One-pot synthesis of small spirocarbocycles through the catalytic cyclometalation reactions of unsaturated compounds

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Dedicated to Professor Usein M. Dzhemilev on the occasion of his 65th birthday

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Abstract

The mild and efficient one-pot methods to synthesize substituted spirocyclopropanes and spirocyclobutanes are reported. The elaborated procedures based on consecutive cycloalumination of methylenecyclopropanes, methylenecyclobutanes or cycloalkynes assisted by alkyl aluminums and Cp_2ZrCl_2 as a catalyst provide the formation of target products through Pd catalyzed carbocyclization of the aluminacyclopentane and aluminacyclopentene intermediates with Me_2SO_4 or allyl chloride.

Keywords: Cyclometallation, cyclopropanation, homogeneous catalysis, spiranes, cyclopropane, cyclobutane, Dzhemilev reaction

Introduction

Small carbocycles are of special interest due to a variety of rearrangements into isomeric unsaturated compounds that have defined their wide use as building blocks for the directed synthesis of strained cyclic organic systems. In addition, among those containing three- and four-membered carbocycles, one can often meet medical and biological preparations, plant protection products, and energy-rich components for jet fuel.

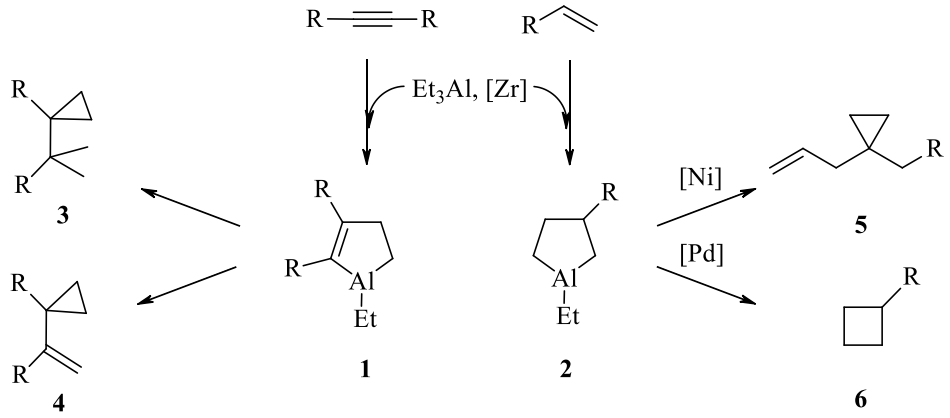
Ordinary approaches to small carbocycles are based on the classical procedures[1] such as 1,ω-elimination, Favorskii rearrangement, Dieckmann, Perkin and Simmons-Smith reactions, cyclopropanation of unsaturated hydrocarbons with diazocompounds as well as through concerted cycloaddition and cyclization reactions and also new ones, e.g. nontrivial

transformations of acetylenes to mono- and biscyclopropanes mediated by aluminum carbenoids.[2]

Of real interest are the methods, elaborated in the last 10–15 years, for the construction of cyclopropane alcohols[3] and ethers[4] by the interaction between esters and Grignard reagents or alkylhalogenalanes in the presence of Ti and Zr complexes through the three-membered metallacarbocycles.

To a number of promising procedures in the synthesis of small carbocycles, in our opinion, it should be also added those including intramolecular transformations of the five-membered nontransition metallacarbocycles such as aluminacyclopentanes[5], aluminacyclopentenes,[6] magnesacyclopentanes[7] and their derivatives *in situ* generated in the cycloalumination and cyclomagnesiation reactions of unsaturated compounds with alkyl aluminums or alkyl magnesiums under the effect of Ti and Zr catalysts (Dzhemilev reaction).[8]

As known,[6d,9] the interaction between 2,3-dialkylsubstituted aluminacyclopent-2-enes **1** and dimethyl sulphate or bromomethyl methyl ether as well as carbocyclization of 3-alkylaluminacyclopentanes **2** with allyl chloride in the presence of $Ni(acac)_2$ provides the formation of cyclopropanes **3–5**. At the same time, the Pd catalyzed intramolecular cyclization of monoalkyl and dialkyl substituted aluminacyclopentanes represents an effective method for the construction of cyclobutanes **6** (Scheme 1).[10]



Scheme 1

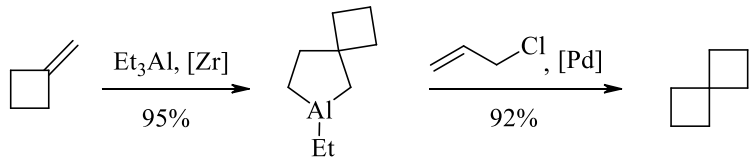
As described above, the aluminum-based transformations of the five-membered metallacarbocycles have been studied on the example of the simplest alkyl substituted aluminacyclopentanes and aluminacyclopent-2-enes. Meanwhile, the investigation of such transformations with the aid of more complicated organoaluminum and organomagnesium compounds is thought to initiate the development of novel one-pot procedures for the synthesis of polycycles containing spirocyclopropane and spirocyclobutane moieties.

In this paper, we report new approaches to small spirocycles via intramolecular carbocyclization of di-, tri- and polycyclic aluminacyclopentanes and aluminacyclopentenes

from methylenecycloalkanes, cycloalkynes, cycloalkadiines and cyclic allenes using the Dzhemilev method.

Results and Discussion

Recently,[11] we have synthesized the first representative of a new class of cyclic organoaluminum compounds (OACs) of a spirane structure, namely 6-ethyl-6-aluminaspiro[3.4]octane **7**, via the interaction between methylenecyclobutane and Et_3Al in the presence of 5 mol% Cp_2ZrCl_2 (pentane, 4 h). It was found that the OAC **7**, without preliminary isolation, can enter into reaction with allyl chloride easily converted into spiro[3.3]heptane **8** (90%) in the presence of 2 mol% $Pd(acac)_2$ (Scheme 2).

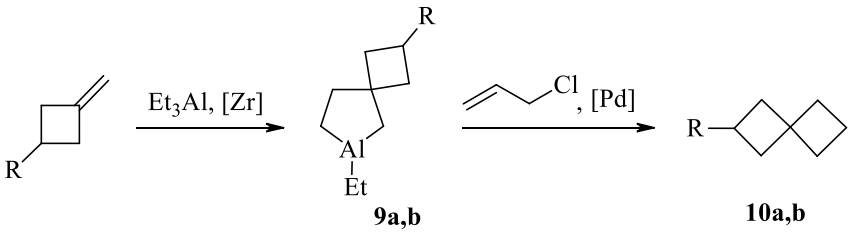


7 **8**

[Zr] = Cp_2ZrCl_2, [Pd] = $Pd(acac)_2$ - $2Ph_3P$

Scheme 2

This reaction is general and can be successfully used in the synthesis of 2-akyl substituted spiro[3.3]heptanes. Thus, the consecutive cycloalumination of 3-pentyl(heptyl) methylenecyclobutanes with Et_3Al catalyzed by Cp_2ZrCl_2 under previously optimized conditions (methylenecyclobutane:Et_3Al:[Zr] = 10:12:0.5, 4 h, r.t., hexane)[11] affords appropriate 2-pentyl-, 2-heptylspiro[3.3]heptanes **10a,b** (82−89%) through the generated *in situ* spiranes **9a,b** and their further carbocyclization mediated by allyl chloride and Pd catalyst (Scheme 3).



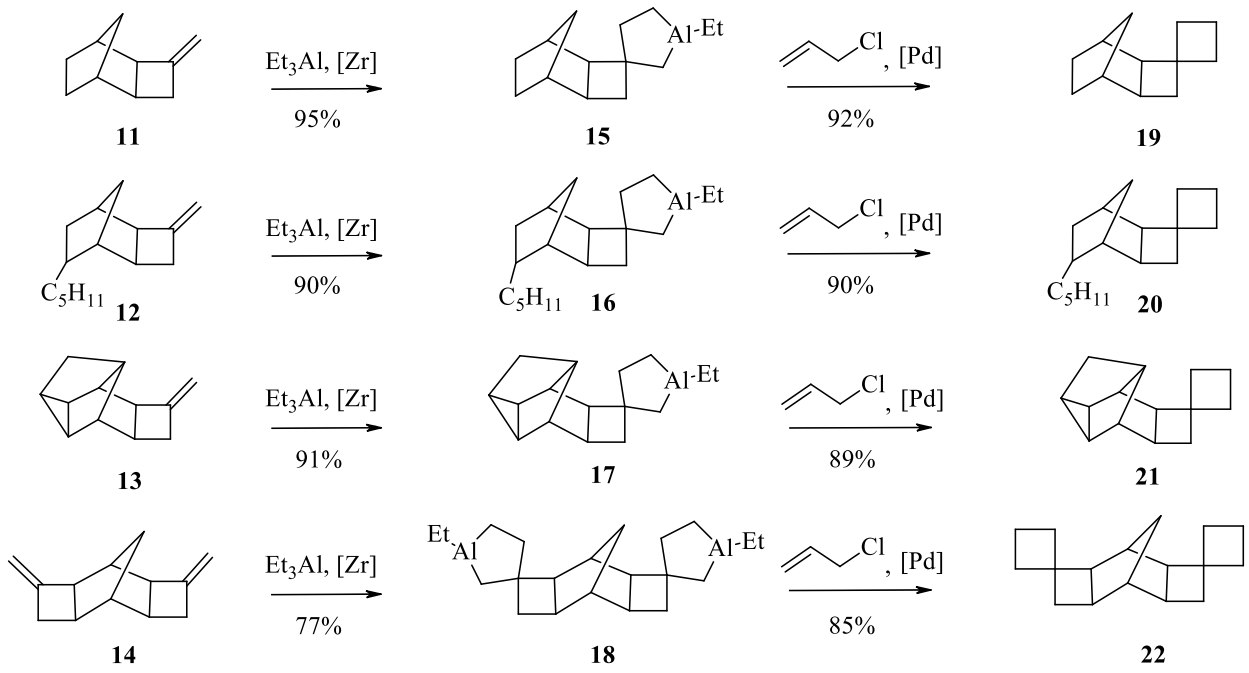
9a,b **10a,b**

[Zr] = Cp_2ZrCl_2; a = n-C_5H_{11}, b = n-C_7H_{15}

Scheme 3

In continuation of these studies and also in order to synthesize polycyclic hydrocarbons of spirane structure, we have studied, for the first time, catalytic transformations of

aluminaspiro[3.4]octanes **15**–**18**[12] as intermediates in cycloalumination of 3-methylene-*exo*-tricyclo[4.2.1.$0^{2,5}$]nonane **11,** 3-methylene-7-pentyl-*exo*-tricyclo[4.2.1.$0^{2,5}$]nonane **12,** 3-methylene-*exo*-pentacyclo[5.4.0.$0^{2,5}$.$0^{6,10}$.$0^{9,11}$]undecane **13** and also 3,9-dimethylene-*exo*-*exo*-tetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]undecane **14**. These spiranes, as we have previously shown, easily reacts *in situ* with an excess of allyl chloride to give the corresponding spiro[3.3]heptanes retaining norbornane skeleton of parent compounds **19**–**22**.

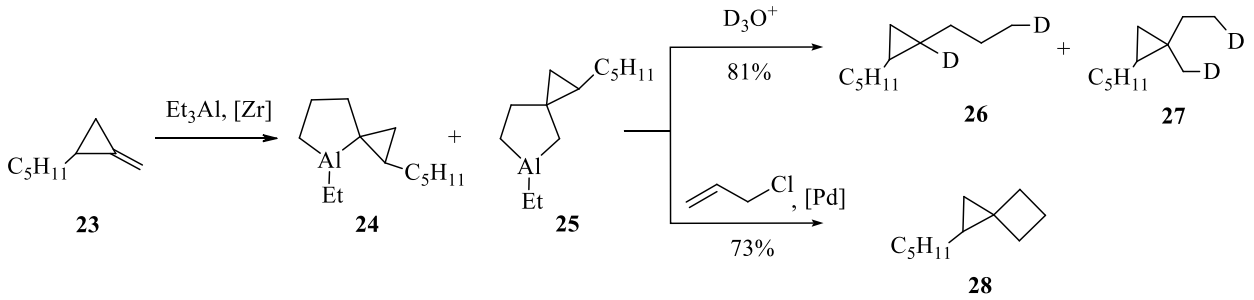


Scheme 4

Very encouraging results, obtained in the course of developing one-pot methods to synthesize spiro[3.3]heptanes by the intramolecular carbocyclization reaction of 6-ethyl-6-aluminaspiro[3.4]octanes, prompted us to apply the same approach to the construction of spiro[2.3]hexane systems.

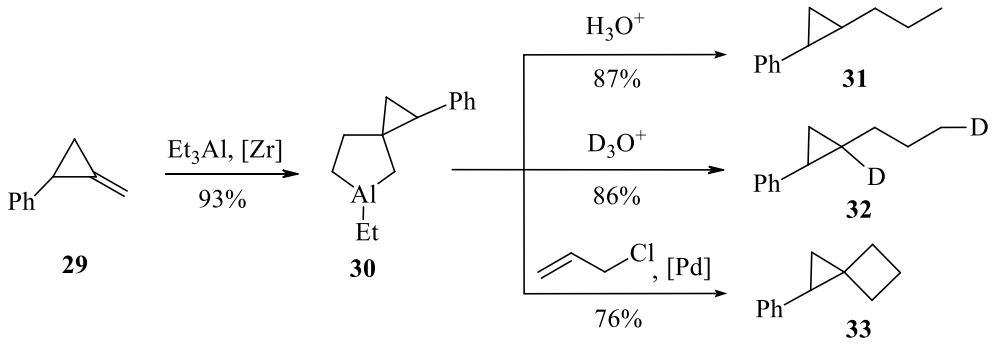
Initially, we investigated the activities of 2-pentyl- and 2-phenylmethylenecyclopropanes, as selected samples, in the reaction of catalytic cycloalumination with Et_3Al and also their ability to give substituted aluminaspiro[2.4]heptanes.

The interaction between Et_3Al and 2-pentyl-1-methylenecyclopropanes in the presence of 5 mol% Cp_2ZrCl_2 (hexane, 4 h) was found to afford a mixture of two theoretically possible regioisomeric aluminacyclopentanes **24** and **25** (81% total) bearing cyclopropane ring in α- and β-position towards to Al atom respectively. Deuterolysis of this regioisomeric mixture led to hydrocarbons **26** and **27** at a 2:1 ratio. The Pd catalyzed reaction with allyl chloride provided the formation of spirocyclobutane **28** in 73% yield (Scheme 5).



Scheme 5

We revealed that the nature of a substituent in the methylenecyclopropane ring determines the selectivity of the reaction. Thus, under previously developed conditions, 2-phenylmethylenecyclopropane entered into reaction with Et_3Al furnishing 4-ethyl-1-phenyl-4 aluminaspiro[2.4]heptane **30** with high regioselectivity (Scheme 6).



Scheme 6

The structure of the new OACs **24**, **25** and **30** has been proven through analysis of the one-dimensional (^{1}H, ^{13}C, APT) and two-dimensional (HH COSY, HSQC and HMBC) NMR spectra of the acid hydrolysis **31** and deuterolysis products **26**, **27**, and **32**.

Thus, the ^{1}H and ^{13}C NMR spectra of the hydrocarbon **31** show the low field signals corresponding to the aromatic protons and carbons of the phenyl ring, while the alkyl substituent and cyclopropane moiety manifest themselves in the high field of the spectra. The methylene protons at the α-carbon [δ(C-10) 30.7 ppm] attributable to the alkenyl substituent are observed as two multiplets [δH (C-10) 0.91 and 1.18 ppm] due to diastereotopic splitting at the chiral C-2 center. 1,2-Disubstituted cyclopropane fragment is represented by a four spin systems associated with two methine [δ H(C-1) 2.13 and δ (H-2) 1.13 ppm] and also two methylene protons [δ H(C-3) 0.67 and 0.99 ppm].

Assignment of *cis* and *trans* isomers has been performed on the basis of vicinal coupling constants (SSCC). Thus, in the ^{1}H NMR spectrum of *trans*-isomer, theoretically, the signal resonated in a low field [δ H (C-1) 2.13 ppm] must comply with one large ($^3J_{cis} \approx 8–10$ Hz) and two average ($^3J_{trans} \approx 4–6$ Hz) coupling constants.

In the experimental spectrum, there are two large vicinal ($^3J_{cis}$ = 8 Hz) and one average ($^3J_{trans}$ = 5 Hz) coupling constants corresponding to the signal at δ 2.13 ppm. These data clear indicate *cis*-arrangement of phenyl and propyl substituents with respect to the cyclopropane ring.

Location of deuteriums in compound **32** obtained from deuterolysis of OAC **30** is determined by the splitting of signals assigned to the methyl C-3 and C-6 carbons (δ 18.9 and 14.0 ppm) with a shift of a triplet centre towards the high field ($\Delta\delta_C$ 0.3 ppm). These data and also the SSCC magnitude ($^1J_{CD}$ = 19 Hz) are the additional arguments for the formation of a cyclic OAC **30**.

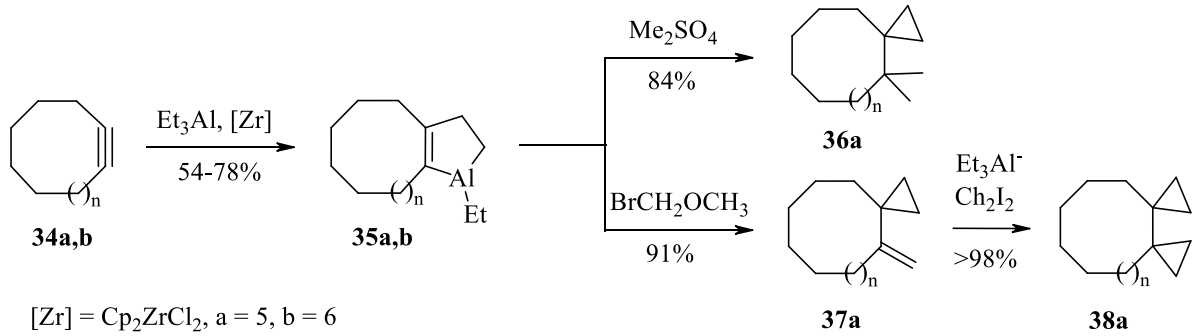
To achieve the stated goals, generated *in situ* aluminaspiro[2.4]heptanes **24**, **25** and **30** under previously developed conditions were subjected to carbocyclization. As a result, 1-pentyl **28** and 1-phenylspiro[2.3]hexane **33** have been obtained in high yields (Scheme 5, 6).

We believe that the above reactions have considerable synthetic potential and their further studies will lead in future to the development of a general method to synthesize spiro[2.3]hexanes, spiro[2.3]heptanes and spiro[4.3]octanes, including those containing functional substituents.

In the development of the other approach to small carbocycles, based on intramolecular carboalumination of 2,3-dialkylaluminacyclopent-2-ene, with the aid of dimethyl sulfate[9] or bromomethyl methyl ether[6d], for the first time the catalytic cycloalumination reaction of cycloalkynes has been performed (Scheme 1).

Thus, we revealed that cycloalkynes, for example, cyclododecyne or cyclotridecyne react with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 (5 mol%) in aliphatic (pentane, hexane, heptane) or aromatic (benzene, toluene) solvents to afford not previously described bicyclic aluminacyclopentanes **35a,b** in 78–89% yield.

Subsequent treatment of *in situ* generated OAC **35a** with an excess Me_2SO_4 or equimolar amounts of bromomethyl methyl ether at 0 °C furnished 4,4-dimethylspiro[2.7]decane **36a** and 4-methylenespiro[2.7]decane **37a** in the yield of 84% and 91% respectively. Using the Et_3Al–CH_2I_2 reagent through the cyclopropanation reaction the latter was converted into dispiro[2.0.2.6]dodecane **38a** (Scheme 7).

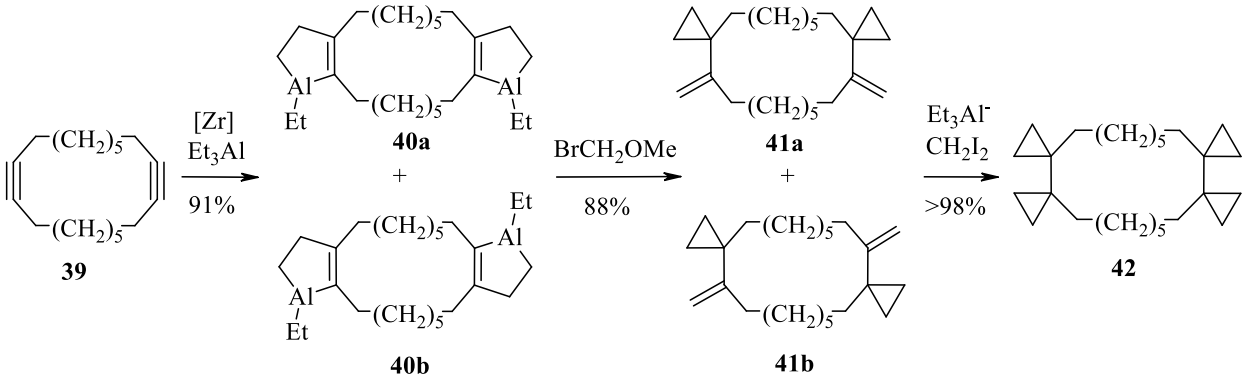


Scheme 7

Taking into account the experimental data obtained from catalytic cycloalumination of disubstituted acetylenes[6c,d] on the example of cyclotetradeca-1,8-diyne **39**, we elaborated reaction conditions (cycloalkadiyne:Et_3Al:[Zr] = 1:6:0.1, hexane, 20−22 ºC, 6 h), under which the pointed cycloalkadiyne entered into the cycloalumination reaction with Et_3Al in the presence of 10 mol% Cp_2ZrCl_2 involving two triple bonds to form isomeric tricyclic bisaluminacyclopentenes **40a** and **40b** in a 1:1 ratio (Scheme 8).

Carbocyclization of OAC **40** aided by equimolar amount of bromomethyl methyl ether gave rise to 12,18-dimethylenedispiro[2.5.2.7]octadecane **41a** and 4,13-dimethylenedispiro[2.6.2.6] octadecane **41b** in 88% overall yield. Treatment of a mixture of regioisomeric dimethylenedispiro(cyclopropane)octadecanes with the cyclopropanation reagent $Et_3Al{-}CH_2I_2$ quantitatively led to tetraspiro[2.0.2^4.5.2^{12}.0.2^{15}.5^3]docosane **42**.

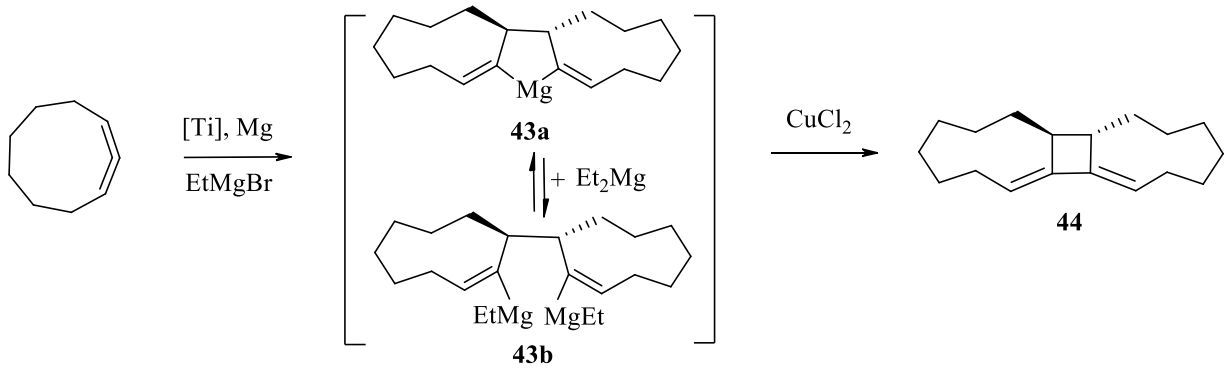
The structure of all compounds synthesized has been rigorously proven by means of one-dimensional (^{1}H, ^{13}C, Dept 135º) and two-dimensional (HSQC, HMBC, HH COSY, NOESY) NMR spectroscopic data.



Scheme 8

For comparison, we presented perhaps the single example of intramolecular cyclization of five-membered magnesacarbocycle successfully obtained from cyclonona-1,2-diene through the catalytic cyclomagnesiation reaction.

Previously,[13] we have shown that selective interaction between cyclic allenes and Grignard reagents mediated by metallic Mg and Cp_2TiCl_2 catalyst affords tricyclic magnesacyclopentadienes in the yields more than 90%. According to the published results on the transformation of the substituted aluminacyclopentanes to the corresponding cyclobutanes in the presence of $CuCl_2$ we have implemented intramolecular carbocyclization of magnesacyclopentane **43** to (10*R*,11*S*)-tricyclo[9.7.$0^{1,11}$.$0^{2,10}$]octadeca-2(3),18-diene **44** in 68% yield (Scheme 9).



Scheme 9

Our proposed approach compares favorably with previously elaborated methods for the synthesis of tricyclic diene **44**, since thermal or catalytic 2π+2π-cyclodimerization of 1,2-cyclononadiene resulted in a mixture of three stereoisomers, in which the maximum content of **44** does not exceed 63%.[14]

In addition, using our methodology one can synthesize diastereomeric pure (10*R*,11*S*)-tricyclo[9.7.$0^{1,11}$.$0^{2,10}$]octadeca-2(3),18-diene **44**.

Conclusions

Thereby, the five-membered organoaluminum and organomagnesium compounds obtained by the *Dzhemilev reaction* have proven to be promising synthons while designing efficient one-pot procedures to obtain various spirocyclopropanes and spirocyclobutanes from accessible methylenecycloalkanes, cyclic 1,2-dienes and acetylenes.

Experimental Section

General. All solvents were dried (hexane over $LiAlH_4$, Et_2O and THF over Na) and freshly distilled before use. All reactions were carried out under a dry argon atmosphere. The reaction products were analyzed using chromatography on a "Shimadzu GC-9A" instrument (2000 x 2 mm column packed with 5% of SE-30 and 15% PEG-6000 on Chromaton N-AW, carrier gas – He). The IR-spectra were recorded on "Bruker VERTEX 70V". Mass spectral measurements were performed on a Finnigan-4021 spectrometer at 70 eV and working temperature 200 °C. Elemental analysis of samples was determined on Carlo Erba, model 1106. The ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on spectrometer "Bruker Avance-400" (100 MHz for ^{13}C and 400 MHz for ^{1}H). The chemical shifts are reported as δ values in ppm relative to internal standard Me_4Si. ^{13}C NMR spectra were edited by *J*-modulation (JMOD) on CH constants. The

yields of organoaluminum compounds **9a,b**, **24**, **25**, **30**, **35a,b**, **40a,b** were determined by GLC analysis of the corresponding deuterium or hydrolysis derivatives. Compound **33** was identified by comparing their physical properties and spectral parameters with those of authentic sample.[15]

Synthesis of spiro[2.3]hexanes and spiro[3.3]heptanes. General procedure Methylidenecyclopropane (methylidenecyclobutane) (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 mL), and Et_3Al (12 mmol) were placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to ambient (20-21 °C) and the reaction mixture was stirred for 4 h, then, Et_2O (10 mL), Ph_3P (0.5 mmol), $Pd(acac)_2$ (0.5 mmol), and allyl chloride (30 mmol) were added at 0 °C, the temperature was raised to ambient and the stirring was continued for 8 h. The reaction mixture was worked up with 7-10% aq. HCl, the reaction products were extracted with diethyl ether, dried with $MgSO_4$ and isolated by distillation *in vacuo*.

2-Pentylspiro[3.3]heptane (10a). IR (film) ν 3050, 2995, 1715, 1460, 1151 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.07-2.10 (m, 3H), 1.97 (t, *J* = 7.1 Hz, 2H), 1.82-1.84 (m, 2H), 1.79-1.83 (m, 2H), 1.50-1.53 (m, 2H), 1.15-1.38 (m, 8H), 0.93 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.0, 39.8, 37.4, 35.6, 35.2, 31.7, 28.6, 22.7, 16.7, 14.0; MS (ES) *m*/*z* $[M]^+$ 166. Anal. Calcd. for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.49; H, 13.31.

2-Heptylspiro[3.3]heptane (10b). IR (film) ν 3045, 2999, 1705, 1456, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.06-2.09 (m, 3H), 1.99 (t, *J* = 6.8 Hz, 2H), 1.86-1.88 (m, 2H), 1.79-1.82 (m, 2H), 1.51-1.53 (m, 2H), 1.16-1.36 (m, 12H), 0.9 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.2, 40.2, 37.2, 35.8, 35.2, 31.9, 29.4, 29.6, 27.4, 22.7, 16.6, 14.1; MS (ES) *m*/*z* $[M]^+$ 194. Anal. Calcd. for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.39; H, 13.49.

Spiro[cyclobutane-1,3'-*exo*-tricyclo[4.2.1.0^{2,5}]nonane] (19). B.p. 77-78 °C (3 Torr). IR (film) ν 1665, 1640, 995, 915, 890 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (br.s, 1H), 1.91-1.93 (m, 1H), 1.88 (br.s, 1H), 1.84-2.03 (m, 4H), 1.64-1.72 (m, 5H), 1.55-1.57 (m, 2H), 1.39-1.41 (m, 2H), 0.96-0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.2, 42.5, 38.9, 38.5, 38.4, 37.1, 36.5, 33.0, 29.7, 28.5, 27.7, 16.5; MS (ES) *m*/*z* $[M]^+$ 162. Anal. Calcd. for $C_{14}H_{26}$: C, 88.82; H, 11.18. Found: C, 88.74; H, 11.19.

7-Pentylspiro[cyclobutane-1,3'-*exo*-tricyclo[4.2.1.0^{2,5}]nonane] (20). B.p. 109-112 °C (1 Torr). IR (film) ν 1665, 1640, 995, 920, 890 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.84-2.04 (m, 8H), 1.72 (m, 2H), 1.59 (m, 2H), 1.53-1.56 (m, 2H), 1.22-1.29 (m, 11H), 0.91 (t, 3H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.8, 42.7, 41.2, 40.0, 38.6, 38.4, 37.4, 36.3, 35.7, 34.3, 32.5, 32.1, 30.4, 28.5, 22.5, 16.2, 14.1; MS (ES) *m*/*z* $[M]^+$ 232. Anal. Calcd. for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 87.79; H, 12.12.

Spiro[cyclobutane-1,3'-*exo*-pentacyclo[5.4.0.0^{2,5}.0^{6,10}.0^{9,11}]undecane (21). B.p. 94-96 °C (5 Torr). IR (film) ν 1680, 995, 905, 885 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.46-2.51 (m, 1H), 2.17-2.19 (m, 1H), 2.10-2.12 (m, 1H), 1.93 (br.s, 1H), 1.84 (br.s, 1H), 1.81-2.04 (m, 4H), 1.66-1.72 (m, 1H), 1.53-1.58 (m, 5H), 1.23-1.25 (m, 1H), 0.89-1.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ 51.3, 46.2, 43.2, 42.2, 38.9, 38.1, 36.6, 36.4, 31.9, 31.5, 29.8, 16.2, 13.9, 12.9; MS (ES) *m*/*z* $[M]^+$ 186. Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.09; H, 9.76.

Dispiro[cyclobutane-1,3'-*exo*-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]undecane-9',1''-cyclobutane] (22). IR (film) ν 1660, 1655, 995, 920, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.98 (br.s, 1H), 1.91-1.94 (m, 2H), 1.83 (br.s, 1H), 1.84-2.03 (m, 8H), 1.63-1.75 (m, 8H), 1.55-1.57 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.2, 41.3, 38.9, 38.5, 38.4, 38.3, 35.9, 34.9, 29.9, 16.6; MS (ES) *m*/*z* $[M]^+$ 228. Anal. Calcd. for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.34; H, 10.57.

2-Deutero-1-pentyl-2-(3-deuteropropyl)cyclopropane (26). IR (film) ν 2170 (CD) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25−1.44 (m, 10H), 1.09−1.15 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.64 (m, 1H), 0.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.1, 30.9, 30.1, 28.9, 23.4, 22.6, 15.8, 15.3 (t, J_{CD} = 19.0 Hz), 14.0, 13.8 (t, J_{CD} = 19.0 Hz), 10.8; MS (ES) *m*/*z* $[M]^+$ 156. Anal. Calcd. for $C_{11}H_{20}D_2$: C, 84.53; H, 12.9; D, 2.57. Found: C, 84.34; H+D, 14.95.

1-(2-Deuteroethyl)-1-deuteromethyl-2-pentylcyclopropane (cis:trans-1:1) (27). IR (film) ν 2160 (CD) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.18−1.44 (m, 10H), 1.03 (s, 2H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 2H), 0.15−0.44 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.4 (34.2), 32.6, 30.5, 28.6, 26.6, 22.6, 20.3 (20.1) (t, J_{CD} = 19.0 Hz), 18.6 (19.0), 14.2, 10.8 (10.7) (t, J_{CD} = 19.0 Hz); MS (ES) *m*/*z* $[M]^+$ 156. Anal. Calcd. for $C_{11}H_{20}D_2$: C, 84.53; H, 12.9; D, 2.57. Found: C, 84.44; H+D, 14.98.

1-Pentylspiro[2.3]hexane (28). IR (film) ν 3069, 2995, 1705, 1460, 1160, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.05-2.10 (m, 4H), 1.92-1.96 (m, 2H), 1.12-1.36 (m, 8H), 0.91 (t, *J* = 6.5 Hz, 3H), 0.49-0.56 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.2, 30.9, 30.4, 29.3, 28.1, 26.4, 22.4, 22.1, 18.1, 17.4, 14.0; MS (ES) *m*/*z* $[M]^+$ 152. Anal. Calcd. for $C_{11}H_{20}$: C, 88.76; H, 13.24. Found: C, 88.68; H, 13.25.

1-Phenyl-2-propylcyclopropane (31). IR (film) ν 3070, 3030, 2995, 1705, 1460, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.30 (m, 2H), 7.21-7.23 (m, 2H), 7.18-7.19 (m, 1H), 2.12-2.14 (m, 1H), 1.31-1.33 (m, 2H), 1.18-1.19 (m, 1H), 1.12-1.14 (m, 1H), 0.98-0.99 (m, 1H), 0.90-0.91 (m, 1H), 0.83 (t, *J* = 7.0 Hz, 3H), 0.66-0.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.8, 129.0, 127.8, 125.8, 30.7, 22.5, 20.9, 18.8, 14.0, 9.6; MS (ES) *m*/*z* $[M]^+$ 160. Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.81; H, 10.04.

2-Deutero-1-phenyl-2-(3-deuteropropyl)cyclopropane (32). IR (film) ν 2160 (CD) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.17−7.31 (m, 5H, Ph), 2.12-2.14 (m, 1H), 1.32-1.33 (m, 2H), 1.19-1.20 (m, 1H), 0.97-0.99 (m, 1H), 0.92-0.94 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 2H), 0.65-0.67 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.1, 30.9, 30.1, 28.9, 23.4, 22.6, 15.8, 15.3 (t, J_{CD} = 19.0 Hz), 14.0, 13.8 (t, J_{CD} = 19.0 Hz), 10.8; MS (ES) *m*/*z* $[M]^+$ 162. Anal. Calcd. for $C_{12}H_{14}D_2$: C, 88.83; H, 8.70; D, 2.47. Found: C, 88.75; H+D, 11.23.

Synthesis of 4,4-dimethylspiro[2.7]decane (36a)

Cyclic alkyne (5 mmol), Cp_2ZrCl_2 (0.25 mmol), hexane (10 mL), and Et_3Al (15 mmol) were placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to

ambient (20-21 °C) and the reaction mixture was stirred for 6 h, then, Me_2SO_4 (8 mmol) were added dropwise at 0 °C, the temperature was raised to ambient and the stirring was continued for 12 h. The reaction mixture was worked up with 7-10% aq. HCl, the reaction products were extracted with diethyl ether, dried with $MgSO_4$ and isolated by distillation *in vacuo*.

4,4-Dimethylspiro[2.7]decane (36a). B.p. 96–98 °C (1 Torr.). IR (film) ν 770, 1050, 1395, 1430, 1498, 2910, 3050, 3070 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.51-1.55 (м, 4H), 1.34-1.43 (m, 16H), 0.75 (s, 6H), 0.31-0.33 (m, 2H), 0.23-0.24 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.6, 35.2, 32.2, 30.1, 27.4, 25.5, 24.8, 24.4, 24.1, 23.1, 22.7, 20.9, 19.8, 5.4; MS (ES) *m*/*z* $[M]^+$ 222. Anal. Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.29; H, 13.57.

Synthesis of 4-methylenespiro[2.7]decane 37a and dimethylenespirooctadecanes 41a,b. General procedure

Cyclic alkyne (10 mmol) or diyne (5 mmol), Cp_2ZrCl_2 (1 mmol), hexane (20 mL), and Et_3Al (30 mmol) were placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to ambient (20-21 °C) and the reaction mixture was stirred for 6 h, then, $BrCH_2OCH_3$ (10 mmol) were added dropwise at -78 °C, the temperature was raised to ambient and the stirring was continued for 12 h. The reaction mixture was worked up with 7-10% aq. HCl, the reaction products were extracted with diethyl ether, dried with Na_2CO_3 and isolated by column chromatography (SiO_2, hexane-benzene, 10:1).

4-Methylenespiro[2.7]decane (37a). Rf 0.67. IR (film) ν 725, 895, 1055, 1460, 1640, 2859, 2920, 2995 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.73 (m, 2H), 2.13 (t, *J* = 8 Hz, 2H), 1.56-1.58 (м, 2H), 1.32-1.44 (m, 16H), 0.53-0.61 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.2, 107.4, 35.2, 32.2, 30.2, 29.4, 26.1, 25.4 24.5, 24.3, 24.0, 23.5, 23.1, 12.2; MS (ES) *m*/*z* $[M]^+$ 206. Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.09; H, 12.72.

12,18-Dimethylenedispiro[2.5.2.7]octadecane (41a). Rf 0.56. IR (film) ν 720, 895, 1048, 1461, 1640, 2859, 2928, 2999 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.76 (m, 4H), 2.06 (t, *J* = 8 Hz, 4H), 1.56-1.64 (m, 4H), 1.38-1.55 (m, 8H), 1.30 (m, 4H), 0.56-0.61 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.6, 107.8, 35.1, 29.5, 27.4, 26.2, 26.0, 25.3, 23.4, 12.0; MS (ES) *m*/*z* $[M]^+$ 272. Anal. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 87.96; H, 11.82.

4,13-Dimethylenedispiro[2.6.2.6]octadecane (41b). 0.49. IR (film) ν 720, 890, 1047, 1464, 1640 (C=CH_2), 2855, 2928, 2990 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.76 (m, 4H), 2.11 (t, *J* = 8 Hz, 4H), 1.56-1.64 (m, 4H), 1.31-1.35 (m, 8H), 1.30 (m, 4H), 0.34 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 109.1, 35.5, 31.2, 26.9, 26.4, 23.8, 23.5, 12.2; MS (ES) *m*/*z* $[M]^+$ 272. Anal. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 11.83.

Synthesis of dispiro[2.0.2.6]dodecane (38a) and tetraspiro[2.0.2^4.5.2^{12}.0.2^{15}.5^3]docosane (42) General procedure

4-Methylenespiro[2.7]decane **37a** (2 mmol) or mixture dimethylenespirooctadecanes **41a,b** (1 mmol), dichloromethane (10 mL), diiodomethane (2.2 mmol) and Et_3Al (2.2 mmol) were placed into a glass reactor under dry argon at 0 °C with stirring. The temperature was elevated to

ambient (20-21 °C) and the reaction mixture was stirred for 6 h. The reaction mixture was worked up with 7-10% aq. HCl, the reaction products were extracted with diethyl ether, dried with Na_2CO_3 and isolated by column chromatography (SiO_2, pentane).

Dispiro[2.0.2.6]dodecane (38a). Rf = 0.41. IR (film) ν 730, 762, 1025, 1185, 1454, 2860, 2925, 2997, 3074 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.55-1.64 (m, 4H), 1.27-1.47 (m, 16H), 0.53-0.62 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.7, 29.7, 27.9, 22.6, 20.4, 9.5; MS (ES) *m*/*z* $[M]^+$ 220. Anal. Calcd. for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.05; H, 12.80.

Tetraspiro[2.0.2^4.5.2^{12}.0.2^{15}.5^3]docosane (42). Rf = 0.39. IR (film) ν 734, 762, 1021, 1185, 1458, 2860, 2929, 2999, 3070 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (m, 8H), 1.29-1.46 (m, 12H), 0.60-0.63 (m, 16H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.3, 20.6, 22.4, 27.3, 35.3; MS (ES) *m*/*z* $[M]^+$ 300. Anal. Calcd. for $C_{22}H_{36}$: C, 87.93; H, 12.07. Found: C, 87.74; H, 12.05.

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