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Catalytic replacement of transition metal atoms in metallacarbocycles by the atoms of nontransition metals

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The phenomenon of catalytic replacement of transition metal atoms in metallacarbocycles by nontransition metal atoms to afford the corresponding organometallic compounds has been discovered and its mechanism is considered.

The first stable metallacarbocycles with transition metals (Ti, Zr, Hf, V, Ta, Cu, Mo, W, Mn, Re, Fe, Ru, Rh, Co and Ni) have been obtained and chemically characterised in the last 10–15 years.[1] Among them five-membered metallacarbocycles with Ti and Zr are the most-used in synthetic practice. The chemistry of these metallacarbocycles is of great interest due to the following reasons: preparative accessibility, stability, possibility of storage and conducting the synthetic transformations at room temperature. Two polar metal–carbon bonds in the metallacycle molecule allow implicating them in reactions with nucleophilic and electrophilic reagents to obtain earlier hard-to-rich functionally substituted acyclic, cyclic and heterocyclic compounds. Furthermore, synthesis and reactivity studies of transition metal metallacarbocycles contribute to further development and understanding of the role of transition metal complexes in catalysis.

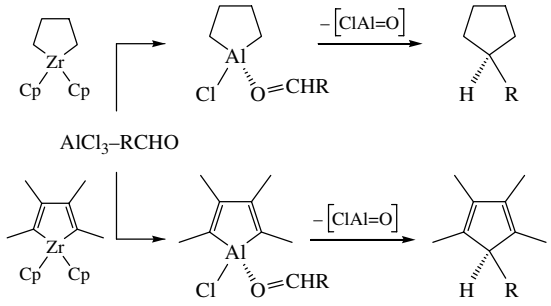
Active studies in this direction during the last years led to the appearance of a new field of organometallic chemistry: the chemistry of nontransition (Mg, Zn, Al, In and Ga) metallacarbocycles.[2–5]

High reactivity of a metal–carbon bond in nontransition metallacarbocycles as compared to the analogous transition metallacarbocycles combined with the sufficiently high stability of these compounds under normal conditions, and also possibility of a synthesis and their synthetic transformations at one preparative stage make this class of metallocycles the most promising in organic and organometallic synthesis.

In our view, the main obstacle on the way of wide investigation and application of nontransition metallacarbocycles was the absence of effective preparative methods for their synthesis, as well as theoretical studies examining thermodynamic stability and possibility of existence of small, medium and macrometallacycles with nontransition metals, for example, aluminacyclopropanes, magnesacyclopropanes, aluminacyclopropenes, aluminacyclopentenes, magnesacyclopentanes and aluminacyclopentadienes.

To solve the above problems, and to develop promising procedures for the synthesis of small and medium metallacarbocycles using available and cheap salts and compounds containing nontransition metals, investigations in the chemistry of magnesium and aluminium, which at first were selected as most suitable and effective, have been expanded with the participation of metal complex catalysts.

The possibility of stoichiometric synthesis and chemical transformations of zircona- and titanacyclopentanes, as well as zirconacyclopentadienes, has been reported.[6–9] The compounds



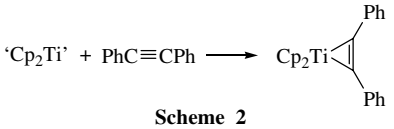
Scheme 1

Usein M. Dzhemilev received his Candidate (Ph.D.) and Doctor of Science (Chemistry) degrees from the Institute of Chemistry of the Academy of Sciences of the USSR in Ufa (nowadays the Institute of Organic Chemistry of Ufa Scientific Centre of the Russian Academy of Sciences). In 1982, he became a professor, and since 1980 he has held the position of a Deputy Director of the same Institute. Since 1992 he has become Director of the Institute of Petrochemistry and Catalysis of Bashkortostan Academy of Sciences, which since 2004 has associated with the Russian Academy of Sciences. He was an invited lecturer in Poland, Czechoslovakia, Bulgaria, Israel, China and the United States.

In 1990, he was elected a Corresponding Member of the Academy of Sciences of the USSR. He is a Laureate of State Prizes of the USSR (1990) and the Russian Federation (2004). His research interests include metal complex catalysis in organic and organometallic synthesis, the chemistry and stereochemistry of strained and cage compounds, the organic chemistry of nontrasition metals (Mg, Al, Zn, Ga and In) and the chemistry of small, low-stable and highly strained molecules.

under the action of an $AlCl_3$–RCHO reagent were converted into appropriate cyclopentanes or cyclopentadiene. In these reactions, the formation of aluminacyclopentanes and aluminacyclopentadienes as key intermediate metallacarbocycles, which underwent carbocyclization to cyclopentanes or cyclopentadienes, was postulated[10,11] (Scheme 1).

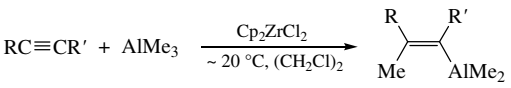
In 1978, Vol'pin and colleagues[12] reported on the synthesis of stable titanacyclopropene by the reaction of stoichiometric quantities of Cp_2Ti^{2+} and tolane (Scheme 2).



Scheme 2

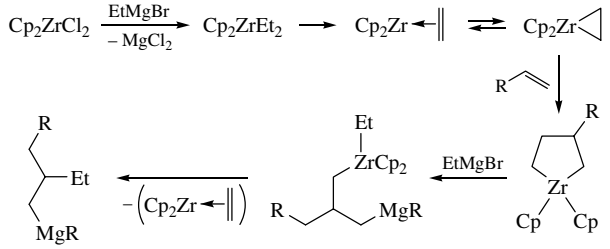
Titanacyclopropene, which was identified by X-ray analysis, gave hope to obtain similar nontransition metal minor cycles and to study their properties.

To the number of essential achievements of this investigated period with the participation of zirconium complexes one should add the reports by Negishi with co-authors[13–15] on the direct regio- and stereoselective carboalumination of 1,2-disubstituted acetylenes with $AlMe_3$ under the action of a Cp_2ZrCl_2 catalyst (Scheme 3).



Scheme 3

By analogy with the carboalumination reaction, in 1983, for the first time, regioselective 1,2-carbomagnesiation of α-olefins with nonactivated double bond (Dzhemilev reaction[16–19]), including those with substituents containing functional groups was published.[20] Zirconacyclopropanes and zirconacyclopentanes were considered as the key intermediates, whose sequential transformations under reaction conditions led to the target 1,2-carbomagnesiation products (Scheme 4).[21,22]

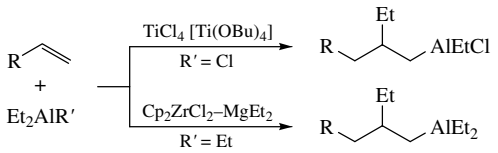


Scheme 4

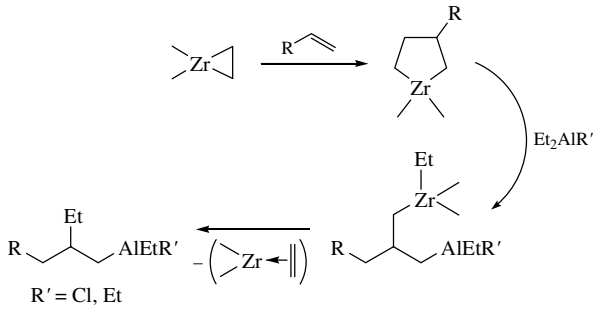
As in the case of 1,2-ethylmagnesiation,[20,21] in the 1,2-ethylalumination reaction of olefins, which for the first time was performed by Dzhemilev and colleagues[23,24] using Et_2AlCl or $AlEt_3$ and $TiCl_4$ [$(Ti(OBu)_4]$ or Cp_2ZrCl_2–$MgEt_2$ as catalysts, zirconacarbocycles have proved to be the key intermediates as well. Their formation is considered to occur according to analogous Scheme 5.

From the examples given above, one can conclude that the catalytic 1,2-carbometallation of olefins with Mg and Al alkyl derivatives affected by Zr and Ti complexes occurs *via* the generation of intermediate transition metallacarbocycles, which are responsible for the formation of target organometallic compounds, under reaction conditions.

The formation and subsequent transformation of zircona- and titanacarbocycles under reaction conditions of 1,2-carbomagnesiation or 1,2-carboalumination were accomplished due to the unique ability of Zr and Ti alkyl or cycloalkyl complexes



Reaction mechanism of the carboalumination of α-olefins

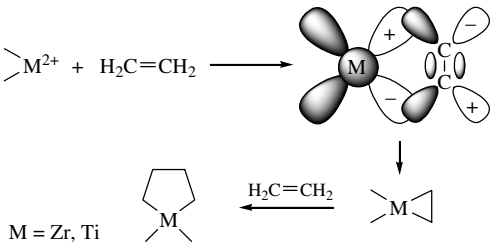


Scheme 5

to transfer their π- and σ-bound ligands onto nontransition metal atoms and *vice versa*.[25–27]

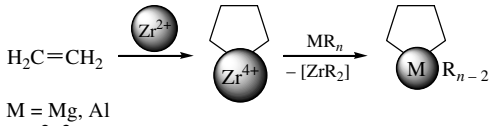
In the 1980s, the author of this survey was the first to announce an idea about the possibility of synthesising magnesa- and aluminacycloalkanes by the catalytic cyclometallation of olefins with Mg or Al alkyl derivatives in the presence of Zr or Ti complexes.

The essence of the advanced idea consisted in the ability of the coordinatively unsaturated Zr or Ti complexes to coordinate olefins to give donor–acceptor complexes in accordance with the Dewar–Chatt–Dunkanson model,[28] leading thus to the activation of initial olefins with the subsequent intramolecular oxidative cyclization of the latter to form three- and five-membered transition metallacarbocycles (Scheme 6).



Scheme 6

Via the interaction between the obtained transition metallacycles and nontransition metal alkyls or alkyl halides, for example, AlR_3 or $MgRR'$, one could hope to replace transition metal atoms in metallacarbocycles by the atoms of nontransition metals to obtain the corresponding nontransition metallacycles according to Scheme 7.

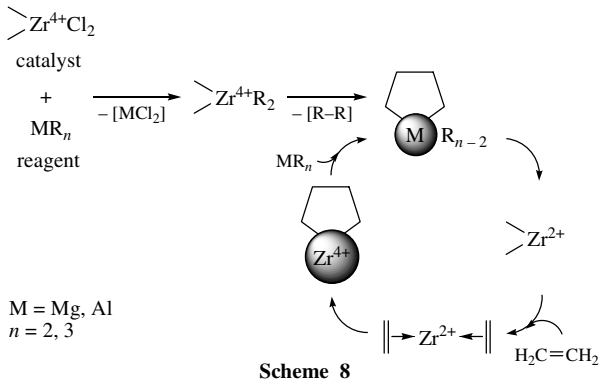


Scheme 7

Certainly, it remained not clear if these reactions will proceed in stoichiometric or catalytic versions (Scheme 8).

This catalytic reaction offered completely new potentials to construct in one preparative stage the reactive metallacarbocycles from olefins, as well as in prospect from acetylenes, obtaining both transition and nontransition metallacarbocycles.

The above formation of the metallacarbocycles with nontransition metals (Al and Mg) was performed in stoichiometric and

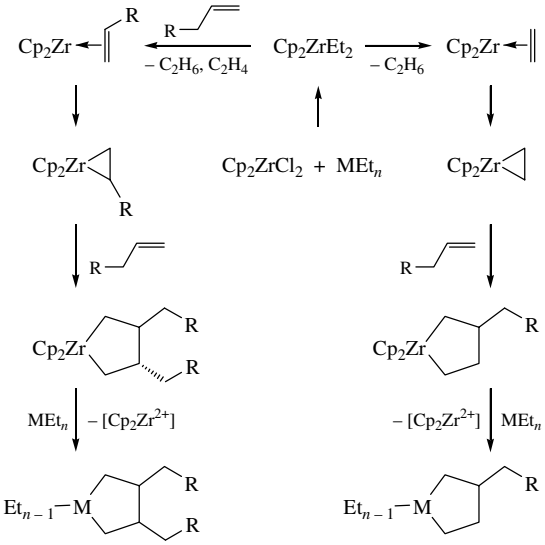


Scheme 8

catalytic versions. In this case, Cp_2ZrCl_2 and Cp_2TiCl_2 proved to be the most active and selective catalysts.

According to Scheme 9, the rapid ligand exchange occurs *via* the interaction between Cp_2ZrCl_2 and EtMgR (R = Et, Cl) or $AlEt_3$ to give Cp_2ZrEt_2, which transforms into zirconocene Cp_2Zr^{2+} as a result of β-elimination of hydrogen atoms. The latter, under reaction conditions, coordinates the molecule of ethylene or a higher olefin to form corresponding zirconacyclopropanes. The subsequent introduction of the initial olefin at the Zr–C bond leads to appropriate 3-substituted or *trans*-3,4-disubstituted zirconacyclopentanes, which in the presence of the excess of magnesium or aluminum alkyl derivatives transmetalate to give the target magnesa- or aluminacyclopentanes.

This reaction is characterised by the extremely high regio- and stereoselectivity allowing in one preparative stage from α-olefins and magnesium or aluminum alkyl derivatives to synthesise five-membered nontransition metallacarbocycles (Mg, Al) in practically quantitative yields.



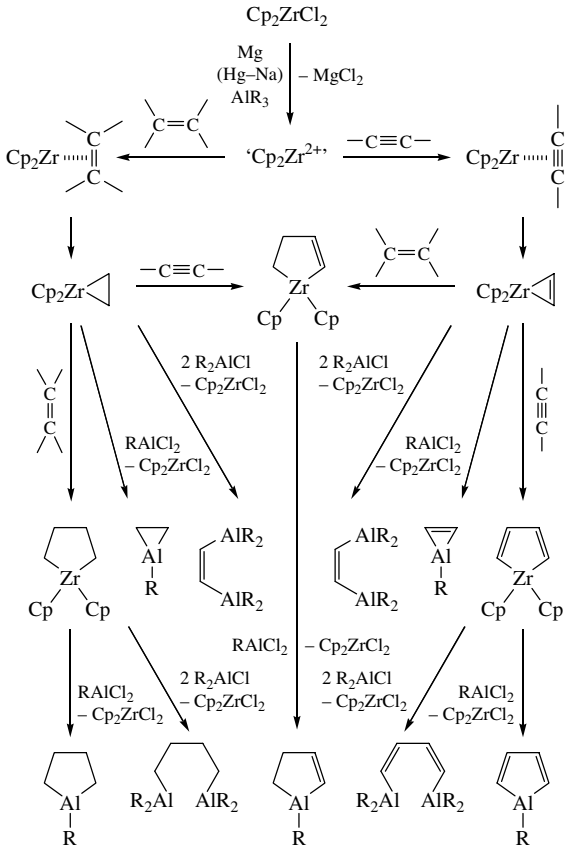
Scheme 9

The above transformations have been initially performed in a stoichiometric version and then with the use of catalytic amounts of Zr or Ti complexes and Hf, Ta and Co as well.

The study of application boundaries of this reaction with the participation of cyclic and acyclic olefins[29–31] resulted in the development of a general catalytic method for the construction of five-membered nontransition metallacarbocycles of different structures.

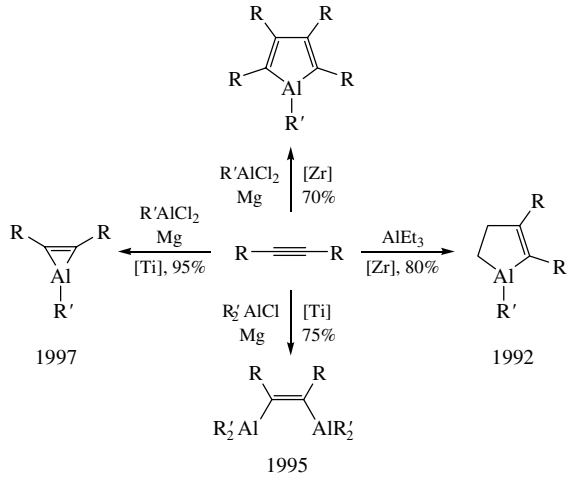
The reaction was called 'catalytic cyclometallation', and it is widely used in synthetic practice.

It remained obscure, if the catalytic cyclometallation reaction is characteristic only of olefins or it can also be applied to acetylenes. In that case one could expect to obtain such transition or nontransition metallacarbocycles as zirconacyclopropenes or titanacyclopropenes, and, consequently, also previously not described aluminacyclopropenes, aluminacyclopentenes, aluminacyclopentadienes, or other similar nontransition metallacarbocycles and their acyclic analogues in the case of their thermodynamic stability as shown in Scheme 10.



Scheme 10

As a result of practical realization of general schemes for the synthesis of cyclic and acyclic aluminum organic compounds (OACs), preparative methods have been developed to synthesise aluminacyclopropanes,[32,33] aluminacyclopropenes, aluminacyclopentanes, aluminacyclopentadienes and 1,2-dialuminioethylenes and to study their physicochemical properties[34–36] (Scheme 11).

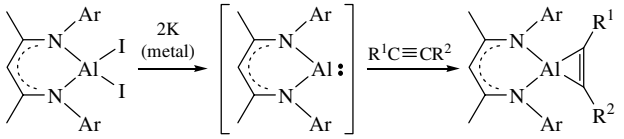


Scheme 11

The above classes of OACs were stable under inert conditions and all reactions described for acyclic aluminum organic compounds were characteristic of them in most cases.

In this family of OACs, the presented aluminacyclopropenes were of special interest, for which in 1990 for the first time Schaeffer has announced the possibility of existence.[37] In 1997, Dzhemilev and coworkers[32,36] have implemented this idea and obtained aluminacyclopropenes. The preparative methods of their synthesis were developed and chemical transformations were studied.

The synthesis of aluminacyclopropenes based on the interaction between diiodoalane stabilized by 1,3-diamine and metallic potassium was reported[38] (Scheme 12).

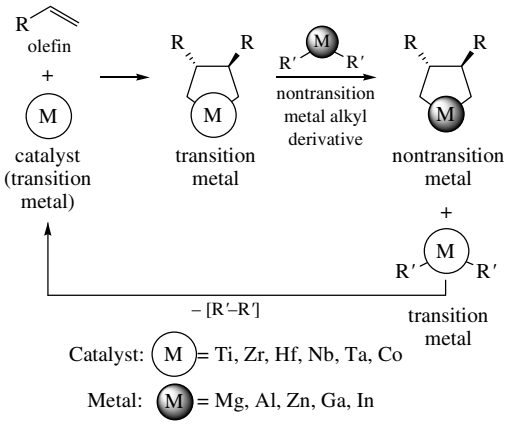


Scheme 12

Thus, the procedures developed[32,36,38] for the synthesis of aluminacyclopropenes open effective pathways to synthesise a new class of organometallic minor cycles, aluminacyclopropenes, and to study their properties. The analysis of data obtained in the study of the catalytic cyclometallation reaction of olefins and acetylenes with the aid of Al or Mg alkyl derivatives in the presence of Zr or Ti complexes showed that all these reactions have general nature. The formation of metallacarbocycles with Al and Mg occurs in all experiments through the formation of transition metallacarbocycles, in particular, zirconium and titanium.

Properly, in all experiments the catalytic replacement of transition metal atoms (Zr, Ti) in the appropriate transition metallacarbocycles by the atoms of nontransition metals (Al, Mg) occurs to form nontransition metallacarbocycles. This reaction is characterised by high regio- and stereoselectivity and makes it possible to conduct the formation of metallacycles at room temperature and in practically quantitative yields.

The catalytic cyclometallation reaction of olefins can be represented by Scheme 13.

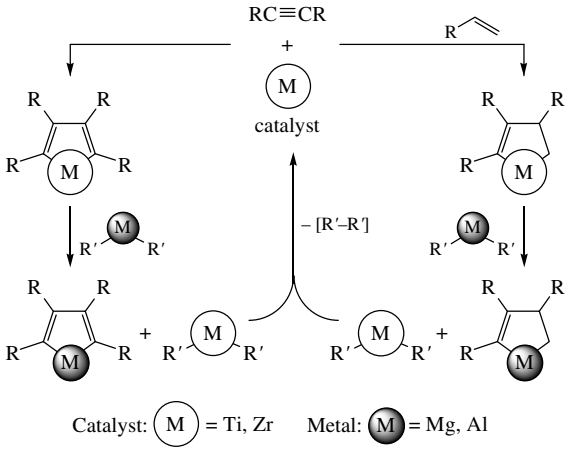


Scheme 13

The catalytic cyclometallation of acetylenes occurs according to Scheme 14.

The wide and active study of the catalytic cyclometallation reaction led to the development of new classes of cyclic and acyclic organometallic compounds and to the discovery of the family of organic and organometallic reactions, which make it possible to synthesise small, medium and macrocyclic compounds, bifunctional monomers with substituents of assigned configuration, heterocycles and other useful synthons from simplest olefins, acetylenes and organometallic reagents (Scheme 15).[39]

Using cycloalumination of olefins with $AlEt_3$ in the presence of catalytic amounts of Cp_2ZrCl_2 as an example, the mechanism of this reaction was studied[31,39] by dynamic NMR spectroscopy with the simultaneous identification of the intermediate Zr–Al



Scheme 14

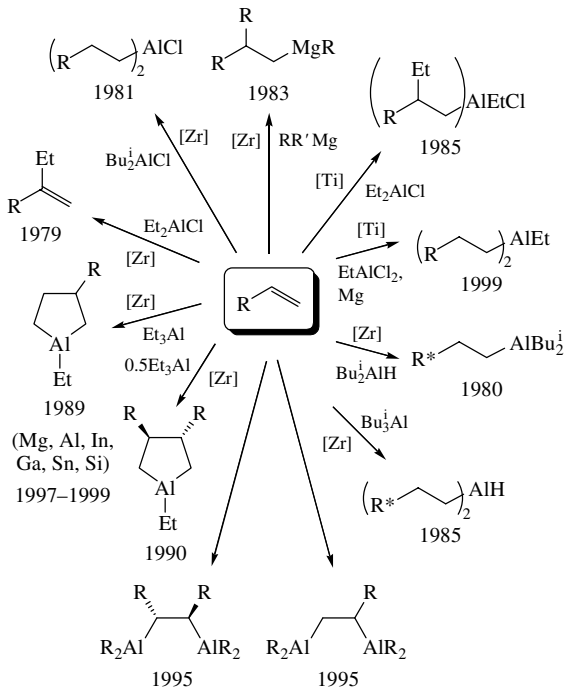
bimetallic complexes responsible for the formation of target aluminacyclopentanes.[40]

This makes it possible to measure and quantum-chemically calculate the rate constants of formation of the intermediate complexes and target metallacarbocycles (Scheme 16).

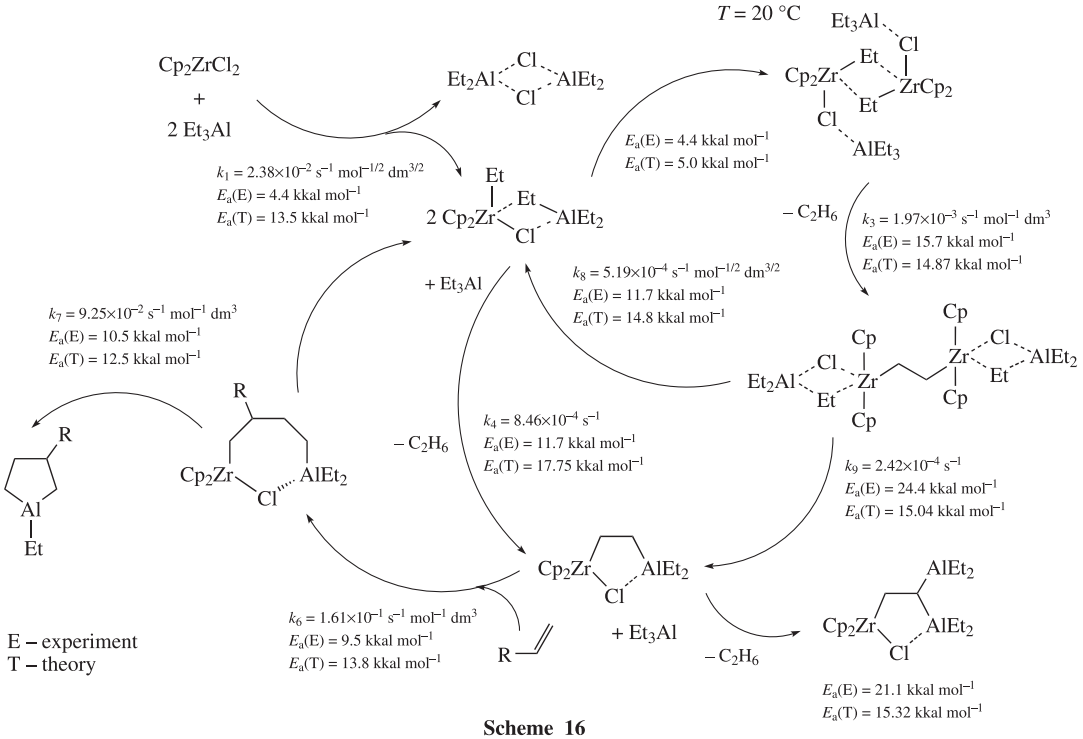
One can see that the replacement of zirconium atoms by aluminum atoms occurs *via* the formation of five- and seven-membered Zr–Al bimetallic complexes with the simultaneous regeneration of catalytically active zirconium complex.

These investigations are at the initial stage of their development and in spite of the success reached there is a number of unsolved problems. Among them are factors the selectivity of catalytic cyclometallation reaction depends on; possible expansion of this reaction over functionally substituted olefins, acetylenes, allenes and conjugated dienes, other transition and non-transition metals, as well as rare-earth metals; the prospects of the reaction, including possible design of gigantic metallacarbocycles, and others.

The further development of investigations in the catalytic cyclometallation reactions of unsaturated compounds with non-transition metal alkyl derivatives in the presence of Ti- and Zr-containing complex catalysts and the solution of the above problems will lead, in our opinion, to the development of a



Scheme 15



Scheme 16

general theory of catalytic metallacarbocycle transmetallation to give insight into the phenomenon of catalytic replacement of transition metals by the atoms of nontransition metals.

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