Professor Usein Memetovich Dzhemilev

A Tribute

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

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Dzhemilev Usein Memetovich was born on May 15, 1946 in Uzbekistan.

In 1963 he finished his school studies in Bekabad (Uzbekistan). In 1968 he graduated from the faculty of Chemical engineering of plastics at Kazakh Chemical-Technological Institute in Shymkent (Kazakhstan). From 1968 to 1969, he was a Senior Laboratory Assistant, then an engineer in the laboratory of Chemistry of alkaloids in the Institute of Chemistry, the Academy of Sciences of the Kazakh SSR (now the National Academy of Sciences of the Republic of Kazakhstan), where he was engaged in research on the chemistry of the steroidal alkaloid - solasodine.

In September 1969, he moved to Ufa (Bashkortostan, Russia) at the invitation of Professor Tolstikov G.A. (now an Academician), where he continued his education in full-time graduate school under his guidance (1969–1972) at the Institute of Chemistry, Bashkirian Branch of the USSR Academy of Sciences.

In 1972, he defended his Ph.D. thesis entitled "Oxidation of organic compounds with hydroperoxides catalyzed by molybdenum salts" and received his Candidate (Ph.D.) degree ahead of schedule.

He received his Doctor of Science (Chemistry) degree from the Institute of Chemistry, Bashkirian Branch of the USSR Academy of Sciences (now the Institute of Organic Chemistry of the Ufa Research Centre of RAS). In 1982, he became a professor, and since 1980 he has held the position of Deputy Director of the same Institute. Since 1992 Professor Dzhemilev has been Director of the Institute of Petrochemistry and Catalysis of Bashkortostan Republic Academy of Sciences, which since 2004 has been associated with the Russian Academy of Sciences. From 1993 to 2006 he was Deputy Chairman of the Presidium of the Ufa Research Center of RAS.

In 1990 he was elected Corresponding Member of the Russian Academy of Sciences. He is a Laureate of State Prizes in the area of Science and Technology of the USSR (1990) and the Russian Federation (2004). In 2009 he was the recipient of the A.M. Butlerov Award for outstanding results achieved in Organic Chemistry.

Dzhemilev has made great contributions to the elaboration of scientific foundations and technological processes for the production of new monomers, flocculants, neutralizers of hydrogen sulfide, corrosion inhibitors, extractants of metals from spent catalysts, phenolic antioxidants, anti-adhesion lubricants, cooling lubricants, microspheric olefin oxychlorination catalysts, modern preparations for medicine and agriculture, and new substances with record high parameters for space rocket technology.

He has published over 1500 scientific papers including more than 600 inventors' certificates and patents, 5 monographs, and 38 reviews in domestic or foreign scientific books and journals. Under the scientific leadership of Professor Dzhemilev 10 doctoral theses and 65 candidate theses have been defended.

Professor Dzhemilev has many other activities, e.g. as a member of the editorial boards of the RAS journals "Nephtekhimiya" (Petroleum Chemistry) and "Zhurnal organichesckoi khimii" (Russian J. Org. Chem.). He is also a member of Russian Mendeleev Chemical Society, and a member of the Scientific Councils on Catalysis and Petroleum Chemistry of the Russian Academy of Sciences.

He has given numerous invited and keynote lectures in universities and research institutes while participating in International scientific meetings since 1982. As a visiting scientist he presented lectures in Poland, Czechoslovakia, Bulgaria, Israel, China and USA.

Usein is happily married and has a son Asan (a businessman) and a daughter Liliya. She is a medic and has a Ph.D. from the Institute of Biochemistry and Genetics of Ufa Scientific Centre of the RAS, where she is engaged in research in the field of hereditary diseases. His wife Galina is a chemist too and received her Ph.D. degree from the same Institute of Chemistry, Bashkirian Branch of the USSR Academy of Sciences. Usein and Galina have five grandchildren – four grandsons and one granddaughter. The eldest, Edward, became a student of the Lomonosov Moscow State Academy of Fine Chemical Technology (MITChT). They all like spending time

in their summer house and work in the garden. Collecting pictures is the other Professor's great hobby.

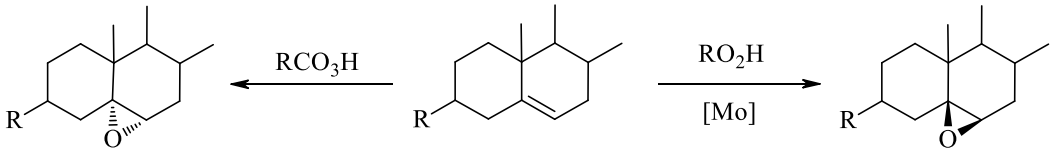
Key research areas

Usein M Dzhemilev is a prominent scientist in the field of design and application of metal complex catalysts in organic and organometallic synthesis. His research interests include chemistry and stereochemistry of strained and cage compounds, organic chemistry of unsaturated and organometallic compounds of nontransition metals (Mg, Al, Zn, Ga, In) as well as chemistry of small, low-stable and high energy molecules.

Dzhemilev is developing one of the most promising areas of modern organic chemistry – goal-oriented synthesis of novel compounds using organometallic reagents and methods of metal complex catalysis in order to create innovative chemical technologies.

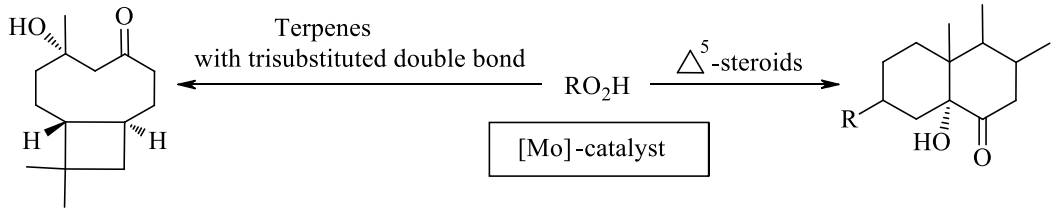
His early scientific work involved epoxidation of natural steroids and terpenes catalyzed by molybdenum complexes and the resultant stereochemistry.

The experiments on oxidation of steroids showed that stereochemistry of epoxidation with hydrogen peroxides differs radically from that of classic epoxidation reagents. In each experiment, predominantly β-oxides were obtained, whereas the classic reagents mainly gave α-oxides (Scheme 1).[1]



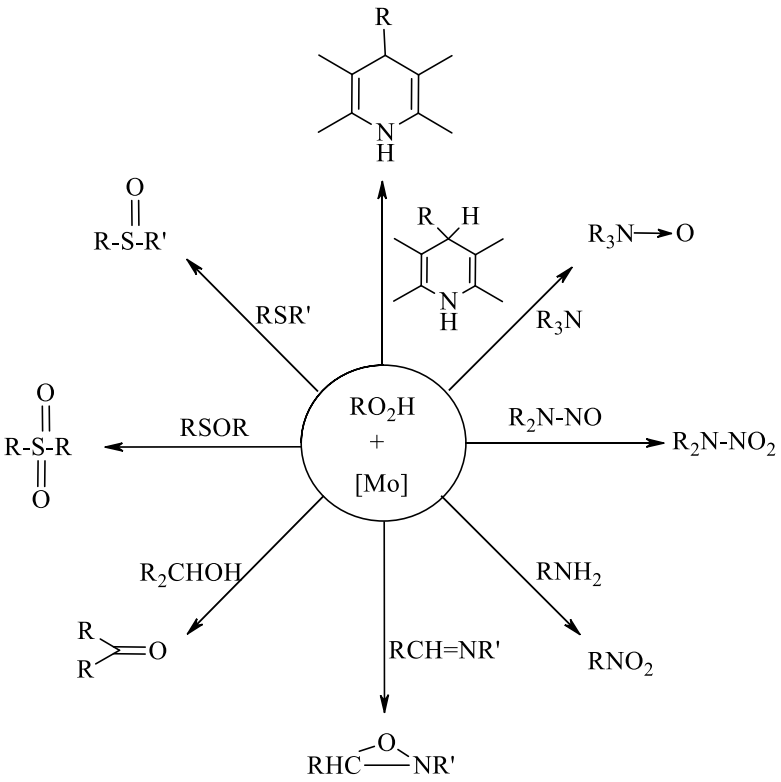
Scheme 1

The investigation of the application boundaries of this new epoxidation method led the young researcher to the discovery of the catalytic oxyketonation reaction of trisubstituted cyclic olefins in a series of steroids, mono-, di- and triterpenes (Scheme 2). This reaction is common in nature and is widely used in synthetic practice.[2]



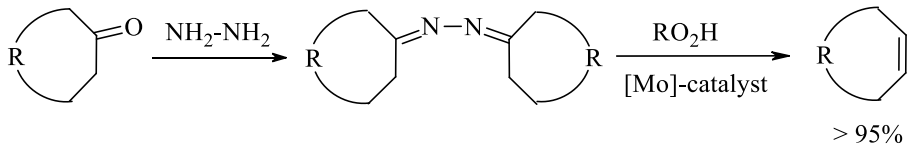
Scheme 2

The synthetic potential of the reagent, composed of hydrogen peroxide and molybdenum compound, was studied further by Dzhemilev by oxidation reactions of amines, nitrosamines, nitrogen heterocycles, sulfides, sulfoxides, dihydropyridines, alcohols and carbohydrates (Scheme 3).[3]



Scheme 3

Among these studies, the reaction that converts cyclic ketones via ketazines into appropriate olefins in one preparative stage is noteworthy.[4]

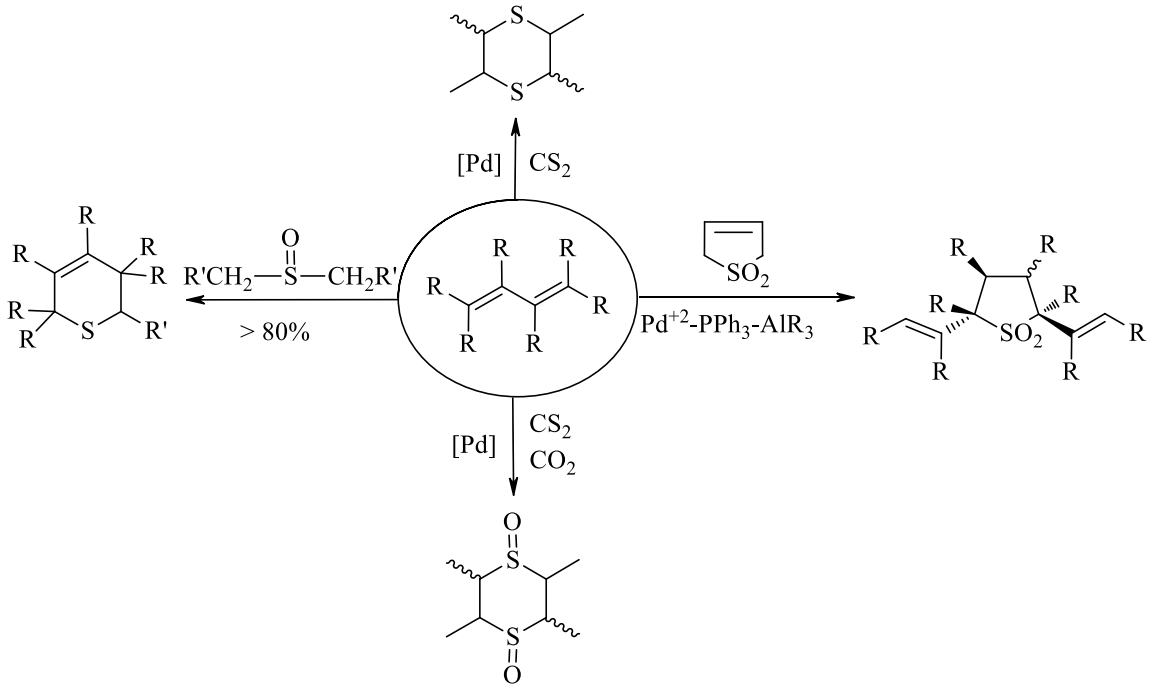


Scheme 4

By mid 1975 study of the hydroperoxide oxidation was complete and in the organized to that time specialized Laboratory of Catalytic Synthesis there were successfully started the works devoted to design and application of metal complex catalysts to different areas of organic chemistry, such as:

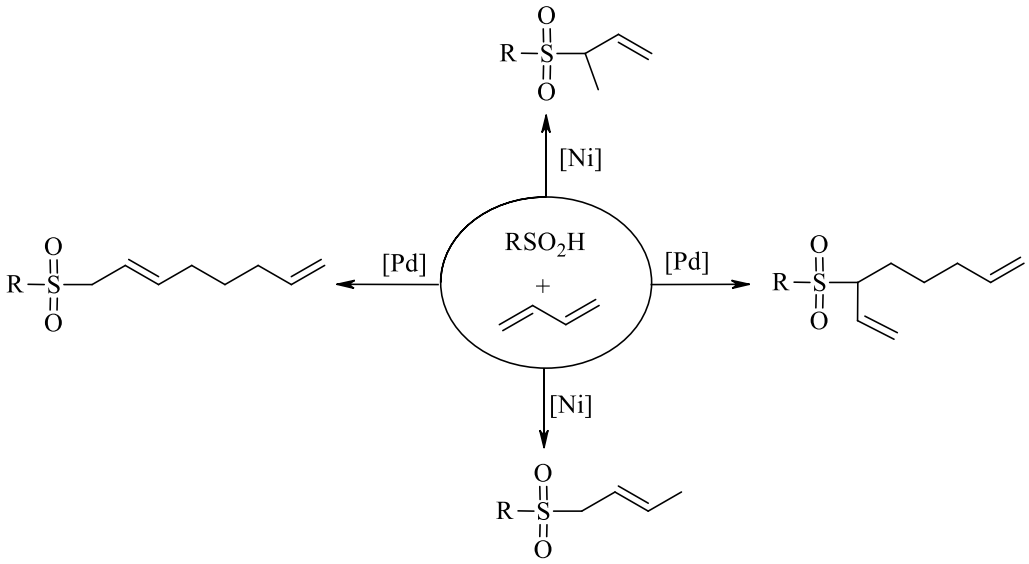
- Linear and cyclic oligomerization of conjugated dienes;
- Telomerization of 1,3-dienes with compounds containing mobile hydrogen atom;
- Synthesis of organosulfur compounds;
- Synthesis of high strained polycyclic compounds;
- Selective functionalization of carbon clusters – fullerenes;
- Chemistry of nontransition organometallics (Mg, Al, Zn, Ga, In);
- Chemistry of small, average as well as gigantic carbo-, hetero- and metallacarbocycles.

Dzhemilev's work on the synthesis of organosulfur compounds involving metal complex catalysts has received well-deserved recognition. Implementation of this work program has resulted in the development of new fundamental reactions, the general principles and efficient one step procedures for heterocyclization of conjugated dienes and acetylenes with small molecules, heteroolefins to give practically important cyclic and acyclic organosulfur compounds (Scheme 5).[5]



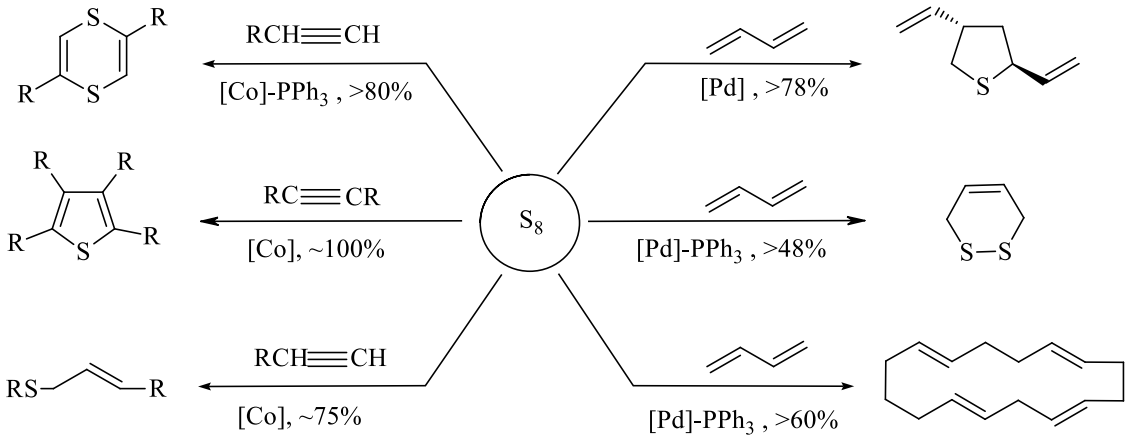
Scheme 5. Metal complex catalysis in synthesis of cyclic organosulfur compounds.

In this series, the research on telomerization of alkyl, cycloalkyl and aryl sulfinic acids with 1,3-dienes in the presence of Pd and Ni low valence complexes, which were carried out by Dzhemilev and coworkers, are the most interesting and promising (Scheme 6).[6]



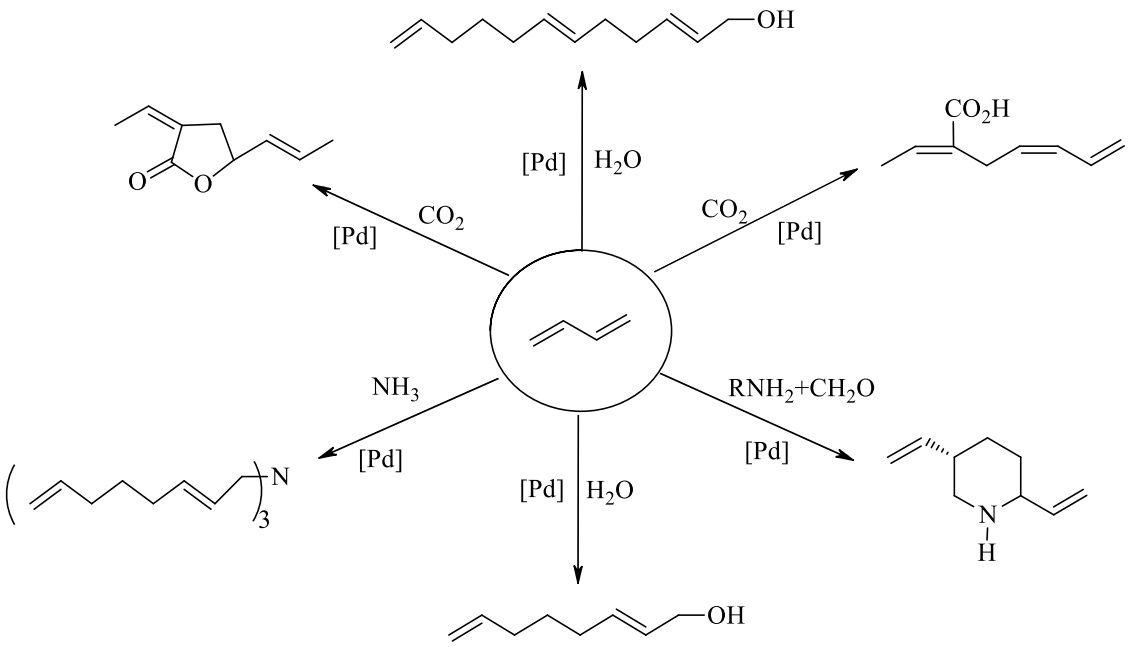
Scheme 6. Metal complex catalysis in chemistry of sulfinic acids.

Researchers in the Scientific School under the leadership of Usein Dzhemilev performed a large number of investigations dealing with reactions of elemental sulfur with acetylene and 1,3-dienes catalyzed by complexes of Co and Pd (Scheme 7).[7–10]



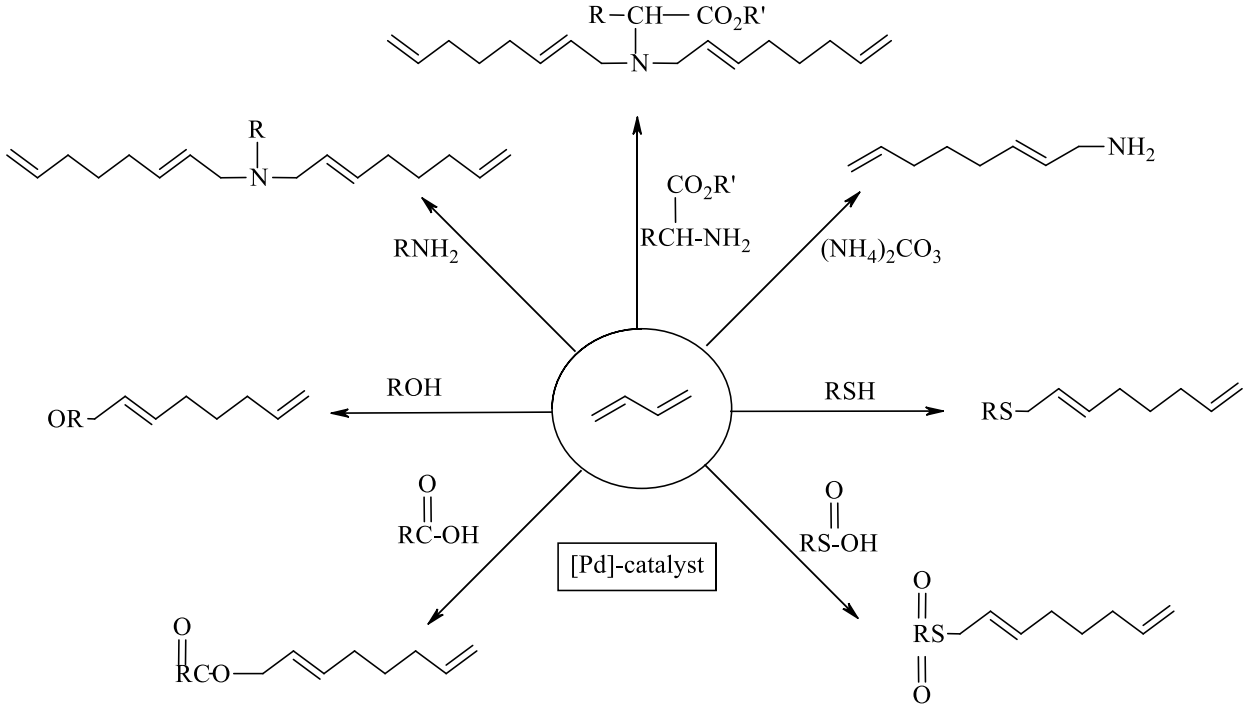
Scheme 7. Metal complex catalysis in chemistry of elemental sulfur.

This work stimulated the development of one of the most promising areas of modern chemistry - the catalytic activation of small and labile molecules in reactions with conjugated dienes (Scheme 8).[11]



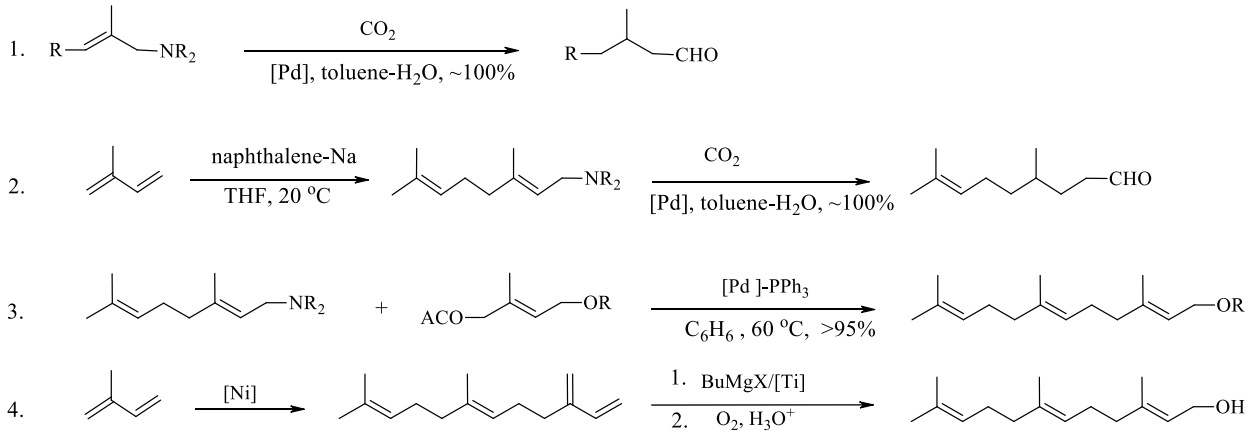
Scheme 8. Metal complex catalysis in chemistry of small molecules.

In continuation of studies in the chemistry of conjugated dienes, Dzhemilev and coworkers have implemented one of the largest programs on catalytic telomerization of cyclic and acyclic 1,3-dienes with compounds containing mobile hydrogen atom (Scheme 9).[12]



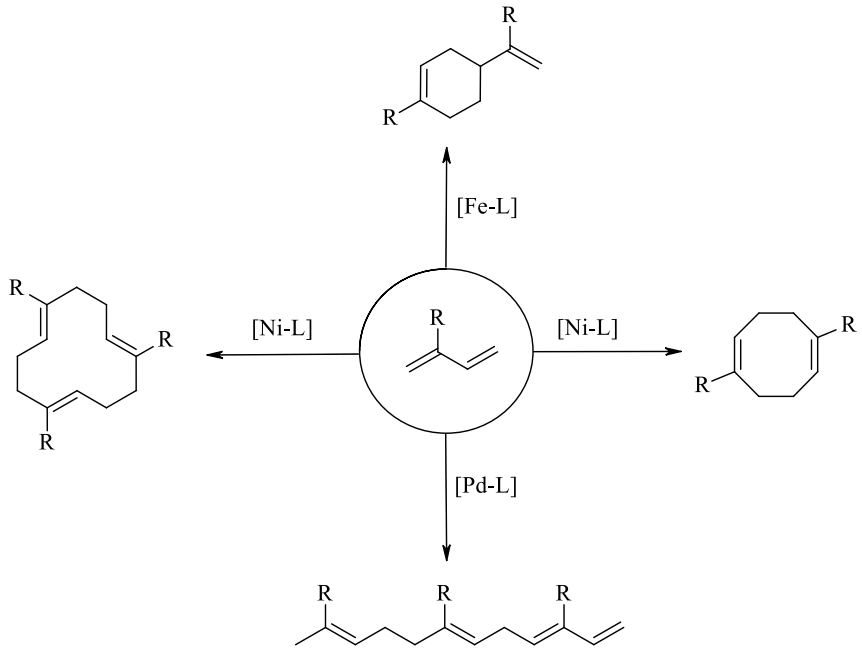
Scheme 9. Metal complex catalysis in chemistry of compounds containing mobile hydrogen.

His next efforts were devoted to linear oligomerization of conjugated dienes mediated by Fe, Co, Ni and Pd catalysts. These investigations made it possible to elaborate original catalytic procedures to synthesize (linear) regular isoprenoids from isoprene (Scheme10).[13]



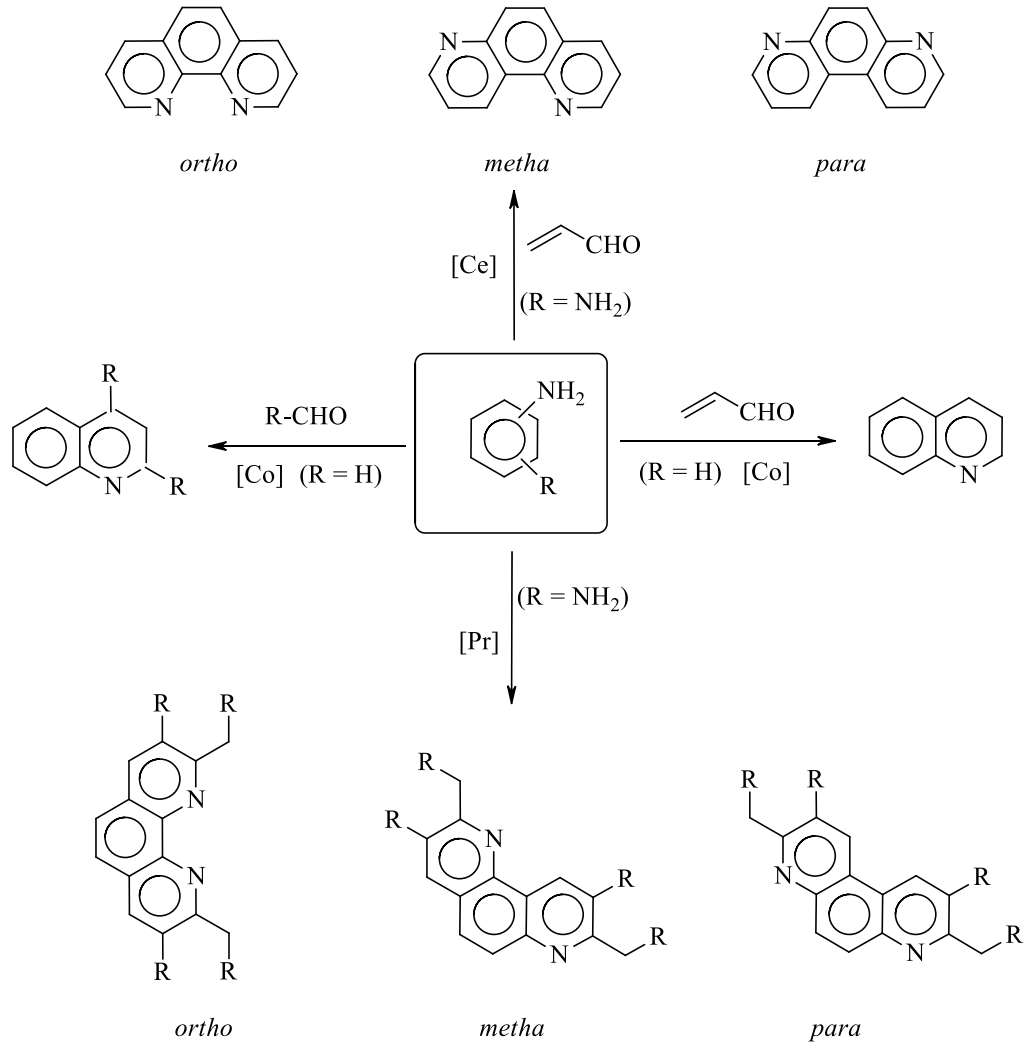
Scheme10. New reactions in synthesis of (linear) regular isoprenoids.

The valuable achievements of Dzhemilev and coworkers should also include the development and use of metal complex catalysis with new types of ligands-activators (L) such as esters of *ortho* and *metha* boric acid, siloxanes, silatranes, borotranes and small molecules (CO_2, SO_2). The wide use of these ligands allowed the elaboration of complex catalysts for regio- and stereoselective linear and cyclic oligomerization of conjugated dienes (Scheme 11).[14]



Scheme 11. Metal complex catalysts for cyclic and linear oligomerization of conjugated dienes.

Fundamental research on the chemistry of nitrogen heterocycles resulted in the development of efficient general methods for the synthesis of pyridines, quinolines, phenanthrolines, and naphthiridines via multicomponent condensation of aliphatic and aromatic amines with carbonyl compounds as well as co-trimerization of acetylenes with nitriles and chloroanhydrides with amines (Scheme 12).[15]



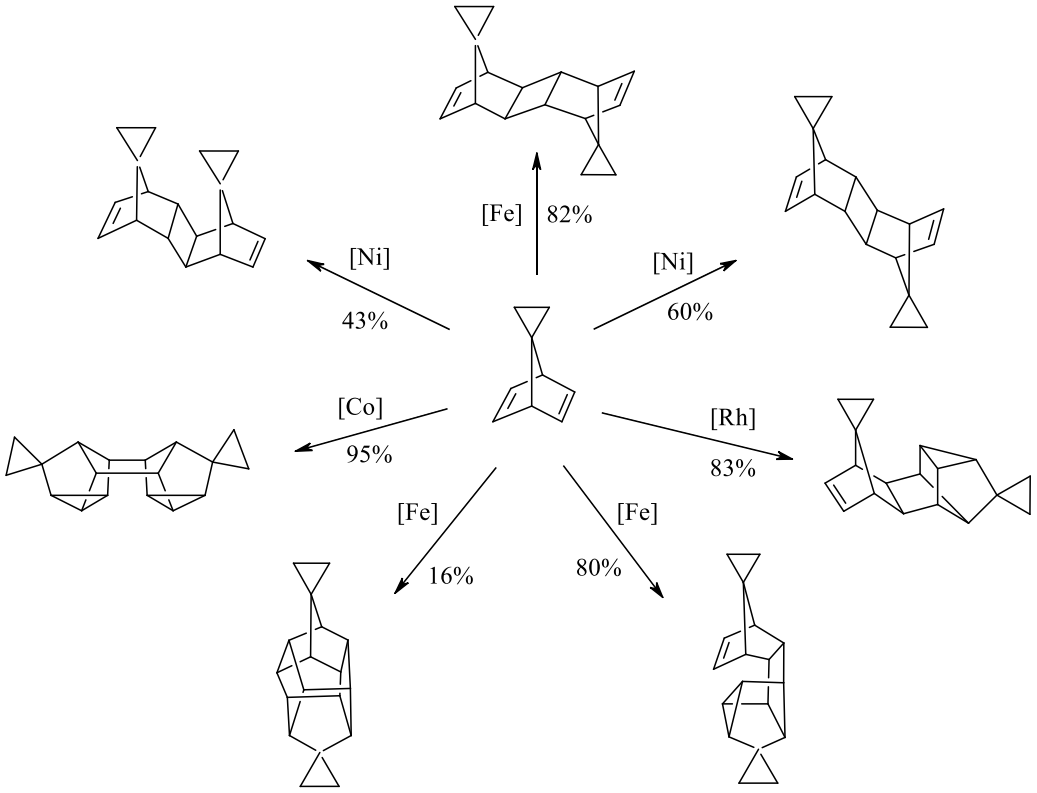
Scheme 12. Metal complex catalysis in chemistry of nitrogenheterocycles.

The synthesis of polycyclic and cage compounds is one of the most attractive areas in the realm of organic chemistry. Basic and applied research in the field of synthesis, properties and application of highly strained polycyclic compounds is the important focus area at the Scientific School under the leadership of Professor Dzhemilev. Among the variety of methods for

synthesizing bridged compounds, catalytic techniques permitting the single-stage transformations of relatively simple substances into the complex compounds rank high.

The implementation of this research program allowed the development of an effective strategy for the one-step synthesis of energy-rich polycyclic compounds constructed from three-, four- and five-membered cycles. More than 1500 types of strained cage hydrocarbons and their derivatives have been synthesized. The physico-chemical properties, stereochemistry, and energy characteristics of the most unique examples, have also been determined (Scheme 13).[14,16]

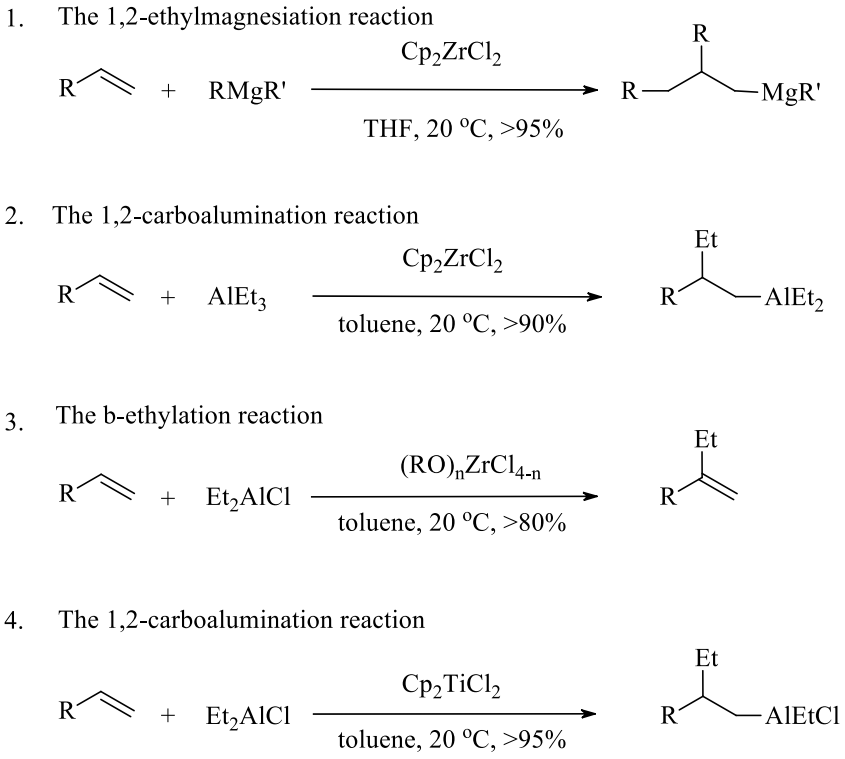
New general reactions and efficient methods to prepare strained polycyclic cage compounds of a specified structure have been discovered and investigated.



Scheme 13. Metal complex catalysis in synthesis of strained polycyclic "cage" compounds.

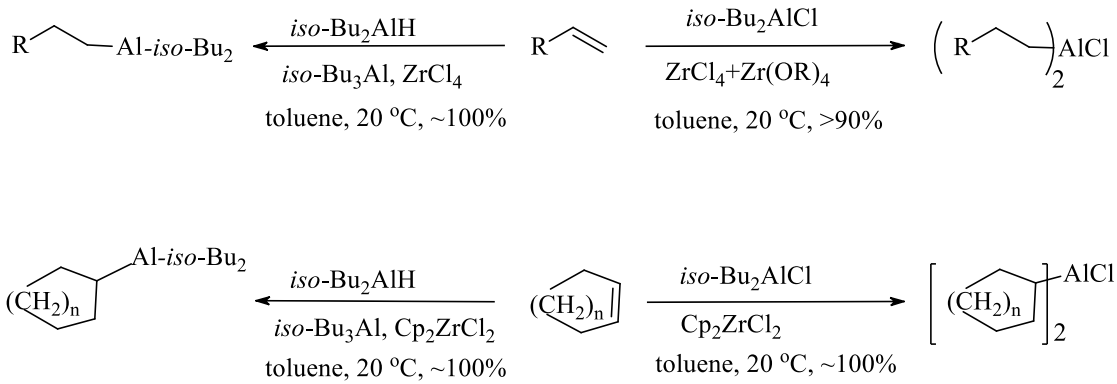
For the past 15–20 years Dzhemilev and coworkers have realized a major program focused on research priorities in catalytic activation of carbon–carbon, metal–carbon and metal–hydrogen bonds. Catalytic chemo-, regio- and stereoselective reactions of hydro-, carbo- and cyclometalation of olefins, dienes, acetylenes and allenes with alkyl and hydride derivatives of non-transition metals (Mg, Zn, Al, In, Ga, B) in the presence of Ti, Zr, Hf, Ta, and Co complexes as catalysts have been successfully performed. These findings stimulated further development of the fundamental catalytic 1,2-ethylmagnesiation, 1,2-carboalumination and β-ethylation reactions of non-activated olefins (Scheme 14).[17-27]

Probably, the most notable discovery of a chemist is that of a reaction that bears his name. The 1,2-ethylmagnesiation reaction is known throughout the world synthetic practice as the *Dzhemilev reaction*.



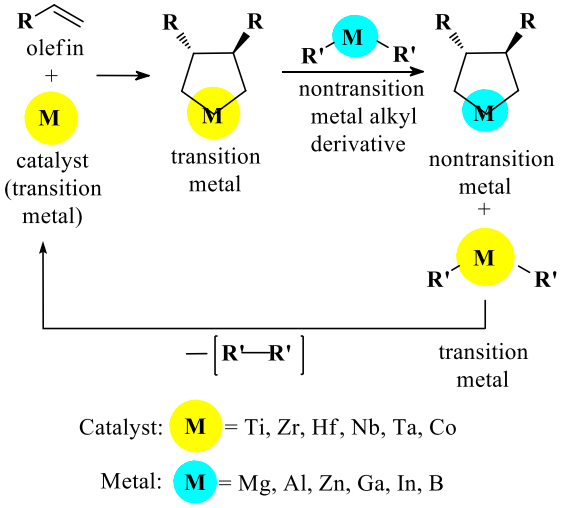
Scheme 14. The new fundamental reactions of non-activated olefins.

In addition to these reactions, the promise for commercial realization of procedures involving higher alanes (Bu^i_2AlH, Bu^i_2AlCl, Bu^i_3Al) and zirconium complex catalysts were also designed to use them for catalytic hydroalumination of different acyclic and cyclic olefins (Scheme 15).[19,20]



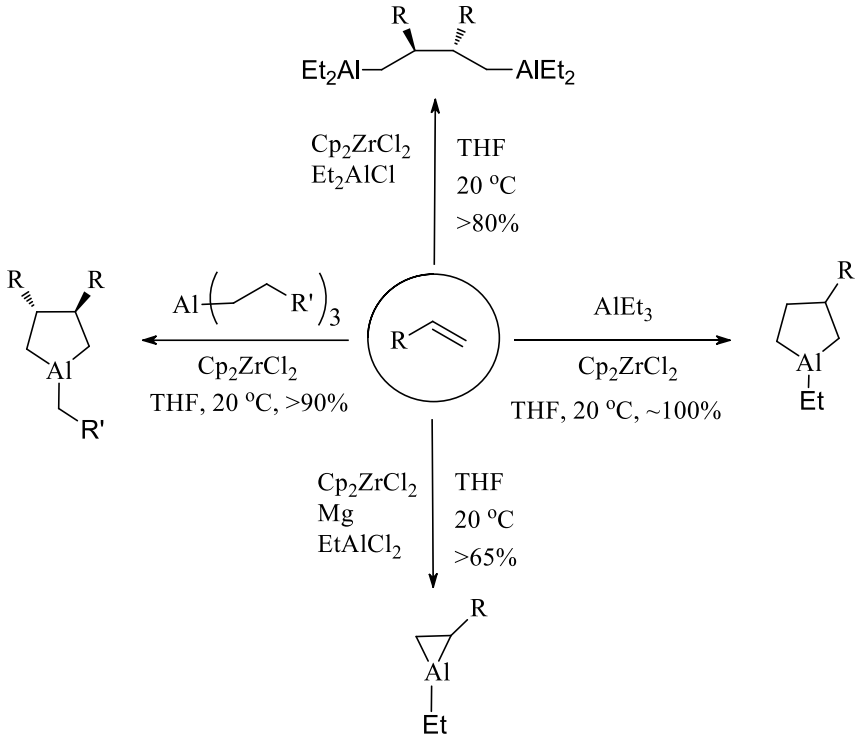
Scheme 15. The efficient methods for hydroalumination of cyclic and acyclic olefins.

The application of metal complex catalysts in the chemistry of non-transition metal compounds, as well as analysis and systematization of the results of investigations, enabled Dzhemilev and co-workers to discover the phenomenon of catalytic replacement of transition metal atoms (Ti, Zr, Hf, Ta, Ga, Co) in metallacarbocycles by non-transition metal atoms (Mg, Zn, Al, Ga, In, B), and to develop the new fundamental catalytic reactions of cycloalumination, cyclomagnesiation and cycloboration of olefins, acetylenes and allenes to afford the corresponding organometallic compounds (Scheme 16).[28]



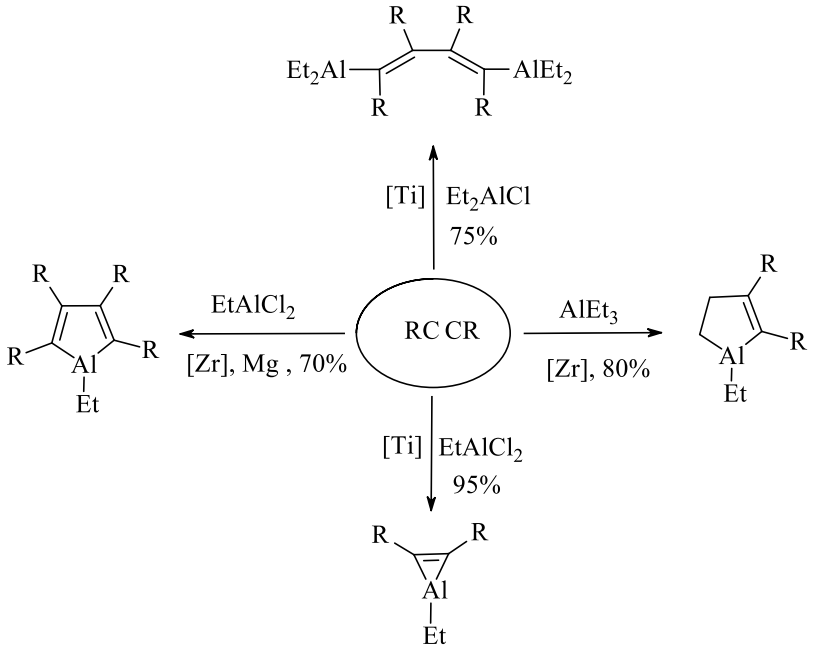
Scheme 16. Catalytic replacement of transition metal atoms in metallacarbocycles by the atoms of nontransition metals.

As a consequence of Dzhemilev's findings, new reactions and original one-pot methods to convert cyclic Mg- and Al-organic compounds into important cyclopropane, cyclobutane, five-membered heterocycles, 1,3-dienes, halogenated alkanes, macrocyclic ketones, α,ω-bifunctional monomers as well as other valuable materials have been developed and incorporated into the practice of organic and organometallic synthesis (Scheme 17).[29]



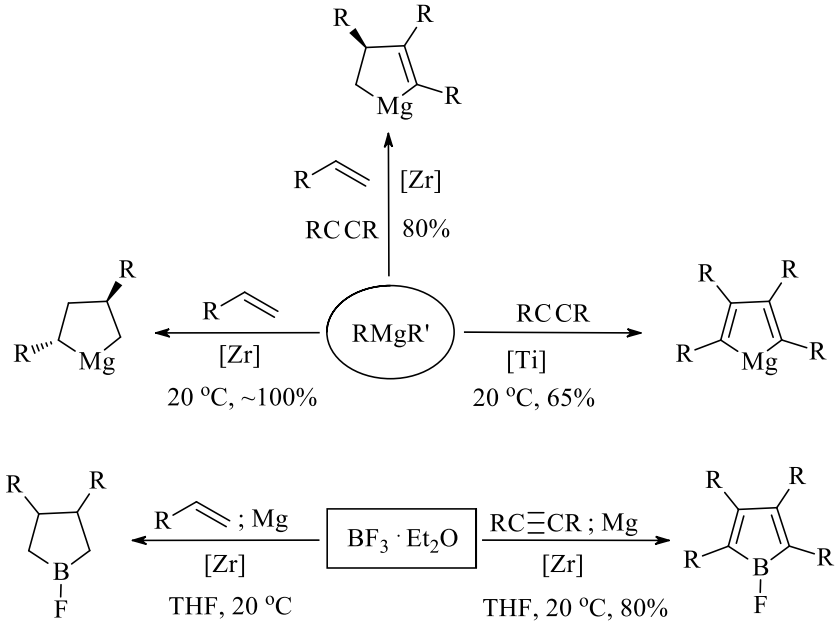
Scheme 17. Catalytic cycloalumination of acyclic α-olefins.

The elaborated reactions have been successfully applied to acetylenes (Scheme 18).[29]



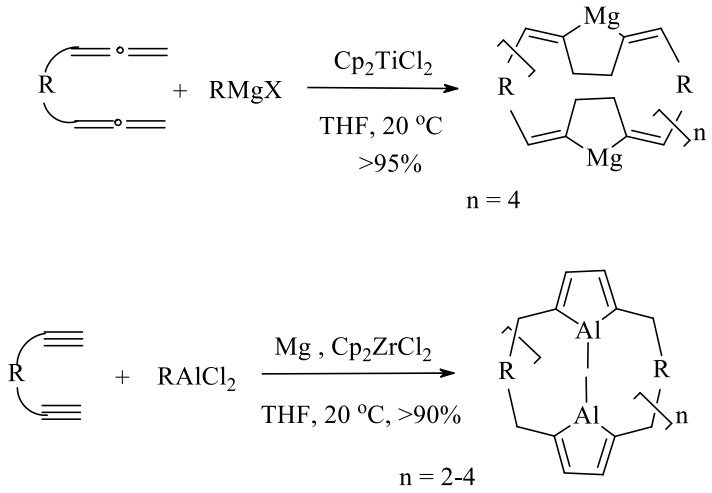
Scheme 18. Catalytic cycloalumination of acetylenes.

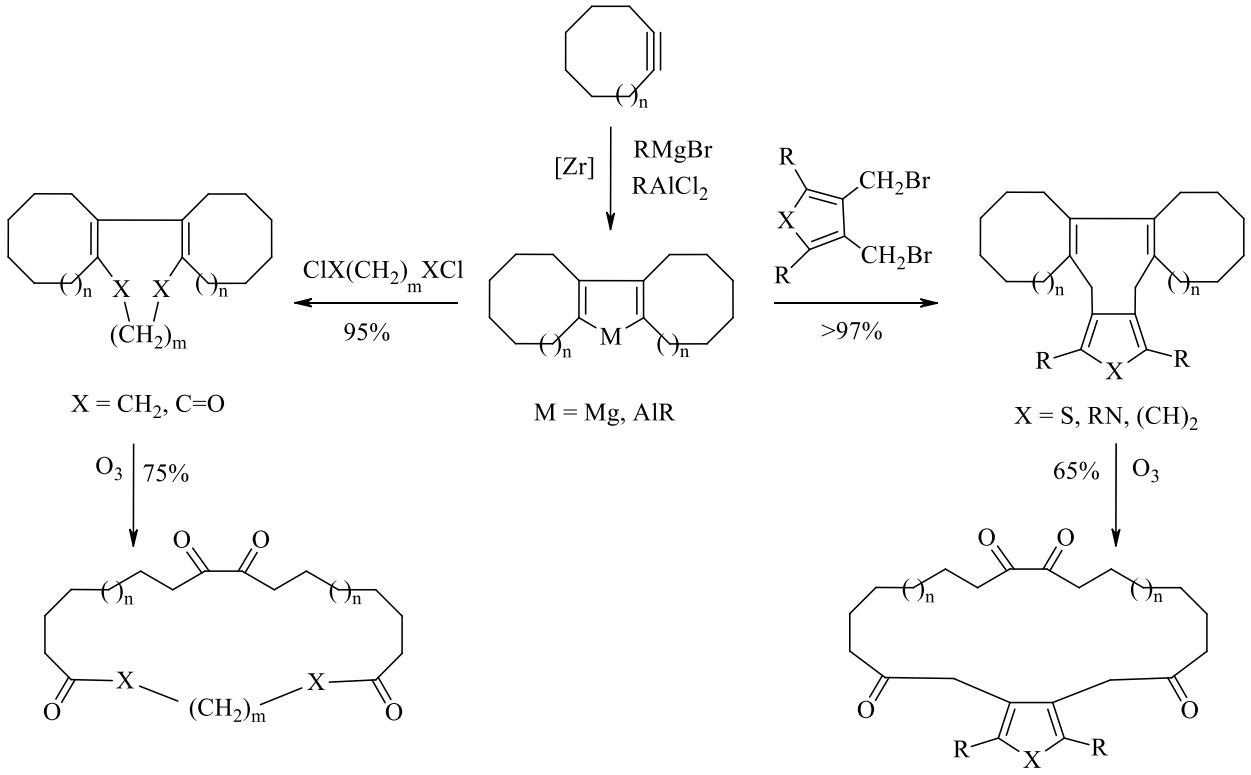
By analogy with the catalytic cycloalumination reaction, Dzhemilev was the first to carry out one-pot cyclomagnesiation and cycloboration to produce appropriate five-membered magnesa- and boracycloalkanes from olefins and acetylenes (Scheme 19).[30]



Scheme 19. Catalytic cyclomagnesiation and cycloboration of olefins and acetylenes.

Of particular interest and practical value are the design of metallacarbocycles and macrocycles using cycloalumination and cyclomagnesiation reactions catalyzed by Ti and Zr complexes (Scheme 20).[31,32]

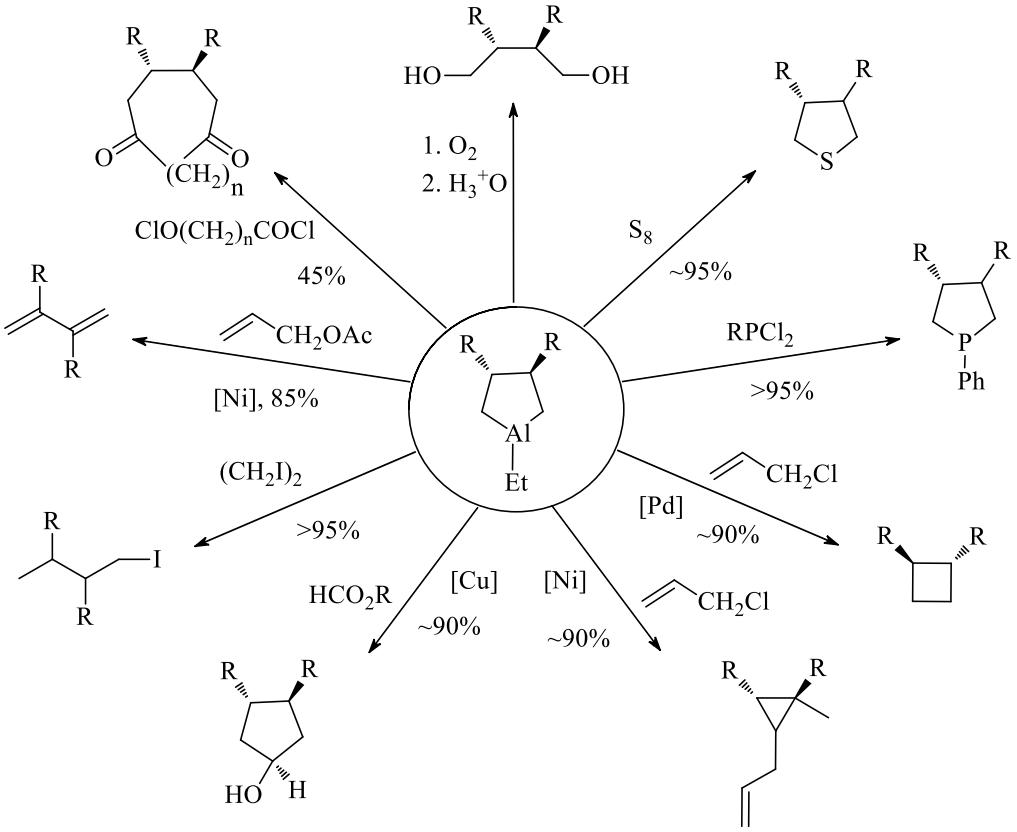




Scheme 20. Catalytic cyclometalation of α,ω-diallenes, α,ω-acetylenes and cycloalkynes in synthesis of gigantic metallacarbocycles and macrocarbocycles.

Basic and applied research conducted by Dzhemilev and co-workers in the field of organometallic chemistry of non-transition metal compounds with the use of catalysts, led to the development of new classes of organometallic and organic reactions, which are valuable in synthetic practice.

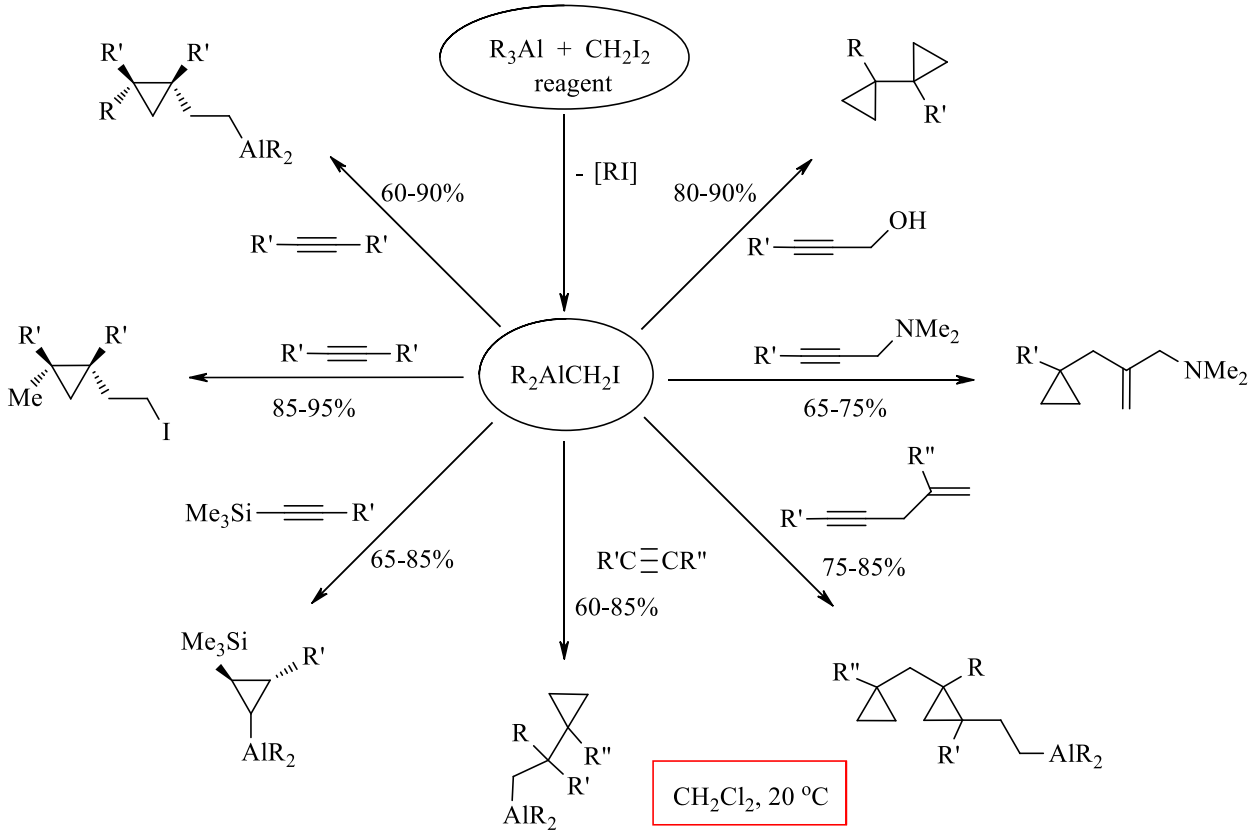
The wide synthetic potential of cyclic organoaluminum compounds involved in one-pot transformations of olefins into monomers, belonging to various classes of compounds, was demonstrated by the example of *cis/trans*-3,4-disubstituted aluminacyclopentanes (Scheme 21).[29]



Scheme 21. Single-stage transformations of α-olefins into practically important types of organic compounds.

In continuation of the investigations described above, a one-pot method for the direct conversion of mono- and disubstituted acetylenes into cyclopropanes (60–90%) was elaborated via the reaction between acetylene and $R_3Al–CH_3I_2$ to yield cyclopropane-containing organometallics. This method is general and may be applied to different acetylenes.

The results create new prospects for facile one-pot synthesis of both cyclopropanes and cyclopropane-containing organoaluminum compounds from acetylenes and aluminum carbenoids (Scheme 22).[33,34]



Scheme 22. Aluminum carbenoids as novel prospective reagents in acetylene chemistry.

Today, the research interests of Professor Dzhemilev deal with hydrocarbon clusters, *viz.*, fullerenes, their selective functionalization, studies of physico-chemical properties and, of course, practical applicability. His attention is focused on gigantic polyfunctinal carbocycles and synthetic transformations of propargyl amines.

On May 15, 2011, Usein Memetovich Dzhemilev celebrates his 65th birthday.

On behalf of colleagues, all his friends and students the author respectfully congratulates Professor Dzhemilev on attaining his 65th birthday and wishes him good health, creative success, new scientific achievements and discoveries.

Dear Professor and Teacher, our Congratulations!

Dr. Vladimir D'yakonov
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Selected Publications of Professor Usein Memetovich Dzhemilev

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