aliphatic α,ω-diynes, undergo catalytic cyclometallation upon the action of BuMgBr or $AlCl_3$ catalyzed with Cp_2ZrCl_2 (10 mol.%) to give the corresponding tricyclic (magnesa)aluminacarbocycles **10a** (61%), **10b** (54%), **11a** (31%), and **11b** (36%) (Scheme 4).

Taking into account our experimental and literature data, we suggested that bicyclic compounds **2** are formed by two possible pathways (Scheme 5). Thus, cycloalumination of α,ω-diynes using $EtAlCl_2$ or $AlCl_3$ (pathway *A*) assumes reduction of zirconocene dichloride with Mg to zirconocene **14**,[24] which, in turn, can coordinate two acetylene groups of the molecules of starting diyne to obtain the corresponding zirconacyclopentadiene intermediate **15**.[25] Transmetallation of the latter upon the action of Et_nAlCl_{3-n} (n = 0, 1) leads to compounds **2** with regeneration of Cp_2ZrCl_2.

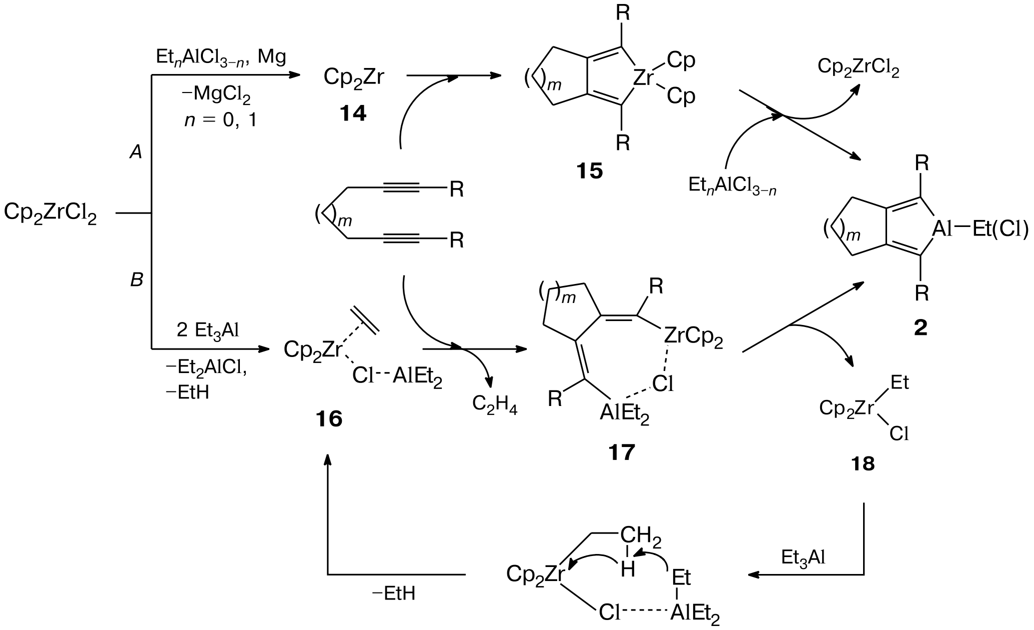
The second pathway *B*, which is realized when Et_3Al is used, is based on the suggestion on the initial formation of Zr,Al-bimetallic complex **16** during the reaction course,[26] which reacts with the diyne to form a seven-membered complex **17** with the bridged Zr—Cl—Al bond,[27—30] which is further transformed to the target bicyclic aluminacyclopentadienes **2** with the liberation of zirconocene ethyl chloride (**18**). The latter reacts with Et_3Al, that leads to the

Scheme 4



9—13: R = Bu (**a**), $SiMe_3$ (**b**); X = H (**12a,b**), D (**13a,b**)

Scheme 5



starting bimetallic complex **16** with elimination of Et—H[26] (see Scheme 5).

In conclusion, we for the first time showed that α,ω-diynes can be exclusively involved under developed by us conditions into intramolecular cyclometallation reaction with RMgR´ or R_nAlCl_{3-n} in the presence of Cp_2ZrCl_2 as a catalyst precursor to furnish unsaturated di- and tricyclic (magnesa)aluminacarbocycles in high yields.

Experimental

Chromatographic analysis was carried out on a Shimadzu GC-9A instrument using a 2000×2 mm column, silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm) was a stationary phase, helium was a carrier gas (30 mL min^{-1}), the temperature was programmed from 50 to 300 °C at 8 deg min^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$, chemical shifts are given relatively to Me_4Si. GLC-MS analysis of compounds were carried out on a Finnigan model 4021 instrument (a 50000×0.25 mm glass capillary column, HP-5 was a stationary phase, helium was a carrier gas, the temperature was programmed from 50 to 300 °C at 5 deg min^{-1}, the temperature of injector was 280 °C, the temperature of the source of ions was 250 °C, 70 eV). IR spectra were recorded on a Bruker VERTEX 70V IR Fourier-spectrometer in $CHCl_3$ or KBr pellets. Elemental analysis of the samples was accomplished on a Karlo Erba model 1106 elemental analyzer. The product yields were determined by GLC. Purity of the reaction products was monitored by chromatography on Silufol UV-254 plates, visualizing in iodine vapors. Reactions with organometallic compounds were carried out under dry argon. Solvents were dried and distilled before use. The catalyst Cp_2ZrCl_2 was synthesized according to the known procedure.[31] Commercially available Et_3Al and $EtAlCl_2$ (92%) were purchased from Redkinsk Experimental Factory, $AlCl_3$ from Acrus. Diynes **9a,b** were synthesized according to the procedure described earlier.[32,33]

Cyclomagnation of diacetylenes upon the action of RMgR´ (R = Bu, Et; R´ = Bu, Br) in the presence of a Cp_2ZrCl_2 catalyst (general procedure). Diacetylene **1a—f**, **9a,b** (1.0 mmol), dry Et_2O (10 mL), RMgR´ (4.0 mmol), and Cp_2ZrCl_2 (0.1 mmol) were sequentially placed into a glass reactor under dry argon at room temperature with stirring. The reaction mixture was stirred for 24—72 h (see Table 1). In order to identify the substituted magnesacyclopentadienes by their deuterolysis or hydrolysis products, the reaction mixture was treated with 5% DCl in D_2O or 5% aqueous HCl. The reaction products were extracted with diethyl ether or hexane, the extracts were dried with $MgSO_4$, the target compounds (**4**, **5**, **12**, **13**) were isolated by fractional distillation.

Cycloalumination of diacetylenes upon the action of Et_nAlCl_{3-n} (n = 0, 1) in the presence of a Cp_2ZrCl_2 catalyst (general procedure). Powdered Mg (8.0 mmol), dry THF (10 mL), diacetylene **1a—f**, **9a,b** (1.0 mmol), Cp_2ZrCl_2 (0.1 mmol), and Et_nAlCl_{3-n} (4.0 mmol) were sequentially placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to ambient and stirring was continued for 8—72 h (see Table 1). In order to identify substituted aluminacyclopentadienes by their deuterolysis or hydrolysis products, the reaction mixture was treated with 5% DCl in D_2O or 5% aq. HCl. The products were extracted with diethyl ether or hexane, dried with $MgSO_4$, the light fractions were evaporated *in vacuo*, the target compounds (**4**, **5**, **12**, **13**) were isolated by fractional distillation.

Cycloalumination of diacetylene 1b upon the action of Et_3Al in the presence of a Cp_2ZrCl_2 catalyst. Dry hexane (5 mL), diacetylene **1b** (1.0 mmol), Cp_2ZrCl_2 (0.1 mmol), and Et_3Al (3 mmol) were sequentially placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to ambient and stirring was continued for 12 h (see Table 1). In order to identify substituted aluminacyclopentadienes by their deuterolysis or hydrolysis products, the reaction mixture was treated with 5% DCl in D_2O or 5% aq. HCl. The products were extracted with diethyl ether or hexane, dried with $MgSO_4$, the light fractions were evaporated *in vacuo*, the target compounds (**4b**, **5b**) were isolated by fractional distillation.

1,2-Bis(trimethylsilylmethylidene)cyclopentane (4a). B.p. 76—78 °C (5 Torr). Found (%): C, 65.23; H, 10.97. $C_{13}H_{26}Si_2$. Calculated (%): C, 65.46; H, 10.99. IR, ν/cm^{-1}: 2910, 1710, 1450, 1230, 1060, 850, 750, 700. ^{1}H NMR, δ: 0.12 (s, 18 H, 6 CH_3); 1.57—1.62 (m, 2 H, CH_2); 2.39—2.49 (m, 4 H, 2 CH_2—C=); 5.87 (s, 2 H, 2 CH). ^{13}C NMR, δ: 0.21 (C(8), C(9), C(10), C(11), C(12), C(13)); 23.93 (C(4)); 32.93 (C(3), C(5)); 116.87 (C(6), C(7)); 157.72 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 238.

1,2-Bis(trimethylsilylmethylidene)cyclohexane (4b). B.p. 89—91 °C (5 Torr). Found (%): C, 66.31; H, 11.16. $C_{14}H_{28}Si_2$. Calculated (%): C, 66.58; H, 11.18. IR, ν/cm^{-1}: 2940, 1700, 1450, 1250, 1100, 1000, 850, 750, 700, 650. ^{1}H NMR, δ: 0.12 (s, 18 H, 6 CH_3); 1.58—1.65 (m, 4 H, 2 CH_2); 2.26—2.36 (m, 4 H, 2 CH_2—C=); 5.48 (s, 2 H, 2 CH). ^{13}C NMR, δ: 0.13 (C(9), C(10), C(11), C(12), C(13), C(14)); 26.66 (C(4), C(5)); 34.51 (C(3), C(6)); 121.96 (C(7), C(8)); 161.57 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 252.

1,2-Bis(trimethylsilylmethylidene)cycloheptane (4c). B.p. 68—70 °C (1 Torr). Found (%): C, 67.31; H, 11.32. $C_{15}H_{30}Si_2$. Calculated (%): C, 67.58; H, 11.34. IR, ν/cm^{-1}: 2920, 1720, 1450, 1250, 1100, 1075, 1050, 920, 850, 760, 700. ^{1}H NMR, δ: 0.14 (s, 18 H, 6 CH_3); 1.55—1.61 (m, 6 H, 3 CH_2); 2.41 (m, 4 H, 2 CH_2—C=); 5.72 (s, 2 H, 2 CH). ^{13}C NMR, δ: 0.21 (C(10), C(11), C(12), C(13), C(14), C(15)); 29.73 (C(4), C(6)); 31.4 (C(5)); 34.36 (C(3), C(7)); 124.11 (C(8), C(9)); 163.13 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 266.

1,2-Bis(trimethylsilylmethylidene)cyclooctane (4d). B.p. 86—88 °C (1 Torr). Found (%): C, 68.25; H, 11.47. $C_{16}H_{32}Si_2$. Calculated (%): C, 68.49; H, 11.49. IR, ν/cm^{-1}: 2920, 1710, 1450, 1250, 1100, 1050, 850, 770, 700, 650. ^{1}H NMR, δ: 0.14 (s, 18 H, 6 CH_3); 1.53—1.61 (m, 8 H, 4 CH_2); 2.23 (t, 4 H, 2 CH_2—C=, J = 7.2 Hz); 5.34 (s, 2 H, 2 CH). ^{13}C NMR, δ: 0.16 (C(11), C(12), C(13), C(14), C(15), C(16)); 26.78 (C(4), C(7)); 28.20 (C(5), C(6)); 34.92 (C(3), C(8)); 123.23 (C(9), C(10)); 161.39 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 280.

1,2-Bis(ethylidene)cyclohexane (4e). B.p. 84—85 °C (40 Torr). Found (%): C, 87.96; H, 11.82. $C_{10}H_{16}$. Calculated (%): C, 88.16; H, 11.84. IR, ν/cm^{-1}: 1650, 900, 800. ^{1}H NMR, δ: 1.56 (d, 6 H, 2 CH_3, J = 8 Hz); 1.46—2.40 (m, 8 H, 4 CH_2); 5.20—5.45 (m, 2 H, 2 CH). ^{13}C NMR, δ: 13.95 (C(8), C(10)); 26.50 (C(4), C(5)); 28.73 (C(3), C(6)); 116.05 (C(7), C(9)); 142.50 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 136.

1,2-Bis(phenylmethylidene)cyclohexane (4f). R_f 0.52 (SiO_2, pentane—benzene (7 : 1)). Found (%): C, 92.06; H, 7.72. $C_{20}H_{20}$. Calculated (%): C, 92.26; H, 7.74. IR, ν/cm^{-1}: 3050, 2850, 1450, 930, 850, 700. ^{1}H NMR, δ: 1.68 (m, 4 H, 2 CH_2); 2.65 (m, 4 H, 2 CH_2); 6.65 (s, 2 H, 2 CH); 7.27 (m, 4 H, Ph); 7.33 (m, 6 H, Ph). ^{13}C NMR, δ: 26.29 (C(4), C(5)); 29.99 (C(3), C(6)); 124.15 (C(7), C(14)); 128.07 (C(9), C(13), C(16), C(20)); 129.49 (C(10), C(12), C(17), C(19)); 138.01 (C(8), C(15)); 144.50 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 260.

1,2-Bis(trimethylsilyldeuteromethylidene)cyclopentane (5a). B.p. 75—77 °C (5 Torr). Found (%): C, 64.79; H + D, 11.67. $C_{13}H_{24}D_2Si_2$. Calculated (%): C, 64.92; H, 10.06; D, 1.67. IR, ν/cm^{-1}: 2210 (C—D), 2171 (C—D). ^{1}H NMR, δ: 0.12 (s, 18 H, 6 CH_3); 1.57—1.64 (m, 2 H, CH_2); 2.41—2.49 (m, 4 H, 2 CH_2—C=). ^{13}C NMR, δ: 0.21 (C(8), C(9), C(10), C(11), C(12), C(13)); 23.95 (C(4)); 32.93 (C(3), C(5)); 116.56 (t, C(6), C(7), J = 24.5 Hz); 157.70 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 240.

1,2-Bis(trimethylsilyldeuteromethylidene)cyclohexane (5b). B.p. 89—92 °C (5 Torr). Found (%): C, 65.91; H + D, 11.74. $C_{14}H_{26}D_2Si_2$. Calculated (%): C, 66.06; H, 10.30; D, 1.58. IR, ν/cm^{-1}: 2165 (C—D). ^{1}H NMR, δ: 0.12 (s, 18 H, 6 CH_3); 1.55—1.64 (m, 4 H, 2 CH_2); 2.24—2.37 (m, 4 H, 2 CH_2—C=). ^{13}C NMR, δ: 0.13 (C(9), C(10), C(11), C(12), C(13), C(14)); 26.63 (C(4), C(5)); 34.52 (C(3), C(6)); 121.64 (t, C(7), C(8), J = 23.0 Hz); 161.54 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 254.

1,2-Bis(trimethylsilyldeuteromethylidene)cycloheptane (5c). B.p. 68—70 °C (1 Torr). Found (%): C, 67.01; H + D, 11.84. $C_{15}H_{28}D_2Si_2$. Calculated (%): C, 67.08; H, 10.51; D, 1.50. IR, ν/cm^{-1}: 2212 (C—D), 2167 (C—D). ^{1}H NMR, δ: 0.13 (s, 18 H, 6 CH_3); 1.57—1.63 (m, 6 H, 3 CH_2); 2.40—2.45 (m, 4 H, 2 CH_2—C=). ^{13}C NMR, δ: 0.22 (C(10), C(11), C(12), C(13), C(14), C(15)); 29.71 (C(4), C(6)); 31.4 (C(5)); 34.37 (C(3), C(7)); 124.11 (t, C(8), C(9), J = 23.5 Hz); 163.15 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 268.

1,2-Bis(trimethylsilyldeuteromethylidene)cyclooctane (5d). B.p. 86—89 °C (1 Torr). Found (%): C, 67.92; H + D, 11.87. $C_{16}H_{30}D_2Si_2$. Calculated (%): C, 68.00; H, 10.70; D, 1.42. IR, ν/cm^{-1}: 2211 (C—D), 2160 (C—D). ^{1}H NMR, δ: 0.13 (s, 18 H, 6 CH_3); 1.53—1.64 (m, 8 H, 4 CH_2); 2.22 (t, 4 H, 2 CH_2—C=, J = 7.2 Hz). ^{13}C NMR, δ: 0.16 (C(11), C(12), C(13), C(14), C(15), C(16)); 26.77 (C(4), C(7)); 28.21 (C(5), C(6)); 34.92 (C(3), C(8)); 122.95 (t, C(9), C(10), J = 24.0 Hz); 161.37 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 282.

1,2-Bis(1-deuteroethylidene)cyclohexane (5e). B.p. 84—86 °C (40 Torr). Found (%): C, 86.67; H + D, 13.09. $C_{10}H_{14}D_2$. Calculated (%): C, 86.88; H, 10.21; D, 2.91. IR, ν/cm^{-1}: 2165 (C—D). ^{1}H NMR, δ: 1.54 (s, 6 H, 2 CH_3); 1.45—2.42 (m, 8 H, 4 CH_2). ^{13}C NMR, δ: 13.97 (C(8), C(10)); 26.51 (C(4), C(5)); 28.73 (C(3), C(6)); 115.79 (t, C(7), C(9), J = 23.5 Hz); 142.52 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 138.

1,2-Bis(phenyldeuteromethylidene)cyclohexane (5f). R_f 0.52 (SiO_2, pentane—benzene (7 : 1)). Found (%): C, 91.36; H + D, 8.38. $C_{20}H_{18}D_2$. Calculated (%): C, 91.55; H, 6.91; D, 1.53. IR, ν/cm^{-1}: 2165 (C—D). ^{1}H NMR, δ: 1.68 (m, 4 H, 2 CH_2); 2.64 (m, 4 H, 2 CH_2); 7.26 (m, 4 H, Ph); 7.35 (m, 6 H, Ph). ^{13}C NMR, δ: 26.28 (C(4), C(5)); 29.97 (C(3), C(6)); 123.88 (t, C(7), C(14), J = 24.5 Hz); 128.06 (C(9), C(13), C(16), C(20)); 129.49 (C(10), C(12), C(17), C(19)); 138.01 (C(8), C(15)); 144.51 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 262.

2,3-Dipentylidene-1,4-dihydronaphthalene (12a). R_f 0.49 (SiO_2, pentane—benzene (10 : 1)). Found (%): C, 89.29; H, 10.49. $C_{20}H_{28}$. Calculated (%): C, 89.49; H, 10.51. IR, ν/cm^{-1}: 3020, 2950, 1450, 920, 860, 695. ^{1}H NMR, δ: 1.04 (t, 6 H, 2 CH_3, J = 7.0 Hz); 1.36—1.57 (m, 8 H, 4 CH_2); 2.26 (q, 4 H, 2 CH_2, J = 7.2 Hz); 3.63 (s, 4 H, 2 CH_2); 5.78 (t, 2 H, 2 CH, J = 7.6 Hz); 7.24 (s, 4 H, 4 CH). ^{13}C NMR, δ: 14.22 (C(15), C(20)); 22.52 (C(14), C(19)); 27.83 (C(12), C(17)); 32.04 (C(13), C(18)); 32.68 (C(1), C(4)); 122.81 (C(11), C(16)); 126.06 (C(7), C(8)); 127.69 (C(6), C(9)); 136.67 (C(2), C(3)); 137.02 (C(5), C(10)). MS (EI, 70 eV), *m/z*: 268.

2,3-Bis(trimethylsilylmethylidene)-1,4-dihydronaphthalene (12b). R_f 0.52 (SiO_2, pentane—benzene (10 : 1)). Found (%): C, 71.72; H, 9.37. $C_{18}H_{28}Si_2$. Calculated (%): C, 71.92; H, 9.39.

IR, ν/cm^{-1}: 3050, 2954, 1450, 922, 890 (Si(CH$_3$)$_3$), 860. ^{1}H NMR, δ: 0.05 (s, 18 H, 6 CH$_3$); 2.25 (s, 4 H, 2 CH$_2$); 7.42 (s, 2 H, 2 CH); 7.19—7.41 (m, 2 H, C$_6$H$_4$); 7.59—7.74 (m, 2 H, C$_6$H$_4$). ^{13}C NMR, δ: –1.34 (C(12), C(13), C(14), C(16), C(17), C(18)); 24.55 (C(1), C(4)); 124.26 (C(7), C(8)); 126.06 (C(11), C(15)); 126.59 (C(6), C(9)); 131.55 (C(5), C(10)); 137.05 (C(2), C(3)). MS (EI, 70 eV), *m/z*: 300.

2,3-Di(1-deuteropentylidene)-1,4-dihydronaphthalene (13a). *R*$_f$ 0.48 (SiO$_2$, pentane—benzene (10 : 1)). Found (%): C, 88.67; H + D, 11.27. C$_{20}$H$_{26}$D$_2$. Calculated (%): C, 88.82; H, 9.69; D, 1.49. IR, ν/cm^{-1}: 2210 (C—D), 2164 (C—D). ^{1}H NMR, δ: 1.03 (t, 6 H, 2 CH$_3$, *J* = 7.0 Hz); 1.36—1.55 (m, 8 H, 4 CH$_2$); 2.24 (t, 4 H, 2 CH$_2$, *J* = 7.2 Hz); 3.62 (s, 4 H, 2 CH$_2$); 7.26 (s, 4 H, 4 CH). ^{13}C NMR, δ: 14.21 (C(15), C(20)); 22.53 (C(14), C(19)); 27.83 (C(12), C(17)); 32.05 (C(13), C(18)); 32.68 (C(1), C(4)); 122.57 (t, C(11), C(16), *J* = 24.0 Hz); 126.06 (C(7), C(8)); 127.68 (C(6), C(9)); 136.67 (C(2), C(3)); 137.01 (C(5), C(10)). MS (EI, 70 eV), *m/z*: 270.

2,3-Bis(trimethylsilyldeuteromethylidene)-1,4-dihydronaphthalene (13b). *R*$_f$ 0.52 (SiO$_2$, pentane—benzene (10 : 1)). Found (%): C, 71.34; H + D, 9.98. C$_{18}$H$_{26}$D$_2$Si$_2$. Calculated (%): C, 71.45; H, 8.66; D, 1.33. IR, ν/cm^{-1}: 2210 (C—D), 2164 (C—D). ^{1}H NMR, δ: 0.05 (s, 18 H, 6 CH$_3$); 2.24 (s, 4 H, 2 CH$_2$); 7.19—7.38 (m, 2 H, C$_6$H$_4$); 7.59—7.68 (m, 2 H, C$_6$H$_4$). ^{13}C NMR, δ: –1.32 (C(12), C(13), C(14), C(16), C(17), C(18)); 24.55 (C(1), C(4)); 124.26 (C(7), C(8)); 125.82 (t, C(11), C(15), *J* = 24.0 Hz); 126.58 (C(6), C(9)); 131.55 (C(5), C(10)); 137.02 (C(2), C(3)). MS (EI, 70 eV), *m/z*: 302.

1,2-Bis(trimethylsilyliodomethylidene)cyclohexane (6). Reaction mixtures obtained by the procedures described above and containing 8-ethyl-7,9-bis(trimethylsilyl)-8-aluminabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**2b´**) or 7,9-bis(trimethylsilyl)-8-magnesabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**3b**) were cooled to 0 °C, followed by addition of CuCl (0.11 mmol) and a dropwise addition of the ethereal solution of I$_2$ (4.2 mmol). The temperature was raised to ambient and the mixture was stirred for 10 h. Then, hexane and 7—10% aq. HCl were added. The organic layer was separated, treated with aq. Na$_2$S$_2$O$_3$, and dried with MgSO$_4$. The reaction product **6** was isolated by vacuum distillation. *R*$_f$ 0.39 (SiO$_2$, pentane). Found (%): C, 33.14; H, 5.18. C$_{14}$H$_{26}$I$_2$Si$_2$. Calculated (%): C, 33.34; H, 5.20. IR, ν/cm^{-1}: 2930 (cyclohexane), 1600 (C=C), 1450 (cyclohexane), 840, 745 (Si(CH$_3$)$_3$), 620, 490, 450 (C—I). ^{1}H NMR, δ: 0.32 (s, 18 H, 6 CH$_3$); 1.26—1.53 (m, 4 H, 2 CH$_2$); 2.17—2.88 (m, 4 H, 2 CH$_2$—C=). ^{13}C NMR, δ: 0.39 (C(9), C(10), C(11), C(12), C(13), C(14)); 29.12 (C(4), C(5)); 36.44 (C(3), C(6)); 107.00 (C(7), C(8)); 165.94 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 504.

1,2-Bis(trimethylsilylpropen-2-ylmethylidene)cyclohexane (7). Reaction mixtures obtained by the procedures described above and containing 8-ethyl-7,9-bis(trimethylsilyl)-8-aluminabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**2b´**) or 7,9-bis(trimethylsilyl)-8-magnesabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**3b**) were cooled to –20 °C, followed by addition of CuCl (0.1 mmol) and slow dropwise addition of allyl bromide (4.5 mmol). The temperature was elevated to ambient and the reaction mixture was stirred for 6 h, treated with 7—10% aq. HCl, the reaction product was extracted with hexane, dried with MgSO$_4$, and isolated by distillation. B.p. 125—127 °C (1 Torr). Found (%): C, 72.01; H, 10.71. C$_{20}$H$_{36}$Si$_2$. Calculated (%): C, 72.21; H, 10.91. IR, ν/cm^{-1}: 3078, 2978, 1635, 1260, 913, 890 (Si(CH$_3$)$_3$), 820, 760. ^{1}H NMR, δ: 0.19 (s, 18 H, 6 CH$_3$); 1.46—1.58 (m, 2 H, C(4)H$_a$, C(5)H$_a$); 1.89—1.92 (m, 2 H, C(4)H$_b$, C(5)H$_b$); 2.00—2.06 (m, 2 H, C(3)H$_a$, C(6)H$_a$); 2.55—2.61 (m, 2 H, C(8)H$_a$, C(12)H$_a$); 2.66—2.69 (m, 2 H, C(3)H$_b$, C(6)H$_b$); 2.92—2.98 (m, 2 H, C(8)H$_b$, C(12)H$_b$); 4.88—4.95 (m, 4 H, 2 CH$_2$); 5.68—5.75 (m, 2 H, 2 CH—C=). ^{13}C NMR, δ: 0.92 (C(15), C(16), C(17), C(18), C(19), C(20)); 29.81 (C(4), C(5)); 36.88 (C(8), C(12)); 38.16 (C(3), C(6)); 114.06 (C(10), C(14)); 126.66 (C(7), C(11)); 138.42 (C(9), C(13)); 155.04 (C(1), C(2)). MS (EI, 70 eV), *m/z*: 332.

2,4-Bis(trimethylsilyl)-3-thiabicyclo[4.3.0^{1,5}]nona-1(2),4(5)-diene (8). ***A.*** A reaction mixture obtained by the procedure described above and containing 8-ethyl-7,9-bis(trimethylsilyl)-8-aluminabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**2b´**) or 7,9-bis(trimethylsilyl)-8-magnesabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**3b**) were cooled to –20 °C, followed by addition of S$_8$ (4.8 mmol) in benzene (10 mL). The reaction mixture was stirred for 8 h at 40 °C, then treated with 7—10% aq. HCl, the reaction product was extracted with hexane, dried with MgSO$_4$, and isolated by vacuum distillation. *R*$_f$ 0.54 (SiO$_2$, pentane—benzene (6 : 1)). Found (%): C, 59.30; H, 9.25. C$_{14}$H$_{26}$SSi$_2$. Calculated (%): C, 59.50; H, 9.27. IR, ν/cm^{-1}: 1490, 1450, 1410 (thiophene ring), 890, 790 (Si(CH$_3$)$_3$). ^{1}H NMR, δ: 0.33 (s, 18 H, 6 CH$_3$); 1.50—1.60 (m, 4 H, 2 CH$_2$); 2.18 (m, 4 H, 2 CH$_2$—C=). ^{13}C NMR, δ: 0.55 (C(10), C(11), C(12), C(13), C(14), C(15)); 31.11 (C(7), C(8)); 39.14 (C(6), C(9)); 137.08 (C(2), C(4)); 146.93 (C(1), C(5)). MS (EI, 70 eV), *m/z*: 282.

B. A reaction mixture obtained by the procedure described above and containing 8-ethyl-7,9-bis(trimethylsilyl)-8-aluminabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**2b´**) or 7,9-bis(trimethylsilyl)-8-magnesabicyclo[4.3.0^{1,6}]nona-1(9),6(7)-diene (**3b**) was cooled to –40 °C, followed by a dropwise addition SOCl$_2$ (2.4 mmol). The temperature was raised to ambient, and the reaction mixture was stirred for 8 h and treated with 7—10% aq. HCl. The reaction product was extracted with hexane, dried with MgSO$_4$, and isolated by vacuum distillation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00046) and the Russian Science Support Foundation.

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Received July 20, 2010;
in revised form January 31, 2011