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Cycloalumination of Cycloalkynes with Triethylaluminum Catalyzed by Zirconium Complexes

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Abstract—Cycloalumination of cycloalkynes with triethylaluminum in the presence of zirconium complexes was performed for the first time, and new bicyclic aluminacyclopentenes were obtained in 74–94% yield.

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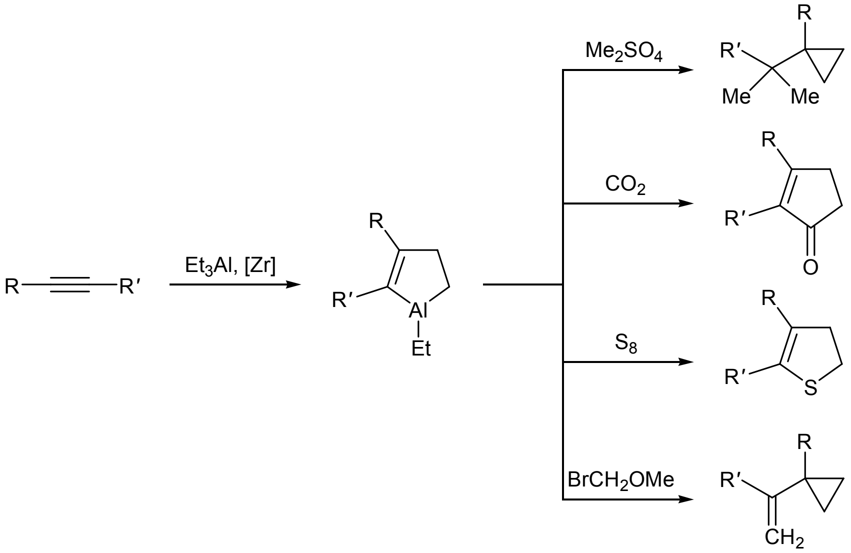
According to published data, disubstituted acetylenes react with Et_3Al in the presence of Cp_2ZrCl_2 to give 2,3-dialkyl(aryl)aluminacyclopent-2-enes in ~90% yield [1–3]; the products are exceptionally interesting as intermediate products in the development of one-pot procedures for the synthesis of substituted cyclopentenones [4, 5], cyclopropanes [6–9], and some other difficultly accessible carbo- and heterocyclic compounds [10] (Scheme 1).

Up to now, cycloalumination of cyclic acetylenes with Et_3Al under catalysis by transition metal complexes has not been reported. We believe that such reactions could give rise to new classes of organoaluminum compounds, fused aluminacyclopent-2-enes, which could be used as a basis for the development of effective one-pot procedures for the synthesis of difficultly accessible high-grade fragrant substances, spirocyclopropanes, and bicyclic heteroatom-containing compounds.

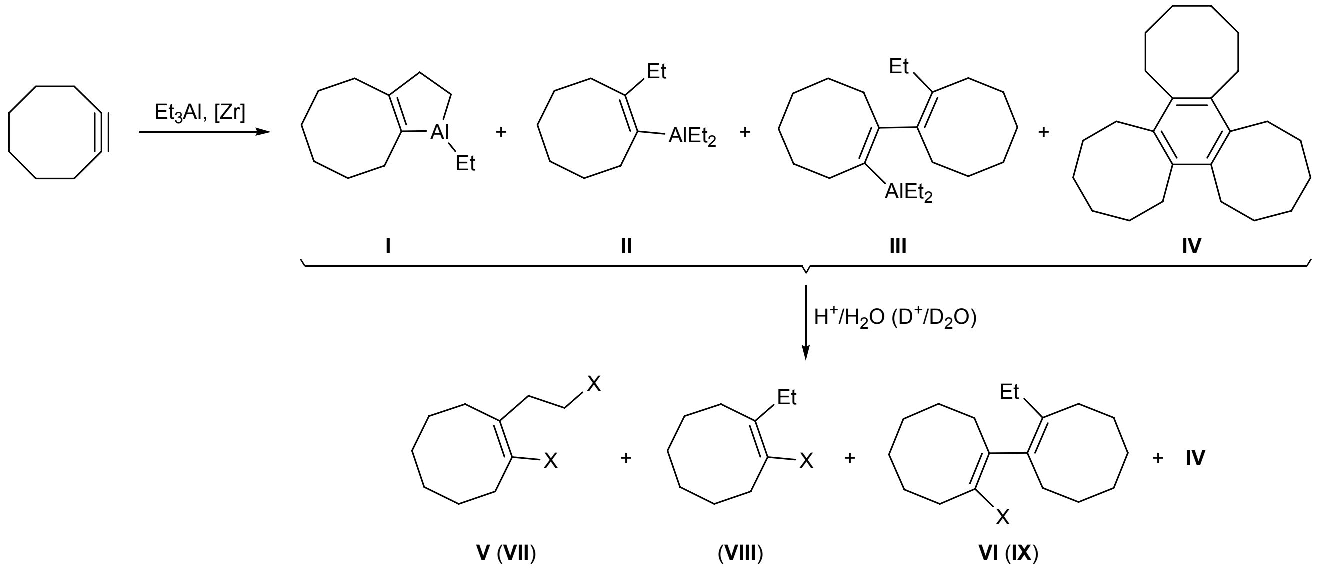
In continuation of our studies on cycloalumination of unsaturated compounds in the present work we examined reactions of some cyclic alkynes (cyclooctyne, cyclodecyne, cyclododecyne, and cyclotridecyne) with Et_3Al in the presence of Cp_2ZrCl_2 as catalyst with a view to synthesize the corresponding aluminacyclopentenes; this catalyst previously showed

Scheme 1.



R = CH_2=$CHCH_2$, Ar; R′ = Alk, Ar, Me_3Si.

Scheme 2.



V, **VI**, X = H; **VII–IX**, X = D.

the highest activity in cyclometalation of olefins, allenes, and acyclic acetylenes [11−16].

Initially, the reaction was carried out with cyclooctyne as substrate under the conditions developed previously for the cycloalumination of acyclic disubstituted acetylenes (substrate–Et_3Al–[Zr] ratio 10 : 30 : 0.5, hexane, 20−25°C, 6 h). The reaction gave a mixture of cyclic and acyclic organoaluminum compounds **I−III** and cyclooctyne cyclic trimer, tris(hexamethylene)benzene (**IV**) (Scheme 2). The structure of compounds **I−III** was determined on the basis of the ^1H and ^{13}C NMR and mass spectra of hydrocarbons **V−IX** obtained by acid hydrolysis (**V**, **VI**) or deuterolysis (**VII−IX**) of the reaction mixture. Thus, the hydrolysis afforded 1-ethylcyclooct-1-ene (**V**), 2-ethyl-1,1′-bi(cyclooct-1-ene) (**VI**), and 1,2:3,4:5,6-tris(hexamethylene)benzene (**IV**) at a ratio of 2 : 6 : 1 in an overall yield of 86%. Likewise, deuterolysis of the reaction mixture gave 1-[(2-$^2H_1$)-ethyl]-(2-$^2H_1$)cyclooct-1-ene (**VII**), (2-$^2H_1$)cyclooct-1-ene (**VIII**), 2-ethyl-(2′-$^2H_1$)-1,1′-bi(cyclooct-1-ene) (**IX**), and trimer **IV**. The presence of monodueterated hydrocarbons **VIII** and **IX** among the deuterolysis products indicated that the process was accompanied by side carboalumination.

While studying the effects of various factors on the product yield and composition, we found that reactions of cyclooctyne with Et_3Al in aliphatic (hexane, cyclohexane) or aromatic solvents (benzene, toluene) in the absence of catalyst lead to formation of only acyclic organoaluminum compounds as a result of 1,2-carbo-

Scheme 3.

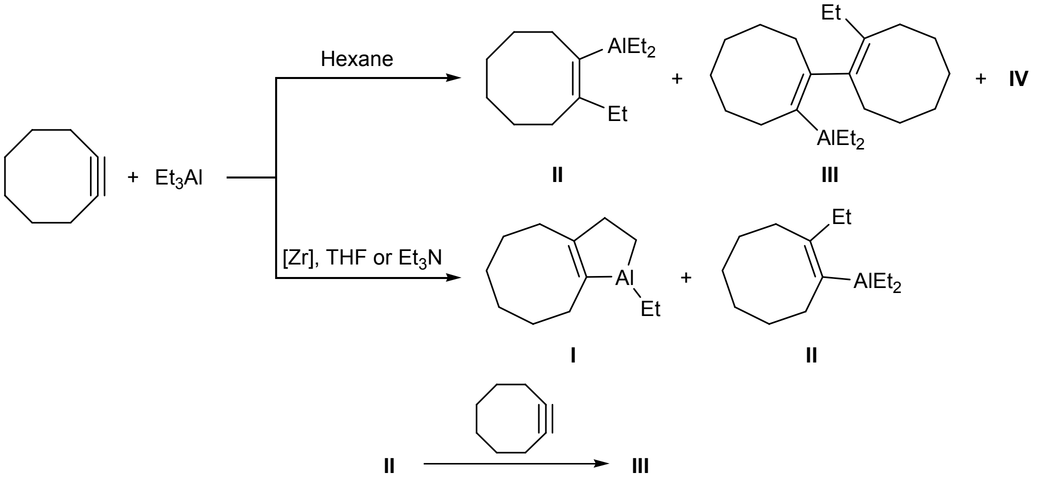


Table 1. Reaction of cyclooctyne with triethylaluminum

Catalyst	Temperature, °C	Solvent	Molar ratio **I–II–III–IV**	Overall yield, %
–	22	–	0:0:0:1	82
–	22	Hexane	0:1:7:1	78
–	22	Benzene	0:4:6:1	76
Cp_2ZrCl_2	22	Hexane	1:1:6:1	86
Cp_2ZrCl_2	22	Benzene	1:3:1:1	85
Cp_2ZrCl_2 ($Et_3Al–Et_3N$)	22	Benzene	3:2:0:0	73
Cp_2ZrCl_2 (Et_3Al–THF)	22	Benzene	3:4:0:0	71
Cp_2ZrCl_2	0	Hexane	2:1:4:0	48

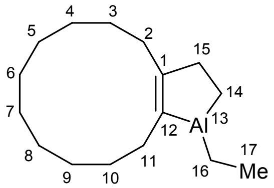
alumination of the initial alkyne with Et_3Al (compound **II**) and intermolecular carboalumination (**III**) [compound **III** can also be obtained by reaction of **II** with cyclooctyne (Scheme 3)]; trimer **IV** is also formed (Table 1). The reaction performed under solvent-free conditions gave 82% of compound **IV**.

By deactivating Et_3Al via complex formation with an equimolar amount of Et_3N or THF we succeeded in considerably increasing the fraction of 9-ethyl-9-aluminabicyclo[6.3.0^{1,8}]undec-1(8)-ene (**I**) in the reaction mixture and avoiding formation of by-products **III** and **IV** (Table 1). Reduced temperature also favors some increase in the yield of bicyclic compound **I**; however, in this case the overall yield considerably decreases despite prolonged reaction (12 h).

The fractions of cyclo- and carboalumination products were determined by GC–MS from the ratio of di- and monodeuterated hydrocarbons.

The low selectivity for aluminacyclopentene **I** is likely to be related to high reactivity of the triple bond in cyclooctyne; therefore, we presumed that increase of the ring size of the initial acetylene should be accompanied by increase in the fraction of the target bicyclic organoaluminum compounds with respect to by-products formed via noncatalytic carboalumination.

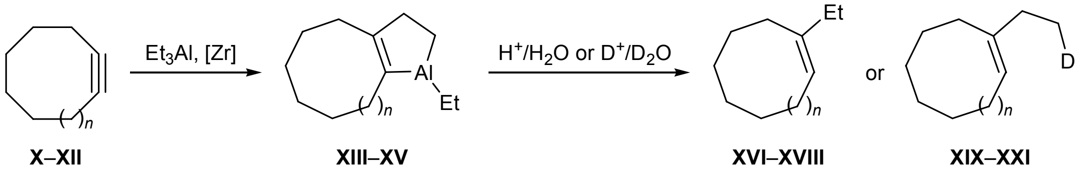
We found that cyclodecyne (**X**), cyclododecyne (**XI**), and cyclotridecyne (**XII**) reacted with 3 equiv of Et_3Al in the presence of a catalytic amount of Cp_2ZrCl_2 (5 mol %) in aliphatic or aromatic hydrocarbons to produce previously unknown bicyclic aluminacyclopentenes **XIII**–**XV** in 82–92% yield (Scheme 4, Table 2). No acyclic organoaluminum compounds were formed as by-products under these conditions. The reaction did not occur in the absence of a catalyst.



XIV

The structure of new organoaluminum compounds **XIII**–**XV** and products of their acid hydrolysis and deuterolysis was determined by 1D and 2D ^1H and ^{13}C NMR spectroscopy (the structure of molecule **XIV** with atom numbering is shown above). The ^{13}C NMR spectrum of compound **XIV** in THF-d_8 contained two singlets at δ_C 157.0 and 147.1 ppm in the region corresponding to sp^2-hybridized carbon atoms. The latter signal had lesser intensity because of broadening and was assigned to C^{12} directly linked to the aluminum atom. Correspondingly, the signal at δ_C 157.0 ppm belongs to C^1, which is confirmed by the HMBC data. The C^1 atom gives two cross peaks in the HMBC spectrum due to coupling with protons on C^2 and C^{15}, whereas the C^{12} atom (δ_C 147.1 ppm) gives only one cross peak with protons on C^{11}. Analysis of the HSQC spectrum allowed us to reliably identify signals from

Scheme 4.



X, **XIII**, **XVI**, **XIX**, $n = 3$; **XI**, **XIV**, **XVIII**, **XX**, $n = 5$; **XII**, **XV**, **XVIII**, **XXI**, $n = 6$.

Table 2. Reaction of cycloalkynes with triethylaluminum in the presence of Cp_2ZrCl_2

Cycloalkyne (no.)	*n*	Solvent	Time, h	Temperature, °C	Product no. (yield, %)
Cyclodecyne (**X**)	3	Hexane	4	20–22	**XII** (87)
Cyclododecyne (**XI**)	5	Hexane	4	20–22	**XIV** (91)
Cyclododecyne (**XI**)	5	Benzene	4	20–22	**XIV** (92)
Cyclododecyne (**XI**)	5	Toluene	4	20–22	**XIV** (91)
Cyclododecyne (**XI**)	5	Hexane	7	0	**XIV** (82)
Cyclododecyne (**XI**)	5	Hexane	1	40	**XIV** (85)
Cyclododecyne (**XI**)	5	Hexane	4	20–22	**XIV** (94)
Cyclododecyne (**XI**)	5	CH_2Cl_2	4	20–22	**XIV** (74)
Cyclododecyne (**XI**)	5	THF	6	20–22	**XIV** (0)
Cyclododecyne (**XI**)	5	Et_2O	6	20–22	**XIV** (0)
Cyclotridecyne (**XII**)	6	Hexane	4	20–22	**XV** (89)

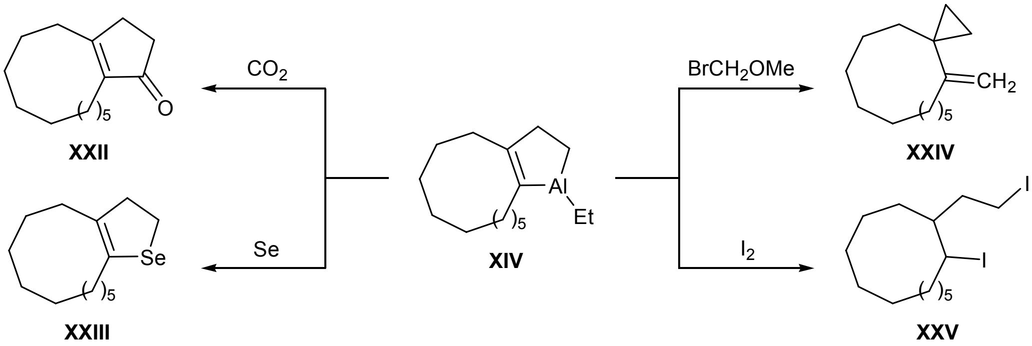
carbon nuclei and protons in positions *2*, *11*, and *15*. The C^{15} (δ_C 34.0 ppm) and 15-H signals (δ 2.21 ppm) were located relatively downfield, the C^2 and C^{11} signals appeared at δ_C 28−29 ppm, and the 2-H and 11-H protons resonated at δ 2.05−2.11 ppm.

According to the COSY HH homonuclear correlation data, methylene protons on C^{15} are actually coupled with those attached to C^{14}; the 14-H signal is displaced upfield to –0.38 ppm due to the presence of neighboring metal atom. Apart from 14-H–15-H interactions, the COSY HH spectrum displayed expected 11-H–10-H and 2-H–3-H couplings in the cyclic fragment (δ 2.05−2.11 to 1.35−1.42 ppm). Thus, the use of two-dimensional homo- and heteronuclear correlation techniques allowed us to confirm the structure of compound **XIV** as 13-ethyl-13-aluminabicyclo[10.3.0]pentadec-1(12)-ene. The aluminum atom in **XIV** gave a signal at δ_{Al} 157.6 ppm in the ^{27}Al NMR spectrum (THF). The signal from C^{10} (in the γ-position with respect to the aluminum atom) is slightly displaced downfield (δ_C 29.5 ppm), which clearly followed from the HSQC spectrum containing a cross peak from C^{10} and ring protons resonating at δ 1.38 ppm. In addition, the C^{14} signal (δ_C 9.0 ppm) is readily distinguishable in the HSQC spectrum. Although the chemical shift of C^{14} is very similar to that of the methyl carbon atom in the $AlCH_2CH_3$ fragment, the chemical shifts of the corresponding protons are appreciably different (δ –0.37 and 1.0 ppm, respectively). In the ^{13}C NMR spectrum of **XIV** recorded from a solution in toluene signals from the double-bonded carbon atoms were observed at δ_C 159.8 (C^1) and 139.3 ppm (C^{12}) ppm, whereas the ^{27}Al NMR spectrum remained almost unchanged (δ_{Al} 156.7 ppm).

Analysis of the structure of new unsaturated bicyclic organoaluminum compounds led us to presume that these metallacycles can be used to develop effective one-pot procedures for the synthesis of difunctional carbo- and heterocyclic compounds, including those having a spiro structure, via transmetalation, cross coupling, and carbocyclization reactions reported by us previously [8−10, 17−19]. For example, reactions of 13-ethyl-13-aluminabicyclo[10.3.0]pentadec-1(12)-ene (**XIV**) generated *in situ* with carbon dioxide, elemental selenium, bromomethyl methyl ether, and molecular iodine gave bicyclo[10.3.0]pentadec-1(12)-en-13-one (**XXII**), 13-selenabicyclo[10.3.0]pentadec-1(12)-ene (**XXIII**), 4-methylidenespiro[2.11]tetradecane (**XXIV**), and 1-iodo-2-(2-iodoethyl)cyclodecene (**XXV**), respectively, in 74−93% yield (Scheme 5). Bicyclo[10.3.0]pentadec-1(12)-en-13-one (**XXII**, yield 84%) is the key intermediate compound in the synthesis of exaltone, muscone, and bicyclo[10.3.0]pentadecan-13-one that are high-grade fragrant substances with musk-like odor [20, 21].

Among tested zirconium-containing catalysts [Cp_2ZrCl_2, $(MeCp)_2ZrCl_2$, Ind_2ZrCl_2, $Zr(acac)_4$, $ZrOCl_2$, $Zr(OBu)_4$, $(Me_2N)_2ZrCl_2$, $(C_5H_5N)_2ZrCl_2$, $ZrCl_4$, $(MeO)_2ZrCl_2$], Cp_2ZrCl_2 showed the highest catalytic activity in the cycloalumination of cyclic alkynes with Et_3Al. The catalyst concentration strongly affected the yield of bicyclic organoaluminum compound **XIV**. Reduction of the amount of Cp_2ZrCl_2 from 5 to 2 mol % required that the reaction be prolonged to 8–10 h to attain the complete conversion and the same yield. Raising the amount of the catalyst to 15–20 mol % considerably reduced the yield, presumably due to polymerization of the initial alkyne.

Scheme 5.



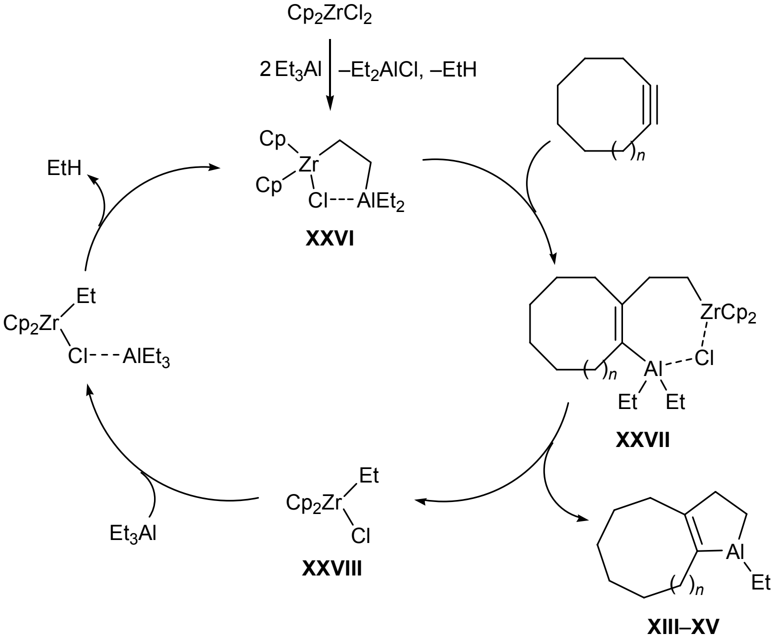
On the basis of our experimental and published data we proposed the following scheme for the formation of bicyclic organoaluminum compounds **XIII–XV** (Scheme 6). Initially formed Zr–Al complex **XXVI** [22] reacts with cycloalkyne to produce seven-membered cyclic complex **XXVII** with bridging chlorine atom. Complex **XXVII** is transformed into bicyclic aluminacyclopentenes **XIII–XV** with liberation of zirconocene complex **XXVIII**, and reaction of the latter with Et_3Al regenerates initial complex **XXVI** via elimination of ethane [2, 22, 23].

To conclude, we were the first to reveal that cyclic alkynes undergo catalytic cycloalumination by the action of triethylaluminum in the presence of zirconium complexes to give in high yield (>85%) representatives of a new class of organoaluminum compounds, unsaturated bicyclic aluminacyclopentenes.

EXPERIMENTAL

Gas chromatographic analysis was performed on a Shimadzu GC-9A instrument equipped with a 2000× 2-mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS (0.125–0.160 mm); carrier gas helium, flow rate 30 ml/min; oven temperature programming from 50 to 300°C at a rate of 8 deg/min. The ^{1}H, ^{13}C, and ^{27}Al NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance-400 spectrometer at 400, 100, and 104 MHz, respectively; the ^{1}H chemical shifts were measured relative to tetramethylsilane. Gas chromatographic–mass spectrometric analysis was performed on a Finnigan 4021 instrument (HP-5 glass capillary column, 50 000 × 0.25 mm; carrier gas helium; oven temperature programming from 50 to 300°C at a rate of 5 deg/min; injector temperature

Scheme 6.



280°C; ion source temperature 250°C; electron impact, 70 eV). The elemental compositions were determined on a Carlo Erba 1106 analyzer. The yields of organoaluminum compounds were determined by GLC analysis of the hydrolysis products. All reactions with organometallic compounds were carried out in a stream of dry argon. Compounds **IV–IX**, **XVI–XVIII**, and **XXII–XXIV** were identified by comparison with authentic samples [7, 9, 10, 19–21, 24].

Reaction of cycloalkynes with triethylaluminum in the presence of Cp_2ZrCl_2 (*general procedure*). A glass reactor was filled with dry argon and charged at 0°C under stirring with 10 mmol of the corresponding cycloalkyne, 0.5 mmol of Cp_2ZrCl_2, 15 ml of hexane, and 11 mmol of Et_3Al. The mixture was allowed to warm up to 20–22°C, stirred for 4 h, treated with a 7–10% solution of HCl in water or of DCl in D_2O, and extracted with hexane. The extract was dried over $MgSO_4$, and the products were isolated by vacuum distillation.

13-Ethyl-13-aluminabicyclo[10.3.0]pentadec-1(12)-ene (XIV). Oily substance. ^{13}C NMR spectrum, δ_C, ppm: –0.1 (C^{16}), 1.0 (C^{17}), 9.0 (C^{14}), 24–28 (C^3–C^9), 28.5 (C^2), 28.8 (C^{11}), 29.5 (C^{10}), 34.0 (C^{15}), 147.14 (C^{12}), 157.0 (C^1). ^{27}Al NMR spectrum (C_7D_8): δ_{Al} 156.7 ppm.

1-[(2-$^2H_1$)Ethyl](2-$^2H_1$)cyclodec-1-ene (XIX). Oily substance. IR spectrum, ν, cm^{-1}: 3090, 2925, 2850, 2160 (C–D), 1450, 905, 790. ^1H NMR spectrum, δ, ppm: 0.96 m (2H, CH_2D), 1.34–1.39 m (12H, CH_2), 2.05–2.10 m (6H, C**H**$_2$CH=C). ^{13}C NMR spectrum, δ_C, ppm: 12.69 t (C^{12}, J_{CD} = 19.0 Hz), 27.32 (C^{11}); 22.41, 22.56, 24.16, 24.44, 24.64, 25.20, 25.68 (C^3–C^9); 27.97 (C^{10}), 140.78 (C^1); no C^2 signal was observed. Found, %: C 84.49; H+D 15.21. *m/z* 168 $[M]^+$. $C_{12}H_{20}D_2$. Calculated, %: C 84.62; H 13.01; D 2.36. *M* 168.

1-[(2-$^2H_1$)Ethyl](2-$^2H_1$)cyclododec-1-ene (XX). Oily substance. IR spectrum, ν, cm^{-1}: 3090, 2925, 2850, 2160 (C–D), 1450, 905, 790. ^1H NMR spectrum, δ, ppm: 0.98 m (2H, CH_2D), 1.36–1.41 m (16H, CH_2), 2.05–2.10 m (6H, C**H**$_2$CH=C). ^{13}C NMR spectrum, δ_C, ppm: 12.61 t (C^{14}, J_{CD} = 19.5 Hz); 22.36, 22.51, 24.05, 24.40, 24.57, 24.64, 25.08 (2C), 25.68 (C^3–C^{12}); 27.47 (C^{13}), 28.77 (C^{12}), 124.11 t (C^2, J_{CD} = 24.0 Hz), 140.89 (C^1). Found, %: C 86.45; H+D 14.22. *m/z* 196 $[M]^+$. $C_{14}H_{24}D_2$. Calculated, %: C 86.63; H 12.32; D 2.05. *M* 196.

1-[(2-$^2H_1$)Ethyl](2-$^2H_1$)cyclotridec-1-ene (XXI). Oily substance. IR spectrum, ν, cm^{-1}: 3080, 2920, 2850, 2160 (C–D), 1450, 910, 790, 720. ^1H NMR spectrum, δ, ppm: 0.99 m (2H, CH_2D), 1.38 m (18H, CH_2), 2.05 m (6H, C**H**$_2$CH=C). ^{13}C NMR spectrum, δ_C, ppm: 12.7 t (C^{15}, J_{CD} = 19.5 Hz), 26.6 (C^{14}); 24.74, 25.6, 25.64, 25.92, 26.35, 26.48, 26.92, 27.29, 28.34 (2C) (C^3–C^{12}); 29.64 (C^{13}), 124.10 t (C^2, J_{CD} = 23.5 Hz), 141.16 (C^1). Found, %: C 85.47; H+D 13.69. *m/z* 210 $[M]^+$. $C_{15}H_{26}D_2$. Calculated, %: C 85.63; H 12.46; D 1.91. *M* 210.

1-Iodo-2-(2-iodoethyl)cyclododecene (XXV). Oily substance. ^1H NMR spectrum, δ, ppm: 1.47–1.57 m (18H), 2.34 t (2H, *J* = 7 Hz), 2.74–2.81 m (2H), 3.17 t (2H, CH_2I, *J* = 9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 1.31 (C^{14}); 25.5, 25.71, 26.04, 26.12, 26.31, 26.63, 27.77, 29.65, 31.58 (C^4–C^{12}); 41.46 (C^3), 47.70 (C^{13}), 103.91 (C^2), 144.12 (C^1). Found, %: C 37.53; H 5.21; I 56.61. *m/z* 446 $[M]^+$. $C_{14}H_{24}I_2$. Calculated, %: C 37.69; H 5.42; I 56.89. *M* 446.

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