

A novel reaction of cycloalumination of olefins and acetylenes mediated by metallocomplex catalysts

U. M. Dzhemilev* and A. G. Ibragimov

Institute of Oil Chemistry and Catalysis, Academy of Sciences of the Bashkortostan Republic,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750

Results obtained in the discovered by the authors catalytic cycloalumination reaction of unsaturated compounds in the presence of complex Ti- and Zr-containing catalysts are generalized. Cycloalumination of olefins and acetylenes proceeds under the action of Ti and Zr complexes in one stage to give novel classes of organoaluminum compounds (OAC): alumacyclopentanes, alumacyclopropanes, alumacyclopropenes, 1,4-dialumabutanes, and 1,2-dialumaethylenes. Based on these cyclic and acyclic OAC, essentially new preparative synthetic methods were elaborated. Novel reactions (β -ethylation, β -vinylation, reductive β -ethylation, and reductive β -vinylation) allow transforming olefins and acetylenes into five-membered heterocycles, cyclopropanes, cyclobutanes, conjugated 1,3-dienes, primary alkyl iodides, 3-substituted alk-1-enes, and *threo*-2,3-disubstituted butane-1,4-diols under mild conditions in high yields. The mechanisms of the presented reactions are discussed.

Key words: organoaluminum compounds, alumacyclopentane, alumacyclopentene, alumacyclopentadienes, alumacyclopropane, alumacyclopropene; cycloalumination, metallocomplex catalysts, titanium and zirconium complexes; olefins; β -ethylation, β -vinylation; pheromones; *E*-isoprenoids; five-membered heterocycles.

In 1954, Ziegler and coworkers discovered the reaction of olefins with aluminum metal and hydrogen,¹ which results in trialkyl alanes. This reaction as well as a method for thermal hydroalumination of unsaturated compounds with aluminum hydrides (alanes)² or AlBu_3 (see Ref. 3), which was developed later, marked the beginning of work on the synthesis of a large number of organoaluminum compounds (OAC) simple enough in structure.

Application of metallocomplex catalysts allowed one not only to change fundamentally the strategy of organoaluminum synthesis but also develop chemo-, regio-, and stereoselective methods for preparation of novel classes of OAC under mild conditions, unlike traditional methods requiring higher pressure and temperature. Among the most effective and widely used catalysts designed for carrying out these reactions are Ti and Zr complexes and, to a lesser degree, compounds of Hf, Cu, Ni, Pd, and rare-earth elements.

Earlier,^{4,5} we already systematized literature data concerning application of metallocomplex catalysts based on Ti and Zr compounds in synthesis and transformations of OAC, but they were published more than 8 years ago, and a large number of new studies dealing with unconventional catalytic methods of synthesis of OAC have appeared since then. Data published in this period have not been generalized up to now. In the present review, we consider results of studies on cycloalumination of alkenes and alkynes, which were

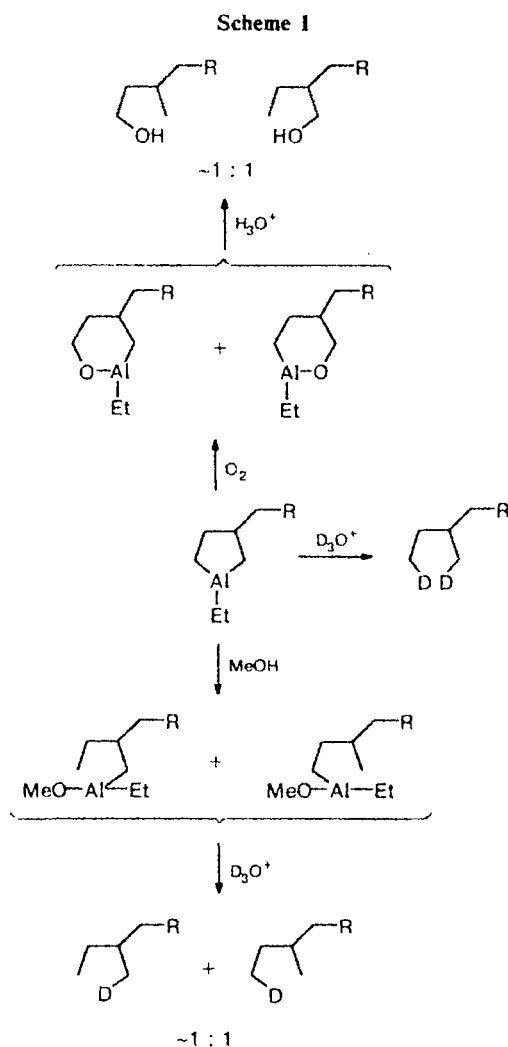
obtained in recent years and laid the foundation for a new line of synthesis of OAC.

Cycloalumination of olefins catalyzed by Ti and Zr complexes

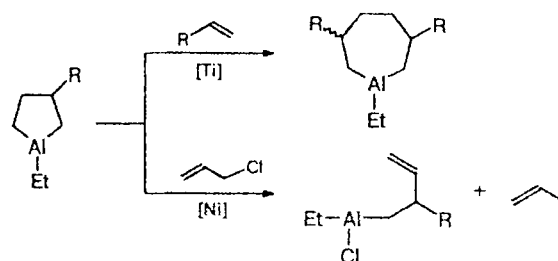
In recent years, application of methods of metallocomplex catalysis to the chemistry of OAC allowed one to significantly extend the range of preparative methods, new reactions, and specific reagents used in organic and organometallic synthesis, which are of constantly increasing interest for organic chemists. Hydro-⁶⁻¹⁶ and carb-¹⁷⁻²⁶alumination of unsaturated compounds, catalyzed by transition metal complexes, remained the basic approaches to the synthesis of not easily available acyclic OAC almost until late 1980s. In 1989, we published our first report²⁷ concerning the synthesis of previously unknown cyclic five-membered OAC by cycloalumination of α -olefins in the presence of catalytic amounts of Cp_2ZrCl_2 . This report marked the beginning of the synthesis of cyclic OAC, a new line in organoaluminum synthesis, and was developed in further publications.²⁸⁻³⁰ The key stage of the cycloalumination reaction discovered by us is catalytic generation of zirconacyclopentane intermediates, whose stoichiometric synthesis and transformations were discussed in a series of publications.³¹⁻³⁵

The method makes it possible to synthesize alumacyclopentanes with alkyl, alkenyl, and aryl substituents as well as with N-, O-, and S-containing ones exclu-

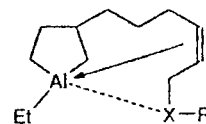
sively in the β -position relative to the Al atom.^{27,36} It was shown experimentally (by incomplete oxidation and alcoholysis) that the Al—C bonds in the five-membered ring are of about equal reactivity but are more active than the Al—Et bond³⁶ (Scheme 1).



Further intense investigations were carried out in our laboratory with the aim of extending applications of the discovered reaction of catalytic cycloalumination. They allowed us to elaborate unconventional methods for the synthesis of macrocyclic and acyclic OAC of various structures. For example, the cycloalumination of α -olefins with triethylaluminum, catalyzed by Cp_2ZrCl_2 and resulting in 3-substituted alumacyclopentanes with subsequent introduction of another olefin molecule at the active Al—C bond of the metal-containing cycle under the action of Ti-containing catalysts, appeared to be a quite simple and effective method for the synthesis of substituted alumacycloheptanes,³⁷ while the presence of Ni-containing catalysts favors the formation of the corresponding unsaturated OAC (Scheme 2).

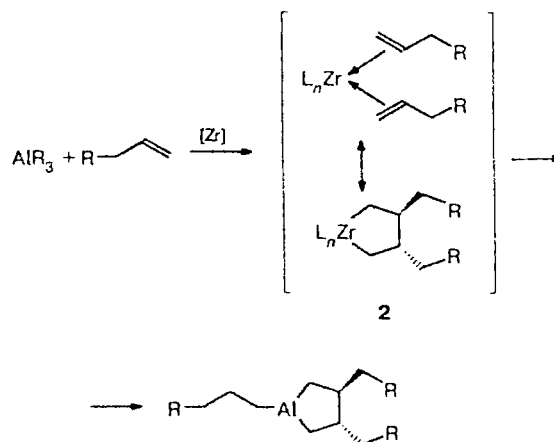
Scheme 2

Along with α -olefins, norbornene compounds were also involved in the cycloalumination catalyzed by Cp_2ZrCl_2 .³⁸ This reaction results in tri- and tetracyclic OAC, cyclometallation occurring at the *exo*-position. In the case of norbornadiene, both double bonds are involved in the interaction with Et_3Al , which leads to polycyclic OAC constructed only from carbon and organometallic rings.³⁸ The positions of the substituents and the configurations of the metal-containing cycles synthesized were determined by ^{13}C NMR spectroscopy (see Refs. 38—43). In addition, it was demonstrated that heteroatomic substituents in the molecules of the initial olefins owing to an unshared electron pair at the O, N, or S atoms form intramolecular donor-acceptor bonds with the Al atom to give type **1** complexes. It cannot be excluded that the allyl double bond is also involved in the formation of the coordination sphere of aluminum.³⁹

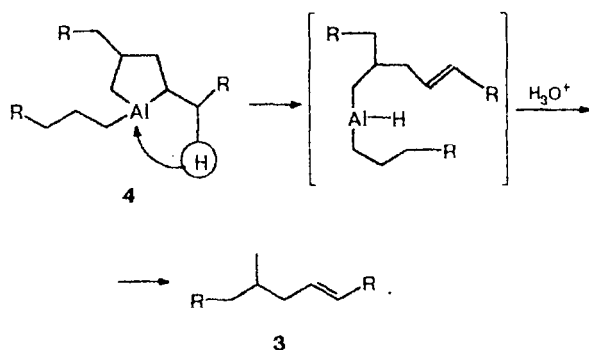
**1**

X = O, S, NR

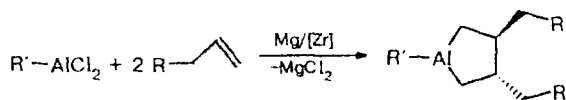
Replacing Et_3Al by higher trialkyl alanes in the cycloalumination of alkenes catalyzed by Cp_2ZrCl_2 can yield 1-alkyl-*trans*-3,4-dialkylalumacyclopentanes,⁴⁴ which attests to a possible analogy between the mechanism of cycloalumination and that of formation of zirconacyclopentane intermediates **2** under the reaction conditions.



In almost every experiment, unsaturated hydrocarbons **3** (5–12%) that contain the *E*-disubstituted double bond were found among products of hydrolysis or deuterolysis of alumacyclopentanes.⁴⁴ These results suggested that 2,4-dialkylsubstituted isomers **4** resulted, along with 3,4-dialkylsubstituted alumacyclopentanes, from the cyclometallation of α -olefins with trialkylalanes. β -Hydride transfer initiated by zirconium complexes and subsequent hydrolysis transform 2,4-dialkylsubstituted isomers **4** into *E*-alkenes according to the scheme



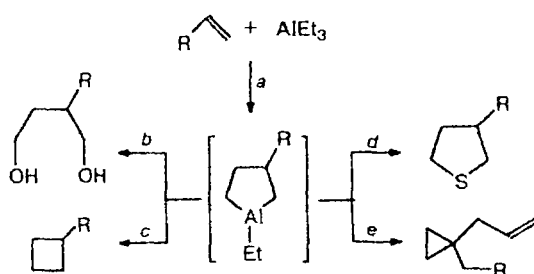
Taking into account that zirconocene " Cp_2Zr " is the key intermediate in the synthesis of alumacyclopentanes,^{27,36,38} we elaborated^{45–49} a new approach for generating zirconocene *in situ*, which differs from the known ones³¹ by its simplicity and consists in reduction of Cp_2ZrCl_2 in THF with magnesium activated with OAC. This allowed us to find a new preparative method for the synthesis of substituted alumacyclopentanes from alkyldihaloaluminum, α -olefins, and magnesium metal. As a result, 1-alkyl-, 1-alkoxy-, 1-amino-, and 1-halo-*trans*-3,4-dialkyl-substituted alumacyclopentanes were synthesized in the presence of catalytic amounts of Cp_2ZrCl_2 or ZrCl_4 with high regio- and stereoselectivity in 70–90% yields.^{45,48,49}



Study of the chemical and physicochemical properties of alumacyclopentanes resulted in the discovery of novel lines of their application in both organic and organometallic synthesis. Of synthetic interest are unconventional "one-pot" methods for transformation of α -olefins into *threo*- and 2,3-disubstituted butane-1,4-diols, thiolane-1-oxides,⁵⁰ compounds of the cyclobutane,^{51,52} cyclopropane,⁵³ thiophane, selenophane,^{54,55} and phospholane⁵⁶ series as well as optically active hydrocarbons⁵⁷ with the participation of alumacyclopentanes obtained *in situ* (Scheme 3).

A novel series of reactions such as β -vinylation,^{58,59} reductive β -vinylation,^{60,61} reductive β -ethylation, and

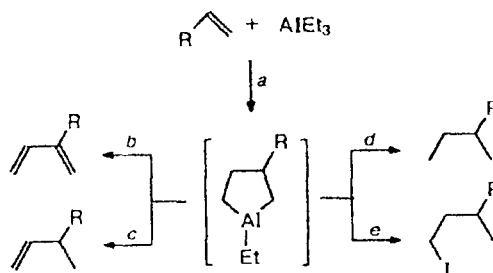
Scheme 3



Reagents: a. [Zr]; b. (1) O_2 , (2) H_2O ; c. $\text{CH}_2=\text{CHCH}_2\text{Hal}$, [Pd]; d. S_8 ; e. $\text{CH}_2=\text{CHCH}_2\text{Hal}$, [Ni].

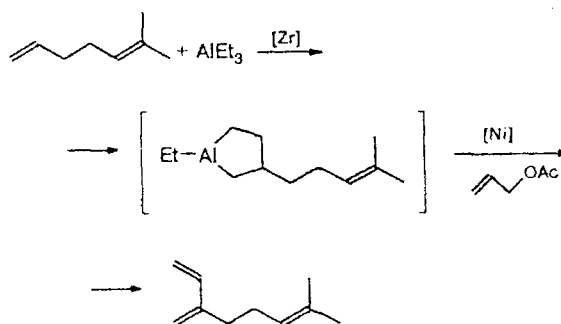
reductive β -iodoethylation⁶² of α -olefins was elaborated based on cycloaluminum of unsaturated compounds, catalyzed by Zr complexes (Scheme 4).

Scheme 4

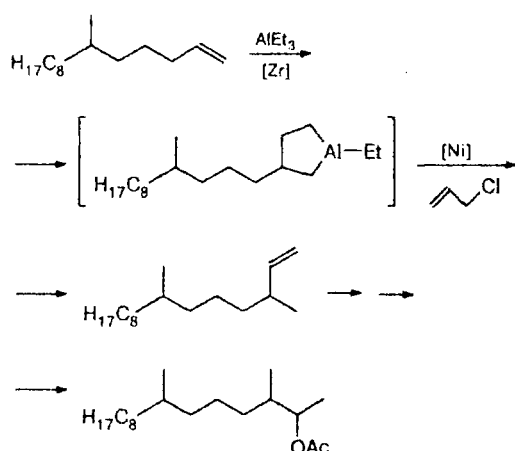


Reagents: a. [Zr]; b. $\text{CH}_2=\text{CHCH}_2\text{OAc}$, [Ni]; c. $\text{CH}_2=\text{CHCH}_2\text{Hal}$, [Ni]; d. H^+ ; e. $(\text{CH}_2\text{I})_2$.

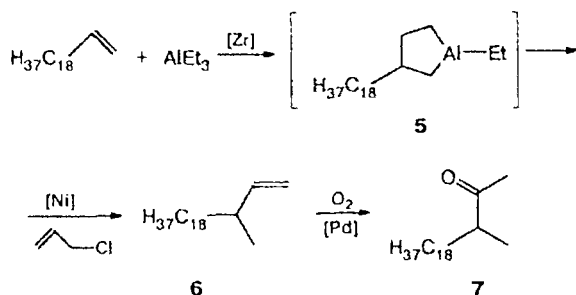
The β -vinylation of α -olefins allows one to obtain 2-substituted 1,3-dienes from comparatively readily available monomers and opens a simple way to the synthesis of linear isoprenoids.^{63,64}



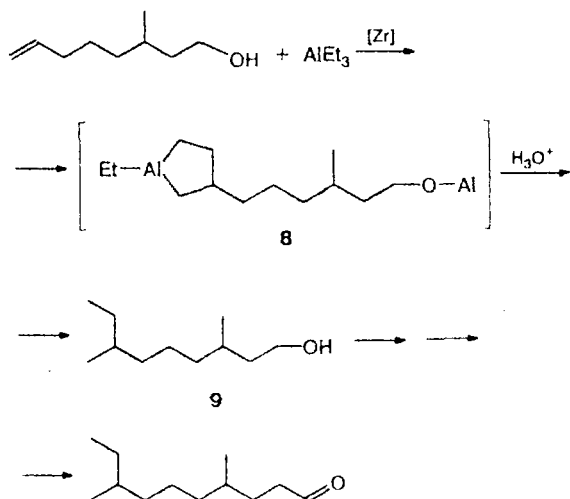
The reductive β -vinylation of α -olefins was used for preparing key intermediates in the synthesis of biologically active compounds, e.g., the pheromone of pine saw fly.⁶⁵



β -Hydrovinylation allows one to synthesize the pheromone of brown cockroach in two steps.⁶⁶ Thus, alkene $\text{C}_{20}\text{H}_{40}$ interacts with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 to give alumacyclopentane **5**, which is involved in the reductive β -vinylation without preliminary isolation. The oxidation of obtained β -vinyl-alkane **6** with oxygen in the presence of a palladium-copper catalyst according to a known procedure yields pheromone **7**.



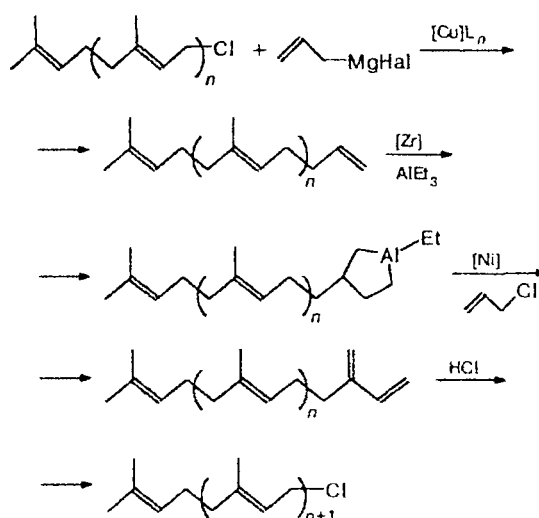
The cyclometallation of α -olefins with the subsequent hydrolysis of OAC formed is a general method for selective introduction of the ethyl substituent into the β -position of α -olefins (reductive β -ethylation). This



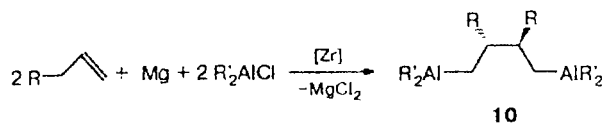
reaction found use in the synthesis of a series of pheromones. For example, the cycloaluminum of 3-methyl-oct-7-en-1-ol with Et_3Al in the presence of Cp_2ZrCl_2 with the subsequent hydrolysis of alumacyclopentane **8** gives the key synthon **9**, which is used in the synthesis of the aggregation pheromone of little and pin meal worms.⁶⁷⁻⁶⁹

Based on the reactions mentioned above,⁵⁸⁻⁶² we elaborated a versatile method for constructing linear *E*-isoprenoids from available monomers and reagents (Scheme 5).

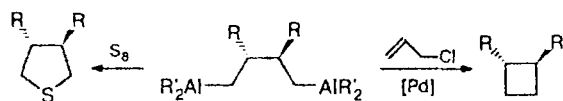
Scheme 5



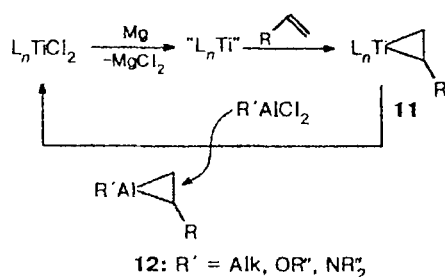
The generation of zirconacyclopentane intermediates and their subsequent transmetalation *in situ* with halogen-containing OAC formed the basis for a new approach to the synthesis of 1,4-dialumacomounds. This reaction allows one to obtain *threo*-2,3-dialkyl-substituted 1,4-dialumabutanes **10** in high yields and selectivity from available α -alkenes, dialkylaluminum chlorides (as well as aluminum amides or aluminum mercaptides), and Mg (Ca, Na) metal acting as an acceptor of halide ions in the presence of catalytic amounts of Cp_2ZrCl_2 or ZrCl_4 in ethereal solvents.⁷⁰



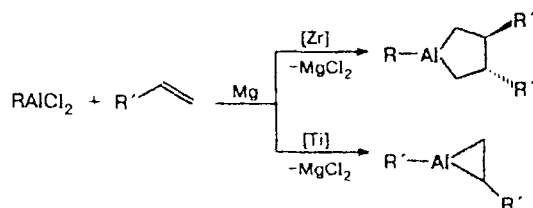
It is interesting to note that most of the reactions characteristic of *trans*-3,4-dialkyl-substituted alumacyclopentanes are also characteristic of 1,4-dialumacomounds, e.g., the reactions with elemental sulfur or allyl chloride, which result in compounds of the thiophane or cyclobutane series, respectively.⁷⁰



In 1963, M. E. Vol'pin with coworkers first synthesized⁷¹ and later studied systematically⁷²⁻⁸⁶ three-membered organotitanium compounds. These results motivated us to carry out studies on elaborating a method for the synthesis of alumacyclopropanes, which were not described earlier.⁸⁷ The method should be based on catalytic generation of titanacyclopropane intermediates **11** with their subsequent transmetalation with alkyl-, alkoxy-, and dialkylaluminum dichlorides according to the scheme



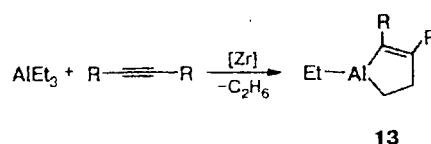
As a result, alumacyclopropanes **12** were first obtained, and their properties were studied. The direction of the reaction of cycloalumination depends on the nature of the catalyst and the structures of OAC and α -olefin. Thus, when the cycloalumination of α -olefins occurs under the action of RAlCl_2 in the presence of catalytic amounts of Cp_2ZrCl_2 , the formation of *trans*-3,4-disubstituted alumacyclopentanes is observed,⁴⁶ while substituted alumacyclopropanes are formed when the reaction is catalyzed by Cp_2TiCl_2 .⁸⁷ At the same time, the cycloalumination of α -olefins with dihaloalanes containing bulky alkoxy or amide substituents in the presence of zirconium catalysts (Cp_2ZrCl_2 or ZrCl_4) results in a mixture of both alumacyclopentanes and alumacyclopropanes, whose ratio depends on the reaction conditions.



The examples cited indicate that the cycloalumination of α -olefins with aluminum halides, which is catalyzed by Ti and Zr complexes, makes it possible to obtain not only cyclic OAC but also substituted 1,2- and 1,4-dialumacomounds in high yields and selectivity.

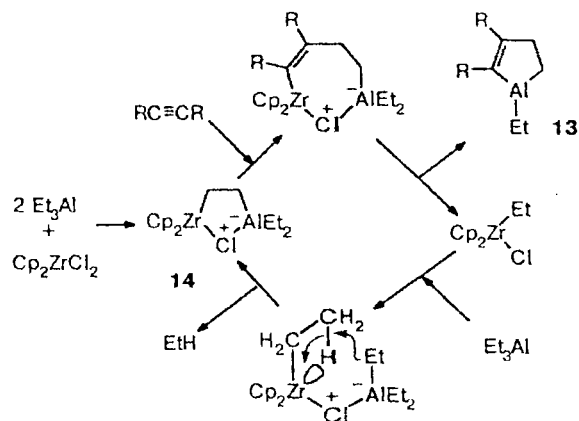
Cycloalumination of acetylenes catalyzed by Ti and Zr complexes

In continuation of the studies on the cycloalumination of olefins under the action of alkyl alanes, we carried out the cyclometallation of mono- and disubstituted acetylene derivatives with trialkyl- and dihaloalanes in the presence of Ti- and Zr-containing catalysts. The cycloalumination of disubstituted acetylene derivatives with triethylaluminum in the presence of Cp_2ZrCl_2 led to the formation of *cis*-2,3-dialkyl(aryl)-substituted alumacyclopent-2-enes, which were thus first synthesized with high regio- and stereoselectivity.^{88,89} The reaction occurs in both aromatic and aliphatic solvents and even in their absence.



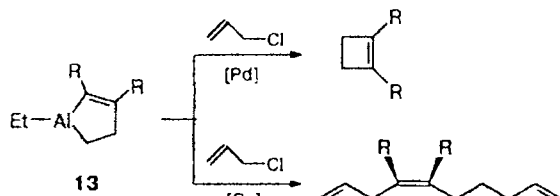
In halogen-containing solvents, acetylenes undergo carbalumination to give alkenylalanes. We assumed⁸⁸ that alumacyclopentenes **13** can be obtained *via* the stage of formation of zirconacyclopentene intermediates with their subsequent transmetalation with the initial OAC. The mechanism of the above reaction⁸⁸ can be explained¹⁶ by the formation of bimetallic complex **14** obtained by the reaction of Cp_2ZrCl_2 with two molar equivalents of Et_3Al .⁹⁰⁻⁹² In this case, the catalytic cycle of the reaction can be represented by Scheme 6.¹⁶

Scheme 6

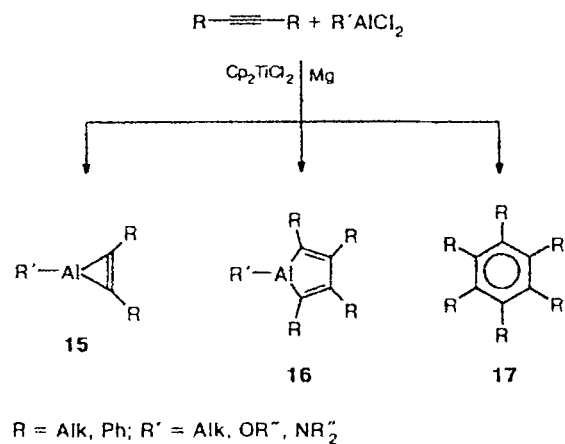


By analogy with alumacyclopentanes, we studied transformations of alumacyclopentenes. Thus, the dealumination of alumacyclopentenes **13** with allyl chloride in the presence of phosphine complexes of palladium allows one to obtain disubstituted cyclobutenes.⁹³ At the same time, the action of copper halides initiates

the reaction of cross-linking giving *cis*-4,5-disubstituted deca-1,4,9-trienes.⁹⁴

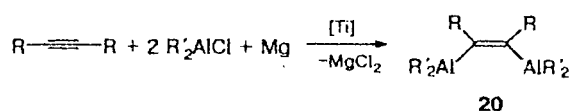


The generation of titanacyclopropene intermediates^{71–86} under the action of activated magnesium powder with the subsequent transmetalation of titanacyclopropenes formed *in situ* with aluminum dihalides gave birth to methods for the synthesis of trisubstituted alumacyclopropenes, a novel class of metal-containing cycles.⁹⁵ The reaction is of general character. Along with alkyldihaloalanes, alkoxy- and dialkylaminodihaloalanes can also be involved in the cyclometallation of acetylenes.



Depending on the reaction conditions, alumacyclopropenes **16** and hexasubstituted benzene derivatives **17** (5–30%) were identified by us among by-products in the above cycloaluminum of acetylenes into alumacyclopropenes **15**. Their formation may be represented by Scheme 7, which includes successive generation of titanacyclopropene (**18**) and titanacyclopentadiene (**19**) intermediates.

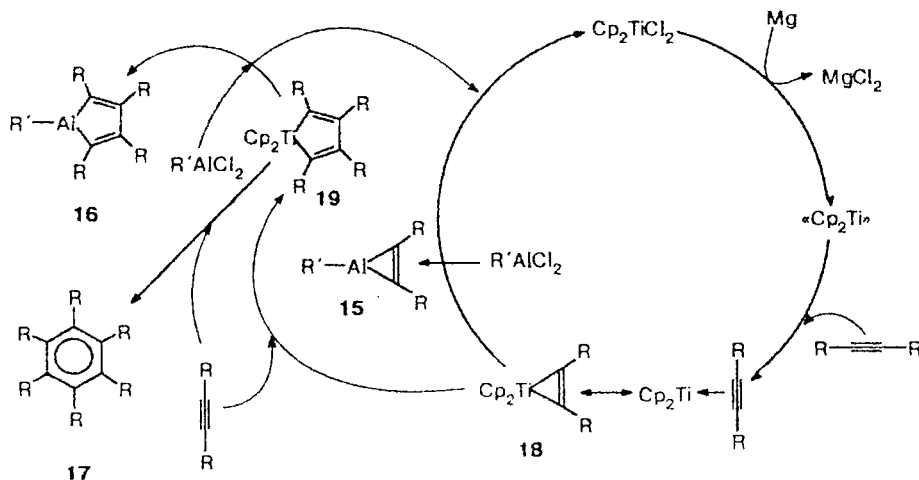
The transmetalation of titanacyclopropene intermediates **18** formed *in situ* with dialkylaluminum halides and halogen-containing aluminum alkoxides or amides allowed one to obtain 1,2-dialumaethylenes **20**, whose chemical and physicochemical properties are being studied intensively at present.



The most significant progress of the last recent years in the field of the synthesis and transformations of OAC is related to the introduction of metallocomplex catalysis in the chemistry of organoaluminum compounds. Regio- and stereoselective reactions of the catalytic hydro- and carbometallation of unsaturated compounds as well as effective synthetic methods and reagents for the construction of new carbon-carbon and metal-carbon bonds were developed. They are widely used for constructing both simple and structurally complex compounds, including natural ones.

Among these achievements, the catalytic cycloaluminum of olefins, dienes, and acetylenes seems to be one of the most promising lines appearing in the chemistry of OAC in the recent 5–8 years. The discovery of this reaction contributed to elaborating a novel methodology of organic and organometallic synthesis,

Scheme 7



developing known reactions, methods, and highly effective reagents, and creating new ones promising for organic and organometallic synthesis.

In connection with this, the most amazing results that will lead to the elaboration of unconventional chemical technology, unique metallic coatings, new polyfunctional catalysts for oligo- and polymerization processes, highly selective complex organometallic reagents for synthetic organic chemistry, and the development of new trends in investigations should be expected in this field of chemistry within a period of 5–10 years.

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