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Cyclomagnesation of Cycloalkynes with the Use of RMgR' Catalyzed by Zirconium Complexes

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Abstract—The intermolecular cyclomagnesation of cycloalkynes and joint cyclomagnesation of cycloalkynes and disubstituted acetylenes was carried out by treating with RMgR' (R, R' = Et, Bu, Hlg) in the presence of Cp_2ZrCl_2 as a catalyst. As a result new unsaturated bi-and tricyclic organomagnesium compounds were obtained in high yields.

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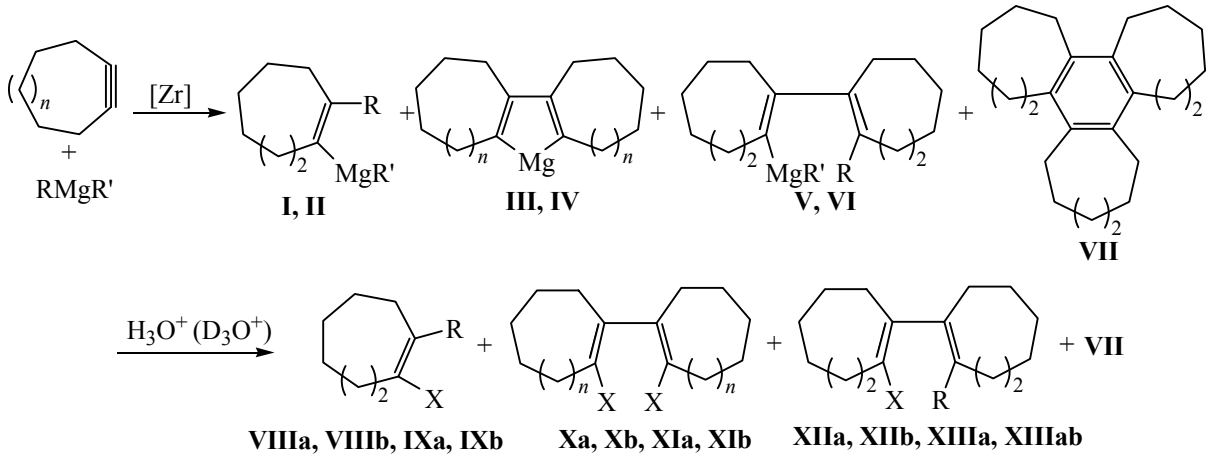
In the course of the investigation of catalytic cyclomagnesation of unsaturated compounds we discovered for the first time that disubstituted acetylenes reacted with Grignard reagents in the presence of Cp_2ZrCl_2 affording tetrasubstituted magnesacyclopenta-2,4-dienes [1].

In continuation of the investigation of this reaction, its extension to cyclic acetylenes, and also aiming at the synthesis of new classes of unsaturated fused tricyclic organomagnesium compounds we studied the reactions of cycloalkynes (cyclooctyne, cyclododecyne) with dialkyl and alkylhalogen magnesium derivatives (EtMgBr, BuMgBr, Et_2Mg, Bu_2Mg) in the presence of zirconium complexes exhibiting a high activity and selectivity in the cyclomagnesation of α-olefins [2–4], acetylenes [1], terminal 1,2-dienes [5, 6], and norbornenes [7].

First the cyclooctyne chosen as model compound was brought into reaction with BuMgBr (Et_2O) under the conditions developed formerly as optimal for the cyclomagnesation of disubstituted acetylenes [1] (~20°C, 2 h, cyclooctyne–BuMgBr–Cp_2ZrCl_2, 10 : 20 : 0.5). As a result of acid hydrolysis and treatment with deuterium oxide of the reaction products a mixture of four hydrocarbons was obtained (according to GLC) in an overall yield ~89%.

Scheme 1.



[Zr] = Cp_2ZrCl_2; X = H (**a**), D (**b**); R = Bu (**I, V, VIII, XII**), Et (**II, VI, IX, XIII**); n = 2 (**III, X**), 6 (**IV, XI**).

Table 1. Effect of the structure of organomagnesium compound and solvent, and also of the temperature on the yield and composition of reaction products obtained at treatment of cyclic acetylenes by Grignard reagents catalyzed with Cp_2ZrCl_2

Cycloalkyne	Organomagnesium compound	Solvent	Temperature, °C	Time, h	[Zr], mol%	Ratio of (**I,II**): :(**III,IV**):(**V,VI**): (**VII**)	Overall yield, %
Cyclooctyne	BuMgBr	Et_2O	20–22	3	5	1:3:1:2	89
Cyclooctyne	BuMgBr	Et_2O	20–22	5	0	3:0:2:0	52
Cyclooctyne	BuMgBr	*i*-Pr_2O	20–22	2	0	1:0:3:1	81
Cyclooctyne	BuMgBr	THF	20–22	8	0	1:0:0:0	10
Cyclooctyne	BuMgBr	THF	20–22	3	5	1:20:1:0	75
Cyclooctyne	BuMgBr	THF	0	8	5	0:1:0:0	56
Cyclooctyne	BuMgBr	THF	40	1	5	2:8:1:2	86
Cyclooctyne	EtMgBr	THF	20–22	3	5	3:8:2:0	90
Cyclooctyne	Bu_2Mg	THF	20–22	3	5	1:14:1:0	80
Cyclooctyne	Et_2Mg	THF	20–22	3	5	4:6:1:0	94
Cyclododecyne	BuMgBr	THF	20–22	8	5	0:1:0:0	46
Cyclododecyne	Bu_2Mg	THF	20–22	8	5	0:1:0:0	54

The structure of organomagnesium compounds **I, III**, and **V** formed in this reaction was established with the use of ^1H and ^{13}C NMR spectroscopy, and also by the mass spectra of the products of their hydrolysis (**VIIIa, Xa, XIIa**) and treatment with D_2O (**VIIIb, Xb, XIIb**) (Scheme 1).

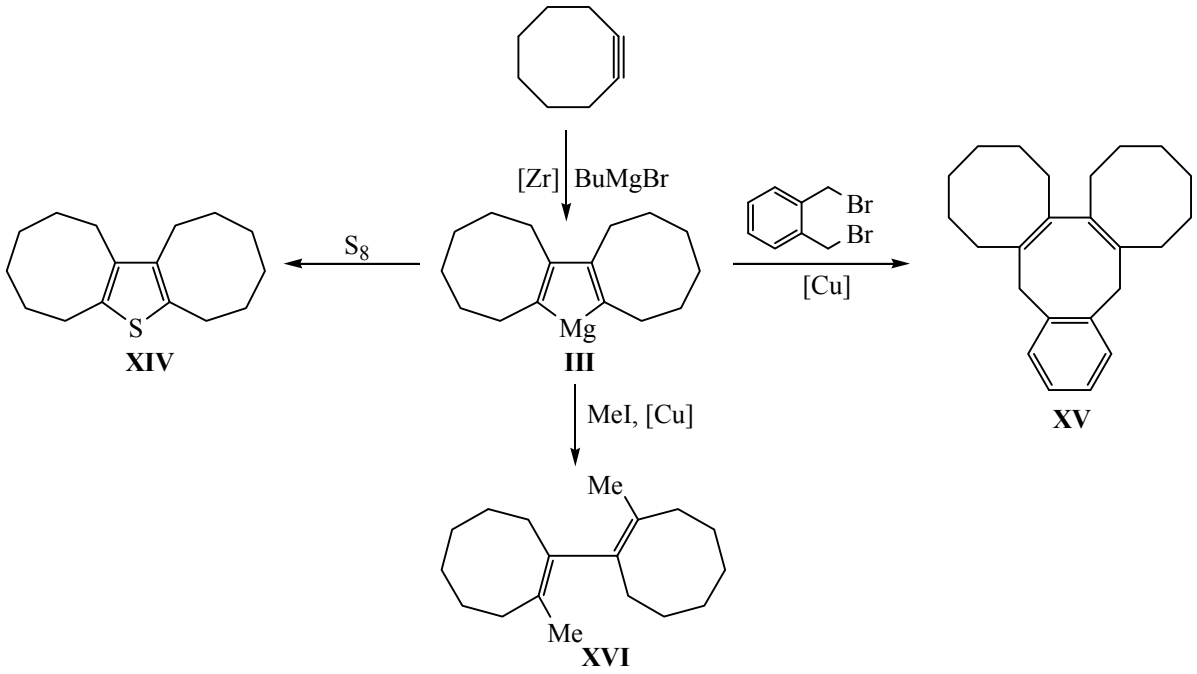
For instance, the ^{13}C NMR spectrum of compound **Xa** contained eight signals: two downfield signals at 125.1 and 139.8 ppm assigned to the carbon atoms of the trisubstituted double bond, and six peaks from sp^3-hybridized carbon atoms of the cyclic fragment in the region 25–31 ppm testifying to the symmetry of the molecule. In the ^{13}C NMR spectrum of partially deuterated compound **Xb** the signal of the carbon atom of the double bond is split into a triplet by coupling with deuterium ($J_{C,D}$ 24.5 Hz) with an α-isotope upfield shift of the triplet center (Δδ– 0.3 ppm) with respect to the same signal in the spectrum of compound **Xa**, and in the ^1H NMR spectrum of compound **Xb** the signal of the proton at the double bond at 5.77 ppm disappears. The molecular mass of compounds **Xa** and **Xb** equal $[M]^+$ 218 and 220 respectively were measured by mass spectrometry. Similarly was established the structure of compounds **I, V** and **VII**.

The above data underlie the assignment to the hydrolysis products the structures of 1-butyl-1-cyclooctene (**VIIIa**), 1,1'-bi(1-cycloocten-1-yl) (**Xa**), and 2-butyl-1,1'-bi(1-cycloocten-1-yl) (**XIIa**), and the deuterated products were identified as 1-butyl-2-deutero-1-cyclooctene (**VIIIb**), 2,2'-dideutero-1,1'-bi(1-cyclo-octen-1-yl) (**Xb**), 2-butyl-2'-deutero-1,1'-bi(1-cycloocten-1-yl) (**XIIb**). 1,4-Dideuterated hydrocarbon **Xb** formed on the treatment with deuterium oxide of compound **III** indicates that in the latter the Mg atom is linked simultaneously to atoms C^9 and C^{11}. Based on the results obtained we assumed for compounds **I, III**, and **V** the structures of [2-butyl(1-cycloocten-1-yl)-1-yl]magnesium bromide, 2-magnesatricyclo[$9.6.0^{1,11}.0^{3,10}$]heptadeca-1(11),3(10)-diene, and [2'-butyl-1,1'-bi(1-cycloocten-1-yl)-2-yl]magnesium bromide respectively.

In order to increase the chemoselectivity of the cyclomagnesation,we studied the effect of various factors (temperature, character of solvent, organomagnesium compound, ligand surrounding of Zr) on the course of this reaction (Table 1).

As a result of the above investigations we established that the reaction of cyclooctyne with BuMgBr in ether solvents (Et_2O, *i*-Pr_2O, THF) without catalyst yielded products of 1,2-carbomagnesation of the initial acetylene by BuMgBr **I** and of intermolecular carbomagnesation **V**; the latter might form by the reaction of compound **I** with the cyclooctyne. The overall yield of compounds **I** and **V** decreased in the solvent series *i*-Pr_2O > Et_2O > THF in good agreement with the published data on the growth of the Grignard reagents activity in various solvents [8]. Based on these results we carried out all further

Scheme 2.



[Zr] = Cp_2ZrCl_2, [Cu] = CuCl.

experiments on cyclomagnesation of cyclic acetylenes with RMgR' (R, R' = Et, Bu, Hlg) catalyzed by Cp_2ZrCl_2 in THF solution.

We established that the variation of the temperature of cyclomagnesation affected both the rate and the chemoselectivity of the reaction. For instance, at 0°C within 8 h we obtained magnesacyclopentadiene **III** in ~56% yield at the selectivity >98%, and at ~40°C in 1 h a complete conversion of the cyclooctyne was attained, but under these conditions alongside organomagnesium compound **III** formed also carbomagnesation products **I, V**, and homocyclotrimer **VII**.

Replacement of BuMgBr by Bu_2Mg, Et_2Mg, or EtMgBr somewhat increased the overall yield of organomagnesium compounds **I–VII** and decreased the chemoselectivity with respect to cyclic compounds **III** and **IV**. Nonetheless, at the use of the above dialkyl and alkylhalogen magnesium derivatives magnesacyclopentadiene **III** was obtained in 51–65% yield.

The change in the ratio of the initial reagents by increasing the content of organomagnesium compound relative to the cycloalkyne did not result in the increase in the overall yield of the target organomagnesium compounds.

Under the developed optimum conditions (BuMgBr, THF, 20-22°C, 3 h) the yield of magnesacyclopentadiene **III** diminished in the series of the tested zirconium-based catalysts: Cp_2ZrCl_2 (68%), Ind_2ZrCl_2 (24%), $ZrCl_4$ (11%), $(BuO)_2ZrCl_2$ (4%), $PyZrCl_6$ (2%).

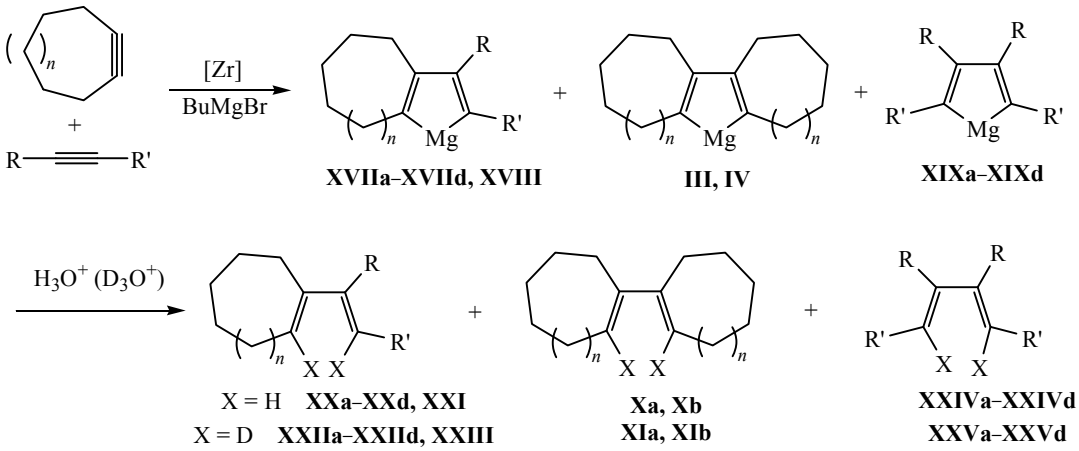
Cyclododecyne like cyclooctyne under the conditions we chose entered the reaction of intermolecular cyclomagnesation with BuMgX (X = Bu, Br) catalyzed by Cp_2ZrCl_2 giving 2-magnesatricyclo[13.10.$0^{1,15}$.$0^{3,14}$]-pentacosa-1(15),3(14)-diene (**IV**) in 46–56% yield. No carbomagnesation products formed in these experiments.

To prove reliably the structure of the obtained magnesacyclopentadiene **III** and to develop new one-pot methods of preparation of difficultly available carbocyclic and heterocyclic compounds we carried out a series of reactions of compound **III** with elemental sulfur, α,α'-dibromo-*o*-xylene, and methyl iodide [9-11] and obtained 2-thiatricyclo-[9.6.$0^{1,11}$.$0^{3,10}$]heptadeca-1(11),3(10)-diene (**XIV**), 3,4-benzotricyclo-[12.6.$0^{1,14}$.$0^{6,13}$]eicosa-1(14),6(13)-diene (**XV**), and 2,2'-dimethyl-1,1'-bi(1-cycloocten-1-yl) (**XVI**) respectively (Scheme 2).

The structure of compounds obtained was confirmed by ^{1}H and ^{13}C NMR spectra and GC-MS method.

Further we attempted a mixed intermolecular

Scheme 3.



[Zr] = Cp_2ZrCl_2; n = 2 (**XVII, XX, XXII**); R = R' = Et (a), Pr (**b**), Bu (**c**); R = Bu, R' = $SiMe_3$ (**d**); n = 6, R = R' = Et (**XVIII**, **XXI, XXIII**).

cyclomagnesation of cyclic acetylenes with acyclic disubstituted acetylenes in order to prepare new class of bicyclic magnesacyclopenta-2,4-dienes.

Actually the reaction of equimolar quantities of cyclooctyne and 3-hexyne that we chose as model compounds with BuMgBr under the conditions developed for homocyclomagnesation of cycloalkynes (BuMgBr, THF, 20-22°C, 3 h) led to the formation of three types of magnesacyclopenta-2,4-dienes in a ratio (**XVIIa**) : (**III**) : (**XIXa**) 1 : 5 : 2 (according to the GLC data for hydrolysis products and products of quenching with D_2O) in 77% yield (Scheme 3). By optimization of the reaction conditions through the variation of the ratio of the initial compounds (cyclooctyne : 3-hexyne: BuMgBr : Cp_2ZrCl_2, 10 : 11 : 22:1, 20–22°C, THF, 4 h) we obtained the mixture of all structural magnesacyclopenta-2,4-dienes **XVIIa, III**, and **XIXa** where the target magnesacyclopenta-2,4-diene **XVIIa** was contained in ~64% yield at the ratio of organomagnesium compounds (**XVIIa**):(**III**):(**XIXa**) 6 : 1 : 1. The overall yield reached 86%.

Based on the data of 1D and 2D NMR experiments and the mass spectra of products from quenching compound **XVIIa** with acidified water **XXa** and deuterium oxide **XXIIa** the structure of compound **XVIIa** was identified as 10,11-diethyl-9-magnesabicyclo-[6.2.$0^{1,8}$]undeca-1(8),10(11)-diene.

Under the conditions mentioned above the joint cyclomagnesation of cyclooctyne with 4-octyne, 5-decyne, butyltrimethylsilylacetylene, or of cyclododecyne and 3-hexyne in excess BuMgBr led to the formation of the corresponding bicyclic magnesacyclopenta-2,4-dienes **XVIIb–XVIId**, and **XVIII** in 45–60% yields (Table 2).

The structure of products of joint cyclomagnesation was reliably proved by spectral methods and by analysis of quenching the target organomagnesium compounds with acidified water and deuterium oxide

Thus we for the first time succeeded in intermolecular

Table 2. Joint cyclomagnesation of cyclic and acyclic acetylenes

Cycloalkyne	Disubstituted acetylene	Yield of magnesacyclopentadienes, %[a]			Overall yield, %
Cyclooctyne	3-Hexyne	64 (**XVIIa**)	12 (**III**)	10 (**XIXa**)	86
Cyclooctyne	4-Octyne	59 (**XVIIb**)	11 (**III**)	12 (**XIXb**)	82
Cyclooctyne	5-Decyne	55 (**XVIIc**)	8 (**III**)	14 (**XIXc**)	77
Cyclooctyne	Butylsilylacetylene	56 (**XVIId**)	8 (**III**)	16 (**XIXd**)	80
Cyclododecyne	3-Hexyne	45 (**XVIII**)	9 (**IV**)	2 (**XIXa**)	56

[a] Yields of magnesacyles were determined by GLC of the products of their acid hydrolysis.

homocyclomagnesation of cycloalkynes and mixed cyclomagnesation of cycloalkynes with disubstituted acetylenes by treatment with dialkyl magnesium and alkylmagnesium halides in the presence of zirconium complexes resulted in preparation of new types of bi- and tricyclic magnesa-cyclopenta-2,4-dienes that as shown on several examples possessed a wide synthetic potential for the synthesis of carbo-and heterocyclic compounds.

EXPERIMENTAL

Products of hydrolysis and quenching with D_2O were analyzed on a chromatograph Chrom-5 in a flow of helium, column 1200 × 3 mm, stationary phase 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (400 and 100 MHz respectively) from solutions in $CDCl_3$, chemical shifts reported with respect to TMS. GC-MS measurements were performed on an instrument Finnigan 4021 (glass capillary column 50000 × 0.25 mm, stationary phase HP-5, carrier gas helium, ramp from 50 to 300°C at a rate 5 deg/min, vaporizer temperature 280°C, ion source temperature 250°C, 70 eV). Elemental analysis was carried out on an analyzer Karlo Erba 1106. The yields of organomagnesium compounds were determined by GLC of hydrolysis products. Reactions with organometallic compounds were performed in a flow of dry argon. The ether solvents were distilled over $LiAlH_4$ just before use. Solutions of RMgR' (R, R' = Bu, Et, Br) in Et_2O and THF were prepared by procedure [12]. Cp_2ZrCl_2 was synthesized from $ZrCl_4$ as described before [13]. Compounds **VII**, **Xa**, **Xb**, **XIa**, **XIb**, **XIV**, **XVI**, **XXa–XXc**, **XXI**, **XXIIa–XXIIc**, **XVIII**, **XXIVa–XXIVd**, **XXVa–XXVd** were identified by comparison with authentic samples [1, 14–18].

Homocyclomagnesation of cycloalkynes with RMgR' (R, R' = Bu, Et, Br in the presence of catalyst Cp_2ZrCl_2. Into a glass reactor under the atmosphere of dry argon at ~0°C was charg-ed while stirring 0.5 mmol of Cp_2ZrCl_2, 10 mmol of cycloalkyne (cyclooctyne, cyclododecyne), and 20 mmol of RMgR' (R, R' = Bu, Et, Br) in an appropriate ether solvent. The temperature was raised to ambient (20–22°C), and the stirring was continued for 3–8 h. For identification of the substituted magnesacyclopentadienes by the deuterated products the reaction mixture was quenched with a 8% solution of DCl in D_2O. The reaction products were extracted with ether or hexane, the extracts were dried with $MgSO_4$, and subjected to fractional distillation.

1-Butyl-1-cyclooctene (VIIIa), bp 109–111°C (20 mm Hg). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, *J* 7 Hz), 1.47 m (12H, CH_2), 2.08 m (6H, $CH_2CH=C$), 5.33 t (1H, CH=C, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 14.0 (C^{12}), 22.6 (C^{11}), 26.2 (C^6), 26.3 (C^5), 26.5 (C^4), 28.9 (C^7), 29.0 (C^3), 30.0 (C^{10}), 30.4 (C^9), 37.3 (C^8), 123.4 (C^2), 141.1 (C^1). Found, %: C 86.67; H 13.33. $[M]^+$ 166. $C_{12}H_{22}$. Calculated, %: C 86.54; H 13.30.

1-Ethyl-1-cyclooctene (IXa), bp 75–77°C (20 mm Hg). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, *J* 7 Hz), 1.45 m (8H, CH_2), 2.11 m (6H, $CH_2CH=C$), 5.37 t (1H, CH=C, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 13.8 (C^{10}), 26.2 (C^6), 26.4 (C^5), 26.5 (C^4), 28.9 (C^7), 29.1 (C^3), 29.7 (C^9), 37.5 (C^8), 123.6 (C^2), 141.3 (C^1). Found, %: C 86.88; H 13.12. $[M]^+$ 138. $C_{10}H_{18}$. Calculated, %: C 86.73; H 13.10.

2-Butyl-1,1'-bi(1-cycloocten-1-yl) (XIIa), bp 154–156°C (1 mm Hg). ^1H NMR spectrum, δ, ppm: 0.94 t (3H, CH_3, J 7 Hz), 1.47 m (20H, CH_2), 2.18 m (10H, $CH_2C=C$), 5.25 t (1H, CH=C, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 14.0, 22.5, 26.5 ($C^{4,4'}$), 26.6 ($C^{5,5'}$), 26.8, 28.7 ($C^{6,6'}$), 29.3 ($C^{3'}$), 29.5 ($C^{7,7'}$), 29.6 (C^3), 29.9 ($C^{8,8'}$), 31.0, 126.1 ($C^{2'}$), 135.2 ($C^{1'}$), 137.9 (C^1), 142.1 (C^2). Found, %: C 87.51; H 12.49. $[M]^+$ 274. $C_{20}H_{34}$. Calculated, %: C 87.44; H 12.45.

2-Ethyl-1,1'-bi(1-cycloocten-1-yl) (XIIIa), bp 136–138°C (1 mm Hg). ^1H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, J 7 Hz), 1.49 m (16H, CH_2), 2.16 m (10H, $CH_2C=C$), 5.24 t (1H, CH=C, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 13.9, 26.4 ($C^{4,4'}$), 26.6 ($C^{5,5'}$), 26.8, 28.7 ($C^{6,6'}$), 29.3 ($C^{3'}$), 29.5 ($C^{7,7'}$), 29.8 (C^3), 29.9 ($C^{8,8'}$), 126.0 ($C^{2'}$), 135.2 ($C^{1'}$), 137.9 (C^1), 142.2 (C^2). Found, %: C 87.73; H 12.27. $[M]^+$ 246. $C_{18}H_{30}$. Calculated, %: C 87.62; H 12.25.

1-Butyl-2-deutero-1-cyclooctene (VIIIb), bp 109–111°C (20 mm Hg). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, J 7 Hz), 1.47 m (12H, CH_2), 2.06 m (6H, $CH_2CH=C$). ^{13}C NMR spectrum, δ, ppm: 14.1 (C^{12}), 22.6 (C^{11}), 26.2 (C^6), 26.4 (C^5), 26.5 (C^4), 28.9 (C^7), 29.1 (C^3), 30.1 (C^{10}), 30.4 (C^9), 37.3 (C^8), 123.1 t (C^2, J 7 Hz), 141.2 (C^1). Found, %: C 86.15; H 12.65; D 1.20. $[M]^+$ 167. $C_{12}H_{21}D$. Calculated, %: C 85.94; H + D 13.50.

1-Ethyl-2-deutero-1-cyclooctene (IXb), bp 75–77°C (20 mm Hg). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J 7 Hz), 1.43 m (8H, CH_2), 2.09 m (6H, $CH_2CH=C$). ^{13}C NMR spectrum, δ, ppm: 13.8 (C^{10}),

26.3 (C^6), 26.4 (C^5), 26.5 (C^4), 28.9 (C^7), 29.2 (C^3), 29.7 (C^9), 37.4 (C^8), 123.4 t (C^2, J 7 Hz), 141.2 (C^1). Found, %: C 86.25; H 12.31; D 1.44. $[M]^+$ 139. $C_{10}H_{17}D$. Calculated, %: C 86.01; H + D 13.16.

2-Butyl-2'-deutero-1,1'-bi(1-cycloocten-1-yl) (XIIb), bp 154–156°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, CH_3, J 7 Hz), 1.48 m (20H, CH_2), 2.19 m (10H, CH_2C=C). ^{13}C NMR spectrum, δ, ppm: 14.1, 22.5, 26.5 ($C^{4,4'}$), 26.6 ($C^{5,5'}$), 26.8, 28.8 ($C^{6,6'}$), 29.3 ($C^{3'}$), 29.5 ($C^{7,7'}$), 29.7 (C^3), 29.9 ($C^{8,8'}$), 31.1 ($C^{2'}$), 135.2 ($C^{1'}$), 137.9 (C^1), 142.2 (C^2). Found, %: C 87.20; H 12.07; D 0.73. $[M]^+$ 275. $C_{20}H_{33}D$. Calculated, %: C 87.03; H + D 12.75.

2-Ethyl-2'-deutero-1,1'-bi(1-cycloocten-1-yl) (XIIIb), bp 136–138°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3, J 7 Hz), 1.49 m (16H, CH_2), 2.17 m (10H, CH_2C=C). ^{13}C NMR spectrum, δ, ppm: 13.9, 26.4 ($C^{4,4'}$), 26.7 ($C^{5,5'}$), 26.8, 28.7 ($C^{6,6'}$), 29.3 ($C^{3'}$), 29.5 ($C^{7,7'}$), 29.8 (C^3), 29.9 ($C^{8,8'}$), *($C^{2'}$), 135.1 ($C^{1'}$), 137.9 (C^1), 142.2 (C^2). Found, %: C 87.37; H 11.81; D 0.81. $[M]^+$ 247. $C_{18}H_{29}D$. Calculated, %: C 87.12; H + D 12.45.

3,4-Benzotricyclo[12.6.0^{1,14}.0^{6,13}]eicosa-1(14),6(13)-diene (XV), mp 158–159°C. ^{1}H NMR spectrum, δ, ppm: 1.48–1.68 m (16H, CH_2), 2.08–2.48 m (8H, CH_2C=C), 3.02 d (2H, $PhCH_2C$=C, J 13 Hz), 3.76 d (2H, $PhCH_2C$=C, J 13 Hz), 7.11 m (4H, Ph). ^{13}C NMR spectrum, δ, ppm: 26.8 ($C^{8,19}$), 26.9 ($C^{11,16}$), 28.7 ($C^{9,18}$), 28.8 ($C^{10,17}$), 30.4 ($C^{12,15}$), 30.9 ($C^{7,20}$), 41.6 ($C^{2,5}$), 126.3 ($C^{21,24}$), 129.0 ($C^{13,14}$), 130.6 ($C^{22,23}$), 136.7 ($C^{1,6}$), 139.1 ($C^{3,4}$). Found, %: C 89.94; H 10.06. $[M]^+$ 320. $C_{24}H_{32}$. Calculated, %: C 89.76; H 10.03.

Joint cyclomagnesation of cyclic and acyclic acetylenes with BuMgBr in the presence of catalyst Cp_2ZrCl_2. Into a glass reactor under the atmosphere of dry argon at ~0°C was charged while stirring 1 mmol of Cp_2ZrCl_2, 10 mmol of cycloalkyne (cyclooctyne, cyclododecyne), 11 mmol of disubstituted acetylene, and 22 mmol of BuMgBr in THF. The temperature was raised to ambient (20–22°C), and the stirring was continued for 3–8 h. For identification of the substituted magnesacyclopentadienes by the deuterated products the reaction mixture was quenched with a 8% solution of DCl in D_2O. The reaction products were extracted with ether or hexane, the extracts were dried with $MgSO_4$, and subjected to fractional distillation.

(2-1-Cycloocten-1-yl-hex-1-en-1-yl)(trimethyl)-silane (XXd), bp 122–124°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.13 s [9H, $(CH_3)_3Si$], 0.92 t (3H, CH_3, J 7 Hz), 1.43 m (12H, CH_2), 2.15 m (6H, CH_2C=C), 5.47 s (1H, SiCH=C), 5.82 t (1H, CH=C, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 0.4 ($C^{15,16,17}$), 14.1 (C^{13}), 23.1 (C^{12}), 25.9 (C^4), 26.1 (C^5), 27.1 (C^6), 27.6 (C^7), 29.1 (C^3), 30.3 (C^8), 32.6 (C^{11}), 33.5 (C^{10}), 123.4 (C^{14}), 127.0 (C^2), 141.7 (C^1), 157.9 (C^9). Found, %: C 77.19; H 12.19; Si 10.62. $[M]^+$ 264. $C_{17}H_{32}Si$. Calculated, %: C 77.04; H 12.15; Si 10.50.

[1-Deutero-2-(2-deutero1-cycloocten-1-yl)-hex-1-en-1-yl](trimethyl)silane (XXIId), bp 122–124°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.14 s [9H, $(CH_3)_3Si$], 0.92 t (3H, CH_3, J 7 Hz), 1.44 m (12H, CH_2), 2.13 m (6H, CH_2C=C). ^{13}C NMR spectrum, δ, ppm: 0.4 ($C^{15,16,17}$), 14.2 (C^{13}), 22.9 (C^{12}), 25.9 (C^4), 26.2 (C^5), 27.1 (C^6), 27.4 (C^7), 29.1 (C^3), 30.3 (C^8), 32.7 (C^{11}), 33.6 (C^{10}), *(C^{14}), *(C^2), 141.7 (C^1), 157.8 (C^9). Found, %: C 76.61; H 11.35; D 1.51; Si 10.54. $[M]^+$ 266. $C_{17}H_{30}D_2Si$. Calculated, %: C 76.44; H + D 12.35; Si 10.50.

Signals marked with asterisk were not observed.

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