



Review

Catalytic cyclometalation reaction of unsaturated compounds in synthesis of magna- and aluminacarbo-cycles

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Dedicated to Professor John M. Birmingham
 on the occasion of his 80th birthday.

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ABSTRACT

The investigation results on design and application of the new catalytic cyclometalation reaction of olefins, dienes, acetylenes and allenes with Al, Mg and halogen alkyls mediated by Ti or Zr based metallocene catalysts to produce novel classes of cyclic organometallics namely aluminacyclopropanes, aluminacyclopentanes, aluminacyclopentanes, aluminacyclopentenes, aluminacyclopenta-2,4-dienes, magnacyclopentanes, magnacyclopentenes, magnacyclopenta-2,4-dienes as well as metallamacrocycles are summarized and systematized. Selected literature data on thermal synthesis of cyclic organoaluminum and organomagnesium compounds for comparison the efficiencies of catalytic and classic synthetic methods are given. Mechanistic aspects of catalytic cyclometalation of unsaturated compounds and chemical transformations of Al and Mg metallacycles are discussed.

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1. Introduction

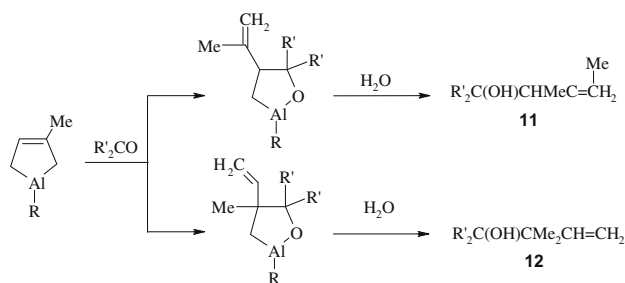
Growing scientific interest in nontransition metallacycles is conditioned by their wide applications in the synthesis of carbo- and heterocyclic compounds including gigantic hydrocarbons and organometallic macrocycles, useful organic and organometallic synthons.

To a number of known, available and stable metallacycles one should add cyclic organoaluminum (OACs) and organomagnesium compounds (OMCs) containing active M–C bonds. The synthetic methods to produce the aforesaid compounds have been mainly developed in the last 10–15 years.

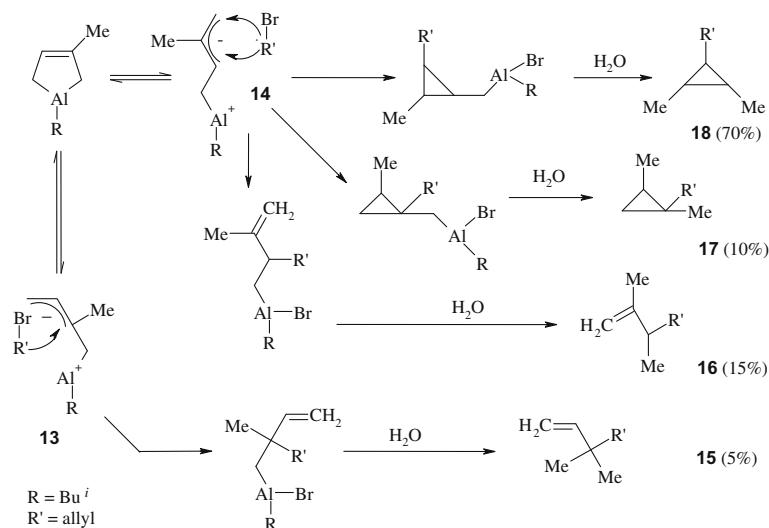
It can be said without exaggeration that all these achievements became possible due to the application of metal complex catalysis to chemistry of OACs and OMCs. As a result, the new regio- and stereoselective fundamental reactions have been successfully elaborated to obtain earlier not described three-membered,

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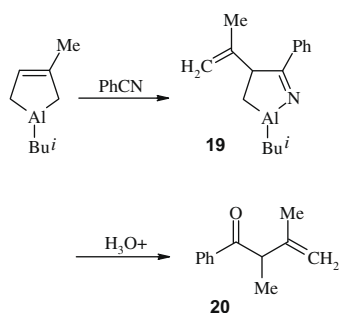
The interaction between aluminacyclopent-3-enes and ketones resulted in unsaturated alcohols **11** and **12** of various structures [6].



Cross-coupling of 3-methylaluminacyclopent-3-ene with allyl bromide was accompanied by cleavage of the cyclopentene cycle yielding regioisomeric unsaturated OACs **13** and **14**. According to the position of the double bond towards the Al atom in the starting cyclic OAC under chosen conditions one can obtain unsaturated acyclic **15** and **16** as well as cyclopropane-containing compounds **17** and **18** [7].

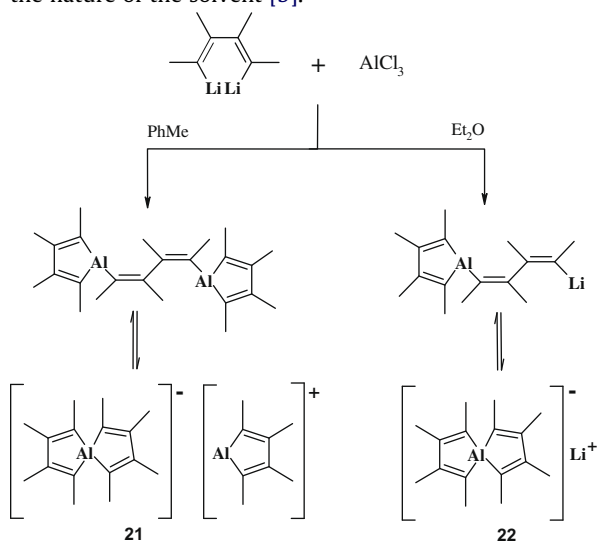


High reactivity of the five-membered OACs have been demonstrated on example of the reaction between 1-isobutyl-3-methylaluminacyclopent-3-ene and PhCN, which through the formation of 4-isopropenyl-1-isobutyl-3-phenyl-1-alumina-2-azacyclopent-2-ene **19** after acid hydrolysis of the latter led to the unsaturated ketone **20** [8].

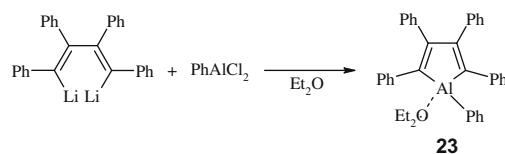


Along with the procedures aforesaid, the method for a synthesis of the five-membered cyclic OACs by the interaction between 1,4-dilithium reagents and aluminum halides is rather common. Treatment of AlCl₃, for example, with excess 1,4-dilithiobutadienes

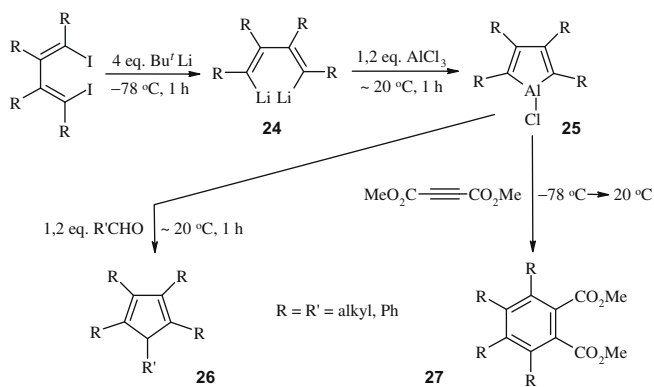
resulted in spiro-ate-aluminacyclopentadienyl complexes **21** and **22**. The structure of these ate complexes was dependent upon the nature of the solvent [9].



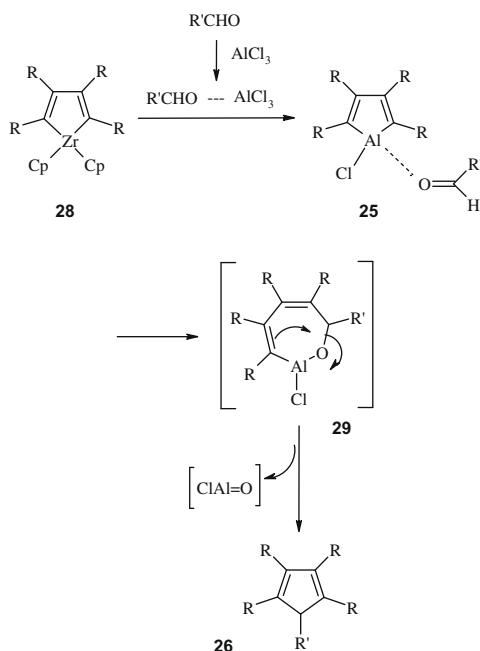
Pentaphenylaluminacyclopenta-2,4-diene etherate **23** has been obtained by transmetalation of 1,2,3,4-tetraphenyl-1,4-dilithiobutadiene with equivalent amount of PhAlCl₂ in toluene [10,11].



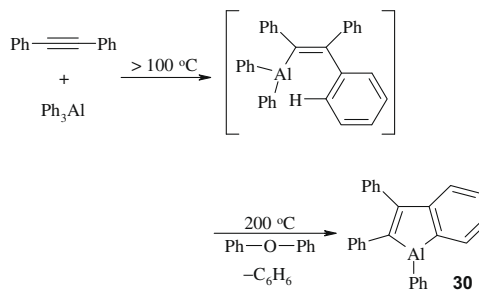
Similar approach was used to synthesize 1-chloro-2,3,4,5-tetraalkyl(phenyl)aluminacyclopentadienes **25** from 1,4-dilithiobuta-1,3-dienes **24** and AlCl₃. Generated *in situ* aluminacyclopenta-2,4-dienes are the effective reagents for the synthesis of cyclopentadienes and aromatic compounds. Thus, the reaction of OAC **25** with aldehydes or dimethylacetylenecarboxylate led to penta-substituted cyclopenta-1,3-dienes **26** or hexasubstituted benzenes **27** [12,13].



The method for a synthesis of aluminacyclopentadiene derivatives through the stoichiometric reaction of zirconacyclopentadienes **28** with aldehydes in the presence of AlCl₃ is considered by the investigators as rather attractive. Using ¹H NMR spectroscopy, Z. Xi and coworkers [13,14] have studied this reaction. They have shown that dienes **28** do not react with aldehydes, but enter the reaction with the latter in the presence of AlCl₃. The generated aluminacyclopentadiene **25** as aldehyde–AlCl₃ adduct via the subsequent interaction with activated aldehyde molecule gave rise to oxoaluminacycloheptane **29**, the intramolecular rearrangement of which facilitated carbocyclization to afford substituted cyclopentadienes **26**.



One should pay attention to the synthesis of aluminacyclopentadiene **30** by thermal (higher than 100 °C) carboalumination of diphenylacetylene with the aid of Ph₃Al suggested by Eisch and Kaska. The intramolecular hydrogen transfer and subsequent cyclization at about 200 °C led to the target product **30** [15,16].



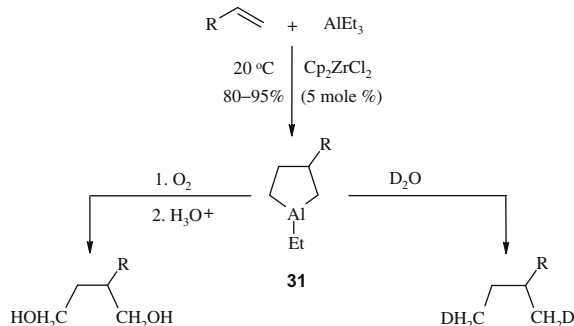
These examples give evidence that thermal procedures to synthesize aluminacyclopentanes, aluminacyclopentenes, and aluminacyclopentadienes are mainly based on the thermal hydro- and carboalumination reactions of olefins and dienes as well as on the reaction of 1,4-dilithium compounds or zirconacyclopentadienes with aluminum halides.

Thermal procedures are characterized by low selectivity and generally do not allow obtaining cyclic OAC in satisfactory yields. They have not been found proper use in synthetic practice as preparative methods for a synthesis of cyclic OACs.

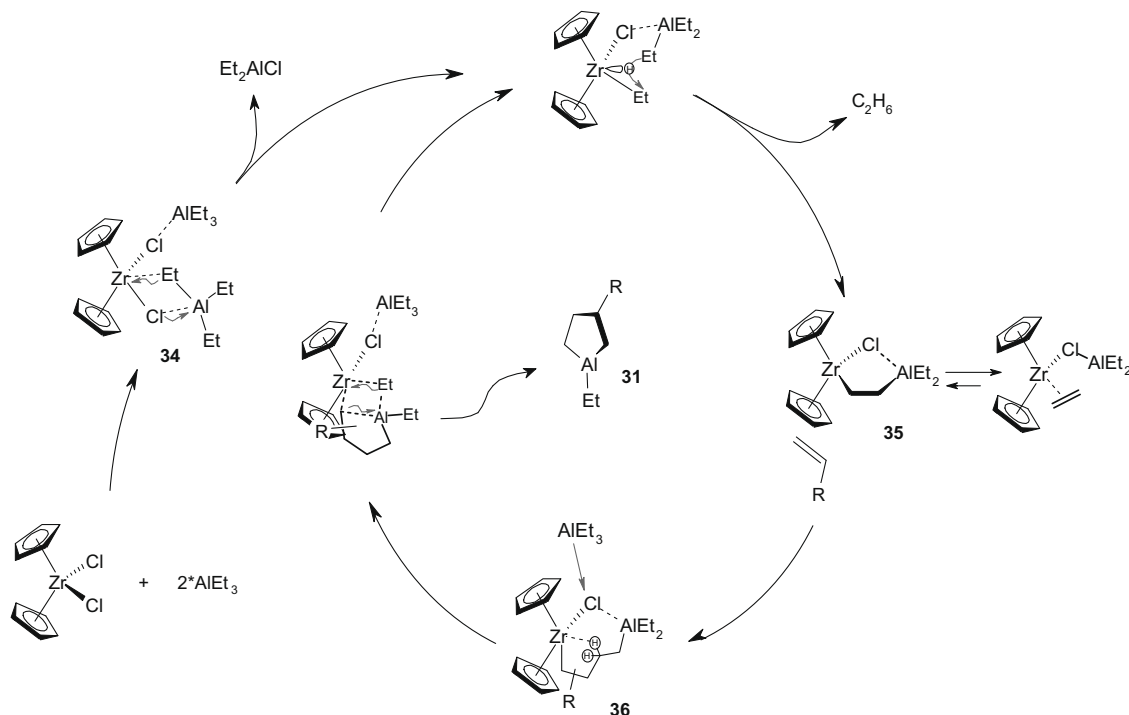
3. Catalytic cycloalumination of olefins and 1,2-dienes

The first report on the possibility of the preparative synthesis of aluminacyclopentanes under catalytic reaction conditions from α-olefins and Et₃Al in the presence of Cp₂ZrCl₂ catalyst, has appeared in 1989 [17], though these results were gained, as noted by the authors of the present survey, in 1985 [18].

Unordinary results obtained, viz., the construction of the five-membered OACs in one preparative stage from acyclic starting reagents with high selectivity (more than 95%) and yields (more than 90%), encouraged the authors [17] to investigate this reaction thoroughly for a more reliable determination of the structure of the target OACs. As a result, the interaction between α-olefins and Et₃Al in the presence of 5 mol% Cp₂ZrCl₂ was established to afford 3-substituted aluminacyclopentanes **31** in high yields. The structure of the latter has been determined by spectral methods after chemical transformations to 1,4-butanediols and 1,4-dideuterobutanes according to the following Scheme:



Very instructive is a history of discovery of this reaction, which allows to synthesize the five-membered OACs **31** from α-olefins. As noted by the authors of this survey, the studies in the field of linear dimerization and codimerization of 1,3-dienes under the effect of Zr-containing catalysts preceded the discovery the

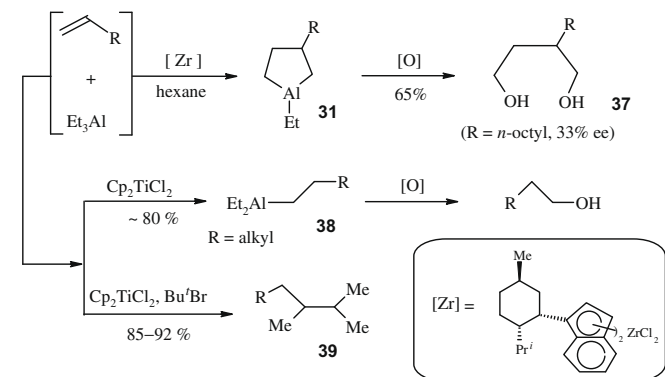
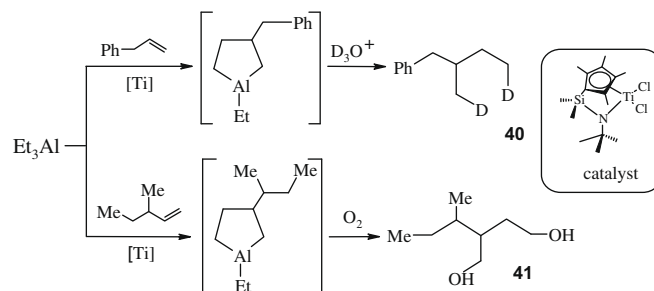


The subsequent efforts of the researchers in the field of organic synthesis of cyclic OACs have been directed towards determination of application boundaries of the said reaction and also to the search of the catalysts able to convert α -olefins in the presence of trialkyl- and alkylhalogenalanes into corresponding substituted aluminacyclopentanes. From a number of the tested catalysts based on salts or complexes of transition metals (Cu, Mn, Cr, Ti, Zr, Hf, H, W, Mo, Fe, Cu, Ni, Pd, Rh) and widely used in metal complex catalysis only cyclopentadienyl Ti, Zr and Co complexes were testified as the most active ones to convert olefins to aluminacyclopentanes with the aid of trialkyl or alkyl halogenides with high yields and selectivity [1,29–31,35–37].

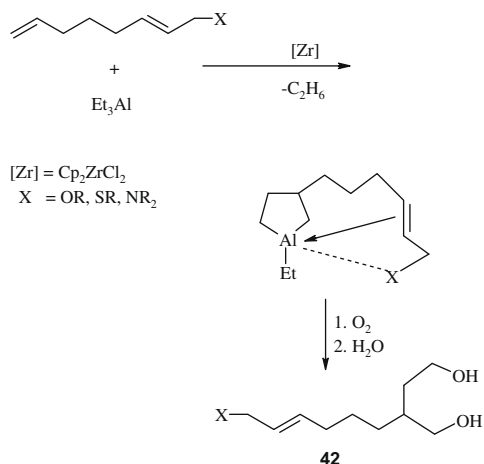
Cycloaluminatation of α -olefins with Et_3Al in the presence of chiral Zr-containing catalysts [38,39] or cocatalysts, viz., amides or aluminum alkoxides [40] was shown to afford cyclic OAC **31**, oxidation of which gave rise to optically active diols **37**.

The reaction is sensitive to the nature of the central metal atom of the catalyst. Thus, the use of Cp_2TiCl_2 as a catalyst instead of Cp_2ZrCl_2 was found to facilitate the formation of the hydroaluminumation products **38** [41], while the reaction of α -olefins with Et_3Al in the presence of *t*-BuBr and Cp_2TiCl_2 catalyst resulted in the hydroalkylation product **39** in 85–92% yield [42].

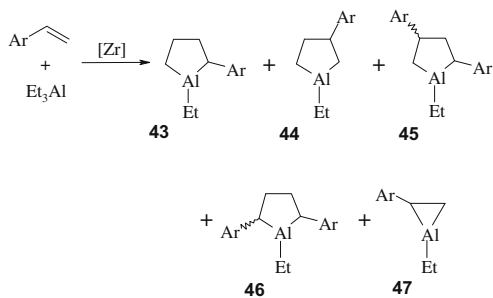
The catalytic cycloaluminatation reaction is sensitive not only to the type of a catalyst but also to the nature of the solvent. Later, Waymouth and co-workers investigated the reaction of α -olefins with AlEt_3 in CH_3CHCl_2 solution affected by cyclopentadienylamidotitanium dichloride $\eta^5\text{-(C}_5\text{Me}_4\text{)SiMe}_2\text{N}(t\text{-Bu)TiCl}_2$ complex. The authors concluded that the reaction proceeds through the formation of the corresponding OACs identified as the deuterolysis **40** and oxidation **41** products [43].



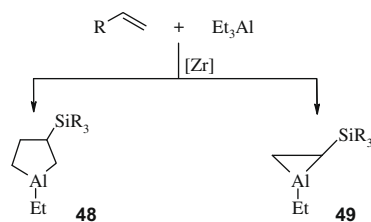
The function substituted N-, O-, and S-containing α -olefins in the presence of catalytic amounts of Cp_2ZrCl_2 enter the reaction with Et_3Al giving aluminacyclopentanes **42**, in which lone electron pairs of the heteroatom such as O, N or S form donor–acceptor complexes [44,45]. One should not exclude the participation of the disubstituted double bond in the formation of the coordination environment of the aluminum atom.



Unlike aliphatic α -olefins, which under the effect of Cp_2ZrCl_2 catalyst enter the reaction with Et_3Al yielding 1-ethyl-3-alkylaluminacyclopentanes, 1-arylolefins such as styrene, *ortho* or *para* methylstyrene under chosen conditions gave a mixture of substituted tri- (**47**) and five-membered **43–46** OACs at a ratio of **43:44:45:46:47** = 50:25:15:3:7 [46]. The authors of the work [46] suggested that formation of cyclic OACs **43–47** occurs through Zr- and Al-containing bimetallic intermediates generated from Cp_2ZrCl_2 and Et_3Al [47–50].



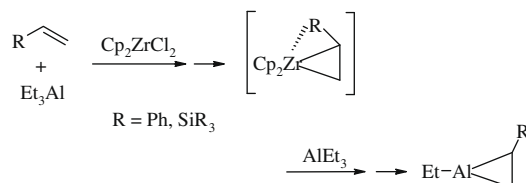
Similar results have been obtained in the course of cycloalumination of vinyl and allyl silanes with Et_3Al in the presence of Cp_2ZrCl_2 catalyst. Thus, the interaction between triethyl(vinyl)silane and Et_3Al (excess) in the presence of Cp_2ZrCl_2 as a catalyst (5 mol%, 10 h, 20 °C) was shown to afford the OAC mixture of 1-ethyl-3-(triethylsilyl)aluminacyclopentane **48** and 1-ethyl-2-(triethylsilyl)aluminacyclopentane **49** at a ratio of 6:1 (total yield ~70%) [51]. Allyl silanes, unlike trialkyl(vinyl)silanes, reacted more selectively to give predominantly 3-substituted aluminacyclopentanes.



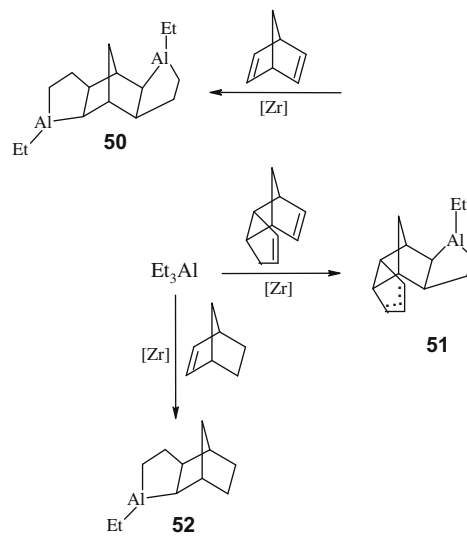
The observed differences in the cycloalumination reaction of aliphatic α -olefins, arylolefins, and vinyl silanes with the aid of Et_3Al can be explained by different structure and nature of substituents in the starting unsaturated compounds. Apparently, che-

moselectivity of cyclic OAC formation is determined by the stage involving generation of Zr- and Al-containing bimetallic complexes [47–50] from zirconacyclopentanes and trialkylallanes under reaction conditions.

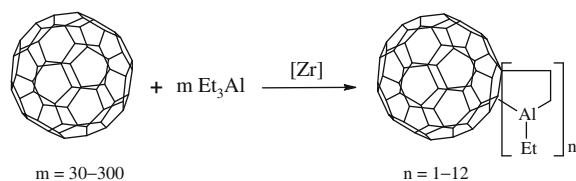
One should believe that intermediate zirconacyclopentanes as a result of cycloalumination of aryl olefins and vinyl silanes with AlEt_3 in the presence of Cp_2ZrCl_2 catalyst are stabilized due to complexation of aryl and silyl substituents in the starting α -olefins with the central atom of the catalyst leading to the appropriate aluminacyclopentanes according to the following Scheme.



High selectivity of the olefin cycloalumination reaction has been demonstrated on the example of cycloolefins such as norbornene, norbornadiene and *exo*-dicyclopentadiene. In each experiment cycloalumination of the double bond in norbornene occurred strongly stereo-selectively to afford appropriate aluminacyclopentanes **50**, **51**, and **52** of *exo*-configuration [52–55].

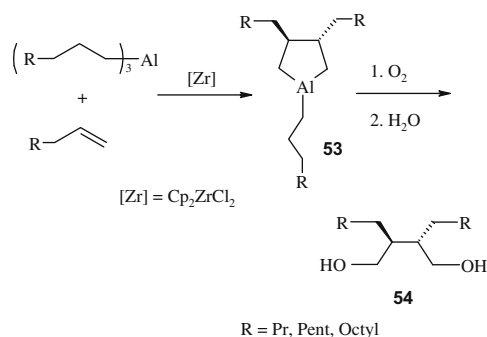


In order to develop these investigations the authors [56–58] have studied cycloalumination of fullerene [60] with AlEt_3 taken in excess. It was shown that under chosen conditions (~23 °C, 36 h, toluene) in the presence of Cp_2ZrCl_2 catalyst the reaction occurs at a 6,6-double bond providing access to adducts with annulated to the fullerene spheroid aluminacyclopentane moieties, the number of which is dependent upon the ratio of the starting reagents.

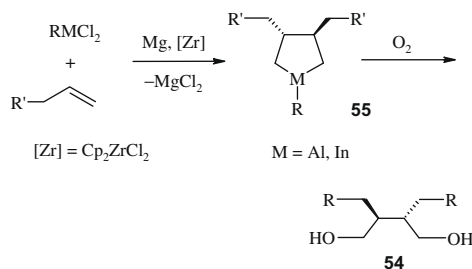


Furthermore, the authors of the works [59,60] showed that, together with Et_3Al , in the cycloalumination reaction higher

trialkylalanes R_3Al can be used. Thus, the interaction between equimolar amounts of α -olefins and higher trialkylalanes in the presence of 3 mol% of Cp_2ZrCl_2 for 12 h at ambient temperature was found to produce selectively 1-alkyl-*trans*-3,4-dialkyl-substituted ACP **53** in 50–75% yield. Based on OAC **53** the preparative method for a synthesis of *threo*-2,3-dialkylbutane-1,4-diols **54** from α -olefins has been developed according to the following Scheme.

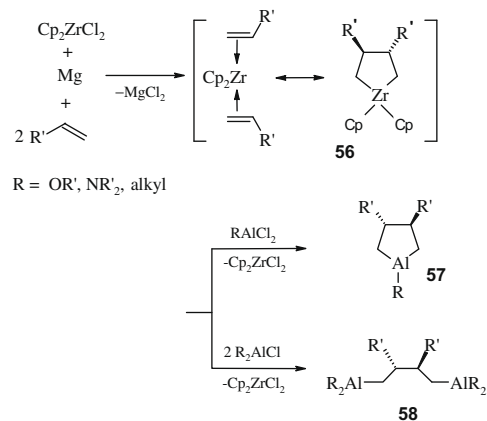


The all aforesaid allow to consider the use of pyrophoric OACs in the synthesis of aluminacyclopentanes as a principal deficiency that noticeably limits the preparative value of the said method. Our proposed method for a synthesis of 1-ethyl-*trans*-3,4-dialkylaluminumacyclopentanes **55** by the interaction between α -olefins and $EtAlCl_2$ in the presence of metallic Mg and catalytic amounts of Cp_2ZrCl_2 at ambient temperature in tetrahydrofuran does not have this limitation [61–63]. In the cycloaluminumation reaction under said conditions together with $EtAlCl_2$ one can use alkoxides, aluminum amides $RAiCl_2$ ($R = OR', NR'_2$) or $AlCl_3$ to provide **55** in 70–90% yield [64,65]. This approach was successfully applied to the preparation of substituted indacyclopentanes [66,67].

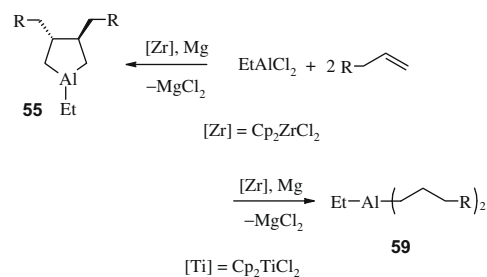


As is evident, the above reactions proceeded through generation from α -olefins and Cp_2ZrCl_2 catalyst zirconacyclopentane intermediates [68–71], transmetalation of which with $RAiCl_2$ led to *trans*-3,4-dialkylaluminumacyclopentanes **57** in high yields with high selectivity.

During these investigations the authors of the works [72,73] extensively studied the reaction for various α -olefins in the presence of Cp_2ZrCl_2 catalyst and metallic Mg (THF, $\sim 20^\circ C$) assisted by dialkyl aluminum chlorides, alkoxides and also aluminum amides of the general formula R_2AlCl ($R = \text{alkyl}, OR', NR'_2$). As a result, *threo*-2,3-dialkyl-1,4-dialuminiobutanes **58** have been synthesized in one preparative stage in 64–84% yield.



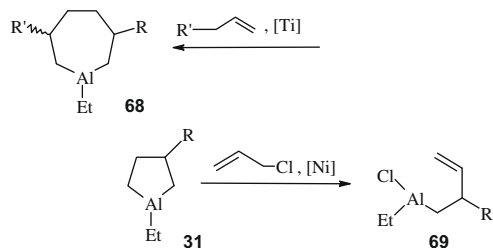
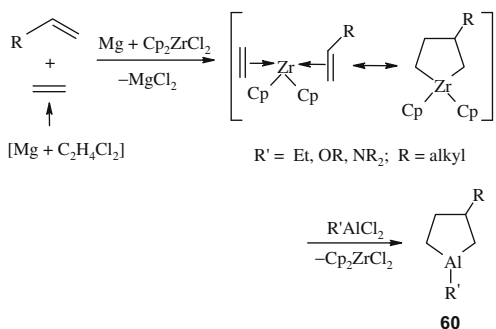
The direction of the given reactions was found to depend upon both the type of the initial reagents and chemical nature of a catalyst. The use of Cp_2TiCl_2 instead of Cp_2ZrCl_2 promoted hydroalumination of α -olefins giving rise to ethyl dialkyl alanes **59** in 60–85% yield [74]. The authors of the work [74] assumed that in this hydrogen atom transfer (HAT) reaction the solvent (THF) can serve as hydrogen donor.



The synthesized by this method 2,3-dialkylsubstituted 1,4-dialuminum compounds contain two asymmetrical C-2 and C-3 carbon atoms being able to form diastereomeric pair. The spectral ^{13}C NMR analysis of 1,4-dialuminum compounds **58**, their hydrolysis and deuterolysis products allowed classify these OACs as *threo* stereoisomers [72]. The structure of aluminacyclopentanes as well as the structure of tri- and tetracyclic OACs, the position of substituents and its configuration have been reliably established by spectral methods [75,76].

High stereoselectivity and efficiency of the preparation method to obtain *trans*-3,4-dialkylaluminumacyclopentanes **55** using available fire and explosion safety reagents *viz.* $AlCl_3$ [61,62,64], specify the prospect of its wide application in synthetic practice.

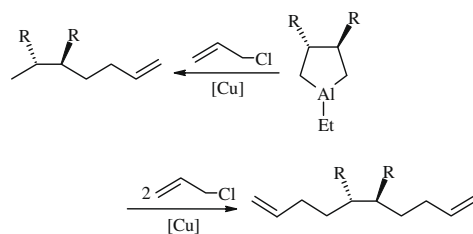
As it follows from the reactions given above, the methodology of catalytic cycloaluminumation of α -olefins with $RAiCl_2$ to *trans*-3,4-disubstituted aluminacyclopentanes does not allow to synthesize 3-substituted aluminacyclopentanes. The authors of the works [77,78] have succeeded in obtaining of 3-alkylsubstituted cyclic OAC **60** with $RAiCl_2$ ($R = Et, OR', NR'_2$) through combined cycloaluminumation of α -olefins and ethylene generated *in situ* from 1,2-dichloroethane with the aid of dihalogenalanes in the presence of metallic Mg (excess) and Cp_2ZrCl_2 catalyst in tetrahydrofuran [77,78]. In these experiments *trans*-3,4-dialkylaluminumacyclopentanes **55** were detected in minor amounts (<10%).



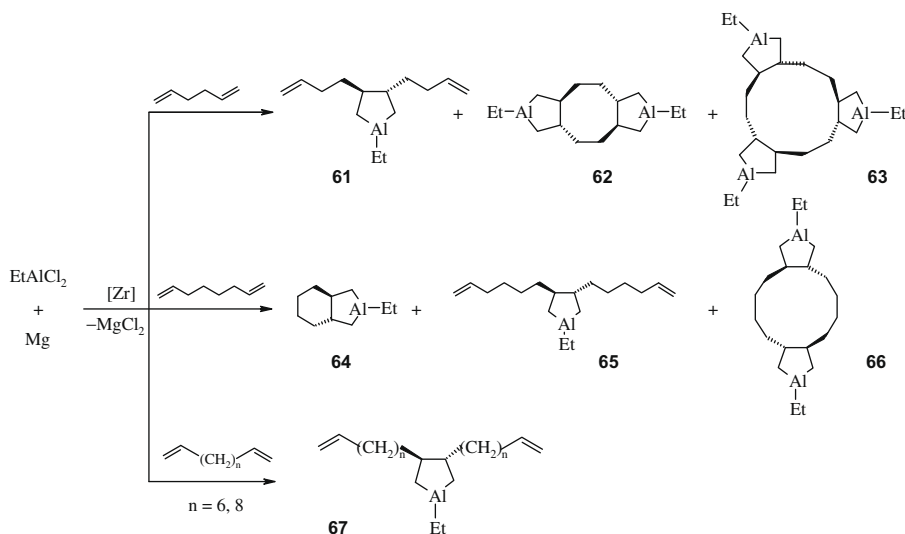
The cross-coupling reaction of substituted aluminacyclopentanes with allyl halogenides affected by CuCl catalyst is a convenient route to the appropriate substituted hept-1-enes and *threo*-5,6-dialkylsubstituted deca-1,9-dienes [85].

These achievements stimulated investigations on intra- and intermolecular cycloaluminum of α,ω -diolefines with RAlCl_2 in the presence of Cp_2ZrCl_2 to produce carbocycles with annulated aluminacyclopentane fragments [79]. Thus, the interaction between hexa-1,5-diene and EtAlCl_2 (1:2 ratio) in the presence of Cp_2ZrCl_2 catalyst (10 mol%) and metallic Mg (acceptor of halogenide ions) in THF ($\sim 20^\circ\text{C}$, 24 h) was found to afford carbocycles **61**, **62** and **63** at a ratio of $\sim 4:3:2$ in 75% common yield. Under indicated reaction conditions cycloaluminum of octa-1,7-diene with EtAlCl_2 led to cyclic OACs **64**, **65** and **66** at a ratio of $\sim 6:3:1$ in 70% total yield.

In contrast with hexa-1,5-diene and octa-1,7-diene the cycloaluminum reaction of deca-1,9-diene and dodeca-1,11-diene gave rise to *trans*-3,4-disubstituted aluminacyclopentanes **67** in 40–45% yield [80].



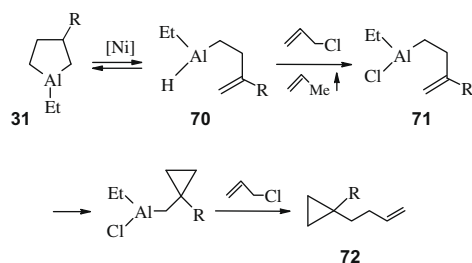
Higher reactivity of Al–C bonds in the aluminacyclopentane ring as compared with Al–Et bond reveals the simple way to the



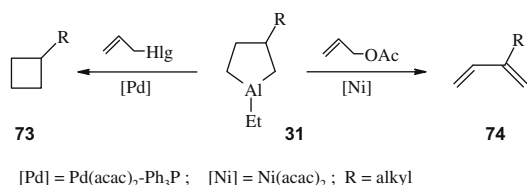
Synthesized and described above monosubstituted and *trans*-3,4-disubstituted aluminacyclopentanes are characterized by high reactivity. Thus, the Al–C bonds in the five-membered cycle manifested higher reactivity as compared with Al–Et bond [44]. For example, 3-alkylaluminacyclopentanes enter the reaction with α -olefins in the presence of Ti catalysts to produce 1-ethyl-3-alkylaluminacyclopentanes **68** [81,82]. The use of allyl chlorides instead of α -olefins as well as Ni or Co catalysts instead of Zr complexes were found to promote the cleavage of the aluminacyclopentane ring giving rise to acyclic allyl halogenalanes **69** [83,84].

synthesis of carbo- and heterocycles from α -olefins through the preliminary generation of the appropriate aluminacyclopentanes. Thus, the interaction between generated *in situ* 1-ethyl-3-alkylaluminacyclopentanes **31** and allyl chloride (excess) in the presence of $\text{Ni}(\text{acac})_2$ catalyst in diethyl ether was shown to afford 1,1-disubstituted cyclopropanes **72** in 55–70% yield [86,87]. According to the Scheme below aluminacyclopentanes **31** under the effect of Ni complex catalyst undergo the intramolecular hydrogen transfer to form but-3-enyl(ethyl)aluminum hydrides **70**, which further react with initial allyl halogenide giving rise to

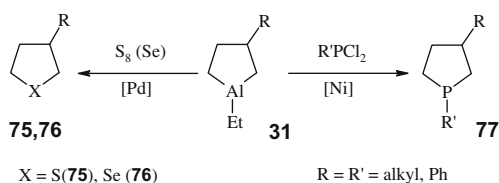
but-3-enyl(ethyl)aluminum halogenides **71**. Subsequent intramolecular carboalumination resulted in the corresponding 1,1-disubstituted cyclopropanes **72** [88,89].



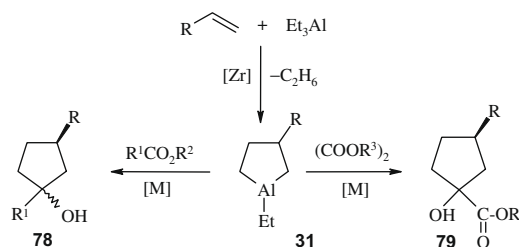
To develop these works the simple procedure to synthesize monoalkylsubstituted cyclobutanes **73** through the reaction of 3-alkylsubstituted aluminacyclopentanes **31** with allyl halogenides (1:3 molar ratio) at ambient temperature have been realized in diethyl ether in the presence of Pd(acac)₂-Ph₃P complex catalyst (5 mol%) in 60–78% yield. The reaction was accompanied by the elimination of propylene and cyclopropane (as a gaseous mixture at a ratio of 5:1) generated from allyl halogenides under the action of low valence Pd complexes [90,91]. Under above conditions one can obtain the corresponding *trans*-1,2-dialkylcyclobutanes with high selectivity from 1-ethyl-*trans*-3,4-dialkylaluminacyclopentanes **55** [92,93]. The reaction is very sensitive to the nature of both allyl compound and central atom of a catalyst. Thus, in the presence of ~3.5-fold excess of allyl acetate and Ni(acac)₂ catalyst (5 mol%) in THF at room temperature 1-ethyl-3-alkylaluminacyclopentanes **31** are converted into 2-alkylbuta-1,3-dienes **74** in 71–76% yield [94–96].



The interaction between cyclooctasulfane (S₈) or selenium (Se) and 3-alkyl-substituted aluminacyclopentanes **31** at a ratio of ~3:1 in benzene (80 °C, 6 h) were shown to afford 3-alkyltetrahydrothiophenes **75** or tetrahydroselenophenes **76** [97–100]. This approach allow to convert α -olefins via a one-pot procedure into *trans*-3,4-dialkyltetrahydrothiophenes with high selectivity in the yields of 65–80% through 1-ethyl-*trans*-3,4-dialkylaluminacyclopentanes **55** preliminary obtained [101,102]. Using the said method tri- and tetracyclic tetrahydrothiophenes have been synthesized from norbornenes [103–106]. The reaction of generated *in situ* substituted aluminacyclopentanes with alkyl(phenyl)dichlorophosphines has been recognized as a convenient rout to transform α -olefins into phospholanes **77** [107–109].

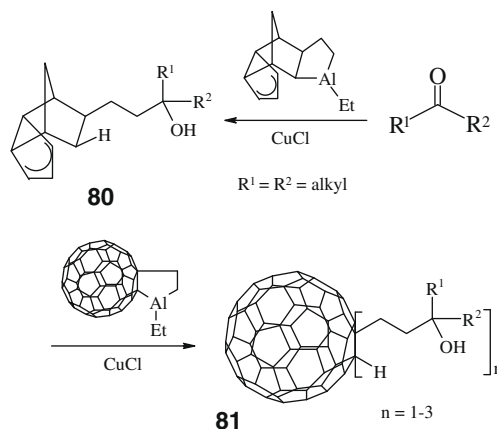


Among known, the method for the synthesis of cyclopentanols **78** and 1-hydroxycyclopentanecarboxylates **79**, which based on consecutive cycloaluminum of α -olefins with trialkylalanes in the presence of Cp₂ZrCl₂ catalyst via subsequent interaction between generated *in situ* aluminacyclopentanes and alkyl carboxylates in the presence of catalytic amounts of Cu, Ni, Pd salts or complexes is considered to be the most attractive [107,110–112].

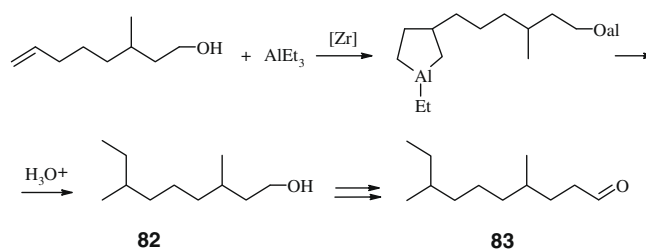


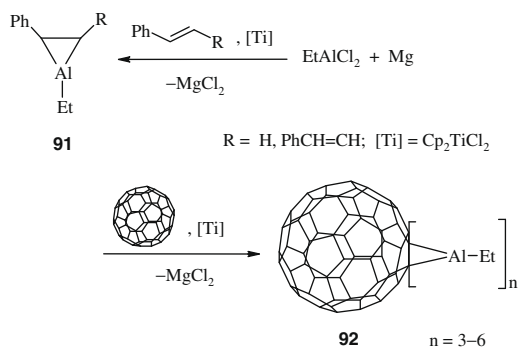
The elaborated method has been successfully applied to the synthesis of secondary and tertiary alcohols via the interaction between generated *in situ* 1-ethyl-3-alkylaluminacyclopentanes **31** at 20 °C and aldehydes or ketones in the presence of catalytic amounts of Cu salts.

Together with OAC **31** 1-ethyl-*trans*-3,4-dialkylaluminacyclopentanes **55**, polycyclic OACs **50** and **51**, 1-ethyl-2,3-fullero[60]aluminacyclopentanes **52** have been implicated in this reaction to synthesize different alcohols including carbocyclic **80** and fullerene-containing **81** ones [113].

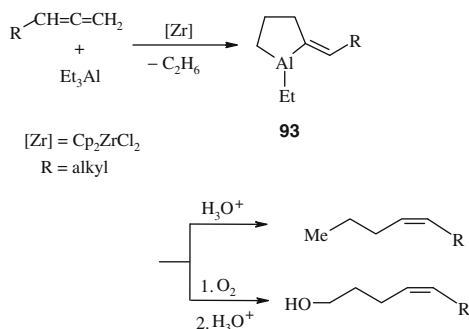


Catalyzed by Cp₂ZrCl₂ cycloaluminum of 3-methyloct-7-en-1-ol with Et₃Al followed by hydrolysis of generated *in situ* ACP gave rise to alcohol **82**, which can be used as a syntone in synthesis of flour beetles, *Tribolium confusum* and *Tribolium costaneum* **83** [114].



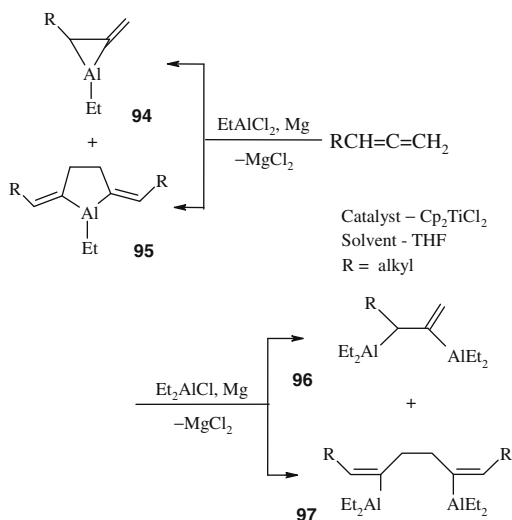


In 2001, 1,2-dienes together with 1,3-dienes have been successfully implicated in the cycloalumination reaction giving rise to the appropriate 2-alkylidenealuminacyclopentanes. As it was shown by the authors of the works [126,127], cycloalumination of 1,2-dienes with Et_3Al under the action of Cp_2ZrCl_2 (5 mol%, $\sim 20^\circ\text{C}$, 4 h) occurs in aliphatic (70–80%), aromatic (75–77%) solvents and also in methylene dichloride (92%) to yield 1-ethyl-2-alkylidenealuminacyclopentanes **93**. In ethereal solvents (THF) or without the solvent the reaction proceeded to afford the product in low yield (less than 20%). In these experiments, 1-ethyl-2-methylene-3-alkylaluminacyclopentanes were detected in minor quantities (3–15%). Chemical transformations of cyclic OAC **93** led to corresponding olefins and alcohols containing Z-disubstituted double bonds [128].

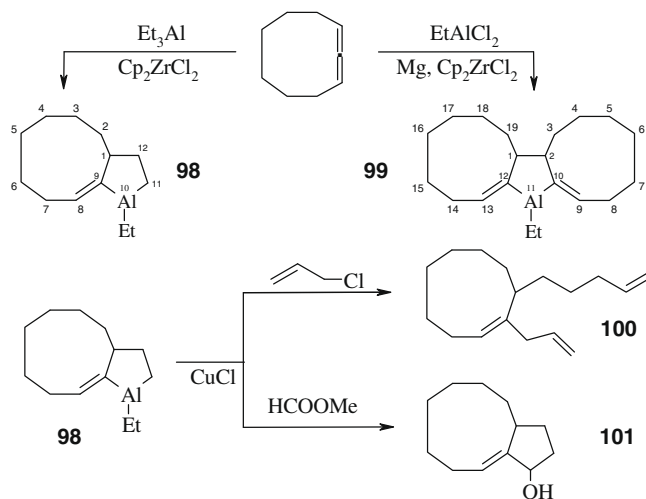


Cycloalumination of acyclic allenes with EtAlCl_2 in the presence of Cp_2TiCl_2 (5 mol%, $\sim 20^\circ\text{C}$) and metallic Mg (acceptor of halogenide ions) was found to provide 1-ethyl-2-methylene-3-alkylaluminacyclopentanes **94** and 1-ethyl-2,5-dialkylidenealuminacyclopentanes **95** in total 80% yield [129,130].

The replacement of EtAlCl_2 by Et_2AlCl allowed to synthesize the corresponding 1,2- **96** and 1,4-dialuminum **97** compounds [129].



D'yakonov and co-workers have succeeded in widening the scope of application of the cycloalumination reaction aforesaid. Thus, the interaction between cyclonona-1,2-diene and Et_3Al (excess) under chosen conditions (5 mol%, Cp_2ZrCl_2 , 4 h) was shown to afford 10-ethyl-10-aluminabicyclo[7.3.0.1,9]dodeca-8-ene **98** with high regioselectivity (>95%) in more than 85% yield [131,132]. Cycloalumination of cyclonona-1,2-diene occurred in aliphatic (hexane, cyclohexane), aromatic (benzol) solvents, and also in CH_2Cl_2 for 4–5 h. In ethereal solvents (THF, diethyl ether) or without the solvent the reaction proceeded in low yields as a result of polymerization of the starting allene.



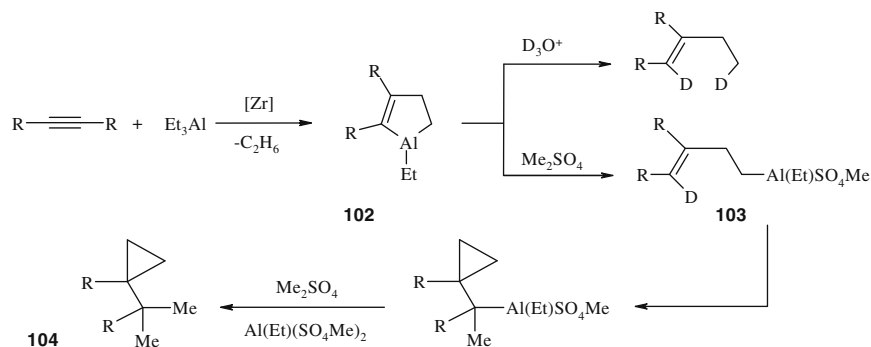
The reaction of OAC **98** with allyl chloride or methyl formate [132] in the presence of CuCl (10 mol%) allowed synthesizing olefin **100** or cyclopentanol **101** by one pot procedure. The intermolecular cycloalumination of cyclonona-1,2-diene with EtAlCl_2 in the presence of metallic Mg and Cp_2ZrCl_2 catalyst in THF gave rise to 11-ethyl-11-aluminatricyclo[10.7.0.1,12.0.2,10]nonadeca-9,12-diene **99**.

The aforesaid procedures to synthesize novel classes of cyclic organoaluminum compounds give evidence that catalytic cycloalumination reaction of unsaturated compounds is universal and allows to convert olefins and dienes into the three-, five-, and seven-membered OACs having very high reactivity.

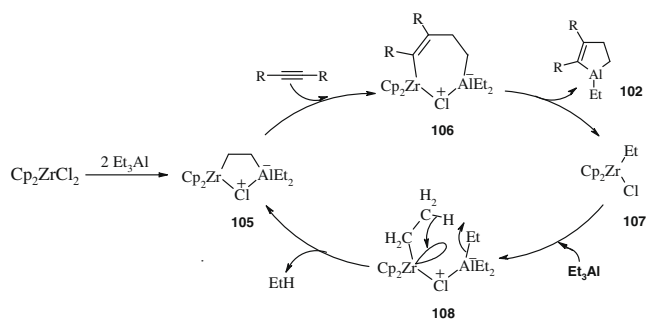
Such reaction has great synthetic potential and can be successfully used in organic and organometallic chemistry.

4. Catalytic cycloalumination of acetylenes

Developed by Dzhemilev in 1989, the catalytic cycloalumination reaction of olefins with Et_3Al affected by Zr catalysts [17] and its further elaboration allowed the authors of the present survey to synthesize in 1990 for the first time the new classes of unsaturated cyclic OACs – aluminacyclopentenes and aluminacyclopentadienes through cycloalumination of acetylenes [133]. The reaction of disubstituted acetylenes with Et_3Al in the presence of Cp_2ZrCl_2 at ambient temperature led to 1-ethyl-2,3-dialkyl(aryl)aluminacyclopent-2-enes **102** in 75–90% yield [134–136]. The structure of the latter was determined by means of ^{13}C NMR spectroscopy [137] and also by chemical transformations [138]. Thus, alkylation of aluminacyclopent-2-enes **102** with dimethyl or diethyl sulfate occurred at the double bond position in aluminacyclopentane cycle to provide homoallyl OAC **103**, which underwent intramolecular carboalumination yielding after additional alkylation 1,1-disubstituted cyclopropanes **104** [139,140].

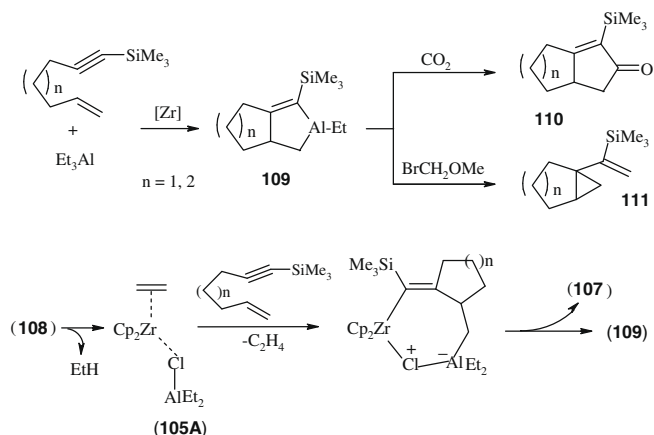


Later the mechanism of the reaction of disubstituted acetylenes with Et_3Al catalyzed by Cp_2ZrCl_2 has been investigated by Ei-ichi Negishi and co-workers [47]. According to the proposed scheme the reaction proceeds through the formation of bimetallic complex **105**. The latter carbometalates the molecule of disubstituted acetylene to give the intermediate **106**, which is transformed to the target product **102** and zirconocene dichloride **107**. Resultant EtZrCp_2Cl **107** in the presence of Et_3Al gives complex **108**, which is converted to bimetallic complex **105** as a result of β -hydrogen transfer and ethane molecule elimination.



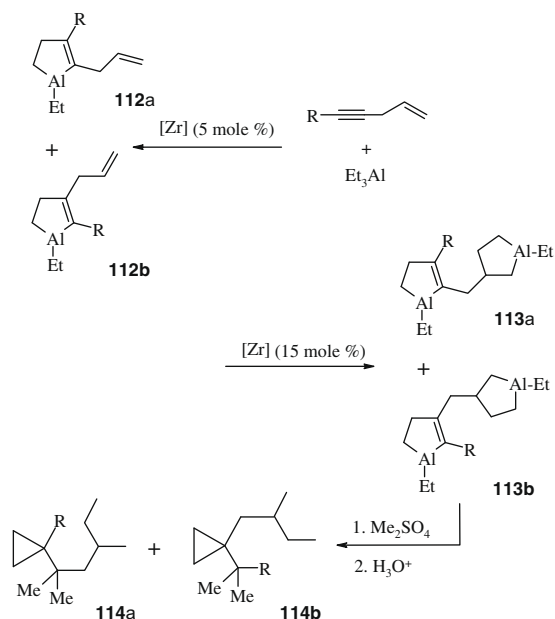
Mechanism proposed by Negishi et al. [47] explains the sequence of the main formation stages for aluminacyclopent-2-enes **102** from disubstituted acetylenes, but this mechanism in a less degree correlates with the experimental data obtained by the same authors during the investigations of the interaction between enynes and Et_3Al in the presence of Cp_2ZrCl_2 (Scheme below) [141]. In this case, the acetylenic and terminal double bonds should be incorporated into the reaction affording aluminacyclopentenes **109**. This fact assumes the formation of the intermediate ethylene-zirconocene complex of **105A** type [70,142–145]. It seems unlikely to obtain **109** through the bimetallic complex **105** with the bridge bond $\text{Zr}-\text{CH}_2\text{CH}_2-\text{Al}$. In our opinion, the primary formation of **105A** with attached Et_2AlCl molecule through the bridge bond $\text{Zr}\cdots\text{Cl}\cdots\text{Al}$, which can be easily transformed to the target bicyclic

aluminacyclopentenes **109**, is the most probable route to synthesize the latter from the complex **108**.

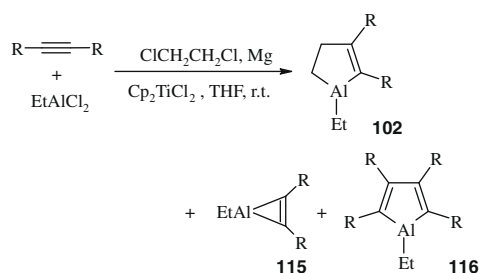


Aluminacyclopentenes **109**, obtained by the reaction of 1,6- or 1,7-enynes with Et_3Al in the presence of Cp_2ZrCl_2 , were found to interact with CO_2 (0 °C, 1 atm) or $\text{ClCH}_2\text{OCH}_3$ (23 °C) yielding bicyclic cyclopentanones **110** or vinylcyclopropanes **111** [141].

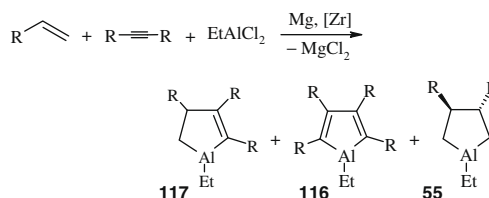
Cycloalumination of 1,4-enynes with Et_3Al under the action of Cp_2ZrCl_2 (5 mol%, ~20 °C, 8 h, hexane) led to regioisomeric mixture of 2,3-disubstituted aluminacyclopent-2-enes **112** with retention of the original double bond at the allylic position [135]. One could incorporate the latter into the cycloalumination reaction only under the interaction between 1,4-enynes and fourfold excess of Et_3Al in the presence of Cp_2ZrCl_2 catalyst (10–15 mol% towards the starting 1,4-enyne, r.t., 8 h). Regioisomeric (~1:1 ratio) (aluminacyclopent-3-ylmethyl)aluminacyclopent-2-enes **113** have been identified as 1,1-dialkylsubstituted cyclopropanes **114** through the transformation under the effect of Me_2SO_4 [146].



The new approach to a synthesis of 2,3-dialkyl(phenyl)aluminacyclopentenes by cycloalumination of disubstituted acetylenes with $EtAlCl_2$ in the presence of ethylene generated from 1,2-dichloroethane and activated Mg under the action of Cp_2TiCl_2 catalyst is considered in the work [147]. The reaction was found to proceed at ambient temperature in tetrahydrofuran. Together with aluminacyclopentenes **102**, the small amounts of aluminacycloprenes **115** and aluminacyclopentadienes **116** have been detected. The yields and ratios of the latter were shown to depend upon the nature of substituents in disubstituted acetylene.

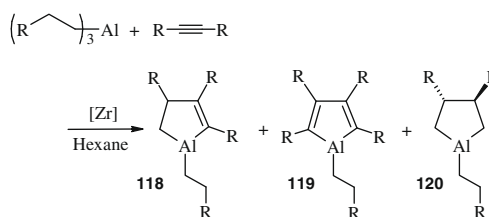


Based on the achievement data above, the authors of the work [148] have elaborated the methodology for the synthesis of tetrasubstituted aluminacyclopent-2-enes by combined cycloalumination of acetylenes and olefins. Thus, the combined cycloalumination reaction of disubstituted acetylene and α -olefin with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 catalyst and metallic Mg (THF, 20–22 °C, 8 h) was found to provide expected 1,2,3,4-tetraalkylaluminacyclopent-2-ene **117** as a major product together with minor amounts of 1,2,3,4,5-pentaalkylaluminacyclopenta-2,4-diene **116** and 1-ethyl-*trans*-3,4-dialkylaluminacyclopentane **55**. The combined product yield reached over 80%.

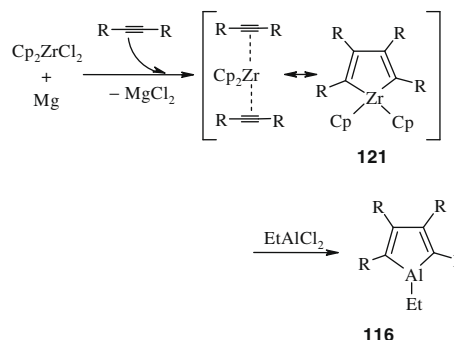


One can alter the course of the chemical reaction towards the predominant formation of aluminacyclopent-2-ene **117**, while slow adding (approximately 6 h) a mixture of α -olefin and $EtAlCl_2$ in THF to the toluene solution of Cp_2ZrCl_2 catalyst containing acetylene and metallic Mg.

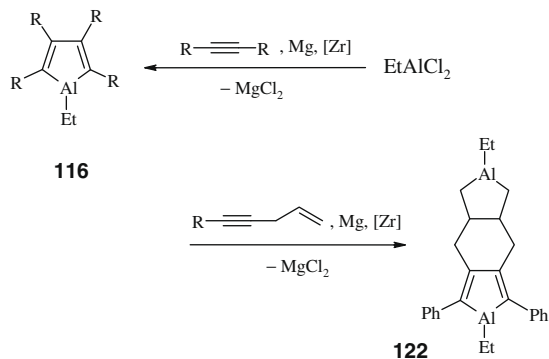
The same procedure as described above has been developed under cycloalumination of disubstituted acetylenes with higher trialkylalanes under the action of Cp_2ZrCl_2 catalyst [148]. As a result, 1,2,3,4-tetrasubstituted aluminacyclopent-2-enes **118** have been obtained in 50–55% yield. Together with **118** in the same experiments the minor amounts (10–15%) of 1,2,3,4,5-tetraalkylsubstituted aluminacyclopenta-2,4-dienes **119** and 1-alkyl-*trans*-3,4-dialkylsubstituted aluminacyclopentanes **120** have been detected in the reaction mixture.



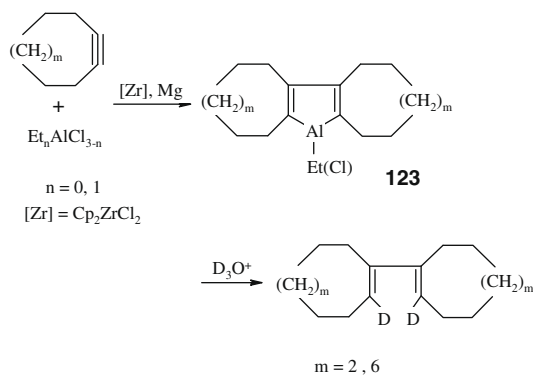
In 1992 the new procedure to synthesize aluminacyclopenta-2,4-dienes (**116**) based on the cycloalumination reaction of disubstituted acetylenes with $AlCl_3$ ($R = Et, BuO, Et_2N, Cl$) affected by Cp_2ZrCl_2 catalyst and widely used in cycloalumination of acetylenes with the aid of Et_3Al has been proposed [134,135,146,149,150]. The authors of the work [146] proceeded from the assumption that reduction of Cp_2ZrCl_2 with Mg in the presence of disubstituted acetylenes gives rise to zirconacyclopentadienes **121** [151], which then are transmetalated with $EtAlCl_2$ into aluminacyclopentadienes **116**.



It should be noted that intermolecular cycloaluminum of phenylcetylene with EtAlCl_2 in the presence of metallic Mg affected by Cp_2ZrCl_2 occurred under the chosen reaction conditions [146,152] with simultaneous incorporation of the double and triple bonds leading selectively to the tricyclic dialuminum compound **122**.

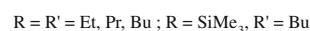
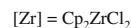
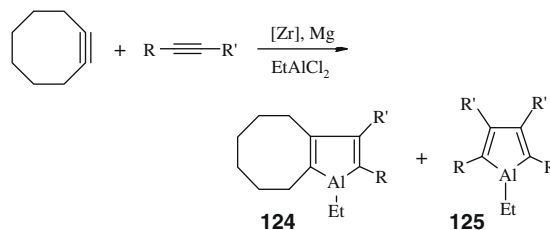


The authors of the work [153] have also succeeded in catalytic cycloaluminum of cyclic acetylenes. Thus, cycloaluminum of cyclooctyne and cyclododecyne with EtAlCl_2 or AlCl_3 in the presence of metallic Mg affected by Cp_2ZrCl_2 catalyst under reaction conditions (r.t., 6 h, THF) opens a convenient synthetic route towards the tricyclic aluminacyclopentadienes **123** in the yields of more than 70% according to the following Scheme:

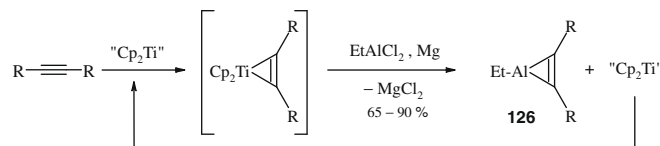


Based on the results above the combined cycloaluminum reaction of cycloalkynes and acyclic disubstituted acetylenes has been realized to obtain the new types of bicyclic aluminacyclopentadienes. Thus, the interaction between cyclooctyne and hex-3-yne with the aid of EtAlCl_2 in the presence of Cp_2ZrCl_2 catalyst and metallic Mg (20 °C, 6 h, THF) has been successfully performed giving rise to 9,10,11-triethyl-9-aluminabicyclo[2.6.0]undeca-1,10-diene **124** in more than 55% yield. Together with the target

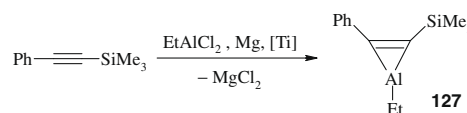
OAC **124** the small amounts (less than 10%) of pentaethylaluminacyclopenta-2,4-diene **125** have been observed as the initial hexyne cycloaluminum product [153].



Based on the achievement data of Vol'pin and co-workers [154–156], viz., the ability of low valence titanium complexes to form titanacycloprenes through the coordination of acetylenes, the authors of the works [157–159] in 1997 have succeeded in synthesizing of aluminacycloprenes **126** via catalytic cycloaluminum of disubstituted acetylenes with EtAlCl_2 . Together with target OAC **126**, the small amounts of substituted aluminacyclopentadienes and substituted benzenes have been obtained. The structure of aluminacycloprenes was determined by spectral methods [160,161].

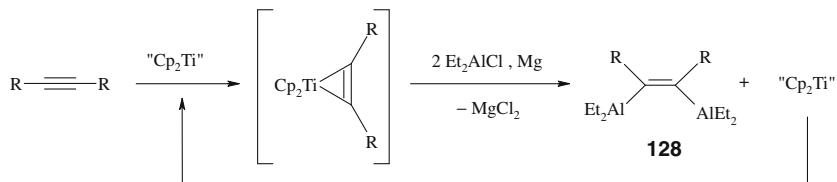


Cyclometalation of acetylenes with bulky substituents, for example, 1-phenyl-2-(trimethylsilyl)acetylene with EtAlCl_2 under reaction conditions [EtAlCl_2 :1-phenyl-2-(trimethylsilyl)acetylene:Mg: $\text{Cp}_2\text{TiCl}_2 = 200:100:100:5$, r.t., 8 h, THF] was shown to afford 1-ethyl-2-phenyl-3-(trimethylsilyl)aluminacyclopent-2-ene **127** in the yield of no more than 15%. However, with the increase in duration of the reaction to 72 h and usage of 10 mol% Cp_2TiCl_2 the yield of target **127** also increased to 55% [162].

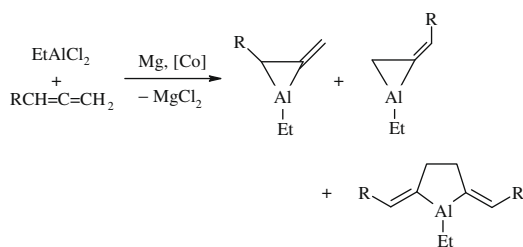


The replacement of EtAlCl_2 by Et_2AlCl_2 changed the direction of the catalytic cycloaluminum reaction giving rise to 1,2-dialuminum ethenes. Toluene entered the said reaction under chosen condi-

tions (Cp_2TiCl_2 , 10 mol%, r.t., 8 h, THF) more selectively to give 1,2-diphenyl-1,2-bis(diethylaluminio) ethene **128** in 70% total yield. In an analogous fashion, substituted 1,2-dialkyl acetylenes underwent cycloalumination to 1,2-dialuminoethenes but the yield in this reaction did not exceed [163–165].

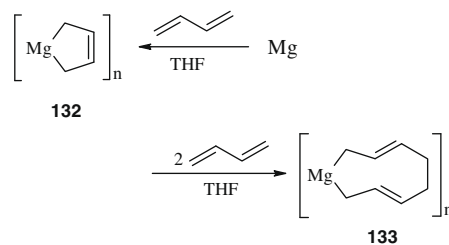


The authors of the work [166] first have announced that together with Ti- and Zr-containing complex catalysts, which were employed in catalytic cyclometalation of unsaturated compounds, Co phosphine complexes could provide appropriate cyclic OACs in the olefin, allene and also acetylene cycloalumination reactions with the aid of trialkyl and alkyl halogenalanes.



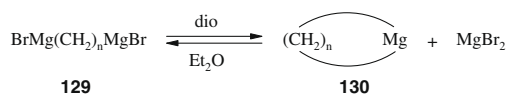
in these reactions was performed with the use of alkyl halogenides [173], anthracene [174], catalytic amounts of ZnCl_2 [175], Ni complexes [176], Fe and Cu halogenides [177] as well.

Buta-1,3-diene easily entered the reaction with magnesium activated by PhI or MeI at 20–40 °C giving rise to dienemagnesium reagents **132** and **133**, in which the size of the cycle was determined by the starting reagent ratio [178,179].

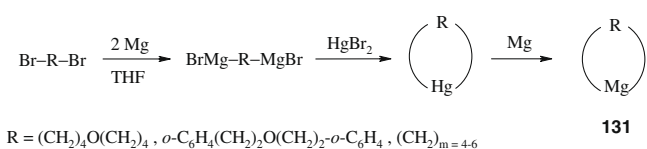


5. Thermal methods to synthesize magnesacarboxycles

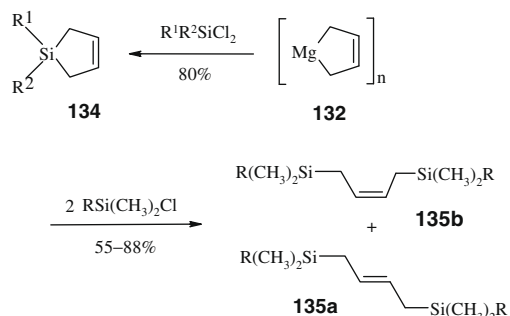
The synthetic method based on the shift change of Shlenk equilibrium between cyclic **130** and acyclic **129** organomagnesium compounds (OMCs), which resulted from the reaction of α,ω -dihalogenalkanes with metallic Mg in ethereal solvents, have been recognized to be the most available and simple one to obtain magnesacyclanes under conditions of organomagnesium synthesis [167,168].



The structure determination of cyclic OMCs obtained through the above described procedure has demanded in due time heavy and near work [169,170]. α,ω -Dimagnesium compounds were specifically converted into magnesacyclanes **131** with the aid of organomercury compounds [170–172].

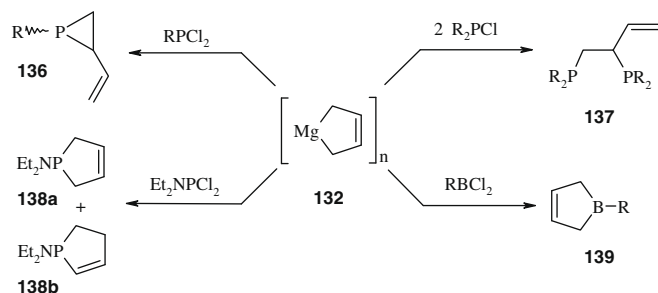


On the basis of cyclic OMCs prepared via the direct metalation of 1,3-dienes with activated magnesium, a number of effective procedures to synthesize organosilicon, organophosphorus and organoboron compounds have been elaborated [179]. Dialkylsilylcyclopentenes **134** and 1,4-bis(organodimethylsilyl)but-2-enes **135a,b** have been synthesized by Richter and coworkers from dialkylchlorosilane or alkylmonochlorosilane, respectively, using the butadiene-magnesium reagent **132** [180,181].

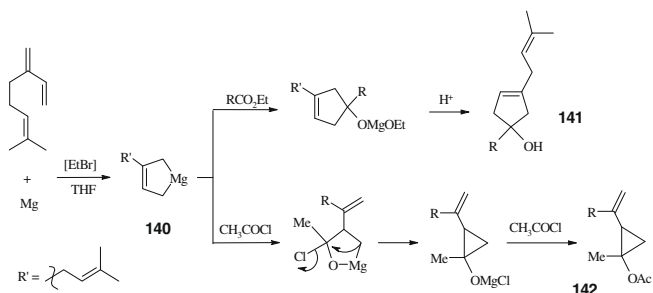


The interaction between the butadiene-magnesium reagent **132** and chlorophosphine were found to run as the 1,2-addition process (Scheme below) providing access to vinylphosphiranes **136** [182] and α -vinyl-P,P'-bis(diorganophosphinyl)ethylene **137** [183].

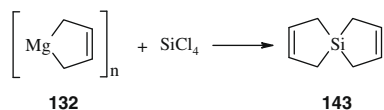
Under similar conditions dichloroethylaminophosphines gave rise to the mixture of 1-(diethylamino)-3-phospholene **138a** and 1-(diethylamino)-2-phospholene **138b** at a ratio of 9:1 [182]. In all experiments with RBCl_2 the appropriate boracyclopentanes **139** have been successfully obtained [184].



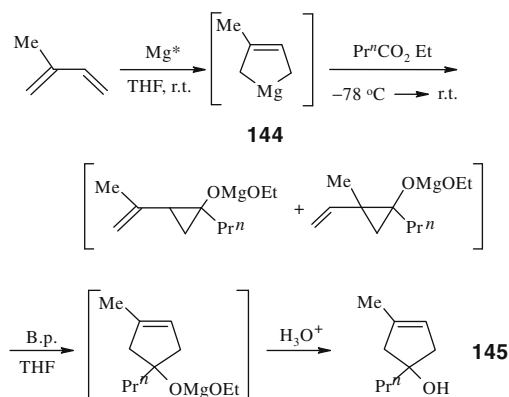
The isoprene-magnesium [185,186] and myrcene-magnesium reagents **140** [187] derived from isoprene and myrcene rather actively entered the reaction with esters or acetyl chloride to afford the corresponding functionally substituted carbocycles **141** and **142** as shown on the Scheme below.



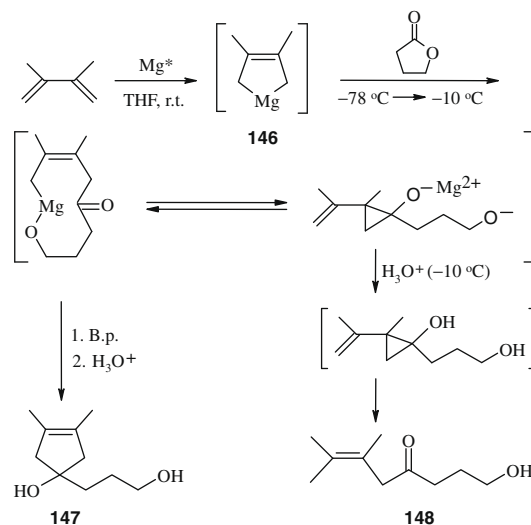
Introduction to synthetic practice in 1972 of highly active Mg^* (Rieke magnesium) [188] allowed direct metalation of buta-1,3-diene without preliminary chemical activation of magnesium. Buta-1,3-diene reacts with Mg^* at room temperature to give the butadiene-magnesium reagent $(\text{MgC}_4\text{H}_6)_n$ **132**, which vigorously react with SiCl_4 yielding 5-silaspiro-4,4'-nona-1,7-dien **143** [189].



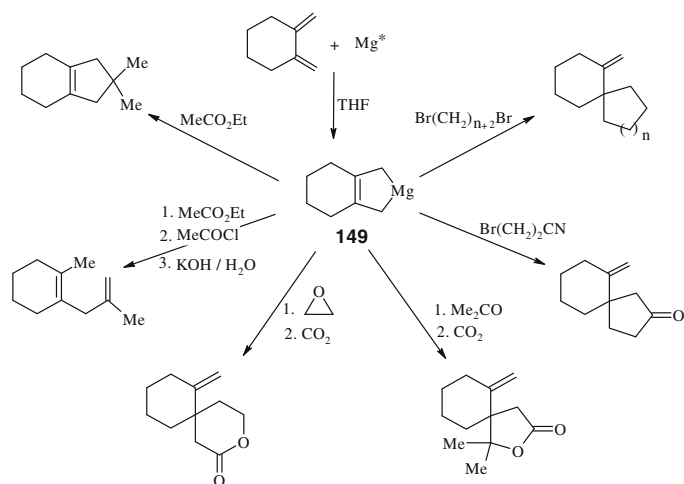
The interaction between isoprene and Mg^* was found to proceed at room temperature to form the isoprene-magnesium reagent **144**, transformations of which provide a convenient mode for the production of cyclopentenols **145** [190].



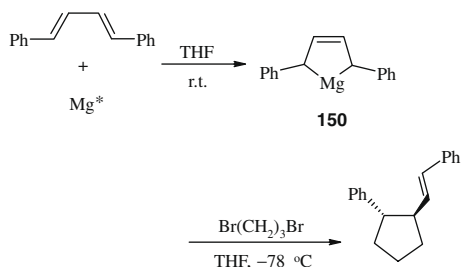
The involvement of 2,3-dimethylbuta-1,3-diene in the reaction with Rieke magnesium resulted in generating 2,3-dimethylmagnesyacyclopent-3-ene **146** as an intermediate. The subsequent reaction of the latter with butyrolactone, depending upon the reaction conditions, led to cyclopent-3-enol **147** or β,γ -unsaturated ketone **148** [190] according the following Scheme:



The aforesaid approach to the synthesis of cyclic OMCs through the direct metalation of 2,3-dialkylsubstituted 1,3-dienes with the aid of highly active Mg^* has been successfully extended to a synthesis of 1,2-dimethylenecycloalkanes **149** in one preparative stage. The latter have been widely employed by investigators in the synthesis of bicyclic alcohols, ketones [191], spiro- $\delta(\gamma)$ -lactones [192,193], and spirocarbocycles [194,195] as well.

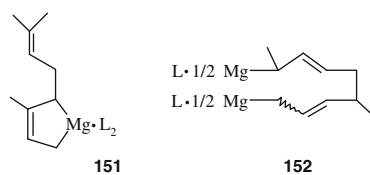


Similar to 2-substituted 1,3-dienes, in a tetrahydrofuran solution 1,4-diphenylbuta-1,3-diene in the presence of highly active Mg^* was transformed into 2,5-diphenylmagnasacyclopentene **150**, the reaction of which with α,ω -dihalogen alkanes opens the convenient route for the synthesis of the five-membered carbocycles [196].



The predominant dimeric myrcene–magnesium complex [197] was generated from myrcene and highly active Mg^* , while in the case of chemically activated Mg one could observe monomeric and in small amounts dimeric myrcene–magnesium reagents [187].

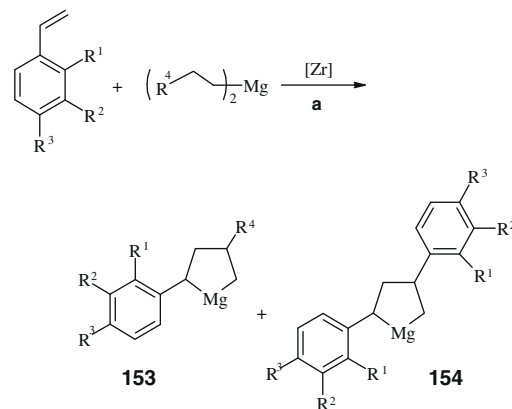
Nerole and linalol have been obtained as a 1:1 mixture from ocymene and highly active magnesium* after oxidation to give evidence for the formation of the monomeric ocymene–magnesium complex **151** under direct metalation conditions. Apparently, the generation of the head-to-tail dimeric piperilene–magnesium complex **152** took place in the case of the reaction with piperilene [197].



High reactivity of cyclic organomagnesium reagents generated *in situ* by direct metalation of 1,3-dienes assisted by chemically activated or highly active magnesium* makes them promising for the use in synthetic organic and organometallic chemistry. Unfortunately, this method has certain limitations as applicable only to conjugated diene.

6. Cyclomagnesiation of olefins and 1,2-dienes affected by Zr and Ti catalysts

The first report on catalytic cyclomagnesiation of olefins with $RMgX$ or R_2Mg to the corresponding magnasacyclopentanes has appeared in 1989. The authors of the work [198] have shown that the reaction of styrene with R_2Mg under the effect of Cp_2ZrCl_2 catalyst led under mild conditions (20 °C, Et_2O/THF) to a 1:3 mixture of magnasacyclopentanes **153** and **154** in a total 80% yield [199]. Similar mixture of magnasacyclopentanes has been obtained as a result of catalytic cyclomagnesiation of *o*-, *m*-, *p*-methyl or *m*-*tert*-butyl styrenes [200,201].



a: solvent – $Et_2O : THF$ (1:1), 20 °C, 7 h

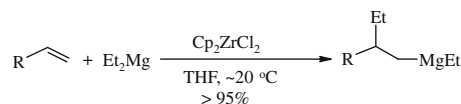
$R^1 = R^2 = R^3 = H$;

$R^1 = Me, R^2 = R^3 = H$; $R^2 = Me, R^1 = R^3 = H$; $R^3 = Me, R^1 = R^2 = H$;

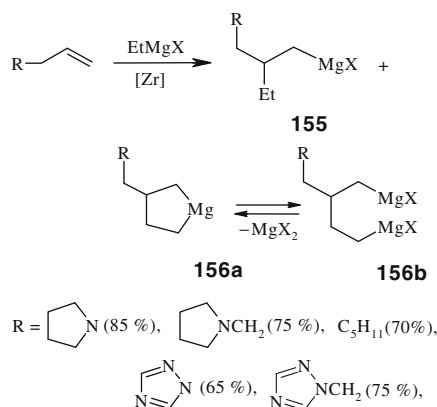
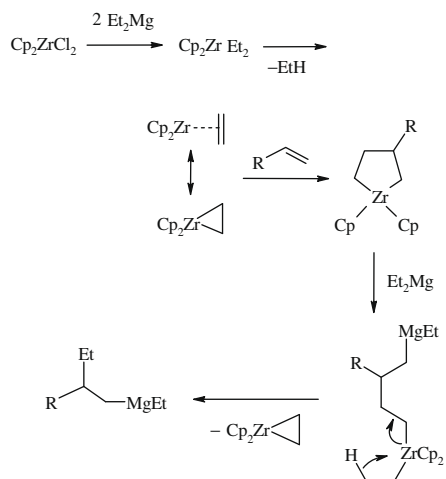
$R^3 = Bu^t, R^1 = R^2 = H$; $R^4 = Me, Et$

It should be noted that before discovery in 1989 of the above catalytic cyclomagnesiation reaction the authors of the present survey have succeeded in studying 1,2-carbomagnesiation of α -olefins containing non-activated double bond assisted by $RMgX$ or R_2Mg [202,203].

The reaction described above is common in nature. It has been efficiently applied to catalytic cyclomagnesiation of various unsaturated compounds including those containing functional substituents and nowadays is used in scientific practice as *Dzhemilev reaction* [204].



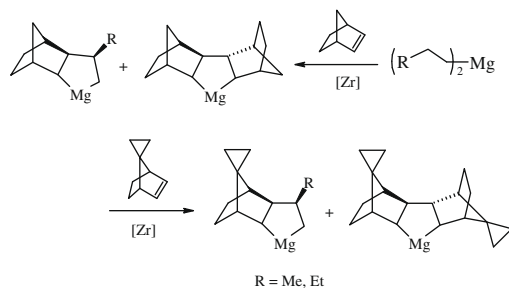
The authors believe this reaction proceeds via the following probable intermediate complex mechanism [205].



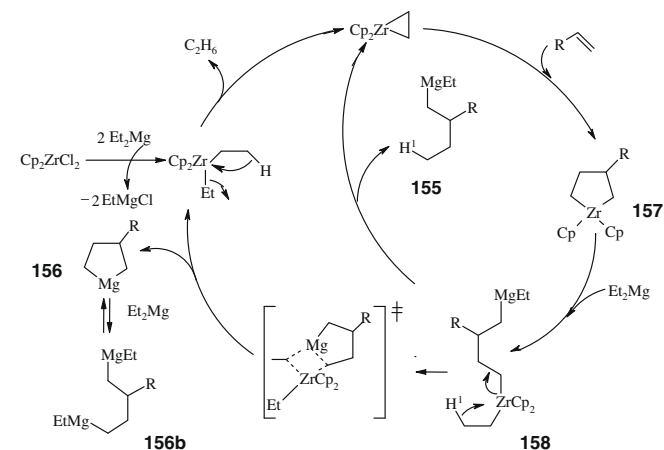
R = N (85 %), NCH₂ (75 %), C₅H₁₁ (70%),
 N (65 %), NCH₂ (75 %),
 PhCH₂O (54 %), PhCH₂OCH₂ (56 %), PhCH₂O(CH₂)₂ (65 %),
 Me₂BuSiO(CH₂)₂ (70 %), PhS (80 %) Me₃Si (63 %); 16 h

The important distinction of olefin catalytic cyclomagnesiation is the necessity of the specified reaction conditions, *viz.*, the use of diethyl ether or in Et₂O–THF mixture (1:1) as a solvent, low reaction temperature from 0 to 20 °C, and also the presence of catalytic amounts of Cp₂ZrCl₂ (3–10 mol%).

Unlike styrene, cyclomagnesiation of norbornenes such as bicyclo[2.2.1]hept-2-ene and spiro[bicyclo[2.2.1]hept-2-ene-7,1'-cyclopropane] with PrⁿMg or BuⁿMg under the action of catalytic amounts of Cp₂ZrCl₂ (3 mol%) in Et₂O/THF solution (22 °C, 8 h) led to diastereomeric pure tri-, tetra-, penta-, and heptacyclic OMCs, *viz.*, *exo,exo*-5-alkyl-3-magnesatrimethylcyclo[5.2.1.0^{2,6}]decane, *exo,exo*-5-alkyl-3-magnesaspiro[tri-cyclo[5.2.1.0^{2,6}]decane-10,1'-cyclopropane], *exo,exo*-9-magnesapenta-cyclo[9.2.1.1^{4,7,0}2,10,0^{3,8}]pentadecane, and *exo,exo*-9-magnesaspiro[pentacyclo[9.2.1.1^{4,7,0}2,10,0^{3,8}]pentadecane-14,1'(15,1')-dicyclopropane] in 80–95% yield [206].

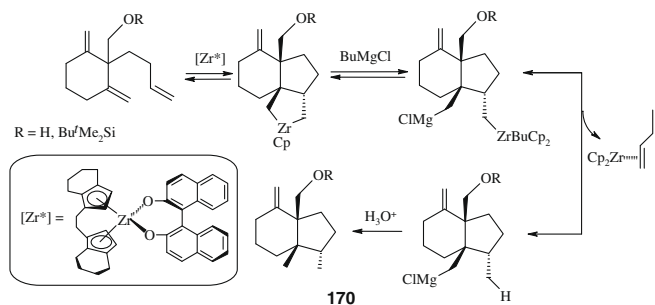


In contradistinction to R₂Mg (R = Pr, Bu, Hex, octyl), the organomagnesium reagents EtMgX and Et₂Mg were found to react with α-olefins in the presence of catalytic amounts of Cp₂ZrCl₂ to yield the ethylmagnesiation or cyclomagnesiation products according to the reaction conditions. In this case, one can regulate the direction of the reaction by controlling the solvent nature, reaction temperature and the ratio of initial reagents. Thus, the interaction between EtMgX and RCH₂CH=CH₂ (2:1 ratio) was shown to afford the ethylmagnesiation products **155** and **156** (95:5 ratio) at ambient temperature in THF. If the reaction was carried out at a ratio Mg:olefin equal to 4:1 in diethyl ether at 0 °C using Et₂Mg instead of EtMgX, magnesacyclopentanes (and/or 1,4-dimagnesium compounds) were predominantly (~85%) obtained [205].

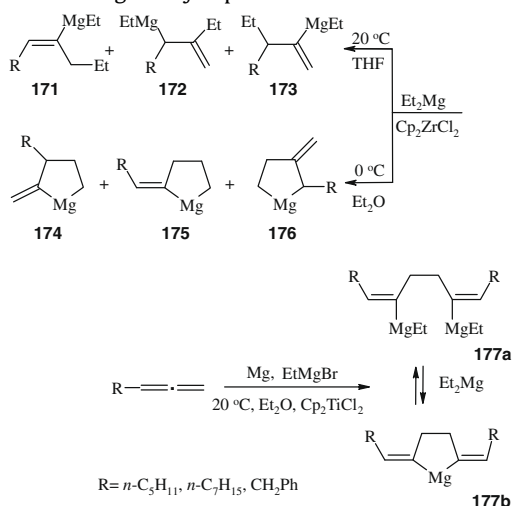


Mechanism of the catalyzed by Cp₂ZrCl₂ ethylmagnesiation and cyclomagnesiation reaction of olefins with nonactivated double bond has been discussed by several authors at one time [199,205,208–210].

Cyclomagnesiation of α-olefins (oct-1-ene, allyl benzene, styrene, *endo*-dicyclopentadiene) with EtMgR (R = Br, Et) affected by Ti-containing catalysts has been reported for the first time in the work [211]. The interaction between EtMgBr or Et₂Mg and

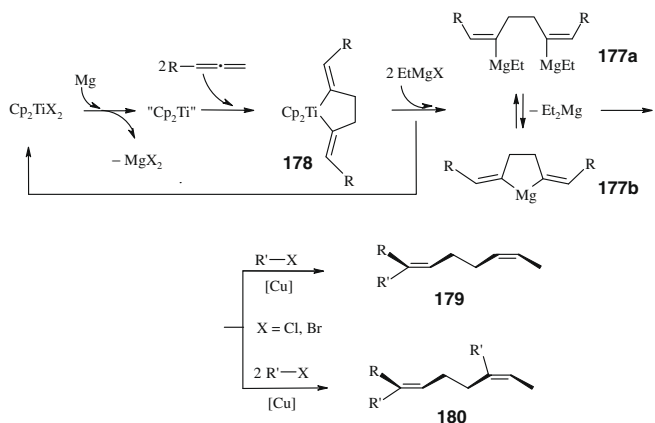


The authors of the work [230] for the first time have succeeded in involving 1,2-dienes into the cyclomagnesian reaction. This reaction led to the carbomagnesian products **171–173** in THF in the presence of Cp_2ZrCl_2 catalyst at ambient temperature. The decrease in temperature to 0°C and Et_2O media favored the formation of magnesacyclopentanes **174–176**.



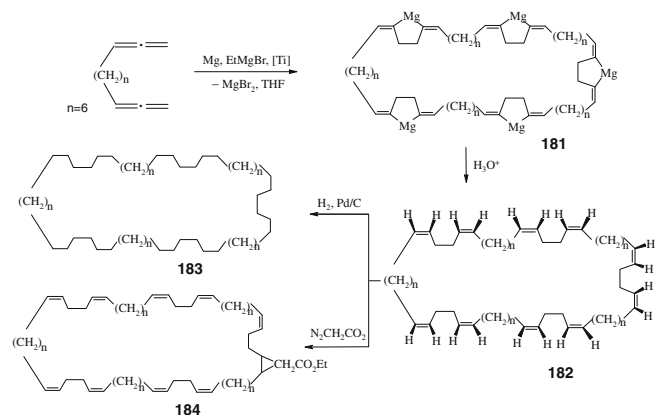
Cyclomagnesian of 1,2-dienes assisted by the two-fold excess of EtMgBr in the presence of chemically activated Mg and catalytic amounts (5 mol%) of Cp_2TiCl_2 under reaction conditions (THF, r.t., 8 h) resulted in 2,5-dialkylidenemagnesacyclopentanes and 1,4-dimagnesium compounds in the **177a:177b** ratio equal to $\sim 1:1$ according to ^{13}C NMR spectral data [230].

Apparently, reduction of Cp_2TiCl_2 to “ Cp_2Ti ”, generation of intermediate 2,5-dialkylidenetitanacyclopentanes **178** and subsequent transmetalation of the latter with EtMgX to target products **177** appeared to be the most probable intermediate steps, which could explain the formation of unsaturated OMC **177a** and **177b**. The studies by the authors [231,232] have shown the possibility of the one pot conversion of **177** to *Z*-diolefins **179** and **180** with the aid of organic halogenides under the action of cuprous salts.



The reaction above was used by the authors for the design of carbo- and macrometallacycles. For example, the synthesis of Mg -containing macrocycle **181** with alternating *cis*-double bonds has been realized from 1,2,10,11-dodecatetraene and EtMgBr in the presence of chemically activated Mg and Cp_2TiCl_2 catalyst (10 mol%) under mild conditions (r.t., THF, 12 h) in high yield (more than 90%) [233].

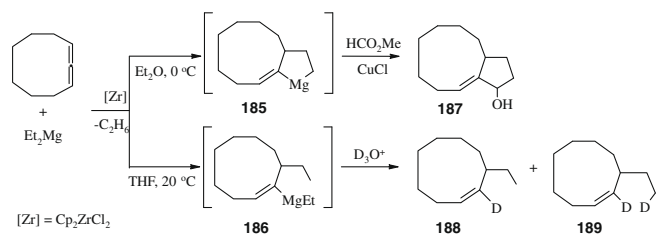
Hydrolysis of the resultant **181** led to unsaturated macrocycle **182** with *Z*-double bonds [234]. Hydrogenation or cyclopropanation of the latter allowed to synthesize the corresponding macrocycles **183** and **184** from α,ω -diallenes through a one pot procedure. As shown, other aliphatic α,ω -diallenes similarly reacted with EtMgBr under above conditions to afford metallacarbo-cycles.



In continuation of these prospective investigations, the authors of the work [235] for the first time have realized catalytic cyclo- and ethylmagnesian of cyclonona-1,2-diene with EtMgR ($\text{R} = \text{Et}, \text{Hlg}$) in the presence of Cp_2ZrCl_2 catalyst (5 mol%) in THF or Et_2O to afford 10-magnesabicyclo[7.3.0.1,9]dodec-8-ene **185** or 3-ethylcyclonon-1-en-2-yl magnesium ethyl **186** depending upon the experimental conditions.

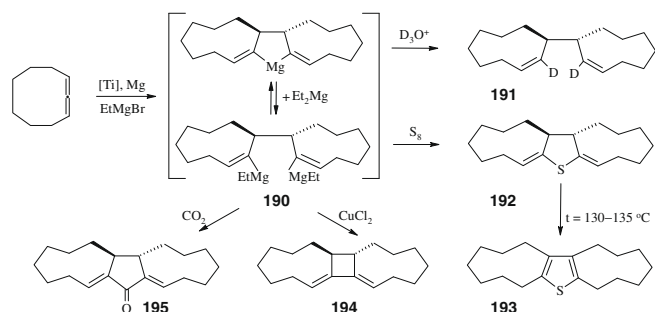
The interaction between Et_2Mg and cyclonona-1,2-diene in the presence of 5 mol% Cp_2ZrCl_2 in diethyl ether at 0°C was found to produce OMC **185** and **186** (91:9 ratio) in 79% combined yield. The action of methyl formate on magnesabicyclane **185** in the presence of CuCl catalyst (10 mol%) gave rise to 10-hydroxybicyclo[7.3.0^{1,9}]dodec-8-ene **187** in 67% yield.

The reaction of EtMgBr with cyclonona-1,2-diene in THF at ambient temperature resulted in the predominant formation of the carbomagnesian product **186**. In this case, deuterolysis of the reaction mixture led to mono- (**188**) and dideuterized **189** hydrocarbons (95:5 ratio) in 56% combined yield.

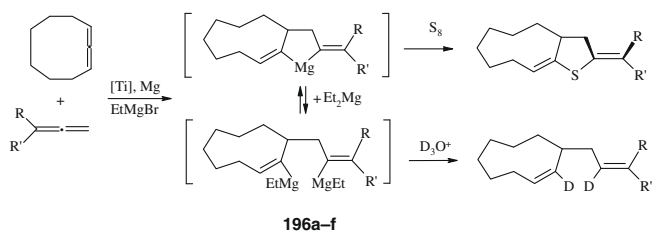


The same authors of the work [236] have established that cyclonona-1,2-dienes easily entered the reaction with EtMgBr in the presence of metallic Mg (acceptor of halogenide ions) and 5 mol% Cp_2TiCl_2 catalyst (Et_2O , 4 h, r.t.) to obtain 11-magnesatricy-

clo[10.7.0^{1,12}.0^{2,11}]nonatrideca-3(4),19-diene (and/or 1,4-dimagnesium compound) **190**. Deuterolysis of the latter led to 2-deutero-3-(2-deutero-2-cyclononyl)-1-cyclononene **191** in 85% yields. The OMC **190** also reacts with elemental sulfur S₈ to provide thiophane (**192**), which isomerizes to thiophene **193**. When dry CO₂ was bubbled through the reaction mixture containing OMC **190**, the latter then transformed to unsaturated tricyclic ketone **195** in 75% yield. The CuCl catalyst initiated intramolecular cyclization of **190** to produce (10*R*,11*S*)-tricyclo[9.7.0^{1,11}.0^{2,10}]octadeca-2(3),18-diene **194** in 68% yield.



The newly developed reaction [235] allowed to involve cyclic and acyclic 1,2-dienes in the combined intermolecular cyclomagnesianation with Grignard reagents and Cp₂TiCl₂ catalyst to obtain new types of bicyclic alkylidenemagnesacyclopentanes (and/or 1,4-dimagnesium compounds). Intermolecular cyclomagnesianation of cyclonona-1,2-diene and hepta-1,2-diene with EtMgBr (excess) in the presence of chemically active Mg and Cp₂TiCl₂ catalyst was shown to afford 11-pentalidene-12-magnesabicyclo[7.3.0]dodec-2(3)-ene **196** under reaction conditions (Et₂O, 4 h, 20 °C) in 88% yield.



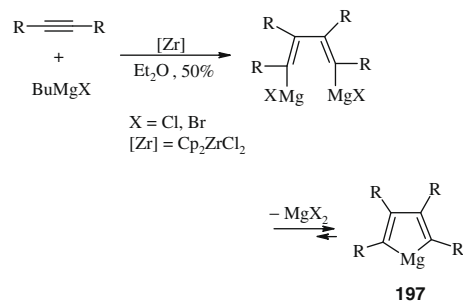
[Ti] = Cp₂TiCl₂; a: R = *n*-Bu, R' = H; b: R = *n*-Hex, R' = H; c: R = Ph, R' = H; d: R = Bn, R' = H; e: R = *n*-Pent, R' = Me; f: R = Ph, R' = Me.

The formation of minor cyclonona-1,2-diene and hepta-1,2-diene homocyclomagnesianation products (~1:1 ratio) has also been observed in the yields of no more than 8–10%.

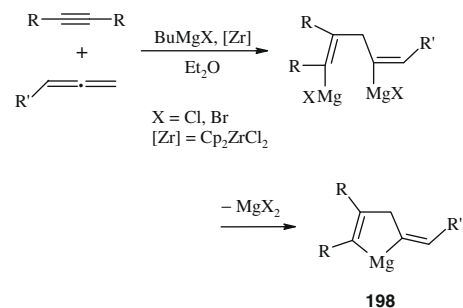
7. Catalytic cyclomagnesianation of acetylenes

The information concerned the catalytic cyclomagnesianation reactions of acetylenes [237] in comparison with the hydro- and carbomagnesianation ones has not been described in scientific literature up to nowadays.

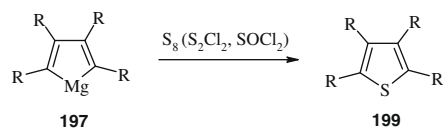
As shown in the 2006–2007, disubstituted acetylenes react with BuMgBr in Et₂O in the presence of Cp₂ZrCl₂ catalyst (10 mol%) under mild conditions (r.t., 2 h) giving rise to tetrasubstituted magnesacyclopentadienes **197** in 50% yield [238,239]. The replacement of BuMgBr by BuMgCl did not noticeably change the yield of the target magnesacyclopentadiene. The yield of **197** did not exceed 15% while using THF as a solvent.



The synthesis of 2,3-dialkyl-5-alkylidenemagnesacyclopent-2-enes **198** has been performed via intermolecular cyclomagnesianation of disubstituted acetylene and allene in equimolar amounts with BuMgX (X = Cl, Br) affected by Cp₂ZrCl₂ in Et₂O under optimized reaction conditions [231,240]. In these experiments together with target magnesacyclopentenes **198** the corresponding magnesacyclopentadienes **197** were shown to obtain as a minor product (<15%).



The reaction of generated *in situ* magnesacyclopentadienes **189** with elemental sulfur (S₂Cl₂, thionyl chloride) under mild conditions led to tetrasubstituted thiophenes **199** [241].



High reactivity of the Mg–C bonds demonstrated by magnesacyclopentenes and magnesacyclopentadienes makes this class of metallocarbycles extremely promising for a synthesis of wide assortment of organic and organometallic compounds.

8. Conclusion

The literature data summarized in the present survey evidence that the most significant breakthrough in the field of organoaluminum and organomagnesium synthesis for the last 15–20 years associates with the discovery of the catalytic cycloalumination and cyclomagnesianation of olefins, dienes and acetylenes with the aid of alkyl and halogen alkyl Al and Mg derivatives and Ti- and Zr-containing catalysts. Available from organic reagents cyclic Al and Mg metallacycles without preliminary isolation can be *in situ* transformed to substituted cyclopropanes, cyclobutanes, thiophanes, phospholanes, cyclopentanol and its esters, butane-1,4-

diols, 1,3-diene hydrocarbons including those of isoprenoid structure, functionally substituted carbon clusters, gigantic metalla- and carbocycles as well.

Nowadays these investigations are under active development. In the nearest future one can expect further progress in several promising directions, in synthesis of major classes of natural compounds such as isoprenoids, prostaglandins, vitamins, medicines and many valuable products through the intermediate Al- and Mg-containing metallocycles.

Undoubtedly, the catalytic cyclometalation reaction of unsaturated compounds discovered by the authors of the present survey will be further developed and will provide a platform for designing the most advanced chemical technologies.

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