Metal Complex Catalysis in Organic and Organometallic Synthesis

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Abstract

Some directions and results of scientific research in the field of metal complex catalysis initiated by Academician G. A. Tolstikov as well as new directions successfully developed today by his followers are considered. The main attention is given to reactions, efficient reagents and promising preparatory methods of metal complex catalysis in organic and organometallic synthesis.

Key words: catalysis, organic and organometallic synthesis, unsaturated compounds, scientific school of Academician G. A. Tolstikov

Contents

INTRODUCTION

January, 2008 marks the 75th anniversary of Academician of the RAS G. A. Tolstikov, an outstanding organic chemist, the head of a brilliant scientific school of chemists. The achievements of this scientific school are known far outside our country; it supports a high authority of Russia on the International scientific Olympus.

The present review is devoted to the consideration of some key directions of research initiated by Academician G. A. Tolstikov in the field of metal complex catalysis with reference to the problems of chemistry of unsaturated compounds. For the objective analysis of the achievements, as well as for distinct ranging ideas put forward and realized by G. A. Tolstikov's scientific school the results obtained are expounded according to a chronological sequence covering both the Ufa period of Academician G. A. Tolstikov's activity (1970–1994) and the next years of his work in the Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS.

HYDROPEROXIDE OXIDATION OF ORGANIC COMPOUNDS CATALYZED BY MOLYBDENUM COMPLEXES

One could say with no exaggeration that the researches in the field of hydroperoxide oxidation of organic compounds under the action of transition metal complexes initiated by Professor G. A. Tolstikov in the beginning of

1970ths at the Institute of Chemistry, Bashkiria Branch of the USSR Academy of Sciences (nowadays the Institute of Organic Chemistry, Ufa Scientific Centre of the RAS), as well as the accumulated experimental operational experience in this field have formed a strong basis for expanding fundamental and applied works for the next years according to the scientific direction "Metal complex catalysis in organic and organometallic synthesis" [1].

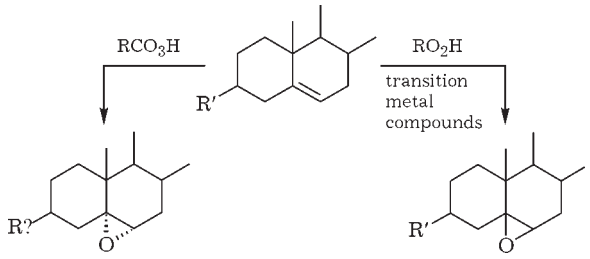
At the first stage we have engaged in the studies on the stereochemistry of epoxidation of olefines (by the example of Δ^5-steroids) by means of *tert*-amyl hydroperoxide, catalyzed by molybdenum complexes. It has been established that the operation with hydroperoxides less hazardous than with such classical epoxidizing reagents as peracids widely used in synthetic practice.

It should be noted that by the moment of beginning the studies on the hydroperoxide oxidation the works by V. Bril, M. Sheng and D. G. Zayachek concerning the epoxidation of simplest olefines by means of such hydroperoxy species as *tert*-butyl, *tert*-amyl, ethylbenzene and cumene hydroperoxides, with the participation of Ti, V, W, Cr and Mo complexes as catalysts had been already published in the world literature. The best results have been obtained with the complexes of molybdenum.

G. A. Tolstikov first has suggested to study the stereochemistry of hydroperoxide-based epoxidation basing on classical objects such as natural steroids and terpenes [2]. The first experiments concerning the oxidation of Δ^5-steroids have demonstrated that the stereochemistry of hydroperoxide epoxidation fundamentally differs from stereoselectivity of other epoxidizing reagents described elsewhere. In each experiment mainly β-oxides were obtained, whereas other reagents resulted in the formation of mostly α-oxides. These results indicated the attack of the double bond in Δ^5-steroids by such a reactant as hydroperoxide- salt molybdenum to proceed from the most shielded β-side.

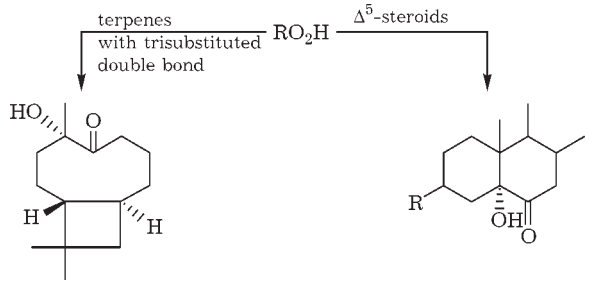
A detailed investigation of the mentioned effect has allowed the researchers to establish that the this reagent is first of all coordinated with the heteroatom bound with C^3-β atom of Δ^5-steroids from the least shielded α-side. Further there proceeds a β-attack of double bond by an activated hydroperoxide molecule to results in the formation of difficult to obtain β-oxides of Δ^5-steroids [3].

The studies carried out have demonstrated that the reaction of β-epoxidation of Δ^5-steroids and other related natural compounds by means of hydroperoxides in the presence of Mo-containing complex catalysts is of general nature, and it offers new possibilities in the field of the synthesis of stereochemically inaccessible derivatives from various classes of organic compounds.

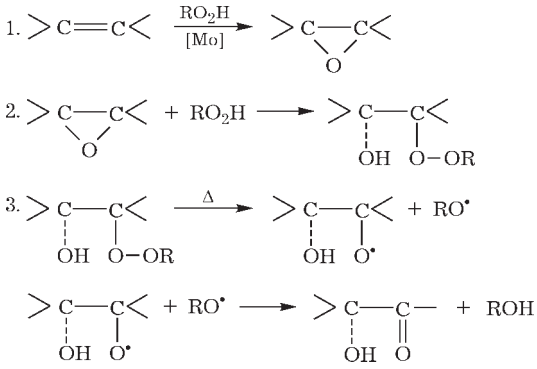


Moreover, in the next experiment concerning the epoxidation of diosgenine acetate by the excess of *tert*-amyl hydroperoxide in the presence of catalyst wherefore $MoCl_5$ was used, the researchers obtained acetate such as 5-oxa-6-ketodiosgenine with a high yield instead of the expected α-oxide of corresponding Δ^5-steroid [4].

We have not realized at once that we had discovered the reaction of one-stage oxyketonation of olefines with triply substituted double bond. The subsequent research concerning the margins of application for the method mentioned by the examples of oxyketonation of steroids, mono-, di- and triterpenes have demonstrated that the reaction is of general nature and it could be widely used in synthetic practice.



Basing on the experimental results obtained G. A. Tolstikov have proposed the most probable scheme of the mechanism for the formation of oxyketones:



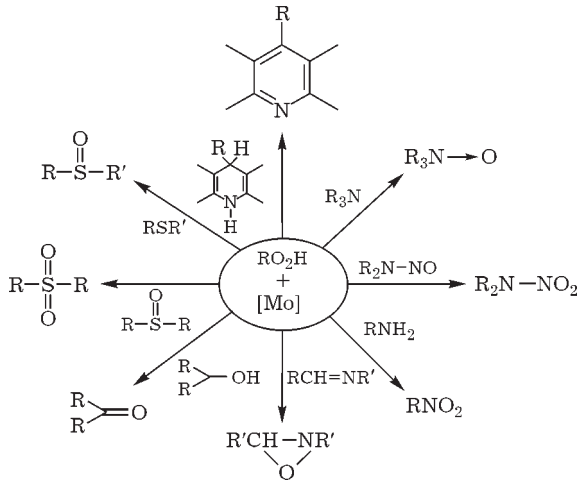
Homolytical transformations presented in this scheme are based on the chemistry of alkylhydroperoxides. However, these reactions have been considered without taking into account the role of intermediate molybdenum complexes.

Further this fertile scientific field was profoundly and carefully "ploughed" by Dutch chemist K. B. Sharpless who succeeded in establishing a detailed mechanism for hydroperoxide oxidation of olefins catalyzed by transition metal complexes as well as identifying the structures of catalytically active complexes. For these works K. B. Sharpless has been rewarded with the Nobel Prize in 2001.

After obtaining so bright results with respect to the hydroperoxide subject G. A. Tolstikov has charged me with studies of the synthetic potentialities of such reagent as hydroperoxide – molybdenum salt in oxidation reactions for various classes of organic compounds – amines (including nitrosoamines), nitrogen-containing heterocyclic compounds, sulphides, sulphoxides, dehydropyridines, alcohols, and carbohydrates.

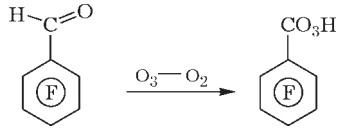
We have found that the reagent mentioned is not only competitive with classical oxidizing reagents in particular, peracids) for the efficiency, reaction selectivity and preparative value, but also surpasses them in the availability and the simplicity of performing the reaction [5, 6].

In addition, another reaction which we have discovered during these studies should be mentioned. In the middle of 1975 Prof. A. M. Moiseenkov (Zelinsky Institute of Organic Chemistry, RAS, Moscow) and Prof. G. B. Bylina (Byelorussia) have suggested us to engage in the studies on oxidizing capabilities such a new reagent as *meta*-carbmethoxyperbenzoic acid formed in the *meta*-carbmethoxybenzaldehyde (a waste from tetraphtalic acid manufacture) oxidation by ozon-oxygen mixture [7].

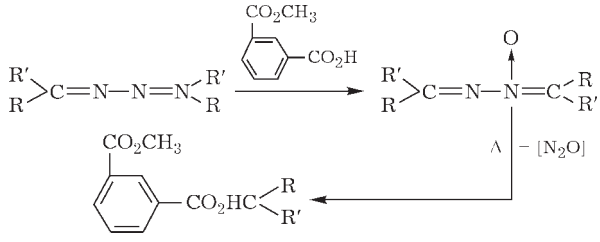


It has been established, that the reagent mentioned exhibits a high stability, whereas as far as the oxidizing ability is concerned, it is similar to that of *meta*-chloroperbenzoic acid widely used abroad.

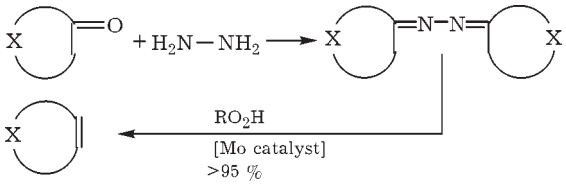
By analogy with the method for *meta*-carbmethoxyperbenzoioc acid we have for the first time obtained stable pentafluoroperbenzoic acid, which pentafluoroperbenzoic acid surpasses all the peracids known up till now in reactivity [8].



So, after the oxidation of ald- and ketazines of *meta*-chloroperbenzoic acid we obtained oxides of azines those thermally decomposed under the conditions chosen and converted into corresponding esters of *meta*-carbmethoxybenzoic acid according to the following scheme [9]:



The results obtained have led me to the idea that peracid in this reaction could be replace by a reagent such as hydroperoxide–molybdenum in order to obtain corresponding olefins. This idea has been successfully realized with ketazines obtained from cyclic ketones



Thus, we have succeeded in discovering another reaction that can allow researchers to convert cyclic ketones into olefins with a high yield using only one preparative stage [10].

By the middle of 1975 the studies in the field of hydroperoxide oxidation were almost completed and a new stage began such as a metal complex period which proceeds to this very day as well. At the initial stage of these researches we have engaged in cyclooligomerization of conjugated dienes.

A primary goal formulated by G. A. Tolstikov consisted in mastering the reactions of isoprene cyclodimerization and trimerization to produce 1,5-dimethyl-*cis,cis*-cyclooctadiene and 1,5,9-trimethyl-*trans,trans,trans*-cyclododecatriene, respectively [11].

To the point, the studies in this direction have just begun with solving the mentioned problem, and for the next years new problems appeared and the first successes of G. A. Tolstikov's scientific school have exhibited in the field of chemistry conjugated dienes with the participation of complex catalysts [12–14].

In several years these studies were already being performed according to the following prospective directions:

• Linear and cyclic oligomerization of conjugated dienes and olefins including strained ones under the action of metal complex catalysts.

• Heterocyclization of conjugated dienes with small molecules and atoms, as well as aliphatic, aromatic and heteroaromatic primary аминов with carbonyl compounds.

• Metal complex catalysis in the chemistry of organosulphur compounds.

• Catalytic telomerization of conjugated dienes with compounds containing labile hydrogen atoms.

• Hydro- and carbometallation of olefins by means of Mg and Al alkyl and hydride derivatives with the participation of Ti, Zr, Hf and Ta complexes.

This is an incomplete list of scientific research directions developed within the period from 1972 to 1991.

Since 1992 the research in the field of organic and organometallic synthesis with the participation of metal complex catalysts were continued at a newly organized Institute of Petrochemistry and Catalysis, RAS (Ufa), and the collective of researchers engaged in the aforementioned work has concentrated the efforts on the development of the following directions:

– Cyclometallation of olefins, acetylenes, allenes by means of Mg, Zn, Al, Jn, Ga, B alkyl derivatives catalyzed by Ti, Zr, Hf, Ta and Co complexes.

– Chemistry small, medium and giant carbo-, hetero- and metallocarbocycles on the basis of non-transition metals (Mg, Al, B).

– Selective heterofunctialization of carbon clusters with the participation of complex catalysts.

– New organometallic reagents for the cyclopropanation of acetylenes, allenes and olefins.

– Mechanisms of catalytic reactions with the participation of transition metal complexes.

– Multicomponental reactions, catalyzed by transition metal complexes for the synthesis of cyclic and acyclic heteroatomic compounds.

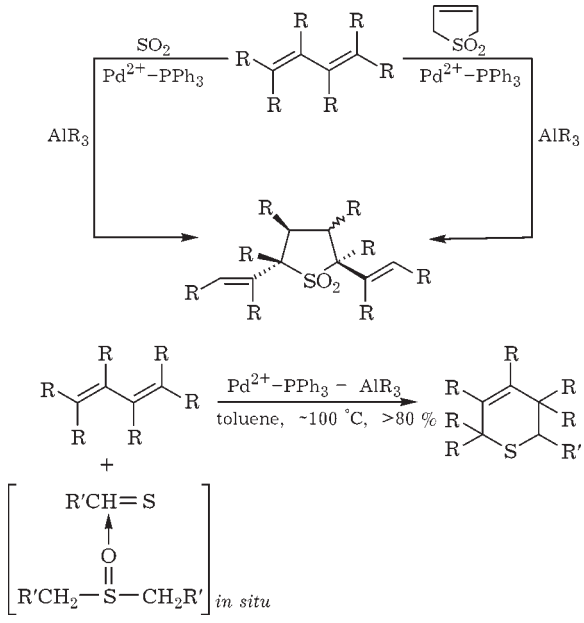
ORGANIC AND ORGANOMETALLIC SYNTHESIS WITH THE PARTICIPATION OF METAL COMPLEX CATALYSTS

Already at the initial stage of coming-to-be the research in the field of metal complex catalysis we postulated the potentiality of applying homogeneous complex catalytic systems for the synthesis of organosulphur compounds those represent poisons for heterogeneous catalysts.

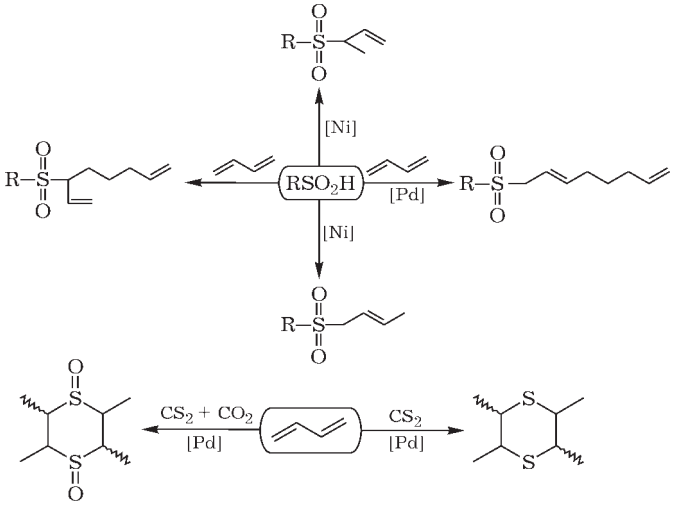
On short notice we succeeded in considerable advancing these work and in developing a new research field such as one-stage catalytic synthesis of cyclic and acyclic unsaturated organosulphur compounds with the participation of homogeneous metal complex catalysts.

The realization of this work program has allowed us to develop novel fundamental reactions, general principles and methods for heterocyclization of conjugated dienes and acetylenes with small molecules and atoms as well as heteroolefins, with the obtaining of a wide class of practically important sulphur-containing compounds [13, 15].

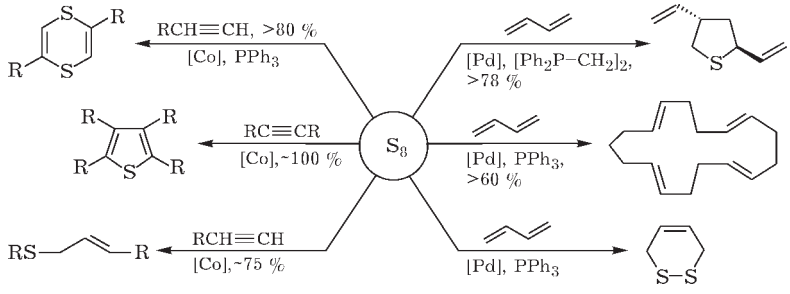
Some novel reactions developed while performing the work program concerning the cre-



Scheme 1.



Scheme 2. Metal complex catalysis in the chemistry of sulphonic acids and carbon bisulphide.



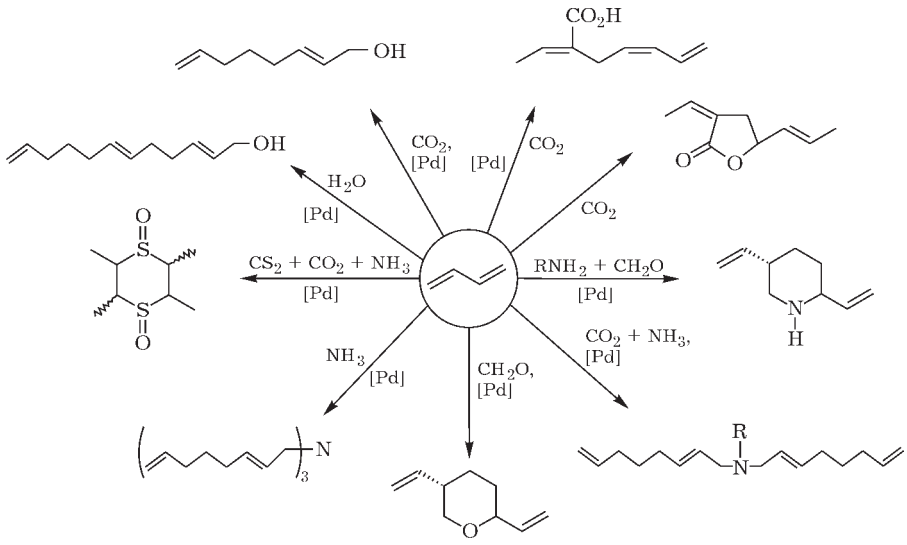
Scheme 3. Metal complex catalysis in the chemistry of elemental sulphur (S_8).

ation of prospective methods for the synthesis of organosulphur compounds, are presented in Schemes 1–3.

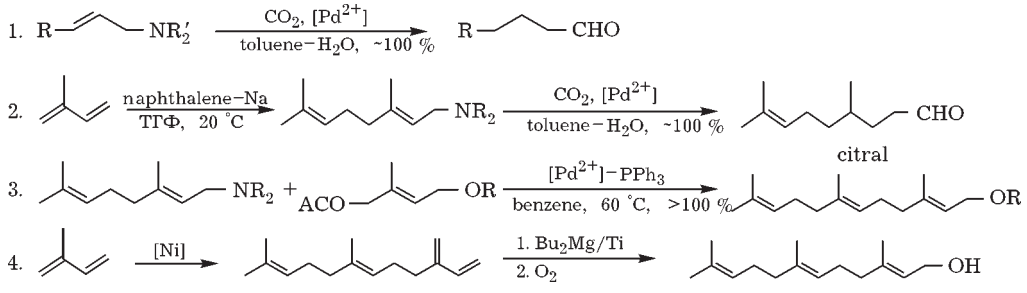
The aforementioned cycle of research has been completed with the development and manufacturing application of efficient flocculating agents, hydrogen sulphide neutralizers, bactericides, inhibitors of sulphate-reducing bacteria, efficient extracting agents and sorbents, pharmaceutical preparations for medicine and agriculture.

The representatives of G. A. Tolstikov's scientific school have drawn an important contribution to the development of one of the most prospective and promising directions of modern chemistry such as catalytic activation of small and low-stable molecules in the reactions with conjugated dienes, and acetylenes.

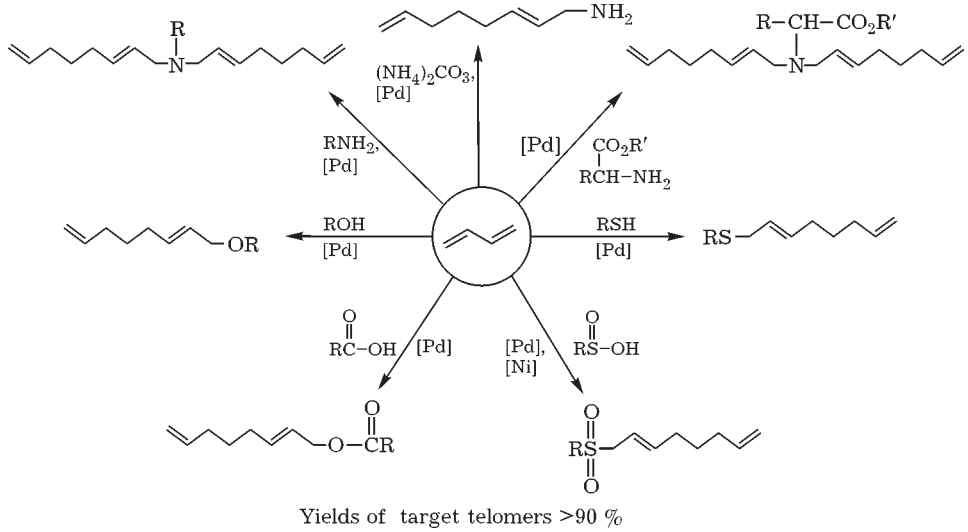
Moreover, they have performed priority studies on the catalytic activation of carbon dioxide, formaldehyde, carbon disulphide, water, ammonia with the obtaining of practi-



Scheme 4. Metal complex catalysis in the chemistry of small molecules and atoms.



Scheme 5. Novel reactions in the synthesis of linear isoprenoids.



Yields of target telomers >90 %

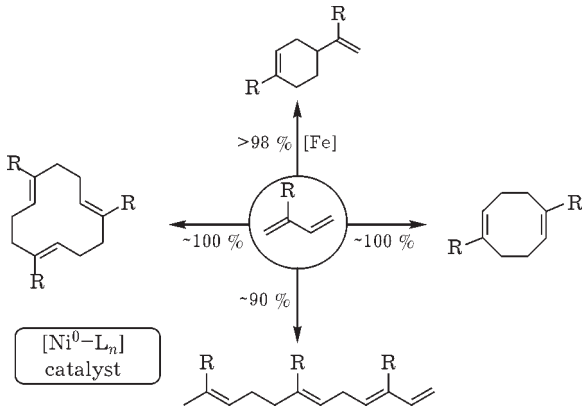
Scheme 6. Metal complex catalysis in the chemistry of compounds containing a labile hydrogen atom.

cally important oxygen-, nitrogen- and sulphur-containing heterocycles, higher amines, alcohols, carbonic acids and other valuable multifunctional compounds (Scheme 4) [13].

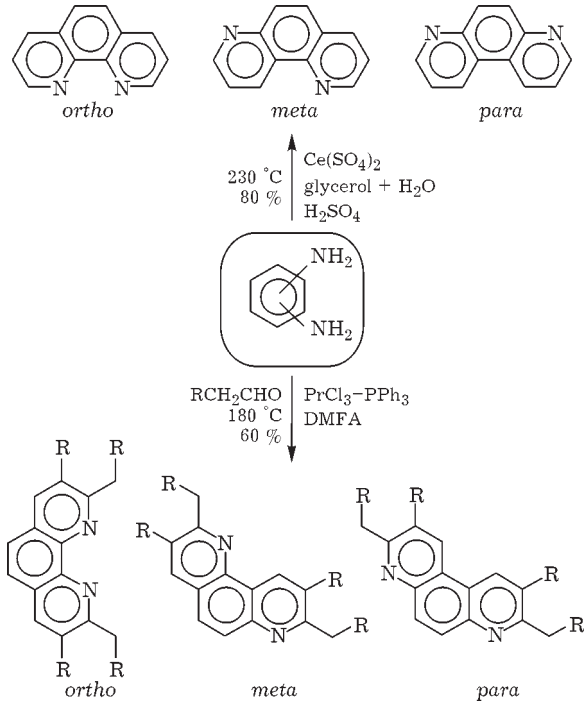
Novel reactions developed according to this direction were used for the synthesis of practically important isoprenoids; in particular citral, farnesol and other derivatives were obtained (Scheme 5).

The researchers G. A. Tolstikov's scientific school have accomplished one of the most large-scale programs concerning catalytic telomerization of conjugated dienes and trienes with aliphatic, aromatic and heteroaromatic primary and secondary amines, alcohols, carbonic and sulphinic acids. This work has resulted in the development of the methods for the synthesis of higher unsaturated amines, amino acids, aminoalcohols, esters of carbonic and sulphinic acids, as well as alcohols (Scheme 6) prospective for practical realization [13].

Due to the investigations carried out aiming at the studies on the mechanism of the formation of metal complex catalysts with the participation of nickel complexes in the reactions of homo- and co-oligomerization of conjugated dienes, the researchers for the first time succeeded in introducing into practice of homogeneous metal complex such activator ligands (L) as the esters of ortho- and metaboric acids, siloxanes, silatranes, boratranes and small molecules (CO_2, SO_2). Basing on these results, catalytic systems with the activity and selectivity earlier unachievable have been obtained both in Russia and abroad.



Basic research in the field of chemistry of nitrogen-containing heterocycles have resulted in the development of general methods for the synthesis of pyridines, quinolines, naphthyridines and phenantrolines prospective for practical realization, based on multicomponent condensation of aliphatic and aromatic amines with carbonyl compounds as well as co-trimerization of acetylenes with nitriles under the action of metal complex catalysts [16].



Together with our colleagues from the laboratory No. 5 of the Zelinsky Institute of Organic Chemistry, RAS (head of the laboratory being Academician O. M. Nefedov) we have developed a new strategy for single-stage catalytic synthesis of polycyclic compounds with unique structure. New general reactions were discovered for obtaining strained polycyclic compounds constructed of three-, four- and five-membered cycles [17].

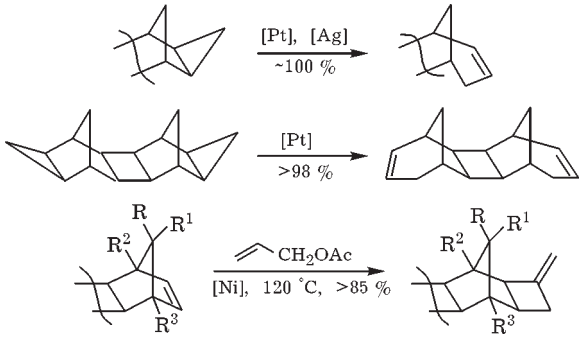
As a result, more than 1500 practically important polycyclic hydrocarbons and their derivatives were synthesized, as well as physical and chemical properties; stereochemistry and energy characteristics have been studied for the most promising samples whose manufacture was mastered on an experimental industrial scale.

In order to realize this work program we have created for the first time in the world practice a single reactor method for cyclopropanation of olefins with no use of toxic and explosive diazonium compounds.

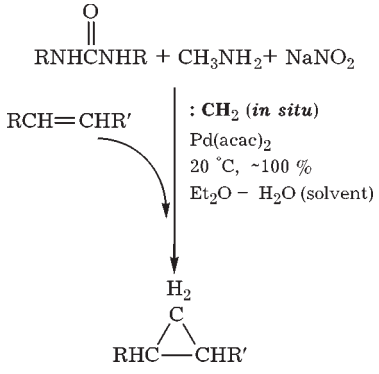
Research performed in this direction allowed fixing the priority of the Russian scientists in the field of synthesis and application of highly strained polycyclic structures, as well as implementing the technologies for obtaining novel materials and products with record characteristics.

Some novel reactions developed within the framework of the mentioned program are presented in Schemes 7, 8.

For the last 10–15 years, priority directions have been developed in the field of catalytic activation of carbon–carbon, metal–carbon and metal–hydrogen bonds, which allowed researchers to carry out chemo-, regio- and stereoselective reactions of catalytic hydro-, carbo- and cyclometallation of olefins, dienes, acetylenes, allenes with the help of alkyl and hydride derivatives of non-transition metals (Mg, In, Al, Zn, Ga, B, *etc.*) with the participation of Ti, Zr, Hf, Ta, Co and other transition metal complexes as catalysts. As a result, fundamental reactions of carbomagnesiation and carboalumination of α-olefins by means of RMgR′, Et_2AlCl, $AlEt_3$ with the participation of complex catalysts based on Ti and Zr compounds have been developed [18–22].



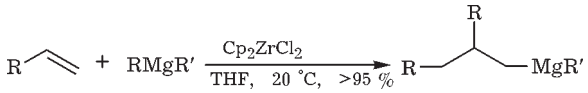
Scheme 7.



Scheme 8. Novel single-reactor method for catalytic cyclopropanation of olefins without preliminary diazomethane obtaining.

CATALYTIC ETHYLMAGNESIATION OF OLEFINS WITH NON-ACTIVATED DOUBLE BOND BY MEANS OF RMgX AND R_2Mg

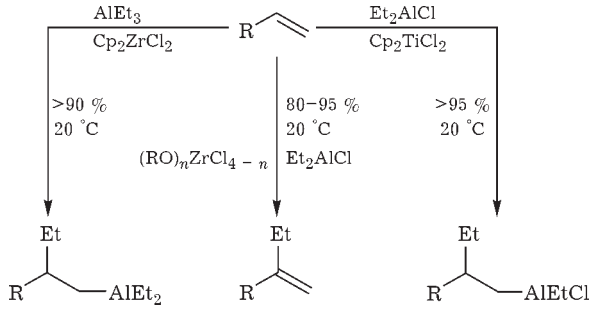
This reaction has received the name Dzhemilev reaction in the world literature; it is widely used in synthetic practice:



In this series of the studies the following reactions were discovered:

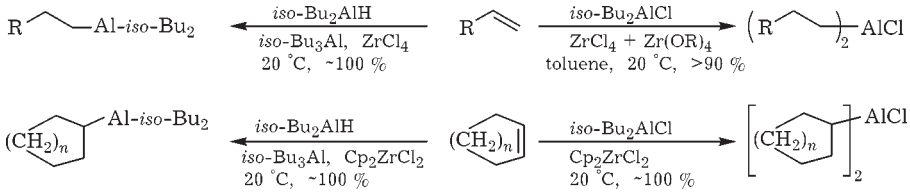
– catalytic 1,2-carboalumination of α-olefins with Et_2AlCl and $AlEt_3$ under the action of Ti and Zr complexes;

– β-alkylation of olefins by means of Et_2AlCl catalyzed by $(RO)_nZrCl_{4-n}$.



Alongside with these achievements, efficient methods are developed for catalytic hydroalumination of cyclic and acyclic olefins by means of *iso*-Bu_2AlH, *iso*-Bu_2AlCl, *iso*-Bu_3Al (Scheme 9).

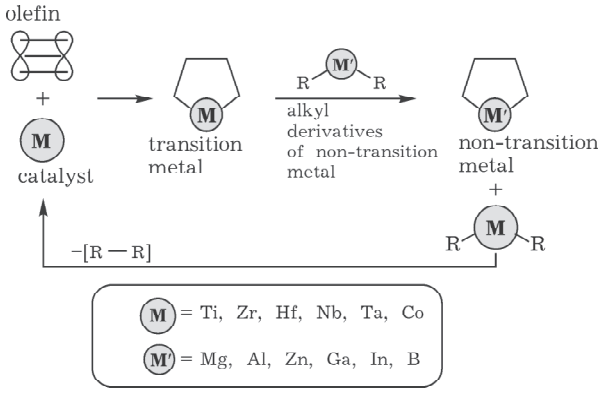
The implementation of the methods of metal complex catalysis in the chemistry of organometallic compounds of non-transition metals has allowed us to discover a phenomenon of catalytic substitution of transition metal atoms (Ti, Zr, Hf, Ta, Hb, Co) in metallocarbocycles



Scheme 9.

by non-transition metal atoms (Mg, Zn, Al, Ga, In, B) as well as to develop novel reagents and fundamental reactions of catalytic cycloalumination, cyclomagnesiation and cycloboration of olefins, acetylenes and allenes.

These studies marked the beginning of the development of a new research field such as the chemistry of small, medium and macrometallocycles containing non-transition metals.

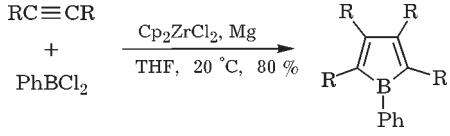


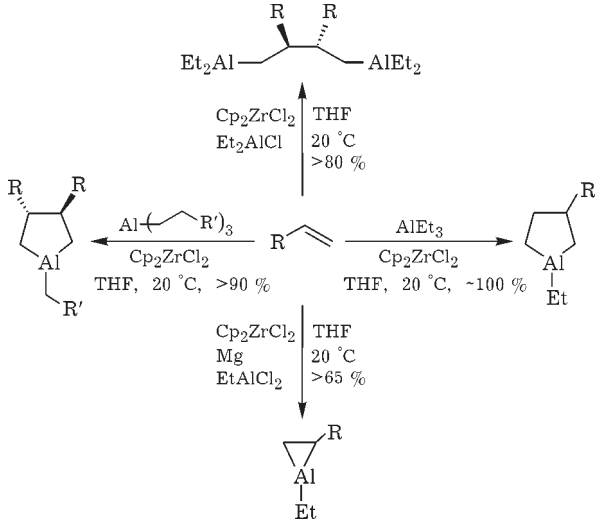
NOVEL REACTIONS OF ORGANOMETALLIC COMPOUNDS OF NON-TRANSITION METALS

The mentioned above research direction is literally "sparkling" with novel reactions and non- trivial transformations of Al- and Mg-organic compounds under the action of metal complex catalysts (Schemes 10, 11).

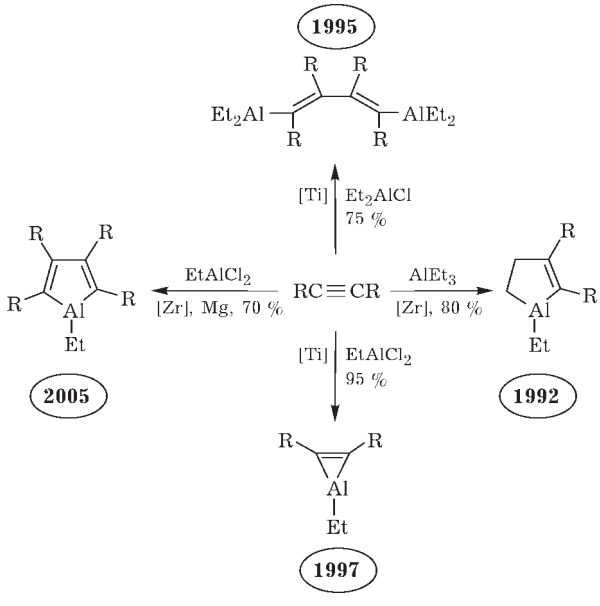
Catalytic cyclomagnesiation of olefins and acetylenes with the help of RMgX and Et_2Mg, catalyzed by Zr complexes allows researchers to obtain magnesacyclopentanes, magnesacyclopentenes and magnesacyclopentadienes with a high yield (Scheme 12).

Catalytic cycloboration of acetylenes by means of such a reagent as $PhBCl_2$ in the presence of a halogenide ion acceptor (metallic Mg) as well as such a catalyst as Cp_2ZrCl_2.

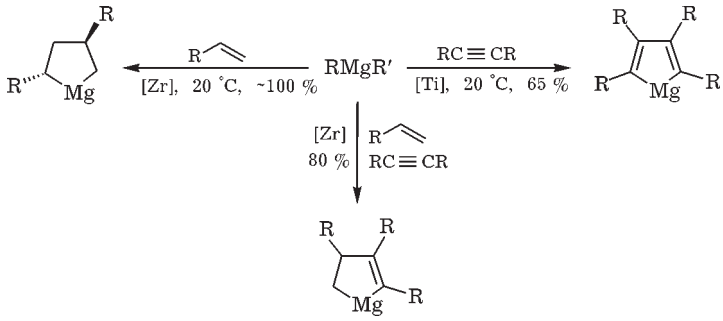




Scheme 10. Cycloalumination of cyclic and acyclic olefins.

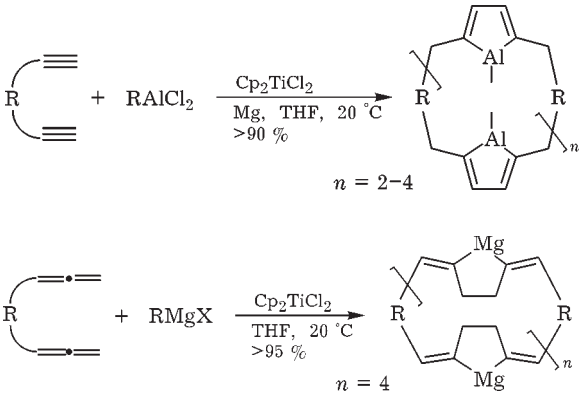


Scheme 11. Cycloalumination of acetylenes.



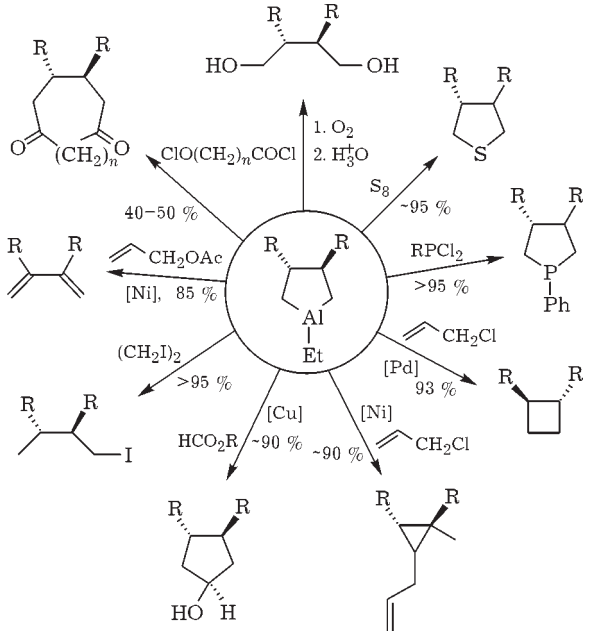
Scheme 12.

As the result of research performed in the field of catalytic cyclometallation of acetylenes and allenes within the recent two or three years, universal single-reactor methods were developed for designing giant organometallic macrocycles of a universal purpose.

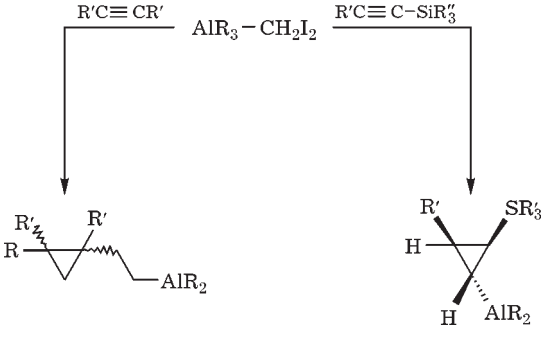


The fundamental and applied research in the field of chemistry of non-transition metal organometallic compounds with the use of complex catalysts based on transition metals have allowed us to develop novel classes of organic and organometallic reactions those are widely used nowadays in the preparative chemistry.

Some of the single-stage synthetic methods developed are presented below:

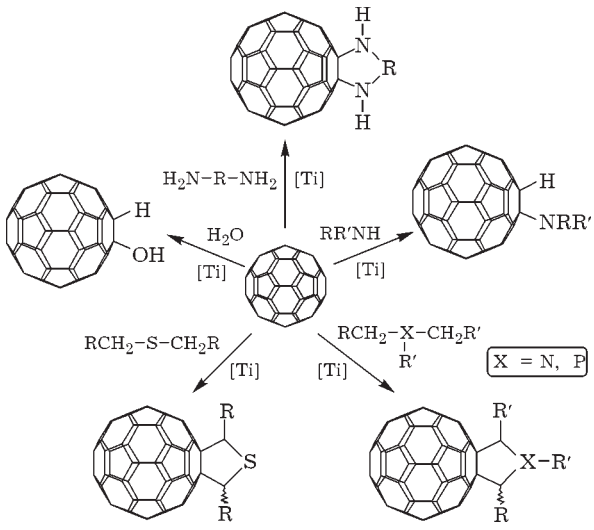


In the series of these studies an efficient reagent such as AlR_3–CH_2I_2 has been developed whose use resulted in performing for the first time a direct cyclopropanation of disubstituted acetylenes with the obtaining of aluminium-containing cyclopropanes (Scheme 13).



Scheme 13. Direct cyclopropanation of distributed acetylenes.

One could consider research concerning the development of general catalytic methods for selective functionalization of carbon clusters with the use of hydroamination by primary and secondary amines, small molecules (H_2O, NH_3, H_2S), as well as [3 + 2]-cycloaddition cyclic and acyclic amines, phosphines, sulphides, sulphoxides to the molecule of fullerene C_{60} to be an important achievement.



Catalysts: Cp_2TiCl_2, Cp_2ZrCl_2, Cp_2HfCl_2

Basing on the developments performed within the framework of the research directions mentioned above, the manufacture of the following chemical products is mastered at the industrial enterprises of Russia: 4-vinylcyclohexene, *trans-trans-trans*-1,5,9-cyclododecatriene, chloronorbornene, norbornadiene, special products with record characteristics, novel efficient neutralizers of hydrogen sulphide, inhibitors for hydrosulphuric corrosion, extracting agents for the regeneration of spent catalysts, phenolic antioxidants, lubricants and lubricoolant liquids, immunostimulants for plants, antifungal preparations for plants and animals.

PROSPECTS OF THE FURTHER RESEARCH DEVELOPMENT IN THE FIELD OF METAL COMPLEX CATALYSIS

For the nearest 5–10 years it is planned to continue the studies on the general mechanism for the action of Ziegler–Natta catalysts by the example of model reactions of hydro-, carbo- and cycloalumination, as well as di-, oligo- and polymerization of olefins under the action of complex catalysts based on zirconium salts and complexes.

Much consideration will be devoted to the studies on the influence of electronic structure of the catalyst's central atom, its ligand surrounding, the stereochemistry of intermediate complexes, as well as to the identification of their structure and to the measurement of kinetic parameters with respect to activity, selectivity and structural selectivity of the aforementioned reactions with the use of catalysts based on zirconium compounds.

There is no doubt that an important role in these studies will be played by quantum chemical calculations of energy profile for these reactions, the construction of a kinetic model.

The investigations of the catalytic cycloalumination and cyclomagnesiation reaction discovered will be continued with the purpose of extending this method over acyclic, cyclic and heterocyclic olefins, including strained heteroolefins, acetylenes, allenes, cumulenes and natural compounds.

Our efforts will be directed at the further development of the discovered phenomenon of catalytic substitution of transition metal atoms in metallocarbocycles by non-transition metal atoms in order to extend this method over metallocarbocycles of other non-transition metals (B, Ge, Ga, Zn, Sn).

Among important and prospective research directions for the nearest 5–10 years one could consider the investigation and development of multicomponent conjugated reactions under the action metal complex catalysts (including heterogenized ones) those would allow researchers to perform a directed self-assembling of complicated cyclic, acyclic and heteroatomic compounds proceeding from simple molecules.

Taking into account the world tendency for the development of chemistry and chemical technologies it is planned to realize novel reactions promising for the creation of modern competitive technologies based on the use of renewable raw materials (H_2O, CO_2, C (carbon raw material), CH_2O, N_2, S_8) with the participation of homogeneous and heterogeneous metal complex catalysts.

Research work concerning the development of promising methods for practical application of selective functionalization of carbon clusters, unsaturated macrocycles, skeletal and polycyclic compounds will be continued and expanded.

An outstanding place among the studies planned will belong to the works connected with the development of essentially new, single-reactor methods of for designing metallo-, carbo- and heterocyclic macrocycles based on the application of the reactions of catalytic cycloalumination and cyclomagnesiation of α,ω-

diacetylenes, α,ω-diallenes, cyclic mono- and diacetylenes, as well as of cyclocotrimerization of cyclic C_8–C_{12} acetylenes with acetonitrile under the action of cobalt-containing complex catalysts, homocyclotrimerization and tetramerization of cyclic acetylenes with the subsequent oxidative scission of double bonds in the unsaturated polycycles formed.

The strategically important directions of research for the nearest 5–10 years also include the development of scientific research aimed at the development of radically new types of chiral complex catalysts on the basis of transition metal ions bound with natural biopolymers such as fibres, nucleic acids, carbohydrates, obtaining and studies on the properties of self-organizing catalytic systems those simulate natural enzymatic systems. The latter is intended for using in order to realize asymmetric reactions of oxidation, reduction, condensation, cycloaddition, hydro-, carbo- and cyclometallation of unsaturated compounds for synthesizing a wide assortment of optically pure substances and materials.

CONCLUSION

This review is devoted to the presentation of the most important results obtained by the disciples and followers of G. A. Tolstikov for the last 30 years within the framework of the direction "Metal complex catalysis in the chemistry of unsaturated and organometallic compounds". The contribution of the disciples of Academician G. A. Tolstikov to the development of one of the most prospective and promising fields of modern organic and organometallic chemistry is demonstrated.

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