Synthesis and transformations of metallacycles

36.* Cycloalumination of macrocyclic diacetylenes with Et_3Al catalyzed by Cp_2ZrCl_2

V. A. D´yakonov, R. A. Tuktarova, T. V. Tyumkina, L. M. Khalilov, and U. M. Dzhemilev*

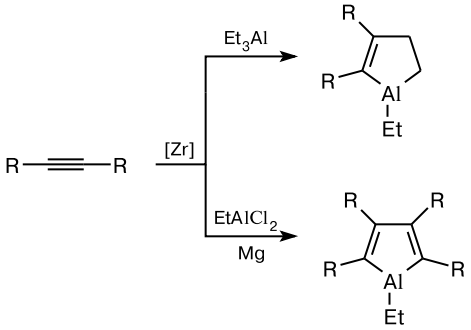
Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Bashkortostan, Russian Federation.
Fax: (347) 284 2750. E-mail: DyakonovVA@rambler.ru

Cycloalumination of macrocyclic diynes with Et_3Al catalyzed by Cp_2ZrCl_2 resulted in unsaturated bi- and tricyclic mono- and dialuminacarbocycles in 76—91% yields.

Key words: organoaluminum compounds, aluminacyclopentenes, cycloalkadiynes, cycloalumination, zirconocene dichloride, triethylaluminum.

Catalytic cycloalumination of disubstituted acetylenes[2—9] including cyclic alkynes[10] under the action of trialkyl- and alkylhaloalanes gives the corresponding aluminacyclopent-2-enes and aluminacyclopenta-2,4-dienes (Scheme 1).

Scheme 1



The resulting metallacycles can be further transformed into various carbocyclic[4,5,11] and heterocyclic[12] compounds as well as in macrocyclic polyketones,[13] for example, musk fragrances.[14]

Earlier,[15—22] we performed Cp_2ZrCl_2-catalyzed cycloalumination of cycloalkadiynes with Et_3Al (Cp_2ZrCl_2 is an efficient catalyst for cycloalumination and cyclomagnesiation of unsaturated compounds). The reactions were studied on the example of symmetrical cyclic diynes, cyclododeca-1,7-diyne (**1a**), cyclotetradeca-1,8-diyne (**1b**), and cyclohexadeca-1,9-diyne (**1c**).[23]

Herein, based on the results obtained previously on cycloalumination of disubstituted acetylenes,[3] we developed conditions (cycloalkadiyne : Et_3Al : [Zr] = 1 : 6 : 0.1, 20—22 °C, hexane, 6 h) for cycloalumination of cyclotetradeca-1,8-diyne (**1b**) as a model compound. Under these conditions, **1b** underwent cycloalumination involving both triple bonds to give isomeric tricyclic bisaluminacyclopentenes **2b** and **3b** in the ratio of 1 : 1 in 91% total yield (Scheme 2).

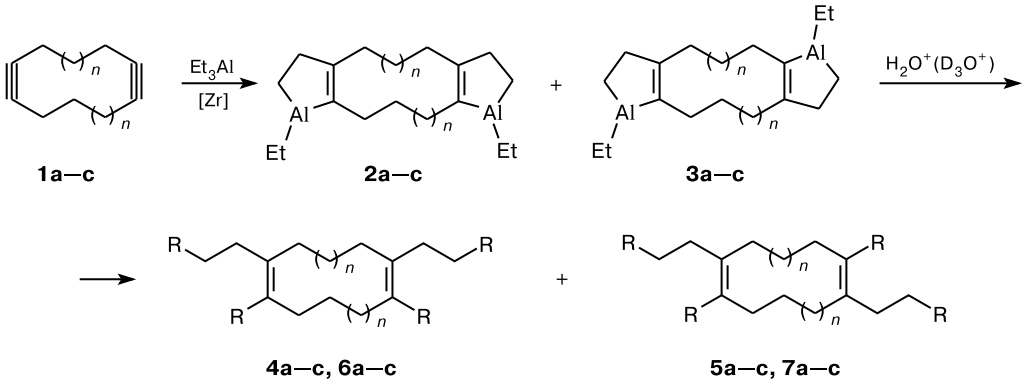
Structures of hitherto unknown organoaluminum compounds (OAC) **2b** and **3b** were established based on 1D and 2D NMR spectroscopy (^1H, ^{13}C, Dept-135, HSQC, HMBC, and HH COSY).

It is known that in solutions, OAC are prone to undergo self-association,[24] therefore in the case of dienes **2b** and **3b** polyassociates could be formed due to two aluminum-containing centers in the molecule. Moreover, due to close spectral parameters of isomers **2b** and **3b**, it is convenient to use the intervals when considering the ^{13}C NMR spectra. Thus, in the ^{13}C NMR spectra of **2b** and **3b** in the low fields, two broadened signals for the carbon atoms of the double bonds were observed in the range of δ_C 152.5—154.0 and 140.0—142.0. The remaining signals for the C atoms have the same multiplicity (triplets), however, using the data from the 2D NMR spectroscopy all signals were attributed. For example, for OAC **2b**, which was used as a reference compound, magnetically equivalent carbon atoms C(9) and C(19) of the aluminacyclopentene fragments were easily identified by the chemical shifts due to strong shielding of the carbon atoms at the α-position to the aluminum atom (δ_H = 8—10). Despite the fact that in the ^{13}C NMR spectra the chemical shifts of the C(9) and C(19) atoms are similar to those for the methyl group of the ethyl substituent, these carbon atoms could be easily distinguished by the chemical shifts of the protons bonded to them: δ_H −0.5 and 0.8, respectively (HSQC data). Moreover, in the homonuclear correlation spectra (HH COSY), correlations between the protons at the C(9) and C(19) carbon atoms and the pro-

For Part 35, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1852—1858, October, 2010.

Scheme 2



[Zr] = Cp_2ZrCl_2; *n* = 2 (**a**), 3 (**b**), 4 (**c**); R = H (**4**, **5**), D (**6**, **7**)

tons vicinal to them, *e.i.*, the protons at the C(10) and C(18), were expectedly observed (Fig. 1). As a result, in the ^1H and ^{13}C NMR spectra, all signals for the alumina-cyclopentene fragment were assigned. Thus, the signal in the range of δ_C 34.0—35.5 was attributed to the C(10) and C(18) carbon atoms. According to the HH COSY spectra, the signal in the range of δ_C 29—31 was assigned to the C(2), C(6), C(12), and C(16) carbon atoms of the macrocyclic fragment adjacent to the allylic carbon atoms.

With the aim at studying the complexing properties of novel OAC **2b** and **3b** with the solvents, THF was added to the solution of the isomers in toluene. This resulted in simplification of the ^{13}C NMR spectra owing to transformation of the broadened signals into narrow singlets, which is due obviously to the formation of the **2b**·THF and **3b**·THF complexes. The signals for the sp^2 hybridized carbon atoms of the **2b**·THF and **3b**·THF complexes shift downfield by ~4 ppm relative to the corresponding signals of OAC in nonpolar solvent and resonate for each isomer at δ_C 157.7, 157.2 and 146.5, 146.1, respectively. It is of note that the correlations found in the 2D NMR spectra in the toluene solutions retained. According to the ^{13}C NMR spectral data of the **2b**·THF and **3b**·THF complexes, the isomers formed in the ratio **2b** : **3b** ≈ 1 : 1. However, due to the proximity of the spectral parameters identification of the isomers is difficult.

Acid hydrolysis and deuterolysis of OAC **2b** and **3b** afforded the pairs of cyclic dienes: 1,9-diethylcyclotetradeca-1,8-diene (**4b**) and 1,8-diethylcyclotetradeca-1,8-diene (**5b**), 2,8-dideutero-1,9-bis(2-deuteroethyl)-cyclotetradeca-1,8-diene (**6b**) and 2,9-dideutero-1,8-bis(2-deuteroethyl)cyclotetradeca-1,8-diene (**7b**), respectively.

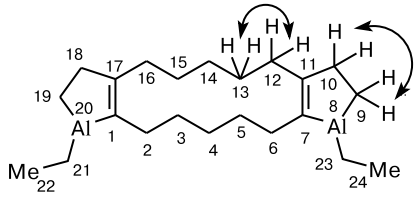


Fig. 1. Correlations in HH COSY spectra on the example of compound **2b**.

The presence of four deuterium atoms in the deuterolysis products **6b** and **7b** as well as the positions of the deuterium atoms at the C(2), C(8), C(16), and C(18) for compound **6b** and at the C(2), C(9), C(16), and C(18) for **7b** indicated the presence of four Al—C bonds in the starting OAC **2b** and **3b** confirming further the suggested structures of 8,20-diethyl-8,20-dialuminatricyclo[15.3.$0^{1,17}$.$0^{7,11}$]-eicosa-1(17),7(11)-diene (**2b**) and 8,18-diethyl-8,20-dialuminatricyclo[15.3.$0^{1,17}$.$0^{7,11}$]eicosa-1(17),7(11)-diene (**3b**).

Similarly to **1b** its homologs, cyclododeca-1,7-diyne (**1a**) and cyclododeca-1,9-diyne (**1c**), underwent cycloalumination following the described-above regularities. In all experiments, formation of pairs of unsaturated tricyclic OAC **2** and **3** in the ratio of ~1 : 1 was observed.

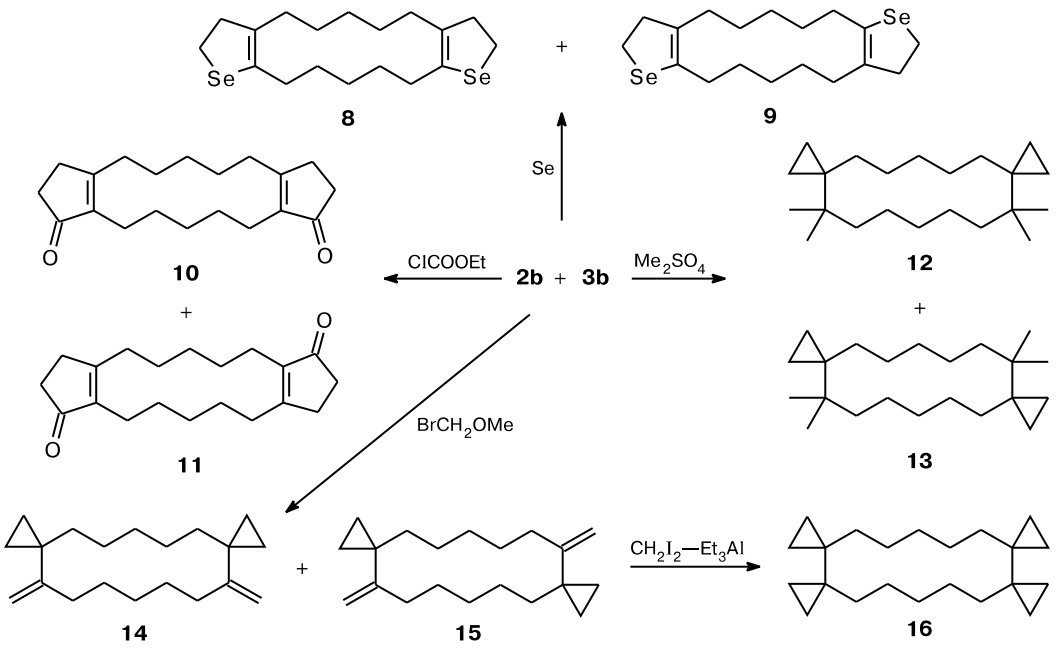
We performed some transformations of generated *in situ* tricyclic OAC **2b** and **3b** with selenium, dimethyl sulfate, ethyl chloroformate, and bromomethyl methyl ether under conditions developed previously for 2,3-dialkylaluminacyclopent-2-enes (Scheme 3).[5,11,12] This serves to an unambiguous assignment of the structures of OAC **2b** and **3b** and allows as studying the possibility of the synthesis on their base of hardly available or hitherto unknown unsaturated carbo- and heterocyclic compounds.

It was found that tricyclic dialuminum compounds **2b** and **3b** easily underwent transmetalation and carbocyclization.

Boiling of generated *in situ* OAC **2b** and **3b** in benzene with an excess of Se for 6 h resulted in a mixture of regioisomeric 8,20-diselenatricyclo[15.3.$0^{1,17}$.$0^{7,11}$]eicosa-1(17),7(11)-diene (**8**) and 8,18-diselenatricyclo-[15.3.$0^{1,17}$.$0^{7,11}$]eicosa-1(17),7(11)-diene (**9**) in 1 : 1 ratio in 69% total yield.

Regioisomeric tricyclo[15.3.$0^{1,17}$.$0^{7,11}$]eicosa-1(17),7(11)-diene-8,20-dione (**10**) and tricyclo[15.3.$0^{1,17}$.$0^{7,11}$]-eicosa-1(17),7(11)-diene-8,18-dione (**11**) were synthe-

Scheme 3



sized by carbocyclization of OAC **2b** and **3b** with ethyl chloroformate for 12 h in 68% yield. Compounds **10** and **11** were separated by column chromatography on silica gel.

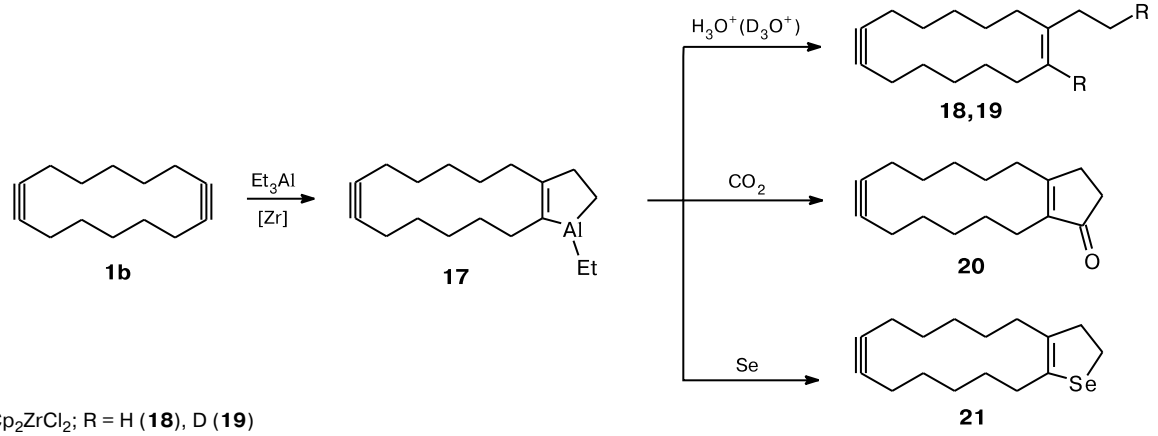
Based on the previously obtained results on the transformations of 2,3-dialkylaluminacyclopent-2-enes into 1,1-disubstituted cyclopropanes,[5,11] regioisomeric 12,12,18,18-tetramethyldispiro[2.5.2.7]octadecane (**12**) and 4,4,13,13-tetramethyldispiro[6.2.6.6]octadecane (**13**) were prepared by treatment of OAC **2b** and **3b** with excess of Me_2SO_4 at 0 °C in 93% total yield. Compound **13** was isolated by crystallization as rhombic crystals, while compound **12** is colorless oil.

Carbocyclization of OAC **2b** and **3b** with equimolar amount of bromomethyl methyl ether led to 12,18-dimethylidenedispiro[2.5.2.7]octadecane (**14**) and 4,13-dimethylidenedispiro[2.6.2.6]octadecane (**15**) in 88% total yield. Cyclopropanation of this mixture with CH_2I_2—Et_3Al afforded pure tetraspiro[2.0.2^4.5.2^{12}.0.2^{15}.5^3]docosane (**16**) in quantitative yield.

Structures of all compounds synthesized were established by 1D and 2D NMR spectroscopy (^{1}H, ^{13}C, Dept-135, HSQC, HMBC, HH COSY, NOESY).

On the further study of cycloalumination of cycloalkadiynes, we attempted to perform monocycloalumination on one triple bond of the starting cycloalkadiyne and subsequent functionalization of the resulting aluminacyclopentene fragment (Scheme 4). It was suggested that this reaction could be used for the development of one-pot

Scheme 4



[Zr] = Cp_2ZrCl_2; R = H (**18**), D (**19**)

synthetic strategy toward unsymmetrically substituted cycloalkynes.

Taking cyclotetradeca-1,8-diyne (**1b**) as an example, we developed the conditions (cycloalkadiyne : Et_3Al : [Zr] = = 1 : 3 : 0.1, 20—22 °C, hexane, 3 h) for the selective cycloalumination at one acetylene bond to give cycloalkyne with annulated aluminacyclopentene moiety **17** in 65% yield. Structure of compound **17** was determined from the structure of acid hydrolysis product **18** and deuterolysis product **19** as well as by transformation of **17** into cyclotetradecyne derivatives **20** and **21**.

In summary, we performed cycloalumination of symmetrical macrocyclic diynes with Et_3Al catalyzed by Cp_2ZrCl_2. Efficient procedures toward novel types of the substituted aluminacyclopentenes were developed. These methods can be used for the synthesis of carbo- and heterocyclic compounds including functionalized cycloakynes of practical importance.

Experimental

Chromatographic analysis was performed on a Shimadzu GS-9A chromatograph, column 2000×3 mm, silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm) was used as stationary phase, helium was used as a carrier gas (30 mL min^{-1}), temperature was programmed from 50 to 300 °C at a rate of 8 °C min^{-1}. ^1H and ^{13}C NMR spectra were run on a Bruker Avance-400 instrument (100 MHz for ^{13}C and 400 MHz for ^1H) in $CDCl_3$ (if not stated otherwise), chemical shifts are given in the δ scale relative to Me_4Si. Chromato-mass spectrometry was performed on a Finnigan 4021 instrument (glass capillary column 50000×0.25 mm, HP-5 was used as stationary phase, helium was used as a carrier gas, temperature was programmed from 50 to 300 °C with a rate of 5 °C min^{-1}, the injector temperature was 280 °C, temperature of the ion source was 250 °C, ionization voltage was 70 eV). Elemental analysis was carried out on a Karlo Erba 1106 analyzer. IR spectra were recorded on a SPECORD 75 IR spectrophotometer (Carl Zeiss Jena) and on a VERTEX 70V Fourier-transform spectrometer (Bruker) in KBr pellets or in solutions in $CHCl_3$. The yields of the products were determined by GC analysis. The purity of the products were monitored by TLC on Silufol UV-254 plates, visualization with iodine vapors. Reactions with organometallic compounds were carried out in a flow of dry argon. Solvents were dried and used freshly distilled. Cycloalkadiynes **1a—c** were synthesized according to the known procedure.[23] Cp_2ZrCl_2 was synthesized from $ZrCl_4$ as described earlier.[25] Commercially available Me_2SO_4, ethyl chloroformate, bromomethyl methyl ether (Aldrich, Acros), and Et_3Al (98%) (Redkino experimental plant) were used as purchased.

Cp_2ZrCl_2-Catalyzed cycloalumination of acetylenes 1a—c with Et_3Al (general procedure). A glass reactor was charged with hexane (5 mL), diacetylene **1** (1.0 mmol, **1a—c** in the case of biscycloalumination or **1b** in the case of monocycloalumination), Cp_2ZrCl_2 (0.1 or 0.05 mmol for bis- and monocycloalumination, respectively), and Et_3Al (6.0 or 3.0 mmol for bis- and monocycloalumination, respectively) under argon at 0 °C with stirring. The mixture was warmed to 20 °C and stirred for 6 h (biscycloalumination) or 3 h (monocycloalumination). The reaction mixture was treated with 5% aqueous HCl (for products **4a—c**, **5a—c**, and **18**) or 5% DCl in D_2O (for products **6a—c**, **7a—c**, and **19**), extracted with hexane or diethyl ether, dried with $MgSO_4$. The solvents were removed *in vacuo*, the residue was filtered through a small layer of neutral aluminum oxide, and the products were purified by distillation under reduced pressure.

The ^1H and ^{13}C NMR spectra of a mixture of aluminacyclopentenes **2b** and **3b** were obtained as follows: the reaction mixture was concentrated *in vacuo*, few drops of toluene-d_8 were added to the residue, the obtained solution was transferred into the NMR tube under argon, and thus prepared sample was used for the NMR spectroscopy.

8,20-Diethyl-8,20-dialuminatricyclo[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene (2b) and 8,18-diethyl-8,20-dialuminatricyclo-[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene (3b). ^1H NMR (THF-d_8), δ: 2.26 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.11 (m, 8 H, 4 C$\underline{H}_2$—CH=); 1.29 (m, 12 H, 6 CH_2); 0.95 (m, 6 H, 2 CH_3); −0.20—−0.30 (m, 8 H, 4 CH_2). ^1H NMR (toluene-d_8), δ: 2.35—2.55 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.00—2.23 (m, 8 H, 4 C$\underline{H}_2$—CH=); 1.20—1.40 (m, 12 H, 6 CH_2); 1.00 (m, 6 H, 2 CH_3); −0.10—0.1 (m, 8 H, 4 CH_2). ^{13}C NMR (THF-d_8), δ: −0.4, 0.1 (both t, C(21), C(23)); 8.3, 8.6 (both q, C(9), C(19), C(22), C(24)); 9.1, 9.3 (both t, C(9), C(19), C(22), C(24)); 27.5, 28.0, 28.3, 28.6, 28.7, 29.0 (all t, C(3), C(4), C(5), C(13), C(14), C(15)); 31.1, 31.8 (both t, C(2), C(6), C(12), C(16)); 32.9, 34.0 (both t, C(10),C(18), C(20) (**3b**)); 146.1, 146.5 (both d, C(1), C(7), C(17) (**3b**)); 157.2, 157.7 (both d, C(11), C(17), C(1) (**3b**)). ^{13}C NMR (toluene-d_8), δ: −1.1, −0.2 (both t, C(21), C(23)); 7.0—10.0 (br.s, C(9), C(19), C(22), C(24)); 26.2—28.8 (br.t, C(3), C(4), C(5), C(13), C(14), C(15)); 29.0—31.0 (br.t, C(2), C(6), C(12), C(16)); 34.0—35.5 (br.t, C(10), C(18), C(20) (**3b**)); 140.0—142.0 (br.d, C(1), C(7), C(17) (**3b**)); 152.5—154.0 (br.d, C(11), C(17), C(1) (**3b**)).

1,8-Diethylcyclododeca-1,7-diene (4a) and 1,7-diethylcyclododeca-1,7-diene (5a). Yield 78%, b.p. 119—121 °C (5 Torr). Found (%): C, 86.99; H, 12.79. $C_{16}H_{28}$. Calculated (%): C, 87.19; H, 12.81. IR, ν/cm^{-1}: 720, 878, 909, 1333, 1368, 1460, 2856, 2927. ^1H NMR, δ: 5.16 (m, 4 H, 4 CH); 2.03—2.27 (m, 16 H, 8 C$\underline{H}_2$—CH=); 1.99 (q, 8 H, 4 C$\underline{H}_2$—CH_3, J = 7.2 Hz); 1.22—1.51 (m, 16 H, 8 CH_2); 0.99 (t, 12 H, 4 CH_3, J = 7.2 Hz). ^{13}C NMR, δ: 12.87 (C(14), C(16)); 24.84, 25.12, 25.38, 25.75, 26.83, 26.97, 27.05, 27.07, 28.69, 28.83 (C(13), C(15)); 123.84, 123.95 (C(2), C(7) (**4a**), C(8) (**5a**)); 140.93 (C(1), C(7) (**5a**), C(8) (**4a**)). MS (EI), m/z: 220 $[M]^+$.

1,9-Diethylcycloteradeca-1,8-diene (4b) and 1,8-diethylcyclotetradeca-1,8-diene (5b). Yield 91%, b.p. 143—145 °C (5 Torr). Found (%): C, 86.82; H, 12.96. $C_{18}H_{32}$. Calculated (%): C, 87.02; H, 12.98. IR, ν/cm^{-1}: 721, 879, 1073, 1335, 1369, 1461, 2856, 2929. ^1H NMR, δ: 5.16 (t, 2 H, 2 CH, J = 7.2 Hz); 5.12 (t, 2 H, 2 CH, J = 7.2 Hz); 2.08 (q, 8 H, 4 C$\underline{H}_2$—CH_3, J = 7.2 Hz); 1.99—2.06 (m, 16 H, 8 C$\underline{H}_2$—CH=); 1.24—1.46 (m, 24 H, 12 CH_2); 1.00 (t, 12 H, 4 CH_3, J = 7.2 Hz). ^{13}C NMR, δ: 12.88, 12.92 (C(16), C(18)); 26.70, 26.72, 26.82, 26.93 (C(3), C(7) (**4b**), C(10) (**5b**)); 27.12, 27.54 (C(5), C(12)); 27.39, 28.14, 28.51, 28.55, 28.64 (C(15), C(17)); 28.89, 28.96 (C(7) (**5b**), C(10) (**4b**), C(14)); 123.51, 123.94 (C(2), C(8) (**4b**), C(9) (**5b**)); 140.74, 141.12 (C(1), C(8) (**5b**), C(9) (**4b**)). MS (EI), m/z: 248 $[M]^+$.

1,10-Diethylcyclohexadeca-1,9-diene (4c) and 1,9-diethylcyclohexadeca-1,9-diene (5c). Yield 89%, b.p. 172—174 °C

(5 Torr). Found (%): C, 86.68; H, 13.10. $C_{20}H_{36}$. Calculated (%): C, 86.88; H, 13.12. IR, ν/cm^{-1}: 721, 859, 1084, 1348, 1368, 1369, 1461, 2855, 2927. ^{1}H NMR, δ: 5.16 (m, 4 H, 4 CH); 2.05—2.06 (m, 8 H, 4 C$\underline{H}_2$—CH_3); 1.99—2.03 (m, 16 H, 2 C$\underline{H}_2$—CH=); 1.28—1.54 (m, 32 H, 16 CH_2); 0.99 (t, 12 H, 4 CH_3, J = 7.2 Hz). ^{13}C NMR, δ: 12.64 (C(18), C(20)); 27.31, 27.41, 27.93, 28.05, 28.24, 28.44, 28.49, 28.68, 28.98, 29.11, 29.18, 29.50, 29.32, 29.38 (C(17), C(19)); 122.98, 123.39 (C(2), C(9) (**4c**), C(10) (**5c**)); 140.90 (C(1), C(9) (**5c**), C(10) (**4c**)). MS (EI): 276 [M]$^+$.

2,7-Dideutero-1,8-bis(2-deuteroethyl)cyclododeca-1,7-diene (6a) and 2,8-dideutero-1,7-bis(2-deuteroethyl)cyclododeca-1,7-diene (7a). Yield 78%, b.p. 119—121 °C (5 Torr). Found (%): C, 85.44; H + D, 14.06. $C_{16}H_{24}D_4$. Calculated (%): C, 85.64; H, 10.78; D, 3.58. IR, ν/cm^{-1}: 723, 1364, 1461, 2214 (C—D); 2173 (C—D); 2855, 2928. ^{1}H NMR, δ: 2.03—2.26 (m, 16 H, 8 C$\underline{H}_2$—CH=); 1.99 (q, 8 H, 4 C$\underline{H}_2$—CH_2D, J = 7.2 Hz); 1.22—1.49 (m, 16 H, 8 CH_2); 0.98 (t, 8 H, 4 CH_2D, J = 7.2 Hz). ^{13}C NMR, δ: 12.88 (C(14), C(16), J_{C-D} = 19 Hz); 24.84, 25.12, 25.37, 25.73, 26.83, 26.97, 27.06, 27.07, 28.68, 28.84 (C(13), C(15)); 123.78, 123.86 (C(2), C(7) (**6a**), C(8) (**7a**), J_{C-D} = = 23 Hz); 140.94 (C(1), C(7) (**7a**), C(8) (**6a**)). MS (EI), *m/z*: 224 [M]$^+$.

2,8-Dideutero-1,9-bis(2-deuteroethyl)cyclotetradeca-1,8-diene (6b) and 2,9-dideutero-1,8-bis(2-deuteroethyl)cyclotetradeca-1,8-diene (7b). Yield 91%, b.p. 143—145 °C (5 Torr). Found (%): C, 85.43; H + D, 13.86. $C_{18}H_{28}D_4$. Calculated (%): C, 85.64; H, 11.18; D, 3.18. IR, ν/cm^{-1}: 721, 1364, 1463, 2214 (C—D); 2173 (C—D); 2855, 2930. ^{1}H NMR, δ: 2.08 (q, 8 H, 4 C$\underline{H}_2$—CH_2D, J = 7.2 Hz); 1.99—2.06 (m, 16 H, 8 C$\underline{H}_2$—CH=); 1.24—1.46 (m, 24 H, 12 CH_2); 0.99 (t, 8 H, 4 CH_2—D, J = 7.2 Hz); 26.70, 26.72, 26.82, 26.93 (C(3), C(7) (**6b**), C(10) (**7b**)); 27.12, 27.54 (C(5), C(12)); 27.39, 28.14, 28.51, 28.55, 28.64 (C(15), C(17)); 28.89, 28.96 (C(7) (**7b**), C(10) (**6b**), C(14)); 123.34, 123.55 (C(2), C(8) (**6b**), C(9) (**7b**), J_{C-D} = 23 Hz); 140.34, 140.98 (C(1), C(8) (**7b**), C(9) (**6b**)). MS (EI), *m/z*: 252 [M]$^+$.

2,9-Dideutero-1,10-bis(2-deuteroethyl)cyclohexadeca-1,9-diene (6c) and 2,10-dideutero-1,9-bis(2-deuteroethyl)cyclohexadeca-1,9-diene (7c). Yield 89%, b.p. 172—174 °C (5 Torr). Found (%): C, 85.44; H + D, 13.98. $C_{20}H_{32}D_4$. Calculated (%): C, 85.64; H, 11.50; D, 2.87. IR, ν/cm^{-1}: 722, 1364, 1461, 2173 (C—D); 2211 (C—D); 2855, 2928. ^{1}H NMR, δ: 2.05—2.08 (m, 8 H, 4 C$\underline{H}_2$—CH_2D); 1.99—2.03 (m, 16 H, 8 C$\underline{H}_2$—CH=); 1.28—1.56 (m, 32 H, 16 CH_2); 0.98 (t, 8 H, 4 CH_2D, J = 7.2 Hz). ^{13}C NMR, δ: 12.62 (C(18), C(20), J_{C-D} = 19 Hz); 27.31, 27.41, 27.93, 28.03, 28.24, 28.43, 28.49, 28.68, 28.98, 29.11, 29.19, 29.50, 29.31, 29.38 (C(17), C(19)); 122.99, 123.45 (C(2), C(9) (**6c**), C(10) (**7c**), J = 23 Hz); 140.87 (C(1), C(9) (**7c**), C(10) (**6c**)). MS (EI), *m/z*: 280 [M]$^+$.

1-Ethylcyclotetradec-1-en-8-yne (18). Yield 65%, b.p. 124—126 °C (5 Torr). Found (%): C, 87.80; H, 11.98. $C_{16}H_{26}$. Calculated (%): C, 88.00; H, 12.00. IR, ν/cm^{-1}: 721, 878, 1333, 1369, 1461, 2856, 2928. ^{1}H NMR, δ: 5.15 (t, 1 H, CH, J = 7.6 Hz); 2.21—2.25 (m, 4 H, 2 CH_2—C≡); 2.02—2.13 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.01 (m, 2 H, CH_2); 1.79 (m, 4 H, 2 CH_2); 1.30—1.54 (m, 8 H, 4 CH_2); 0.99 (t, 3 H, CH_3, J = 7.2 Hz). ^{13}C NMR, δ: 12.91 (C(16)); 18.36 (C(7), C(10)); 26.97 (C(3)); 27.28 (C(6); C(11)); 27.77, 28.16, 29.19 (C(4), C(5), C(12), C(13)); 28.83 (C(15)); 29.33 (C(14)); 80.77, 81.16 (C(8), C(9)); 124.46 (C(2)); 140.81 (C(1)). MS (EI), *m/z*: 218 [M]$^+$.

2-Deutero-1-(2-deuteroethyl)cyclotetradec-1-en-8-yne (19). Yield 65%, b.p. 124—126 °C (5 Torr). Found (%): C, 87.00; H + D, 12.46. $C_{16}H_{24}D_2$. Calculated (%): C, 87.20; H, 10.98; D, 1.82. IR, ν/cm^{-1}: 722, 1364, 1461, 2214 (C—D); 2173 (C—D); 2855, 2928. ^{1}H NMR, δ: 2.21—2.25 (m, 4 H, 2 CH_2—C≡); 2.02—2.13 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.01 (m, 2 H, C$\underline{H}_2$—CH_2D); 1.79 (m, 4 H, 2 CH_2); 1.30—1.54 (m, 8 H, 4 CH_2); 0.99 (t, 2 H, CH_2—D, J = 7.2 Hz). ^{13}C NMR, δ: 12.89 (C(16), J_{C-D} = 19 Hz); 18.36 (C(7), C(10)); 26.97 (C(3)); 27.28 (C(6), C(11)); 27.75, 28.15, 29.19 (C(4), C(5), C(12), C(13)); 28.83 (C(15)); 29.33 (C(14)); 80.77, 81.17 (C(8), C(9)); 124.44 (C(2), J = 23 Hz); 140.81 (C(1)). MS (EI), *m/z*: 220 [M]$^+$.

Synthesis of selenium-containing cyclic compounds 8, 9, and 21 (general procedure). The glass reactor was charged with hexane (5 mL), diacetylene **1b** (1.0 mmol), Cp_2ZrCl_2 (0.2 mmol for products **8** and **9** or 0.5 mmol for product **21**), and Et_3Al (6.0 mmol for products **8** and **9** or 3.0 mmol for product **21**) under argon at 0 °C with stirring. The mixture was warmed to 20 °C and stirred for 6 h (products **8** and **9**) or 3 h (product **21**). Then benzene (6 mL) and Se (6 mmol for products **8** and **9** or 3.0 mmol for product **21**) were added and the reaction mixture was heated at 80 °C for 6 h. The mixture was treated with 7—10% aqueous HCl, extracted with hexane, the extracts were washed with aqueous Na_2CO_3 until neutral, dried with $MgSO_4$, and the products were isolated by column chromatography (silica gel L, 180—250 μm, elution with hexane).

8,20-Diselenatricyclo[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene (8). Yield 34%. Found (%): C, 53.53, H, 6.99. $C_{18}H_{28}Se_2$. Calculated (%): C, 53.73; H, 7.01. ^{1}H NMR, δ: 3.14 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 8.0 Hz); 2.79 (t, 4 H, 2 CH_2—Se, J = 8.0 Hz); 2.34 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 6.8 Hz); 2.11 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 6.8 Hz); 1.32—1.48 (m, 12 H, 6 CH_2). ^{13}C NMR, δ: 22.78 (C(10), C(18)); 26.99 (C(3), C(5)); 27.16 (C(14)); 27.33 (C(4)); 28.40 (C(13), C(15)); 29.21 (C(2), C(6)); 29.52 (C(12), C(16)); 41.81 (C(9), C(19)); 131.53 (C(11), C(17)); 133.59 (C(1), C(7)). MS (EI), *m/z*: 402 [M]$^+$.

8,18-Diselenatricyclo[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene (9). Yield 35%. Found (%): C, 53.53; H, 6.99. $C_{18}H_{28}Se_2$. Calculated (%): C, 53.73; H, 7.01. ^{1}H NMR, δ: 3.14 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 8.0 Hz); 2.79 (t, 4 H, 2 CH_2—Se, J = 8.0 Hz); 2.34 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 6.8 Hz); 2.11 (t, 4 H, 2 C$\underline{H}_2$—CH=, J = 6.8 Hz); 1.17—1.31 (m, 12 H, 6 CH_2). ^{13}C NMR, δ: 22.78 (C(10), C(20)); 26.80 (C(5), C(15)); 26.83 (C(4), C(14)); 28.58 (C(3), C(13)); 29.11 (C(6), C(16)); 29.68 (C(2), C(12)); 41.81 (C(9), C(19)); 131.36 (C(1), C(11)); 133.84 (C(7), C(17)). MS (EI), *m/z*: 402 [M]$^+$.

15-Selenabicyclo[12.3.0^{1,14}]heptadec-1(14)-en-7(8)-yne (21). Yield 65%, b.p. 167—169 °C (1 Torr). Found (%): C, 64.87; H, 8.18. $C_{16}H_{24}Se$. Calculated (%): C, 65.07; H, 8.19. IR, ν/cm^{-1}: 735, 912, 1081, 1330, 1427, 1461, 1637, 2855, 2927. ^{1}H NMR, δ: 3.14 (t, 2 H, C$\underline{H}_2$—CH=, J = 8.0 Hz); 2.82 (t, 2 H, CH_2—Se, J = 8.0 Hz); 2.36 (m, 2 H, 2 C$\underline{H}_2$—CH=); 2.19—2.25 (m, 4 H, 2 CH_2—C≡); 2.13 (m, 2 H, C$\underline{H}_2$—CH=); 1.43—1.58 (m, 12 H, 6 CH_2). ^{13}C NMR, δ: 18.38 (C(6), C(9)); 22.69 (C(17)); 27.06, 27.20, 27.23, 27.99, 28.16, 28.76 (C(3), C(4), C(5), C(10), C(11), C(12)); 29.89 (C(13)); 30.46 (C(2)); 42.27 (C(16)); 81.00 (C(7), C(8)); 131.81 (C(1)); 133.90 (C(14)). MS (EI), *m/z*: 295 [M]$^+$.

Synthesis of tricyclodienediones 10, 11 and bicyclic ketone 20 (general procedure). A glass reactor was charged with hexane (5 mL), diacetylene **1b** (1.0 mmol), Cp_2ZrCl_2 (0.02 mmol for products **10** and **11** or 0.05 mmol for product **20**), and Et_3Al (6.0 mmol for products **10** and **11** or 3.0 mmol for product **20**) at 0 °C under argon with stirring. The mixture was warmed to 20 °C

and stirred for 6 h (products **10** and **11**) or 3 h (product **20**). The resulting solution was cooled to 0 °C, then ClCOOEt (6 mmol for products **10** and **11** or 3 mmol for product **20**) was added dropwise, and stirring was continued at 23 °C or 12 h. The reaction mixture was treated with 7—10% aqueous HCl, the organic layer was extracted with diethyl ether, washed with aqueous Na_2CO_3 until neutral, and dried with $CaCl_2$. The obtained regioisomers **10** and **11** were isolated by column chromatography (silica gel L, 180—250 μm, elution with ethyl acetate).

Tricyclo[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene-8,20-dione (10). Yield 34%. Found (%): C, 79.76; H, 9.37. $C_{20}H_{28}O_2$. Calculated (%): C, 79.96; H, 9.39. IR, ν/cm^{-1}: 771, 921, 1437, 1464, 1625 (C=O); 1674 (C=O); 1755 (C=O); 2859, 2931. ^{1}H NMR, δ: 2.43 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.35 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.30 (m, 4 H, 2 CH_2—C=O); 2.10 (m, 4 H, 2 C$\underline{H}_2$—CH=); 1.58 (m, 4 H, 2 CH_2); 1.40 (m, 4 H, 2 CH_2); 1.21—1.36 (m, 4 H, 2 CH_2). ^{13}C NMR, δ: 22.87 (C(2), C(6)); 25.48 (C(13), C(15)); 26.42 (C(3), C(5)); 27.62 (C(14)); 27.78 (C(4)); 28.73 (C(10), C(18)); 29.78 (C(12), C(16)); 34.16 (C(9), C(19)); 139.92 (C(1), C(7)); 173.29 (C(11), C(17)); 210.16 (C(8), C(20)). MS (EI), *m/z*: 300 [M]$^+$.

Tricyclo[15.3.0^{1,17}.0^{7,11}]eicosa-1(17),7(11)-diene-8,18-dione (11). Yield 34%, m.p. 121—122 °C. Found (%): C, 79.76; H, 9.37. $C_{20}H_{28}O_2$. Calculated (%): C, 79.96; H, 9.39. IR, ν/cm^{-1}: 725, 758, 919, 1434, 1460, 1641 (C=O); 1677 (C=O); 1747 (C=O); 2841, 2936. ^{1}H NMR, δ: 2.44 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.38 (m, 4 H, 2 C$\underline{H}_2$—CH=); 2.33 (m, 4 H, 2 CH_2—C=O); 2.12 (m, 4 H, 2 C$\underline{H}_2$—CH=); 1.60 (m, 4 H, 2 CH_2); 1.44 (m, 4 H, 2 CH_2); 1.22 (m, 4 H, 2 CH_2). ^{13}C NMR, δ: 23.13 (C(6), C(16)); 25.77 (C(3), C(13)); 26.49 (C(5), C(15)); 27.70 (C(4), C(14)); 28.59 (C(10), C(20)); 29.61 (C(2), C(12)); 34.14 (C(9), C(19)); 140.50 (C(7), C(17)); 173.45 (C(1), C(11)); 210.24 (C(8), C(18)). MS (EI), *m/z*: 300 [M]$^+$.

Bicyclo[12.3.0^{1,14}]heptadec-1(14)-en-7(8)-yn-15-one (20). Yield 70%. Found (%): C, 83.35; H, 9.88. $C_{17}H_{24}O$. Calculated (%): C, 83.55; H, 9.90. IR, ν/cm^{-1}: 771, 921, 1437, 1464, 1625 (C=O); 1674 (C=O); 1755 (C=O); 2846, 2960. ^{1}H NMR, δ: 2.49 (m, 2 H, C$\underline{H}_2$—CH=); 2.45 (t, 2 H, C$\underline{H}_2$—CH=, *J* = 7.2 Hz); 2.37 (m, 2 H, CH_2—C=O); 2.16—2.26 (m, 6 H, 3 CH_2); 1.67 (m, 2 H, CH_2); 1.39—1.62 (m, 10 H, 5 CH_2). ^{13}C NMR, δ: 17.92 (C(6)); 18.42 (C(9)); 23.17 (C(13)); 26.30 (C(3)); 26.59, 27.12, 27.32, 28.26, 28.34 (C(4), C(5), C(10), C(11), C(12)); 29.06 (C(17)); 34.21 (C(16)); 80.17 (C(8)); 81.25 (C(7)); 140.31 (C(14)); 174.05 (C(1)); 210.38 (C(15)). MS (EI), *m/z*: 244 [M]$^+$.

Synthesis of tetramethyldispirooctadecanes 12 and 13 (general procedure). A glass reactor was charged with diacetylene **1b** (1.0 mmol), Cp_2ZrCl_2 (0.2 mmol), hexane (5 mL), and Et_3Al (6 mmol) at 0 °C under dry argon with stirring. The mixture was warmed to 20 °C and stirred for 6 h. The resulting solution was cooled to 0 °C, dimethyl sulfate (6 mmol) was added dropwise, and stirring was continued at 20—22 °C for 12 h. The reaction mixture was treated with 7—10% aqueous HCl, the organic phase was extracted with diethyl ether, washed twice with aqueous Na_2CO_3 solution until neutral, and dried with $CaCl_2$. Compounds **12** and **13** were purified by distillation under reduced pressure.

12,12,18,18-Tetramethyldispiro[2.5.2.7]octadecane (12). Yield 46%. Found (%): C, 86.56; H, 13.22. $C_{22}H_{40}$. Calculated (%): C, 86.76; H, 13.24. IR, ν/cm^{-1}: 770, 1050, 1395, 1430, 1498, 2910, 3050 (cyclopropane); 3070 (cyclopropane). ^{1}H NMR, δ: 1.51—1.57 (m, 4 H, 2 CH_2); 1.34—1.38 (m, 12 H, 6 CH_2); 1.02—1.11 (m, 4 H, 2 CH_2); 0.78 (s, 12 H, 4 CH_3); 0.32 (m, 4 H, 2 CH_2, cyclopropane); 0.25 (m, 4 H, 2 CH_2, cyclopropane). ^{13}C NMR, δ: 5.21 (C(1), C(2), C(10), C(11)); 19.85 (C(14), C(16)); 20.95 (C(5), C(7)); 22.73 (C(3), C(9)); 25.71 (C(19), C(20), C(21), C(22)); 27.08 (C(6)); 27.36 (C(4), C(8)); 28.97 (C(15)); 35.04 (C(12), C(18)); 38.66 (C(13), C(17)). MS (EI), *m/z*: 304 [M]$^+$.

4,4,13,13-Tetramethyldispiro[2.6.2.6]octadecane (13). Yield 46%, m.p 83—84 °C. Found (%): C, 86.56; H, 13.23. $C_{22}H_{40}$. Calculated (%): C, 86.76; H, 13.24. IR, ν/cm^{-1}: 750, 1020, 1395, 1490, 2835, 2910, 3050 (cyclopropane); 3080 (cyclopropane). ^{1}H NMR, δ: 1.40—1.48 (m, 8 H, 4 CH_2); 1.36 (m, 4 H, 2 CH_2); 1.12—1.19 (m, 8 H, 4 CH_2); 0.78 (s, 12 H, 4 CH_3); 0.35 (m, 4 H, CH_2, cyclopropane); 0.20 (m, 4 H, CH_2, cyclopropane). ^{13}C NMR, δ: 6.20 (C(1), C(2), C(11), C(12)); 20.91 (C(6), C(15)); 21.96 (C(8), C(17)); 23.23 (C(3), C(10)); 25.86 (C(19), C(20), C(21), C(22)); 28.55 (C(7), C(9), C(16), C(18)); 35.04 (C(4), C(13)); 40.65 (C(5), C(14)). MS (EI), *m/z*: 304 [M]$^+$.

Synthesis of dimethylidenedispirooctadecanes 14 and 15 (general procedure). The glass reactor was charged with diacetylene **1b** (1.0 mmol), Cp_2ZrCl_2 (0.2 mmol), hexane (5 mL), and Et_3Al (6 mmol) at 0 °C under dry argon with stirring. The mixture was warmed to 20 °C, stirred for 6 h, and then cooled to −78 °C. $BrCH_2OMe$ (2.0 mmol) was added and the stirring was continued at 20—22 °C for 12 h. The reaction mixture was treated with 7—10% aqueous HCl, extracted with diethyl ether or hexane, the extracts were washed with aqueous Na_2CO_3 until neutral, and dried with $CaCl_2$. Compounds **14** and **15** were isolated by column chromatography (silica gel L, 180—250 μm, elution with hexane).

12,18-Dimethylidenedispiro[2.5.2.7]octadecane (14) and 4,13-dimethylidenedispiro[2.6.2.6]octadecane (15). Yield 88%. Found (%): C, 87.95; H, 11.81. $C_{20}H_{32}$. Calculated (%): C, 88.16; H, 11.84. IR, ν/cm^{-1}: 720, 895, 1048, 1461, 1640 (C=CH_2); 2859, 2928, 2999 (cyclopropane); 3077 (cyclopropane). MS (EI), *m/z*: 272 [M]$^+$.

Compound **14**. ^{1}H NMR, δ: 4.76 (m, 4 H, 2 CH_2=); 2.06 (t, 4 H, 2 C$\underline{H}_2$—CH=, *J* = 8 Hz); 1.56—1.64 (m, 4 H, 2 CH_2); 1.38—1.55 (m, 8 H, 4 CH_2); 1.30 (m, 4 H, 2 CH_2); 0.51—0.56 (m, 8 H, 4 CH_2, cyclopropane). ^{13}C NMR, δ: 12.05 (C(1), C(2), C(10), C(11)); 23.44 (C(14), C(16)); 25.30 (C(5), C(7)); 25.96 (C(3), C(9)); 26.24 (C(6)); 27.41 (C(15)); 29.54 (C(13), C(17)); 35.08 (C(4), C(8)); 107.85 (C(19), C(20)); 151.64 (C(12), C(18)).

Compound **15**. ^{1}H NMR, δ: 4.76 (m, 4 H, 2 CH_2=); 2.11 (t, 4 H, 2 C$\underline{H}_2$—CH=, *J* = 8 Hz); 1.56—1.64 (m, 4 H, 2 CH_2); 1.31—1.35 (m, 8 H, 2 CH_2); 1.30 (m, 4 H, 2 CH_2); 0.34 (m, 8 H, 4 CH_2, cyclopropane). ^{13}C NMR, δ: 12.21 (C(1), C(2), C(11), C(12)); 23.47 (C(6), C(15)); 23.82 (C(8), C(17)); 26.40 (C(7), C(16)); 26.94 (C(3), C(10)); 31.18 (C(5), C(14)); 35.47 (C(9), C(18)); 109.10 (C(19), C(20)); 151.82 (C(4), C(13)).

Tetraspiro[2.0.2^4.5.2^{12}.0.2^{15}.5^3]docosane (16). The glass reactor was charged with a mixture of dimethylidenedispirooctadecanes **14** and **15** (1.0 mmol), CH_2Cl_2 (5 mL), diiodomethane (2.2 mL), and Et_3Al (2.2 mmol) at 0 °C under argon with stirring. The mixture was warmed to 20 °C and stirred for 6 h. The resulting reaction mixture was treated with 7—10% aqueous HCl, extracted with diethyl ether or hexane, the organic layer was washed with aqueous Na_2CO_3 until neutral, and dried with $CaCl_2$. The reaction products were isolated by column chromatography (silica gel L, 180—250 μm, elution with hexane). Yield 98%. Found (%): C, 87.74; H, 12.03. $C_{22}H_{36}$. Calculated (%):

C, 87.93; H 12.07. IR, ν/cm^{-1}: 734, 762, 1021, 1185, 1458, 2860, 2929, 2999 (cyclopropane); 3070 (cyclopropane). ^{1}H NMR, δ: 1.59 (m, 8 H, 4 CH_2); 1.29—1.46 (m, 12 H, 6 CH_2); 0.60 (m, 16 H, 8 CH_2, cyclopropane). ^{13}C NMR, δ: 9.27 (C(1), C(2), C(5), C(6), C(13), C(14), C(16), C(17)); 20.58 (C(3), C(4), C(12), C(15)); 22.43 (C(8), C(10), C(19), C(21)); 27.27 (C(9), C(20)); 35.27 (C(7), C(11), C(18), C(22)). MS (EI), *m/z*: 300 $[M]^+$.

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

References

1. V. A. D´yakonov, R. K. Timerkhanov, T. V. Tyumkina, U. M. Dzhemilev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 2378 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, **58**, 2456].
2. *Vazhneishie rezul´taty v oblasti estestvennykh i obshchestvennykh nauk za 1990 god* [*Major Results in the Field of Natural and Social Sciences for 1990*], Report of the Academy of Sciences of the USSR, Moscow, 1991 (in Russian).
3. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, *Mendeleev Commun.*, 1992, 135.
4. E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.*, 1996, **118**, 9577.
5. E. Negishi, J.-L. Montchamp, L. Anastasia, A. Elizarov, D. Choueiry, *Tetrahedron Lett.*, 1998, **39**, 2503.
6. U. M. Dzhemilev, A. G. Ibragimov, I. R. Ramazanov, M. P. Luk´yanova, A. Z. Sharipova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 465 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 484].
7. U. M. Dzhemilev, A. G. Ibragimov, L. O. Khafizova, L. R. Yakupova, L. M. Khalilov, *Zh. Org. Khim.*, 2005, **41**, 684 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2005, **41**, 667].
8. I. R. Ramazanov, A. G. Ibragimov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2008, **44**, 793 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2008, **44**, 781].
9. L. O. Khafizova, L. R. Yakupova, A. G. Ibragimov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2007, **43**, 1802 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 1804].
10. V. A. D´yakonov, L. F. Galimova, A. G. Ibragimov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2008, **44**, 1308 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2008, **44**, 1291].
11. U. M. Dzhemilev, A. G. Ibragimov, I. R. Ramazanov, M. P. Luk´yanova, A. Z. Sharipova, L. M. Khalilov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 1092 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1086].
12. V. A. D´yakonov, A. G. Ibragimov, L. M. Khalilov, A. A. Makarov, R. K. Timerkhanov, R. A. Tuktarova, L. F. Galimova, *Khim. Geterotsikl. Soedin.*, 2009, **45**, 393 [*Chem. Heterocycl. Compd. (Engl. Transl.)*, 2009, **45**, 317].
13. V. A. D´yakonov, A. A. Makarov, U. M. Dzhemilev, *Tetrahedron*, 2010, **66**, 6885.
14. V. A. D´yakonov, *Dzhemilev Reactions in Organic and Organometallic Synthesis*, NOVA Sci. Publ., New York, 2010, p. 96.
15. U. M. Dzhemilev, A. G. Ibragimov, *Usp. Khim.*, 2000, **69**, 134 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2000, **69**, 121].
16. U. M. Dzhemilev, *Tetrahedron*, 1995, **51**, 4333.
17. D. Y. Kondakov, E. Negishi, *J. Am. Chem. Soc.*, 1996, **118**, 1577.
18. E. Negishi, D. Y. Kondakov, *Chem. Soc. Rev.*, 1996, **26**, 417.
19. D. P. Lewis, R. J. Whitby, R. V. H. Jones, *Tetrahedron*, 1995, **51**, 4541.
20. V. A. D´yakonov, R. K. Timerkhanov, U. M. Dzhemilev, A. G. Ibragimov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 2156 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 2232].
21. V. A. D´yakonov, R. K. Timerkhanov, T. V. Tumkina, A. G. Ibragimov, U. M. Dzhemilev, *Tetrahedron Lett.*, 2009, **50**, 1270.
22. V. A. D´yakonov, E. Sh. Finkelshtein, A. G. Ibragimov, *Tetrahedron Lett.*, 2007, **48**, 8583.
23. R. Gleiter, R. Merger, B. Treptow, W. Wittwer, G. Pflasterer, *Synthesis*, 1993, 558.
24. T. Mole, E. A. Jeffery, *Organoaluminium Compounds*, Elsevier, New York, 1972, p. 85.
25. R. Kh. Freidlina, E. M. Brainina, A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1969, **138**, 1369 [*Dokl. Chem.* (*Engl. Transl.*), 1969, **138**].

Received March 25, 2010;
in revised form July 16, 2010