Catalytic synthesis and transformations of magnesacycloalkanes
3. Cyclomagnesation of norbornenes catalyzed by Cp_2ZrCl_2

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Catalytic cyclometallation of bicyclo[2.2.1]hept-2-ene, spiro{bicyclo[2.2.1]hept-2-ene-7.1'-cyclopropane} and *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (dicyclopentadiene) with R_2Mg (R = *n*-Pr, *n*-Bu) leading to the formation of polycyclic magnesacyclopentanes (MC) has been studied. The yield of MC and the selectivity of the reaction have been shown to depend on the ratio of starting reagents, the solvent, and temperature. The most probable scheme of the transformation studied is proposed.

Key words: synthesis, catalysis, magnesacycloalkanes, norbornenes, cyclometallation, Zr-complex, selectivity, mechanism, zirconacyclopentanes.

Recently we accomplished cyclometallation of styrenes with *n*-R_2Mg (R = Pr, Bu, C_6H_{13}) catalyzed by Cp_2ZrCl_2, leading to magnesacycloalkanes in one step.[1]

These results have stimulated research along this line with the aim of widening the application field of the discovered reaction, as well as investigation of the possibility of cyclomagnesation of cyclic olefins to produce new types of polycyclic organomagnesium compounds (OMC). Bicyclo[2.2.1]hept-2-ene (**1**), spiro{bicyclo[2.2.1]hept-2-ene-7,1'-cyclopropane} (**2**), and *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**3**) were chosen as the objects of study, and $(n\text{-Pr})_2Mg$, and $(n\text{-Bu}_2)Mg$ served as organometallic reagents. It should be noted that Et_2Mg reacts with norbornenes in the presence of Cp_2ZrCl_2 according to the carbomagnesation scheme,[2] while beginning with $(n\text{-Pr})_2Mg$, cyclometallation is observed.

Preliminary experiments have shown that the optimal conditions for cyclometallation of the norbornenes mentioned are: ~25°C, 7—8 h, the solvent mixture Et_2O—THF (1:1), and the catalyst concentration 2-3 mol. % in relation to the olefin. Thus, interaction of **1** with an equimolar amount of R_2Mg (R = *n*-Pr, *n*-Bu) in the presence of Cp_2ZrCl_2 in the conditions chosen gives OMC **4**, **5**, and **6** in an overall yield of ~80%. The reaction is accompanied by liberation of propane or butane*, depending on the starting OMC (Scheme 1).

Hydrolysis or deuterolysis of the reaction mixture obtained from $(n\text{-Pr})_2Mg$ and norbornene yields *exo*-2-isopropylbicyclo[2.2.1]heptane (**7**) and *exo,exo*-2,2'-bis-bicyclo[2.2.1]heptyl (**8**), or partially deuterated compounds, *exo*-2-(1-deuteriomethyl)ethyl-3-deuteriobicyclo[2.2.1]heptane (**9**) and *exo,exo*-2,2'-bis-3-deuteriobicyclo[2.2.1]heptyl (**10**), which were isolated by vacuum distillation and identified by spectroscopy.

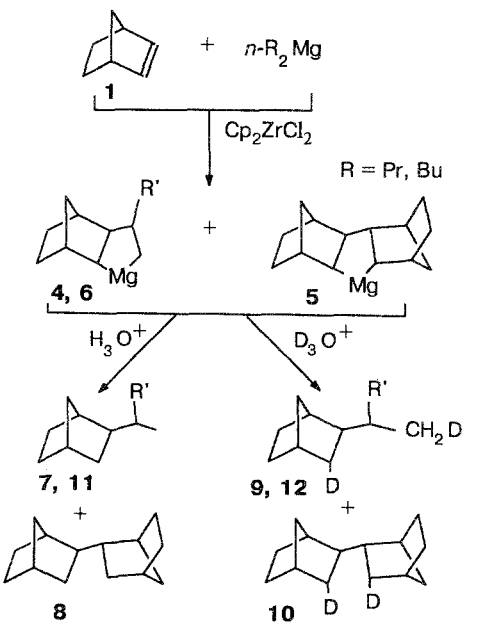
* Up to 5-6% of propene and 1-butene, respectively, were detected in a gaseous product.

In the case of $(n\text{-Bu})_2Mg$, *exo*-2-*sec*-butylbicyclo[2.2.1]heptane (**11**) and **8**, or *exo*-2-(1-deuteriomethyl)propyl-3-deuteriobicyclo[2.2.1]heptane (**12**) and **10**, respectively, were obtained.

As in the case of styrene cyclometallation[1], the choice of reaction conditions is of great importance in obtaining the cyclometallation products of norbornene (NB) in high yield and high selectivity (Table 1).

Note that an increase in the starting OMC content favors the reaction selectivity with respect to **4**, which can be as high as 99%. The temperature of the process

Scheme 1



R' = Me(**4**, **7**, **9**); Et(**6**, **11**, **12**)

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 1, pp. 165-169, January, 1993.

exerts considerable effect on the yield and composition of the products. With an increase in cyclometallation temperature up to 40°C, the content of **5** rises to 89%.

The assignment of the signals in the ^{13}C NMR spectra of the compounds and determination of their configuration was carried out by comparison with the authentic NB derivatives.[3] Stereochemical individuality of the "dimeric" compound **8** was established by comparing the chemical shifts for the C(6) and C(7) atoms (30.30 ppm, t, and 30.50 ppm, t, respectively), which are the most sensitive to *exo*-, *endo*-configuration change, with those for C(6) (30.64 ppm, t) and C(7) (35.50 ppm, t) of compound **7**, having *exo*-configuration. Similar chemical shift values for these carbon atoms, as well as a series of seven magnetically non-equivalent signals imply that compound **8** has *exo,exo*-configuration and symmetrical structure.

The spectral characteristics obtained for compounds **7**, **8**, **9**, **10**, **11**, and **12** allow one to conclude that interaction of NB with R_2Mg in the presence of Cp_2ZrCl_2 proceeds as *exo*-cyclometallation to form tri- and pentacyclic metalocycles with *exo*-orientation of the magnesacyclopentane fragment.

In order to reveal the effect of the olefin structure on the route and stereochemistry of cyclometallation, we studied reactions of **2** and **3** with R_2Mg (R = *n*-Pr, *n*-Bu) in the presence of 3 mol.% of Cp_2ZrCl_2 in the conditions outlined above. In the case of **2** we obtained MC **13**, **14** and **15**, **14** in an overall yield of ~80% for each reaction. The regularities of the process are the same as those for **1**.

Hydrolysis and deuterolysis of the obtained metalocycles lead only to *exo*-substituted norbornanes **16**, **17**, **18**, and to dideuterionorbornanes **19**, **20**, **21** (Scheme 2).

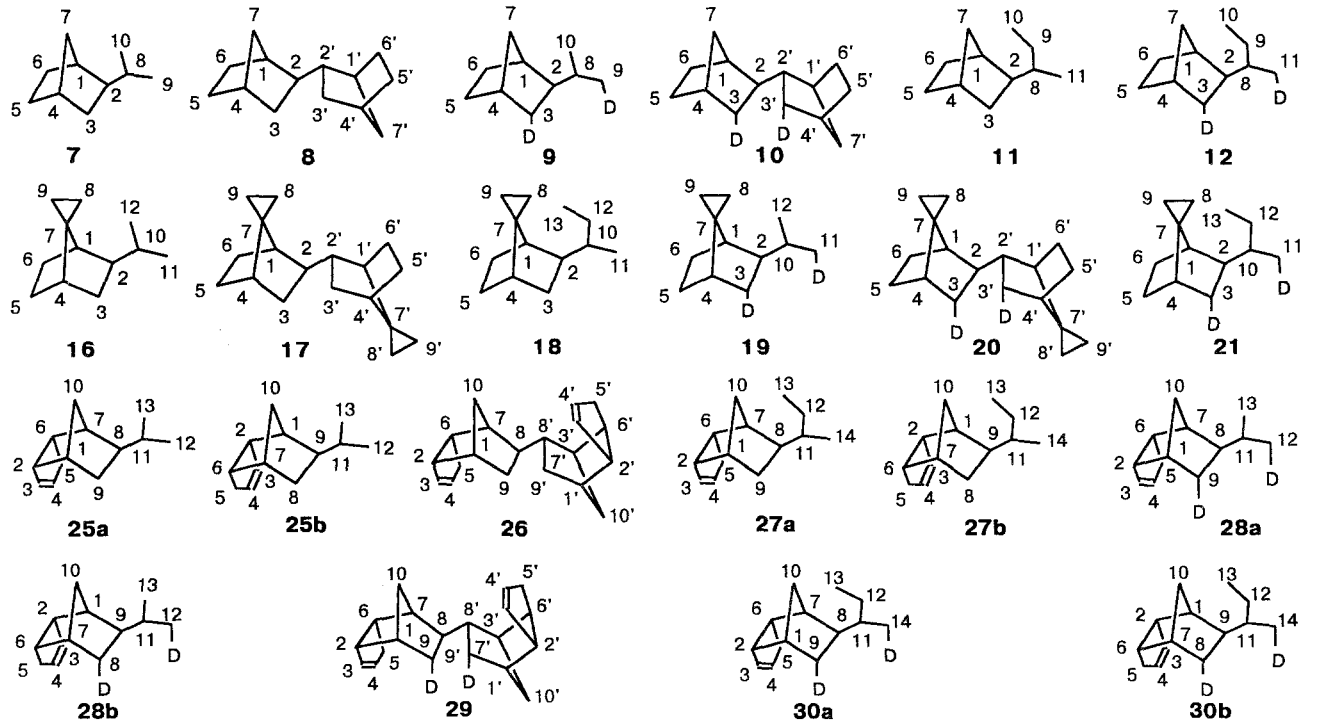
Table 1. The effect of the ratio of starting reagents on the yield and composition of the cyclometallation products of norbornene (NB) with $(n\text{-Pr})_2Mg$*

No	NB:$(n\text{-Pr})_2Mg$	Yield 4+5, %	Products ratio 4	5
1	2:1	58	29	71
2	1:1	81	80	20
3	1:2	86	95	5
4	1:3	98	99	1
5	1:1**	95	11	89
6	1:1***	40	26	74

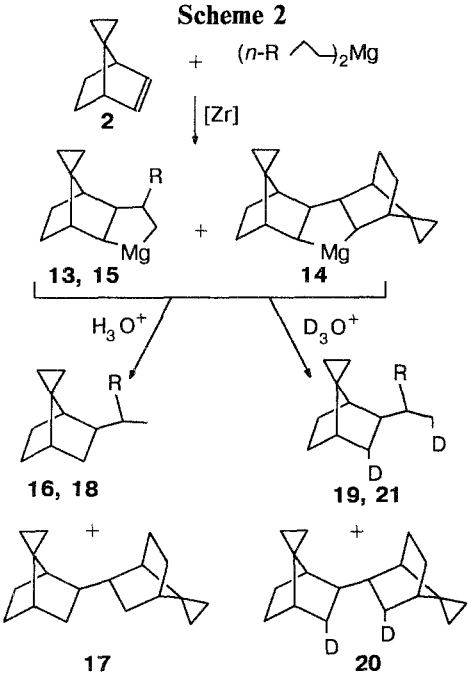
*Reaction conditions: Cp_2ZrCl_2 : $(n\text{-Pr})_2Mg$ = 2.5 : 100; ether — THF (1 : 1) solvent mixture; 20°C, 8h, concentration of $(n\text{-Pr})_2Mg$, 0.6 mmol/ml. Yields of **4**, **5**, based on the starting NB, were calculated from the hydrolysis products of the reaction mixture. The regularities for the reaction with $(n\text{-Bu})_2Mg$ are the same as for $(n\text{-Pr}_2)Mg$.
**The reaction was carried out for 4 h at 40°C.
***The reaction was carried out in ether for 8 h at 20°C.

Similar results were obtained in cyclometallation of *endo*-dicyclopentadiene **3**, which under these reaction conditions gives a mixture of five-membered regioisomeric magnesacycles **22a**, **22b**, **24a**, **24b** (Scheme 3), built of one *endo*-dicyclopentadiene molecule, a magnesium atom, and an alkyl radical, and of the magnesacycle **23**, built of two molecules of **3** and a magnesium atom. After hydrolysis and deuterolysis of the OMC mixture, hydrocarbons **25a**, **25b**, **26**, **27a**, **27b**, **28a**, **28b**, **29**, **30a**, **30b** were isolated, and their structure and proportion were determined by spectral methods.

The ratio of regioisomers **25a**:**25b**, **27a**:**27b**, and **28a**:**28b**, **30a**:**30b** is ~3:2. Compounds **26** and **29** are present as single isomers.



Scheme 2



R = Me(**13**, **16**, **19**); Et(**15**, **18**, **21**)

The known data on olefin cycloalumination with R_3Al[4] catalyzed by zirconium complexes, on the mechanism of the decomposition of dialkylzirconium derivatives, and on the synthesis of zirconocene-alkene complexes,[5,6] as well as the results of our experiments allow one to propose a probable scheme for the mechanism of NB cyclomagnesation with R_2Mg in the presence of Cp_2ZrCl_2 (Scheme 4).

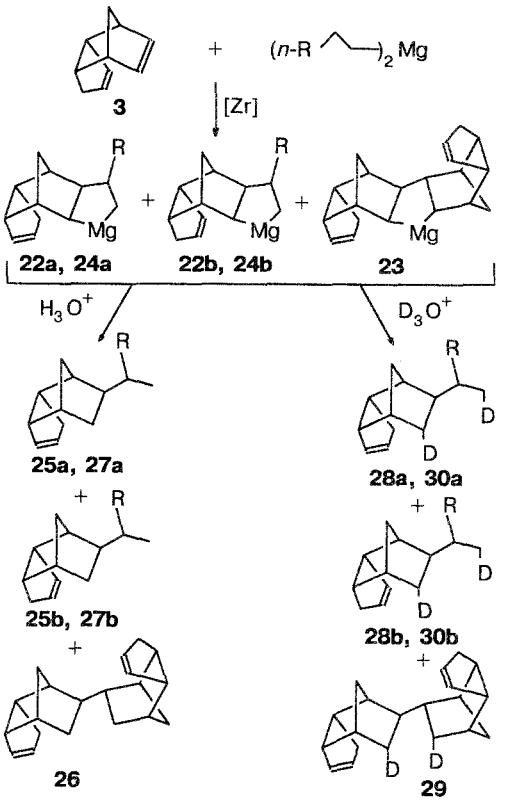
The scheme includes the initial formation of the dialkylzirconium complex **31**, its decomposition gives the zirconocene-alkene complex **32** and alkane **33**, which corresponds to the alkyl radical in the starting OMC, the formation of zirconacyclopentanes **34**, **37**, and recovery of **31**.

Thus, catalytic cyclomagnesation of norbornene is of a general character and leads to the formation of polycyclic magnesacyclopentanes.

Experimental

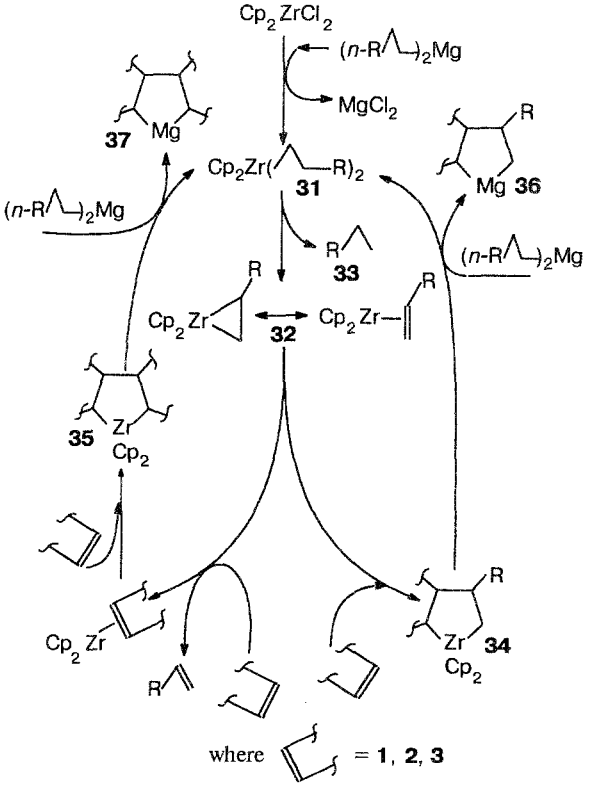
Cyclometallation was carried out under dry argon. Compounds **1** and **2** were synthesized according to the known procedures.[7,8] Solutions of dialkylmagnesium derivatives were prepared according to ref.[9] IR spectra were recorded on a UR-20 spectrophotometer. ^1H NMR spectra were obtained on a Tesla-487 spectrometer (100 MHz), using TMS as an internal standard and $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on JEOL-FX-900 (22.5 MHz) and Bruker AM-300 spectrometers. Mass spectra were obtained on a MKh-1320 instrument at ionizing potentials of 12 and 70 eV and at ionization chamber temperature 150°C. Reaction mixtures were analyzed after appropriate treatment on a Chrom-5 chromatograph equipped with a flame ionization detector and 3.7 m and 2.4 m columns at working temperatures of 50-300°C and 50-70°C, respectively, with stationary phases SE-30 (5%) and PEG-6000 (15%) on Chromaton N-AW-DMCS (0.16-0.20 mm), with helium as the carrier gas. Processing of chromatog-

Scheme 3



R = Me(**22a**, **22b**, **25a**, **25b**, **28a**, **28b**); Et(**24a**, **24b**, **27a**, **27b**, **30a**, **30b**)

Scheme 4



rams of the reaction mixtures was accomplished using an internal standard (decane). Gaseous hydrocarbons were analyzed on a Chrom-4 apparatus, with a 3 mm x 3.7 m column packed with β,β'-oxydipropionitrile on Chromaton N-AW-DMCS (0.16-0.20 mm), at 25°C.

General procedure of cyclomagnesation of norbornenes. Into a glass reactor (100 ml) equipped with a magnetic stirrer were placed under Ar 20 mmol of OMC in ether (1.2 mmol/ml), 20 mmol of the corresponding norbornene, 0.175 g (0.6 mmol) of Cp_2ZrCl_2, and 16.7 ml of THF. The resulting solution was stirred for 7-8 h at a specified temperature, cooled to 0°C, hydrolyzed with 5% HCl or DCl, extracted with ether (3x50 ml), dried with $MgSO_4$, evaporated, and the residue was analyzed by GLC. The following compounds were isolated from the reaction mixture by distillation *in vacuo*.

***exo*-2-Isopropylbicyclo[2.2.1]heptane (7)**, b.p. 51°C (38 Torr), n_D^{20} 1.4584. IR spectrum (ν, cm^{-1}): 1370, 1385, 1450, 1460, 2840, 2980. ^1H NMR spectrum (δ, *J*, Hz): 0.80-0.95 (d, 6 H, CH_3, *J* = 6.0), 1.1-1.7 (m, 10H, CH_2, CH), 2.05-2.25 (m, 2 H, CH). ^{13}C NMR spectrum (δ): 38.71 (d, C-1), 50.58 (d, C-2), 36.86 (t, C-3), 36.71 (d, C-4), 28.61 (t, C-5), 30.64 (t, C-6), 35.50 (t, C-7), 32.90 (d, C-8), 20.24 (q, C-9), 21.85 (q, C-10). Found, %: C 86.74; H 13.06. $C_{10}H_{18}$. Calculated, %: C 86.96; H 13.04. Mass spectrum, *m/z*: 138 $[M]^+$.

***exo,exo*-2,2'-Bis-bicyclo[2.2.1]heptyl (8)**, b.p. 62°C (4 Torr), n_D^{20} 1.4953. IR spectrum (ν, cm^{-1}): 1460, 2880, 2930, 2970. ^1H NMR spectrum (δ): 0.95-1.8 (m, 18H, CH_2, CH), 2.0-2.3 (m, 4H, CH). ^{13}C NMR spectrum (δ): 40.66 (d, C-1), 48.11 (d, C-2), 36.02 (t, C-3), 36.63 (d, C-4), 20.04 (t, C-5), 30.30 (t, C-6), 35.50 (t, C-7). Found, %: C 88.27; H 11.63. $C_{14}H_{22}$. Calculated, %: C 88.42; H 11.58:. Mass spectrum, *m/z*: 190 $[M]^+$.

3-Deuterio-*exo*-2-(1-deuteriomethylethyl)bicyclo[2.2.1]heptane (9), b.p. 51°C (38 Torr), n_D^{20} 1.4546. IR spectrum (ν, cm^{-1}): 1460, 2185 (C-D), 2880, 2970. ^1H NMR spectrum (δ, *J*, Hz): 0.85, (d, 5 H, CH_3, CH_2D, *J* = 6.0), 1.05-1.7 (m, 10 H, CHD, CH), 2.0-2.3 (m, 2H, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 38.52 (d, C-1), 50.46 (d, C-2), 36.57 (t, C-3, $J_{^{13}C\text{-}D}$ = 19.5), 36.85 (d, C-4), 28.54 (t, C-5), 30.63 (t, C-6), 35.47 (t, C-7), 32.83 (d, C-8), 20.02 (t, C-9, $J_{^{13}C\text{-}D}$ = 19.5), 21.84 (q, C-10). Found, %: C 85.43; H 14.42. $C_{10}H_{16}D_2$. Calculated, %: C 85.75; H 14.29. Mass spectrum, *m/z*: 140 $[M]^+$.

3,3'-Dideuterio-*exo,exo*-2,2'-bis-bicyclo[2.2.1]heptyl (10), b.p. 62°C (4 Torr), n_D^{20} 1.5014. IR spectrum (ν, cm^{-1}): 1455, 2190 (C-D), 2860, 2960. ^1H NMR spectrum (δ): 0.9-1.8 (m, 16 H, CH_2, CHD, CH), 2.0-2.25 (m, 4 H, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 40.67 (d, C-1), 47.97 (d, C-2), 35.54 (t, C-3), 36.55 (d, C-4), 28.98 (t, C-5), 30.29 (t, C-6), 35.54 (t, C-7, $J_{^{13}C\text{-}D}$ = 19.5). Found, %: C 87.44; H 12.5. $C_{14}H_{20}D_2$. Calculated, %: C 87.50; H 12.50. Mass spectrum, *m/z*: 192 $[M]^+$.

***exo*-2-(*sec*-Butyl)bicyclo[2.2.1]heptane (11)**, b.p. 60°C (16 Torr), n_D^{20} 1.4601. IR spectrum (ν, cm^{-1}): 1390, 1470, 2885, 2970. ^1H NMR spectrum (δ): 0.85-0.95 (m, 6H, CH_3), 1.05-1.65 (m, 12 H, CH_2, CH), 2.0-2.2 (m, 8 H, CH). ^{13}C NMR spectrum (δ): 38.58 (d, C-1), 48.26 (d, C-2), 36.80 (t, C-3), 36.75 (d, C-4), 28.71 (t, C-5), 30.82 (t, C-6), 35.68 (t, C-7), 39.14 (d, C-8), 27.86 (d, C-9), 10.98 (q, C-10), 16.13 (q, C-11). Found, %: C 86.57; H 13.08. $C_{11}H_{20}$. Calculated, %: C 86.84; H 13.16. Mass spectrum, *m/z*: 152 $[M]^+$.

3-Deuterio-*exo*-2-(1-deuteriomethylpropyl)bicyclo[2.2.1]heptane (12), b.p. 52°C (14 Torr), n_D^{20} 1.4575. IR spectrum (ν, cm^{-1}): 1475, 2170 (C-D), 2890, 2970. ^1H NMR spectrum (δ): 0.8-0.95 (m, 5 H, CH_3, CH_2D), 1.1-1.6 (m, 11 H, CH_2, CHD, CH), 2.0-2.25 (m, 2 H, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 38.56 (d, C-1), 48.12 (d, C-2), 36.40 (t, C-3, *J* = 19.5), 36.74 (d, C-4), 28.70 (t, C-5), 30.80 (t, C-6), 35.65 (t, C-7), 39.05 (d, C-8), 27.88 (t, C-9), 10.97 (q, C-10), 15.82 (t, C-11, $J_{^{13}C\text{-}D}$ = 19.5). Found, %: C 85.43; H 14.15. $C_{11}H_{18}D_2$. Calculated, %: C 85.71; H 14.29. Mass spectrum, *m/z*: 154 $[M]^+$.

***exo*-2-Isopropyl-spiro{bicyclo[2.2.1]heptane-7,1'-cyclopropane} (16)**, b.p. 72°C (10 Torr), n_D^{20} 1.4727. IR spectrum (ν, cm^{-1}): 1025, 1380, 1395, 1470, 2880, 2969, 3080. ^1H NMR spectrum (δ, *J*, Hz): 0.15—0.65 (m, 4 H, cyclopropane CH_2), 0.85 (d, 6H, CH_3, *J* = 5.5), 1.2-1.7 (m, 8 H, CH_2, CH), 1.8—2.0 (m, 2H, CH). ^{13}C NMR spectrum (δ): 41.67 (d, C-1), 52.46 (d, C-2), 37.93 (t, C-3), 42.68 (d, C-4), 28.63 (t, C-5), 30.98 (t, C-6), 32.74 (s, C-7), 3.29 (t, C-8), 6.55 (t, C-9), 37.72 (d, C-10), 20.66 (q, C-11), 22.15 (q, C-12). Found, %: C 87.61; H 12.37. $C_{12}H_{20}$. Calculated, %: C 87.80; H 12.20. Mass spectrum, *m/z*: 164 $[M]^+$.

***exo,exo*-2,2'-Bis-spiro{bicyclo[2.2.1]heptyl-7,1'-cyclopropane} (17)**, m.p. 79°C. IR spectrum (ν, cm^{-1}): 1020, 2870, 2990, 3080. ^1H NMR spectrum (δ): 0.18-0.26 (m, 4 H, cyclopropane CH_2), 0.28-0.66 (m, 4H, cyclopropane CH_2), 1.20-1.85 (m, 18 H, CH_2, CH). ^{13}C NMR spectrum (δ): 43.37 (d, C-1), 49.24 (d, C-2), 36.81 (t, C-3), 42.43 (d, C-4), 29.04 (t, C-5), 30.65 (t, C-6), 32.86 (s, C-7), 3.14 (t, C-8), 7.22 (t, C-9). Found, %: C 89.21; H 10.76. $C_{18}H_{26}$. Calculated, %: C 89.26; H 10.74. Mass spectrum, *m/z*: 242 $[M]^+$.

***exo*-2-(*sec*-Butyl)spiro{bicyclo[2.2.1]heptane-7,1'-cyclopropane} (18)**, b.p. 108°C (60 Torr), n_D^{20} 1.4749. IR spectrum (ν, cm^{-1}): 1010, 1385, 1460, 2870, 2980, 3080. ^1H NMR spectrum (δ): 0.15-0.6 (m, 4 H, cyclopropane CH_2), 0.75-0.9 (m, 6 H, CH_3), 1.2-1.6 (m, 10 H, CH_2, CH), 1.65-1.90 (m, 2H, CH). ^{13}C NMR spectrum (δ): 43.26 (d, C-1), 50.06 (d, C-2), 37.95 (t, C-3), 42.65 (d, C-4), 28.69 (t, C-5), 30.99 (t, C-6), 32.77 (s, C-7), 3.38 (t, C-8), 6.68 (t, C-9), 38.92 (d, C-10), 27.96 (t, C-11), 10.66 (q, C-12), 16.47 (q, C-13). Found, %: C 87.44; H 12.40. $C_{13}H_{22}$. Calculated, %: C 87.64; H 12.36. Mass spectrum, *m/z*: 178 $[M]^+$.

3-Deuterio-*exo*-2-(1-deuteriomethylethyl)spiro{bicyclo[2.2.1]heptane-7,1'-cyclopropane} (19), b.p. 88°C (20 Torr), n_D^{20} 1.4708. IR spectrum (ν, cm^{-1}): 1020, 1380, 1475, 2185 (C-D), 2880, 2960, 3075. ^1H NMR spectrum (δ, *J*, Hz): 0.15-0.60 (m, 4H, cyclopropane CH_2), 0.87 (d, 5 H, CH_3, CH_2D, *J* = 5.5), 1.1-1.7 (m, 7 H, CH_2, CHD, CH), 1.8-2.0 (m, 2 H, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 43.60 (d, C-1), 52.42 (d, C-2), 37.67 (t, C-3, $J_{^{13}C\text{-}D}$ = 19.5), 42.63 (d, C-4), 28.59 (t, C-5), 30.94 (t, C-6), 32.70 (s, C-7), 3.20 (t, C-8), 6.53 (t, C-9), 37.60 (d, C-10), 20.30 (t, C-11, $J_{^{13}C\text{-}D}$ = 19.5), 22.13 (q, C-12). Found, %: C 86.61; H 13.17. $C_{12}H_{18}D_2$. Calculated, %: C 86.75; H 13.25. Mass spectrum, *m/z*: 166 $[M]^+$.

3,3'-Dideuterio-*exo,exo*-2,2'-bis-spiro{bicyclo[2.2.1]heptyl-7,1'-cyclopropane} (20), m.p. 79°C. IR spectrum (ν, cm^{-1}): 1015, 2185 (C-D), 2870, 2980, 3075. ^1H NMR spectrum (δ): 0.16-0.24 (m, 4 H, cyclopropane CH_2), 0.27-0.64 (m, 4H, CH_2), 1.16-1.75 (m, 16 H, CH_2, CHD, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 45.38 (d, C-1), 49.07 (d, C-2), 36.32 (t, C-3, $J_{^{13}C\text{-}D}$ = 19.5), 42.35 (d, C-4), 29.06 (t, C-5), 30.64 (t, C-6), 32.81 (s, C-7), 3.08 (t, C-8), 7.19 (t, C-9). Found, %: C 88.50; H 11.45. $C_{18}H_{24}D_2$. Calculated, %: C 88.52; H 11.48. Mass spectrum, *m/z*: 244 $[M]^+$.

3-Deuterio-*exo*-2-(1-deuteriomethylpropyl)spiro{bicyclo[2.2.1]heptane-7,1'-cyclopropane} (21), b.p. 54°C (28 Torr), n_D^{20} 1.4732. IR spectrum (ν, cm^{-1}): 1000, 1375, 1460, 2190 (C-D), 2860, 2980, 3070. ^1H NMR spectrum (δ): 0.2-0.65 (m,

4H, cyclopropane CH_2), 0.75-0.90 (m, 5H, CH_3, CH_2D), 1.1-1.6 (m, 9 H, CH_2, CHD, CH), 1.6—1.9 (m, 2 H, CH). ^{13}C NMR spectrum (δ, *J*, Hz): 43.21 (d, C-1), 50.02 (d, C-2), 37.71 (t, C-3, $J_{^{13}C\text{-}D}$ = 19.5), 42.61 (d, C-4), 28.65 (t, C-5), 30.95 (t, C-6), 32.73 (s, C-7), 3.29 (t, C-8), 6.63 (t, C-9), 38.79 (d, C-10), 27.91 (t, C-11), 10.66 (q, C-12), 16.43 (t, C-13, $J_{^{13}C\text{-}D}$ = 19.5). Found, %: C 86.59; H 13.37. $C_{13}H_{20}D_2$. Calculated, %: C 86.67; H 13.33. Mass spectrum, *m/z*: 180 $[M]^+$.

***exo*-8-Isopropyl-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (25a)/*exo*-9-isopropyl-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (25b)** = 3/2, b.p. 90°C (14 Torr). IR spectrum (ν, cm^{-1}): 1375, 1390, 1480, 2860, 2940, 3055. ^1H NMR spectrum (δ): 0.8-0.9 (m, 6 H, CH_3), 1.1—1.8 (m, 6 H, CH_2, CH), 2.0—2.3 (m, 3 H, CH), 2.4—2.8 (m, 2 H, CH_2), 2.85-3.1 (m, 1 H, CH), 5.5—5.8 (m, 2H, CH=CH). ^{13}C NMR spectrum (δ) **25a**: 40.18 (d, C-1), 53.88 (d, C-2), 132.55 (d, C-3), 130.90 (d, C-4), 31.99 (d, C-5), 41.70 (d, C-6), 44.77 (d C-7), 50.38 (d, C-8), 34.68 (t, C-9), 38.58 (t, C-10), 32.77 (d, C-11), 20.37 (q, C-12), 21.76 (q, C-13); **25b**: 46.21 (d, C-1), 52.23 (d, C-2), 131.98 (d, C-3), 130.38 (d, C-4), 32.38 (t, C-5), 42.69 (d, C-6), 41.83 (d, C-7), 29.34 (t, C-8), 49.02 (d, C-9), 38.66 (t, C-10), 32.12 (d, C-11), 15.21 (q, C-12), 22.06 (q, C-13). Found, %: C 88.47; H 11.41. $C_{13}H_{20}$. Calculated, %: C 88.64; H 11.36. Mass spectrum, *m/z*: 176 $[M]^+$.

***exo,exo*-8,8'-Bis-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-enyl (26)**, m.p. 128°C. IR spectrum (ν, cm^{-1}): 1615, 2870, 2980, 3075. ^1H NMR spectrum (δ): 1.18-1.95 (m, 10 H, CH_2, CH), 2.05—2.25 (m, 6 H, CH_2), 2.30-2.75 (m, 4H, CH_2), 2.8—3.15 (m, 2 H, CH), 5.55—5.60 (m, 4 H, CH=CH). ^{13}C NMR spectrum (δ): 41.04 (d, C-1), 53.79 (d, C-2), 132.59 (d, C-3), 130.91 (d, C-4), 32.24 (t, C-5), 41.99 (d, C-6), 41.96 (d C-7), 52.81 (d, C-8), 36.03 (t, C-9), 38.53 (t, C-10). Found, %: C 90.21; H 9.75. $C_{20}H_{26}$. Calculated, %: C 90.23; H 9.77. Mass spectrum, *m/z*: 266 $[M]^+$.

***exo*-8-(*sec*-Butyl)-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (27a)/*exo*-9-(*sec*-butyl)-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (27b)** = 3/2, b.p. 80°C (4 Torr). IR spectrum (ν, cm^{-1}): 1475, 1620, 2890, 2980, 3060. ^1H NMR spectrum (δ): 0.7-0.95 (m, 6 H, CH_3), 1.1—1.7 (m, 6 H, CH_2, CH), 2.1-2.35 (m, 3 H, CH), 2.35—2.7 (m, 2 H, CH_2), 2.85—3.2 (m, 1 H, CH), 5.5—5.8 (m, 2 H, CH=CH). ^{13}C NMR spectrum (δ) **27a**: 38.88 (d, C-1), 53.96 (d, C-2), 132.59 (d, C-3), 130.38 (d, C-4), 31.99 (t, C-5), 41.74 (d, C-6), 42.78 (d, C-7), 48.83 (d, C-8), 32.38 (t, C-9), 38.22 (t, C-10), 40.18 (d, C-11), 27.87 (t, C-12), 10.49 (q, C-13), 16.12 (q, C-14); **27b**: 43.30 (d, C-1), 52.32 (d, C-2), 132.37 (d, C-3), 131.03 (d, C-4), 32.38 (t, C-5), 42.17 (d, C-6), 41.26 (d C-7), 29.39 (t, C-8), 47.26 (d, C-9), 38.40 (t, C-10), 39.05 (d, C-11), 27.44 (t, C-12), 10.84 (q, C-13), 16.12 (q, C-14). Found, %: C 88.03; H 11.74. $C_{14}H_{22}$. Calculated, %: C 88.42; H 11.58. Mass spectrum, *m/z*: 190 $[M]^+$.

***exo*-8-(1-Deuteriomethylethyl)-9-deuterio-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (28a)/8-deuterio-*exo*-9-(1-deuteriomethylethyl)-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (28b)** = 3/2, b.p. 90°C (14 Torr). IR spectrum (ν, cm^{-1}): 1370, 1480, 1620, 2190 (C-D), 2860, 2960, 3060. ^1H NMR spectrum (δ): 0.9-1.1 (m, 5 H, CH_3, CH_2D), 1.2-1.8 (m, 5 H, CH_2, CH_2D), 2.0-2.4 (m, 3H, CH), 2.7—3.0 (m, 2 H, CH_2), 3.0-3.4 (m, 1 H, CH), 5.4-5.6 (m, 2 H, CH=CH). ^{13}C NMR spectrum (δ, *J*, Hz) **28a**: 38.74 (d, C-1), 53.92 (d, C-2), 132.58 (d, C-3), 130.88 (d, C-4), 32.05 (t, C-5), 41.91 (d, C-6), 44.85 (d, C-7), 50.17 (d, C-8), 32.38 (t, C-9, $J_{^{13}C\text{-}D}$ = 19.5), 38.58 (t, C-10), 32.69 (d, C-11), 20.36 (t, C-12, $J_{^{13}C\text{-}D}$ = 19.5), 21.74 (q, C-13); **28b**: 45.74 (d, C-1), 52.99 (d, C-2), 132.58 (d, C-3), 130.42 (d, C-4), 32.38 (t, C-5), 42.71 (d, C-6), 41.91 (d C-7), 29.07 (t, C-8, $J_{^{13}C\text{-}D}$ = 19.5), 48.63 (d, C-9), 38.74 (t, C-10), 32.05 (d, C-11), 14.57 (t, C-12, $J_{^{13}C\text{-}D}$ = 19.5), 22.06 (q, C-13). Found, %: C 87.57; H 12.01. $C_{13}H_{12}D_2$. Calculated, %: C 87.64; H 12.36. Mass spectrum, *m/z*: 178 $[M]^+$.

9,9'-Dideuterio-*exo,exo*-8,8'-bis-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-enyl (29), m.p. 128-129°C. IR spectrum (ν, cm^{-1}): 1610, 2190 (C-D),2860, 2980, 3060. ^1H NMR spectrum (δ): 1.15—1.90 (m, 8 H, CH2, CHD, CH), 2.0—2.25 (m, 6 H, CH), 2.25—2.70 (m, 4 H, CH_2), 2.75—3.15 (m, 2H, CH), 5.55-5.60 (m, 4 H, CH=CH). ^{13}C NMR spectrum (δ, *J*, Hz): 41.06 (d, C-1), 53.66 (d, C-2), 132.58 (d, C-3), 130.88 (d, C-4), 32.31 (t, C-5), 41.97 (d, C-6), 43.97 (d, C-7), 52.84 (d, C-8), 35.47 (t, C-9, $J_{^{13}C\text{-}D}$ = 19.5), 38.51 (t, C-10). Found, %: C 89.53; H 10.40. $C_{20}H_{24}D_2$. Calculated, %: C 89.55; H 10.45. Mass spectrum, *m/z*: 268 $[M]^+$.

9-Deuterio-*exo*-8-(1-deuteriomethylpropyl)-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (30a)/8-deuterio-*exo*-9-(1-deuteriomethylpropyl)-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (30b) = 3/2, b.p. 80°C (4 Torr). IR spectrum (ν, cm^{-1}): 1470, 1610, 2190 (C-D), 2870, 2980, 3055. ^1H NMR spectrum (δ): 0.7—0.9 (m, 5 H, CH_3, CH_2D), 1.0—1.6 (m, 5 H, CH_2, CHD, CH), 2.0—2.25 (m, 3 H, CH), 2.35—2.7 (m, 2 H, CH_2), 2.8—3.2 (m, 1 H, CH), 5.5—5.8 (m, 2 H, CH=CH). ^{13}C NMR spectrum (δ, *J*, Hz) **30a**: 38.71 (d, C-1), 53.98 (d, C-2), 132.62 (d, C-3), 130.36 (d, C-4), 31.98 (t, C-5), 41.78 (d, C-6), 42.64 (d, C-7), 47.64 (d, C-8), 31.87 (t, C-9, $J_{^{13}C\text{-}D}$ = 19.5), 38.31 (t, C-10), 40.21 (d, C-11), 27.83 (t, C-12), 10.51 (q, C-13), 14.57 (t, C-14, $J_{^{13}C\text{-}D}$ = 19.5); **30b**: 43.27 (d, C-1), 52.35 (d, C-2), 132.57 (d, C-3), 130.14 (d, C-4), 32.31 (t, C-5), 42.16 (d, C-6), 41.23 (d C-7), 29.03 (t, C-8, $J_{^{13}C\text{-}D}$ = 19.5), 47.29 (d, C-9), 38.43 (t, C-10), 39.62 (d, C-11), 27.41 (t, C-12), 10.83 (q, C-13), 14.96 (t, C-14, $J_{^{13}C\text{-}D}$ = 19.5). Found, %: C 87.36; H 12.39. $C_{14}H_{20}D_2$. Calculated, %: C 87.50; H 12.50. Mass spectrum, *m/z*: 192 $[M]^+$.

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Received October 15, 1991