4th International
symposium dedicated to
the 100th anniversary
of academician
Mark Vol'pin

Modern Trends in Organometallic
Chemistry & Catalysis
23-27 May 2023

BOOK
OF ABSTRACTS

Professor
Mark E. Vol'pin
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The day of May 23 2023 is the 100th anniversary of the birth of Mark Efimovich Vol'pin, chemist of genius and one of Russia's leading scientists.

Mark Efimovitch Vol'pin started his career as an organic chemist, then moved into organometallic chemistry, and ended it in bioinorganic chemistry. From 1988 he was the director of the A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS) of the Russian Academy of Sciences.

Vol'pin came from a medical background but, after service during the Second World War, he graduated in Chemistry from Moscow State University in 1949. He first became well-known in the mid-1950s for his studies on the chemistry of tropylium, a remarkable organic compound with seven carbons in a ring, bearing a positive charge, which was isolable due to its 6-electron «aromatic» character. He later expanded the chemistry of such organic positively charged ions to the 3-membered ring, 2-electron analogues. For that work he was awarded the Lenin Prize in 1963. Deriving from this he became interested in the highly reactive unsaturated single carbon species called carbenes, which in turn led him to investigate related systems, including some highly reactive and unsaturated metal complexes. The successful synthesis of diphenylcyclopropenone via the reaction of dihalocarbenes with tolane led Vol'pin to very important theoretical generalizations for the concept of "carbenoids", heteroanalogs of carbenes (R_2Ge, R_2Sn, RB).

An interesting sidelight on the path of pure scientific research in the hands of a master like Vol'pin is seen in his progression from organic chemistry to a most remarkable discovery in inorganic chemistry: a metal complex with the ability to «fix» atmospheric nitrogen under very mild conditions. The catalytic system that Vol'pin and V.B. Shur developed offered a signpost to many other workers. For this research Vol'pin was awarded the USSR State Prize in 1982, as well as numerous other honours, and was elected to full membership of the USSR Academy of Science in 1987.

In his later work he studied biological metal complexes that could generate very active species, in this case free radicals. The object of these researches was to find compounds that were absorbed by tumours and would destroy them without harming healthy tissue. He felt that this work represented his most satisfying achievement.

In his later career he was the intellectual powerhouse that drove the research staff of INEOS by example and inspiration. Characteristically he ran a relatively small group himself and did not have his name on all the Institute publications, as was the custom elsewhere. He was a very approachable, gentle and nice man; and he was appointed Director on three separate occasions. Vol'pin was a tall youthful-looking man with a ready smile. He was a most convivial companion, and much enjoyed entertaining friends and visitors.

1923
Mark Vol'pin
Symposium
2023

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“Modern trends in organometallic chemistry
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anniversary of the academician M. E. Vol’pin
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23-27 May 2023

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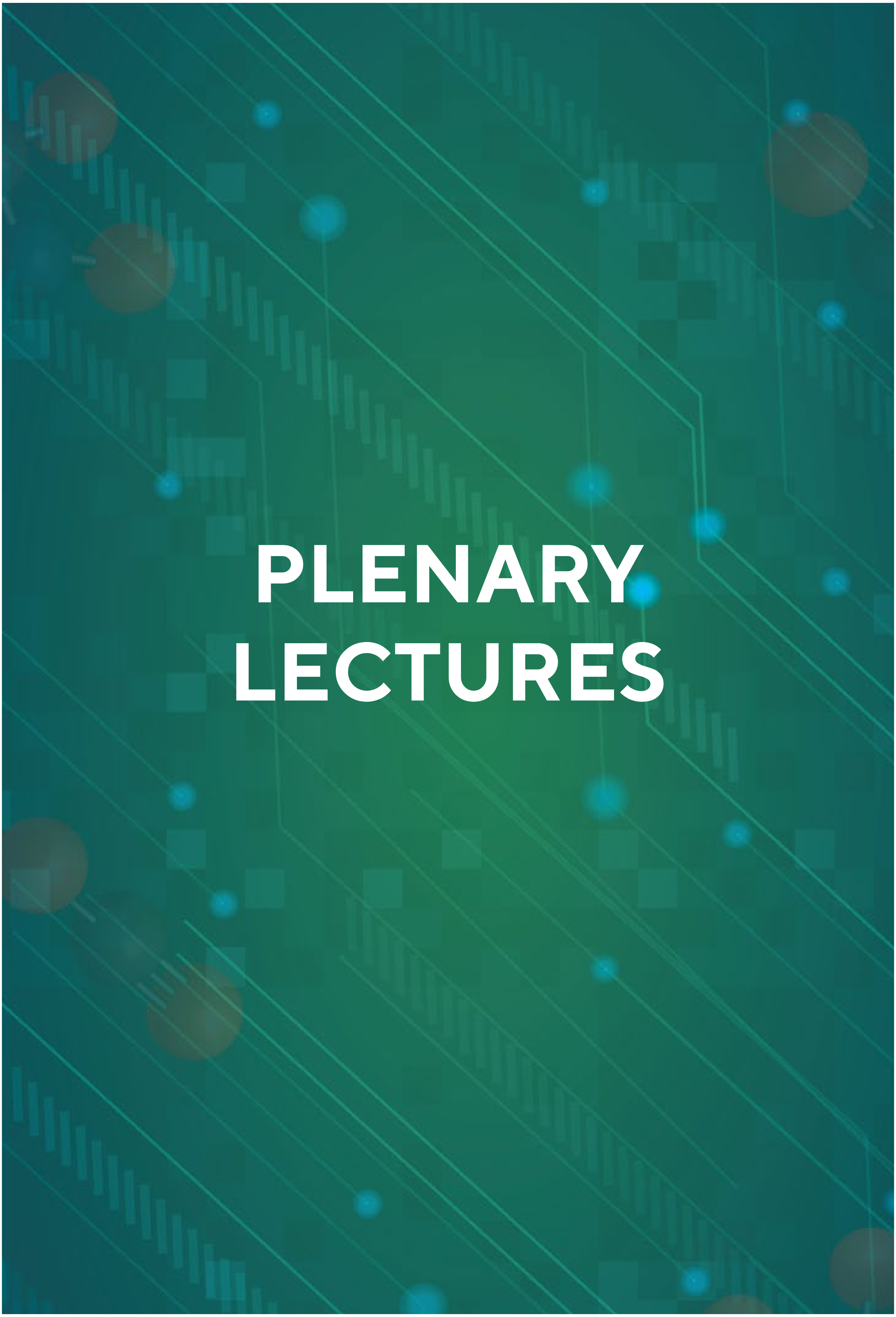
CONTENT



PLENARY LECTURES

Carboxylates as non-innocent L-ligand – metal-bound carboxylate radicals in Ni-catalyzed C-H activation

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Metals have the ability to stabilize a variety of transient species through coordination. A particularly interesting situation arises when the metal-bound species adjusts its oxidation state to match the electronic demands of the metal and the reaction, i.e., behave as a "non-innocent ligand" (NIL). Although carboxylates are capable of forming complexes with a wide range of transition metals, they generally behave as one-electron X-ligands and form a covalent M-O bond with the loss of radical character.

We show that the carboxylate radical acts as a L-ligand with certain high-spin transition metal centers. Such coordination preserves the O-radical character needed for C-H activation *via* HAT. Capture of the new C-radical by the metal and subsequent reductive elimination leads to formal C-H acyloxylation. Decarboxylation of the RCO_2 radical[1] is minimized through hybridization effects introduced by spiro-cyclopropyl moiety.[2]

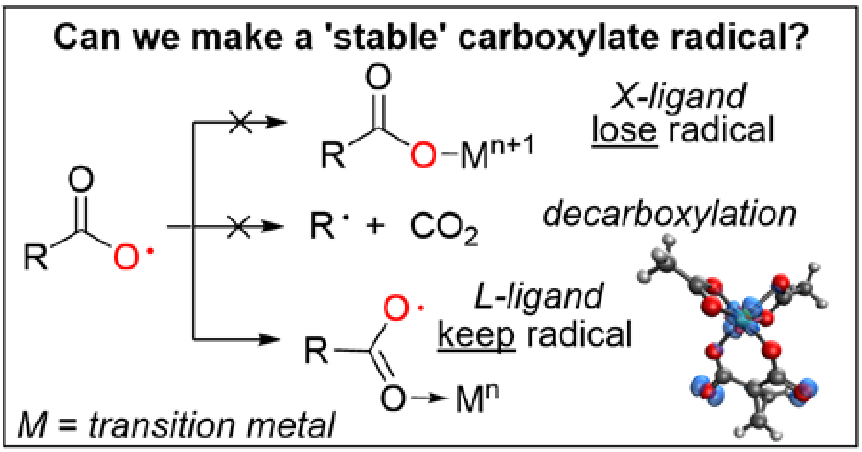

Figure 1. Two ways to use carboxylate as a ligand. Top: Carboxylate acts as an X-ligand and loses radical character. Bottom: Carboxylate maintains radical character when forming a bond as an L-ligand.

Acknowledgements

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2. Carboxylate as a non-innocent L-ligand – computational and experimental search for metal-bound carboxylate radicals. Kuhn, L.; Vil', V. A.; Barsegyan, Y. A.; Terent'ev, A. O.; Alabugin, I. V. *Org. Lett.* **2022**, *24*, 3817–3822. https://pubs.acs.org/doi/10.1021/acs.orglett.2c01356. Creating, preserving, and directing carboxylate radicals in Ni-catalyzed Csp3-H acyloxylation of ethers, ketones, and unactivated alkanes with diacyl peroxides. V. A. Vil', Y. A. Barsegyan, L. Kuhn, A. O. Terent'ev, I. V. Alabugin, *Organometalllics,* **2023**, https://pubs.acs.org/doi/10.1021/acs.organomet.2c00663.

Artificial intelligence in chemical research: what to expect in the 21st century?

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The rapid growth of the amount of accumulated experimental data, the complexity of the studied phenomena at the molecular and nanoscale levels, and the need for a qualitatively new leap in the development of new chemical technologies lead to the active introduction of artificial intelligence algorithms in chemical research. On the example of particular chemical tasks the actual trends in the development of practical applications of artificial intelligence algorithms for creating highly active catalysts[1,2], spectral data analysis[3] and understanding of the mechanisms of formation and functioning of micro- and nanoscale systems[4,5] will be discussed in this report.

Acknowledgements
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Metal catalysis in the substitution and addition reactions

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The lecture will consider the application of the metal complexes in the substitution reactions (cross-coupling, carbonylation, carboxylation with CO_2) and addition reactions (hydrogenation, hydrosilylation, hydroboration, hydrothiolation of alkenes and alkynes, Michael addition). Divirgent addition controlled by the catalyst will be discussed as well.

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Catalysis: a key to Polypyridines, Fused Heterocycles, Functional Phosphines and to catalyst improvement

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key words: C-H bond functionalization, polypyridines, fused heterocycles, functional phosphines, improvement of Ru and Rh catalysts

Pyridines in metal complexes are key ligands to promote selective catalytic reactions, and as photocatalysts such as $\{Ru(bipy)_3]^{2+}\}$[1]. Many phosphine ligands control the activity of molecular metal catalysts for numerous useful catalytic reactions used in industry.

Fast modifications of these P[2] and N ligands via C-H bond functionalization[3] have potential to quickly create more efficient catalysts for useful applications.

The lecture will present several aspects of functionalization of pyridines, N- heterocycles and phosphines from C-H bond functionalizations and will give evidence for the improvement of Phosphine-Metal catalysts.

i) Pyridines

-Ruthenium(II) catalysts in water solvent without surfactant can promote sp^2C-H bond activation and can be directed to produce polyheterocycles : hexapyridine compounds and hexa(heteroaryl)benzenes leading to simple Ru(II) or Pd(II) complexes and catalysts[4].

-Ruthenium(II) catalysts can be driven for partial reduction of N-Heteroarenes for tandem functionalization via diastereoselective Annulation of Azaarenes into Fused N- heterocycles[5].

ii) Phosphines

-Ruthenium(II)-catalyzed selective sp^2C-H bond alkylations with alkenes of arylphosphine oxides can be controlled to give access to bifunctional phosphines with carboxylic group[6].

-Rhodium(I) catalysts promote the regioselective mono or dialkylation and dialkenylation of the biaryl ortho'C-H bonds of phosphines to produce functional dialkylated phosphines even with long chain[7], or bulky dialkenylphosphines[8].

Examples of increased activity of catalysts using modified phosphines will be presented for carboxylation with CO_2 of arylhalides or for C-N bond cross couplings[7,8]

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Luminescent Metal-organic Frameworks for Detection of Biologically Active Substances and Environmental Pollutants

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Recently, more and more attention is being paid to the sensory properties of luminescent metal-organic frameworks (LMOFs). LMOFs with their well-defined crystalline nature, structural diversity, permanent porosity as well as adjustable functionality stand out as a unique type of sensors compared to other traditional luminescent materials. One of the most important areas of research is the development of highly sensitive/highly selective and easy-to-use luminescent sensors based on porous MOFs for the detection of biologically active compounds, pollutants of organic and inorganic nature in the environment.

In this report, approaches to the synthesis of new classes of metal-organic frameworks with photoluminescence properties will be considered.[1-3] Such LMOFs are interesting for their sensory properties, since the presence of various analytes (for example, metal ions, organic compounds) in the pores of the framework leads to a change in the electron density on the fluorophore and, consequently, to a change in the photophysical properties (luminescence intensity, emission band position, etc.) (Fig. 1).

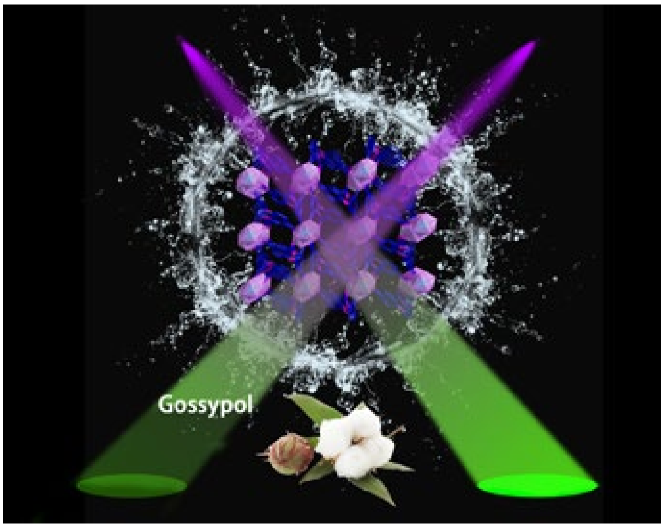

Figure 1. L-MOF with exceptionally high sensitivity towards gossypol

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Compounds with Low-Valent p-Block Elements

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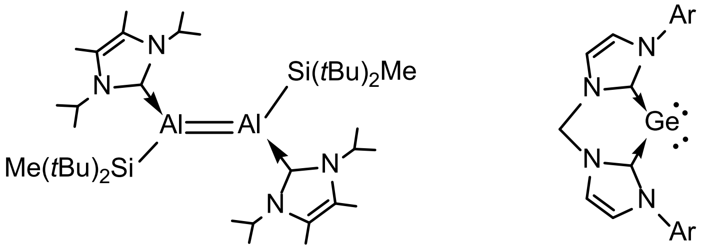
Compounds containing a low-oxidation center of p-block elements is one of the topical directions in modern organometallic chemistry. Their reactivity is prototypical for late transition metals, that makes them suitable catalysts for different processes. The stabilization of the low valent main group centers is achieved by combination of kinetic and thermodynamic stabilization methods, which can be tuned through ligand design. Kinetic stabilization is provided by using of sterically bulky ligands, while thermodynamic stabilization is obtained by choosing of heteroatom inside the ligand. [1-3] Additional stabilization can be provided externally through coordination of Lewis acids and bases (Figure 1). N-heterocyclic carbene (NHC) and cyclic (alkyl)(amino)-carbenes (CAACs) are often used in this role.[4]



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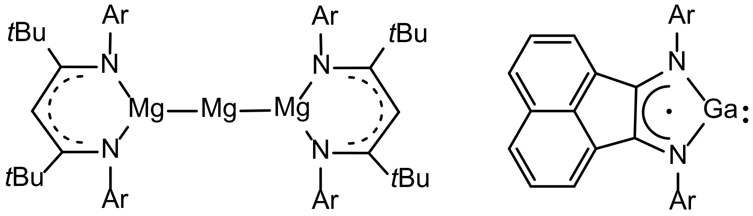

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Figure 1

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Tetrapyrrolic Photosensitizers: Design, Synthesis and Application in Medicine

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Photodynamic therapy (PDT) is a perspective socially significant method of treatment successfully applied both for tumor neoplasms and microbial infections caused by poly-resistant pathogens. Among photosensitizers generating reactive oxygen species, special attention is paid to tetrapyrrolic macrocycles of both natural and synthetic origin.[1,2] Due to their remarkable photophysic properties such compounds can be also apply for imaging, temperature sensing etc. (Figure 1).

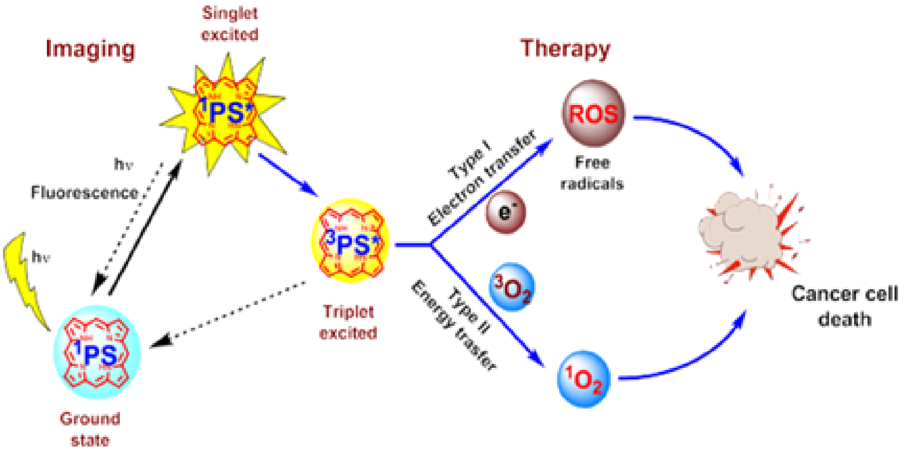

Figure 1. Application of tetrapyrrolic photosensitizers in medicine.[1]

This report is summarized the recent results on the design, synthesis and application in medicine of tetrapyrrolic compounds including the results of our scientific group.[3-9]

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Phosphine ligands with dynamic 3D architecture – a new tool of coordination chemistry

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Tertiary diphosphins are essential ligands for coordination chemistry and homogeneous catalysis due to their unique ability to form stable bonds with transition metals at low oxidation states. Due to the preorganized arrangement of phosphorus atoms, the pre-defined structure of the coordination polyhedron of the transition metal are designed. In addition the substitutes at phosphorus atoms form a sufficiently stable three-dimensional environment around the coordination center, which is responsible for the selectivity of the metal catalyst.

Methodology of covalent self-assembly of macrocyclic systems such as P, N-containing corands, cyclofanes and cryptands was developed in our laboratory during the last two decades. Such macrocyclic systems are the unique building blocks to produce brand new coordination compounds and materials.[1] Kinetic lability of key endocylic phosphine aminomethyl fragment was demonstrated for these molecular systems. The lability is manifested in the form of mutual transformations of stereoisomers and intermolecular exchange of endocyclic framents, as well as reactions of narrowing and expansion of heterocycles. Dynamic 3D architecture of these phosphines significantly complicates both the formation and the behavior of metal complexes with this type of ligands.[2-5] Dynamic behavior predetermines catalytic activity and stimuli response of metal complexes.[6-8] It is shown that luminescent metal complexes immobilization in the polymer matrix leads to kinetically stable, low cytotoxic biocompatible nanoparticles. The luminescence of nanoparticles can be used to visualize penetration into organelles, as well as to determine the concentration of biotiols, pH and temperature in cells, which opens up the prospects for biomedical applications of the luminescent materials.[9-12]

Acknowledgements
This work was supported by the Russian Science Foundation (grant №22-13-00147)

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Coordination Chemistry of Functionalized Group 14 and 15 Amides

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The report is focused on coordination chemistry of silane- and phosphaneamido ligands represented in Figure 1 as well as of their heavy analogues containing As, Sb, Ge and Sn.

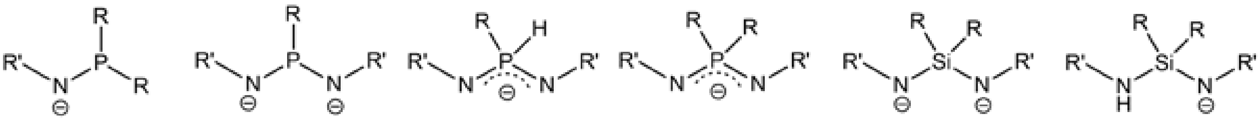

Figure 1. The main types of the silane- and phosphaneamido ligands considered in this report.

A peak of interest to the chemistry of group 14 and 15 amides dates from the last two decades of XX century, while their coordination chemistry towards both transition metals and main group elements is related to XXI century. Structural diversity of the complexes, interesting steric and electronic properties of the ligands prompted us to synthesize silane- and phosphaneamido ligands as well as their heavy analogues containing heterocyclic R' substituents known as good luminophores (Figure 2).[1-4]

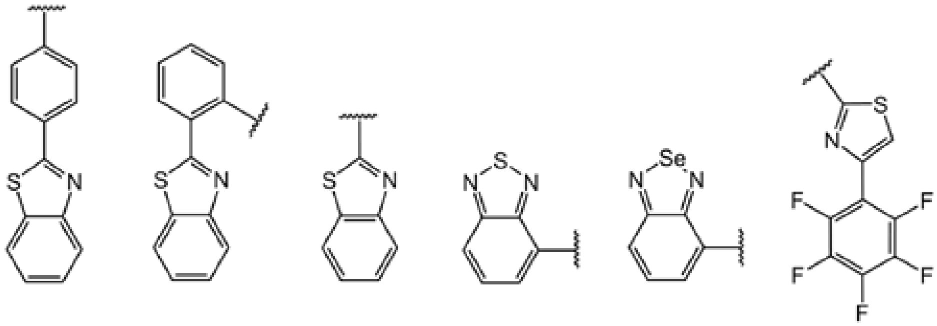

Figure 2. The examples of heterocyclic R' substituents used for creation of fluorescent ligands.

Herewith the results of synthetic experiments as well as of investigation of structural features and photophysical properties of the new ligands/proligands and their complexes with *d*- and *f*-elements are discussed.

Acknowledgements
This work was supported by the Russian Science Foundation (project no. 21-13-00287).

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σ- AND π-HOLE INTERACTIONS IN CHEMISTRY

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An avalanche-like increase in the number of publications related to the topic of intermolecular interactions has been observed in recent years. In spite of the low energy of non-valent interactions, in many cases they act collectively, and the sum of their actions may play an important role in various chemical transformations, synthesis, and catalysis, including organocatalysis. The phenomenon of the formation of multiple weak non-valence bonds is the basis of crystal design and, ultimately, the production of functional materials.

Nonmetallic centres carrying unshared pairs, such as O, N, S, C, etc., are usually used as acceptors in those variants of crystal design, where interactions with σ-[1] or π-hole donors are exploited[2]. In the scientific group of the reporter it was found that even positively charged metallocenes can serve as efficient σ-hole acceptors[3] and in particular Ni^{II}, Pd^{II}, Pt^{II}, Rh^{I}, Au^{I} and Au^{III} with a certain ligand environment behave as nucleophiles. While interaction of positively charged metallic centers with σ-hole donors even up to now is unusual, the interaction with donor π-hole centers is almost unique and only few examples of π-hole type contacts are known. In this lecture all these examples will be considered and the corresponding data are systematized.

Acknowledgements

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Synthesis, reactivity and catalytic applications of 2D-materials based on exfoliated black phosphorus

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The possibility to modify the properties of 2D exfoliated black phosphorus (2D-BP) by chemical methods is still attracting great interest in view of the exciting applications that could arise following the chemical modification of the 2D-material. However, this goal is still far from being fully accomplished and a trustworthy structural characterization of the functionalized material is seldom achieved. In our laboratory, we have demonstrated that high quality of phosphorene flakes [1] may be easily decorated with nickel nanoparticles forming nanohybrid Ni/2D-BP species, which show higher stability with respect to pristine BP [2]. These nanostructured materials have been tested as catalysts for the selective hydrogenation of phenylacetylene showing high conversion and selectivity towards styrene. These features were preserved after recycling tests revealing the high stability of the nanohybrid. More intriguingly, 2D-BP was used as a platform for homogeneously dispersed palladium nanoparticles directly grown by a wet chemical process. EEELS-STEM (electron energy loss spectroscopy-scanning transmission electron microscopy) analysis evidences a strong interaction between palladium and the Phosphorus atoms of the phosphorene nanosheets [3]. A quantitative evaluation of this interaction was obtained from XAS measurements that disclosed the occurrence of a very short Pd−P distance (2.26 Å), attesting for the first time the existence of a undocumented Pd−P coordination bond of covalent nature. The average Pd−P coordination number of about 1.7 suggested that bP behaves like a polyphosphorus ligand toward the surface of the Pd atoms of the nanoparticles, thus preventing their agglomeration and inferring with structural stability. These unique properties result in a very good performance in the catalytic hydrogenation of chloronitroarenes to chloroanilines, with better chemoselectivity in comparison to other heterogeneous catalysts based on palladium.

Finally, we have demonstrated the first complete structural characterization of 2D-BP functionalized with rare discrete Pd_2 units, obtained through mild decomposition of the organometallic dimeric precursor $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ in the presence of exfoliated BP [4]. A multitechnique approach, including HAADF-STEM, Solid State NMR, XPS and XAS spectroscopy, has been used to study in detail the morphology of the palladated nanosheets (Pd_2/BP) and to unravel the coordination of the Pd_2 units to phosphorus atoms of 2D-BP. In particular, EXAFS spectroscopy, backed up by DFT modelling, revealed the existence of unprecedented interlayer Pd–Pd units, sandwiched between stacked BP layers. Preliminary application of Pd_2/BP as catalyst for the hydrogen evolution reaction (HER) in an acidic medium highlighted an activity increase ascribable to the presence of Pd_2 units.

Acknowledgements

MP thanks all the coworkers listed in the references for their invaluable help and enthusiasm in developing this chemistry. Thanks are expressed to the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 670173) for funding the project PHOSFUN by an ERC Advanced Grant to MP.

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A new pathway for borrowing hydrogen transformations under Cp^*Co^{III} catalysis

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The “borrowing hydrogen” approach elegantly expands the scope of catalysis at the service of organic synthesis. On the other hand, interest in replacing precious metals with more abundant metals (3*d* or “base” metals) is growing. In our groups, various substrates (anilines,[1] aromatic ketones,[2] oxindoles,[3] *etc.*) could be alkylated by secondary alcohols via a borrowing hydrogen strategy under the catalytic action of Cp^*Co^{III} compounds (Figure 1).

The observed higher activity (in specific cases) for the coordinatively saturated **3** led to detailed mechanistic studies by a combined experimental-computational approach, revealing an unprecedented pathway for the dehydrogenative activation of the secondary alcohol. The key feature is the transfer of the β-H atom as a proton to an internal (coordinated) or external base, rather than as a hydride ligand to the metal (Figure 2).[4] This unsuspected new pathway may also be operational for previously published processes catalyzed by other metals.

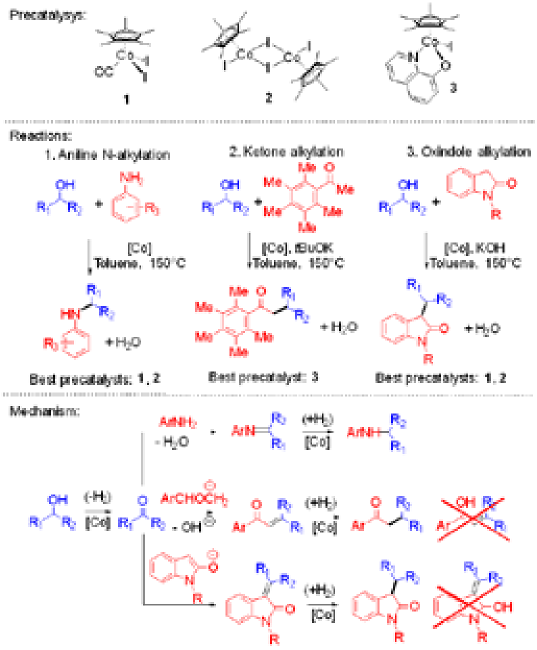

Figure 1. Cp*CoIII-catalyzed alkylations.

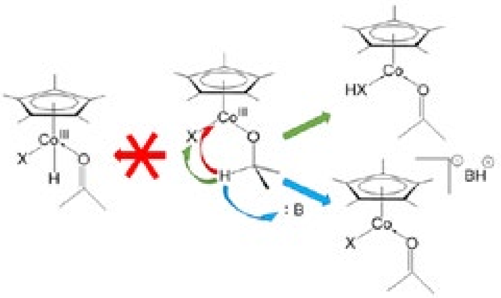

Figure 2. Mechanistic highlight.

Acknowledgements
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Coordination Polymers and Metal-Organic Frameworks (MOFs) in Selected Catalytic Reactions

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In memory of Prof. Mark Vol'pin and Prof. Georgiy Shul'pin

Various coordination polymers and metal-organic frameworks (MOFs), mainly of 1st-row transition metals and bearing amidocarboxylate, polyaromatic carboxylate or N,O-type linkers, are discussed, as well as their catalytic applications in selected reactions which have been investigated in the author´s research laboratory.

The reactions are aimed towards the synthesis of added value compounds under sustainable conditions, being aligned with some of the UN Sustainable Developments Goals, and include the following types:

C-H bond activation (e.g., oxidation of alkanes, alcohols and toluene), C-C bond formation, electrocatalytic water splitting (oxygen evolution and hydrogen evolution reactions) and electrocatalytic oxygen reduction reaction.

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Non-covalent interactions in hydride chemistry: from stoichiometric reactions to catalytic processes

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One of the most important non-covalent interaction in hydride chemistry is dihydrogen bonding. The dihydrogen bond, an interaction between a transition-metal or main-group hydride (M-H) and a protic hydrogen moiety (H-X, H-M'), is arguably the most intriguing type of hydrogen bond. Various structural, energetic, and spectroscopic aspects of these unconventional hydrogen bonds have been revealed both experimentally and computationally for a wide variety of transition-metal and main-group hydrides.[1] Dihydrogen bonds play a role in, among other aspects of chemistry, crystal packing, potential hydrogen-storage materials, and organometallic reaction mechanisms Figure 1. Being a weak interaction, dihydrogen bonding entails the lengthening of the participating bonds as well as their polarization (repolarization) as a result of the electron density redistribution. These changes lead to the activation of both MH and XH bonds in one step, facilitating proton and hydride transfer and preparing these bonds for further transformations,[2] and making DHB a driving force in hydrides chemistry. The implications of dihydrogen bonding in different stoichiometric and catalytic reactions, such as alcoholysis and aminolysis, hydrogen evolution, hydrogenation, and dehydrogenation, will be discussed.[3-7]

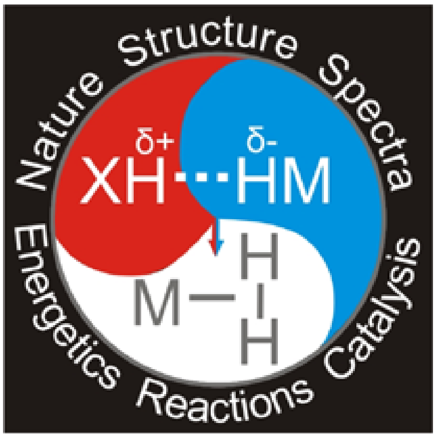

Figure 1

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INVITED LECTURES

Renaissance of phosphorescent Mn(II) complexes: the selected stories

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In the last decade, there has been a renaissance in the chemistry of phosphorescent Mn^{II} complexes because of their remarkable emission properties, eco-friendless, cheapness and elementary earth-abundance (manganese, 0.1% of the Earth’s crust). Recently, a number of emissive Mn^{II} complexes have been highlighted as efficient phosphors, triplet dopants for OLEDs, stable X-ray scintillators, optical sensors, triboluminescent materials, anti-counterfeiting dyes, etc.

Our research group is focused on designing highly emissive Mn^{II}-organic compounds based on P=O-functionalized and halido ligands. We have developed new approaches to the design of effective Mn^{II}-based emitters featuring bright room temperature phosphorescence, dual phosphorescence, triboluminescence, vapor-/solvatochromic emission as well as X-ray radioluminescence and circular polarized luminescence.

In the report, it will be discussed:

- chiral Mn^{II} complexes with strong X-ray radioluminescence and circular polarized luminescence [1];
- dual emissive of “two-in-one” $Mn^{II}(O_h)$-$Mn^{II}(T_d)$ and Mn^{II}-Cu^{I} complexes [2, 3];
- photo- and triboluminescence of Mn^{II} polymers based on *m*-carborane-derived ligands [4];
- polymorphic luminescence of Mn^{II} halide complexes with P,P’-dioxide of Xantphos [5];
- first observation of luminescence from Mn^{II} ion in a square-pyramidal ligand field [6].

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Hydrosilylation – Key Catalytic Approach to Si–C-Bonds Formation

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Hydrosilylation, i.e., the addition of hydrosilanes to unsaturated hydrocarbons, mainly alkenes, is a key method for creating Si–C-bond. This reaction is used on a large scale and presents the most successful example of homogeneous catalysis in industrial application. Moreover, hydrosilylation opens a way to a wide variety of organosilicon products, which are widely used in the main areas of industry from aviation and space to agriculture and medicine.[1]

Industrial hydrosilylation catalysts are Pt^0-complexes – Speier's and Karstedt's catalysts, which have been employed since the middle of XXth century. However, intensive studies of this reaction and development of the new catalysts continue until today. On the one hand, it is related to high platinum cost and its irretrievable "scattering", products contamination by colloid platinum, etc. On the other hand, it is because of low activity to sterically hindered compounds, low selectivity in functionalized[2] alkenes/alkynes hydrosilylation, etc.

There are several approaches in modern chemistry, aimed to solve these economical, ecological, chemical and technological problems:[3] (1) development of [M]-free hydrosilylation; development of new homogeneous [M]-catalysts based on (2) cheaper and more accessible earth-abundant transition metals[4] and (3) platinum series metals,[5,6] in particular, single-atom catalysts; and transition to reusable and recyclable heterogeneous[4] and heterophase[7] catalytic systems. Our scientific group continues research in all directions described, which will be discussed in this presentation.

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Catalytic addition reactions of alkynes

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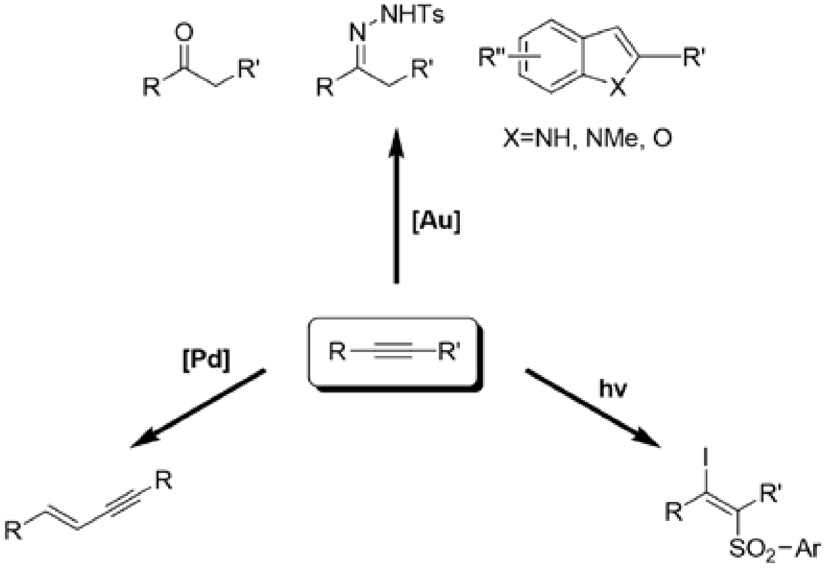
Alkynes are important building blocks in organic chemistry and are easily converted into many other compounds. In recent decades, the chemistry of acetylene has received intense attention from chemists due to the use of alkynes as building blocks or versatile intermediates for the synthesis of a wide variety of chemicals. This development in alkyne chemistry has been driven mainly by the development of new synthetic methodologies based on transition metal catalysis, a field in which gold and palladium has always been at the first place.

Currently, photocatalytic methods for the functionalization of alkynes are among emerging trends of research. Recent methods for the catalytic functionalization of alkynes will be presented and discussed based on our recent results.[1-5]



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Intramolecular Nicholas reaction in the synthesis of cyclic alkynes and diynes

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Intramolecular Nicholas reaction is a unique synthetic tool for the construction of various cyclic alkyne derivatives. We have shown that the Nicholas-type macrocyclization can be used for synthesis of heteroenediynes to create promising analogues of natural enediyne antibiotics[1,2]. This synthetic methodology is also very efficient for obtaining heterocycle-fused cycloalkynes as new SPAAC reagents[3].

The scope and limitation of this approach for synthesis of 10-membered C-, N-, and O-enediynes fused to five- and six-membered heterocycles of different types as well as heterocycloalkynes for bioconjugation will be discussed.

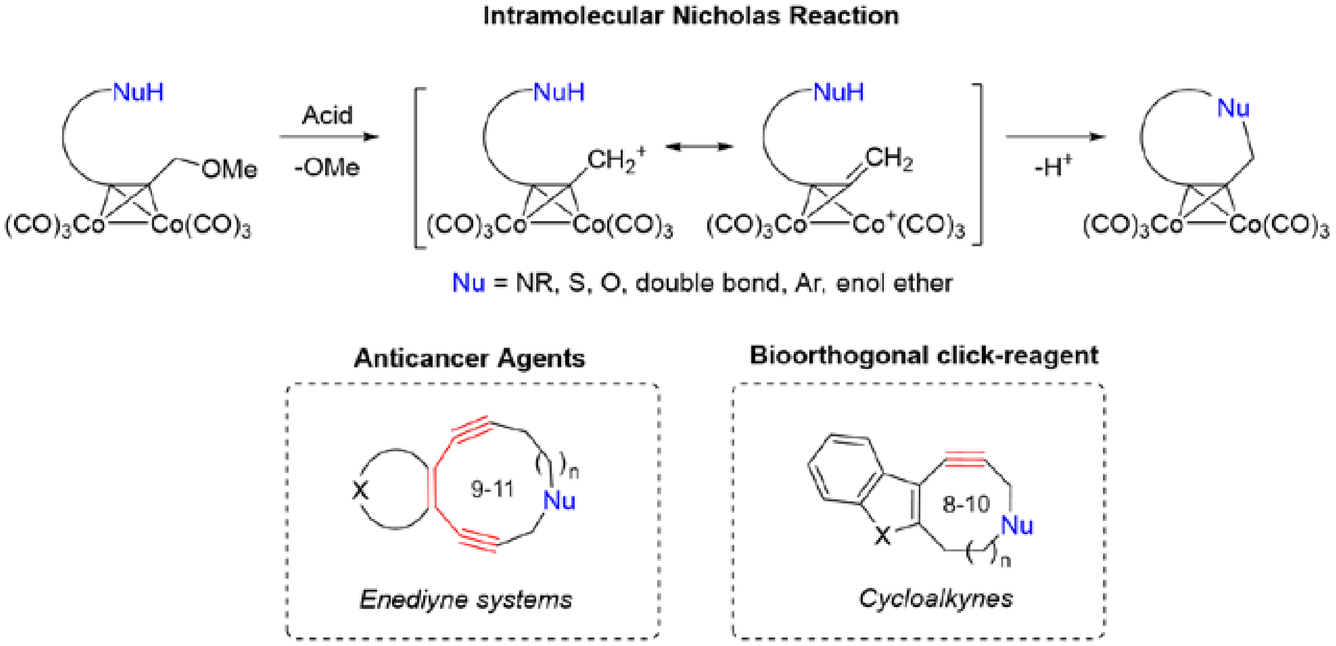

Figure 1. Intramolecular Nicholas reaction in the synthesis of strained cyclic alkynes.

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Luminescent octahedral cluster complexes of molybdenum and rhenium: from synthesis to applications

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Octahedral cluster complexes described by the general formulas $[\{Mo_6X_8\}L_6]^n$ and $[\{Re_6Q_8\}L_6]^m$ (X = Cl, Br or I; Q = S or Se; L = apical inorganic or organic ligands) (Figure 1), harmoniously combine promising for various applications chemical and physical properties.[1–3] In particular, such complexes exhibit high chemical and photostability of the $\{Mo_6X_8\}^{4+}$ and $\{Re_6Q_8\}^{2+}$ cluster cores, which are responsible for the triplet excited state of luminescence. Compounds based on these clusters are characterized by broad luminescence spectra extending in the red/near infrared region (from ~550 to more than 950 nm), emission quantum yields that are impressive for inorganic materials, and are effective photosensitizers of the singlet oxygen generation. Various research groups have confirmed the biocompatibility and low toxicity of various octahedral metal cluster complexes. These properties make the molybdenum and rhenium octahedral cluster complexes attractive objects for creating luminescent materials, as well as for use in catalysis and in biomedical applications (for example, as photosensitizers for photodynamic therapy and luminescent markers for bioimaging).

Some details about the synthesis, structure and properties of various octahedral cluster complexes of molybdenum and rhenium as well as materials based on them will be presented at the conference.

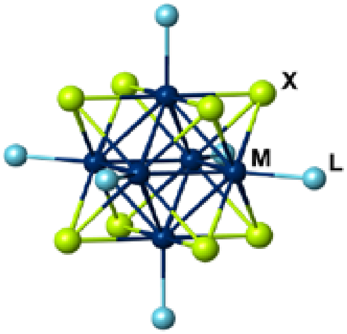

Figure 1. Structure of a cluster complex $[\{M_6X_8\}L_6]^n$

Acknowledgements

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From acetylene complexes of titanocene to five-membered metalla-cyclocumulenes and metallacyclopentynes, compounds that should not have existed

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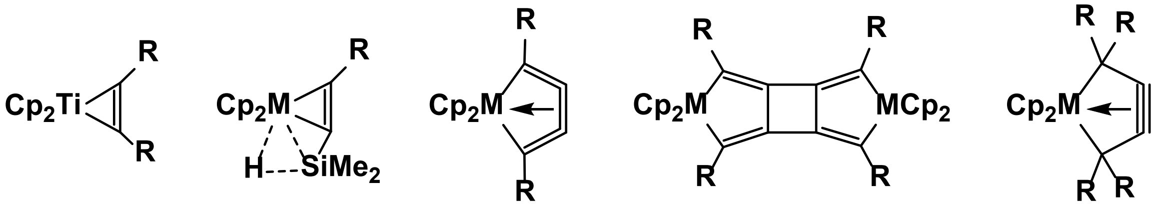
In 1981, M.E. Volpin initiated research on the development of a method for the synthesis of acetylene complexes of titanocene not containing additional stabilizing ligands. A year later, we developed sach general method for the synthesis of acetylene complexes of titanocene and synthesized the first $Cp_2Ti(RC_2R)$ complexes (**1**)[1] that did not contain additional ligands. Analogous acetylene complexes with various substituents in the Cp-rings and, in particular, the first acetylene complexes of ansa-titanocene derivatives were obtained in a similar way. The developed method was successfully used for the synthesis of various acetylene complexes of zirconocene and its Cp-substituted derivatives. Later, unusual complexes of titanocene and zirconocene with *trans*-acetylene ligands (**2**)[2], as well as the first hafnium acetylene complexes, were synthesized.

Later, when studying the reactions of group IVB metallocenes (generated in various ways) with conjugated di- and polyacetylenes, we first synthesized and structurally characterized stable five-membered metallacyclocumulene complexes $Cp_2M(\eta^4\text{-}RC_4R)$, where M = Ti, Zr, Hf (**3**)[3], and the first organometallic radialens (**4**). We have shown for the first time that the metallocene particle is able to migrate along the polyacetylene chain.

In 2002-2004, the reaction of group IVB metallocenes with reduced 1,4-dichlorobutine produced the first metallacyclopentine complexes of titanium and zirconium (**5**)[4,5].



(1) **(2)** **(3)** **(4)** **(5)**

Figure 1. The complexes 1-5.

Acknowledgements
This work was supported by the Russian Science Foundation (Project code 22-23-00701)

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Amines are our everything and more

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It is difficult to overestimate the role of amines in the modern world. However, there can be many difficulties in obtaining them. Here we will look at how different reductants and catalysts can affect the production of certain amines.[1-9]

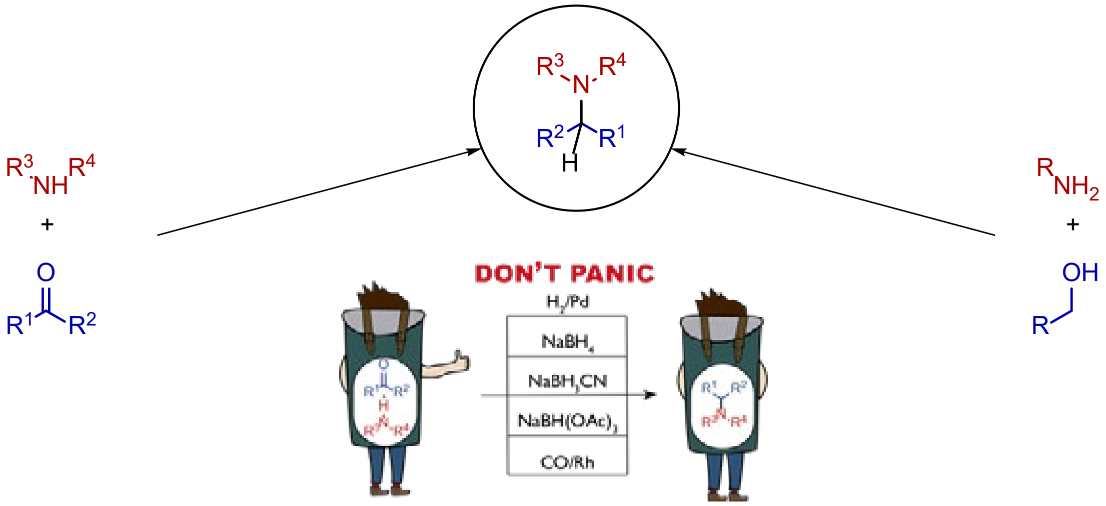

Figure 1. Different approaches to amine synthesis.

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Azacrown compounds and their conjugates with nanoparticles, antibodies and peptides as a platform for radiopharmaceuticals

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In the field of nuclear medicine, work is underway to create radiopharmaceuticals that provide a selective effect on the affected tissue with minimal toxic effects on healthy cells and the human body as a whole, thus increasing their effectiveness and reducing side effects. The main fundamental problems that exist in the development of radiopharmaceuticals are the search for chelating components that provide high binding strength of the radionuclide and the selection of conjugation conditions with vector molecules that selectively deliver the radionuclide to the desired organ.

The paper presents a series of nitrogen-containing macrocyclic and acyclic complexons containing rigid benzene and priridine fragments, as well as various substituents at nitrogen atoms, which determine the selectivity to certain types of radionuclides, as well as covalent conjugation with a functional fragment. The study of complex formation was carried out with radionuclides ^{68}Ga, ^{89}Zr, ^{177}Lu, ^{90}Y, ^{213}Bi, ^{225}Ac, ^{212}Pb, ^{227}Th, using the methods of potentiometric titration, mass spectrometry, NMR spectroscopy and X-ray diffraction analysis. When binding radionuclides, the synthesized ligands showed resistance to radiation, and experiments *in vitro* and *in vivo* demonstrated the promise of ligands for their use in biomedical purposes.

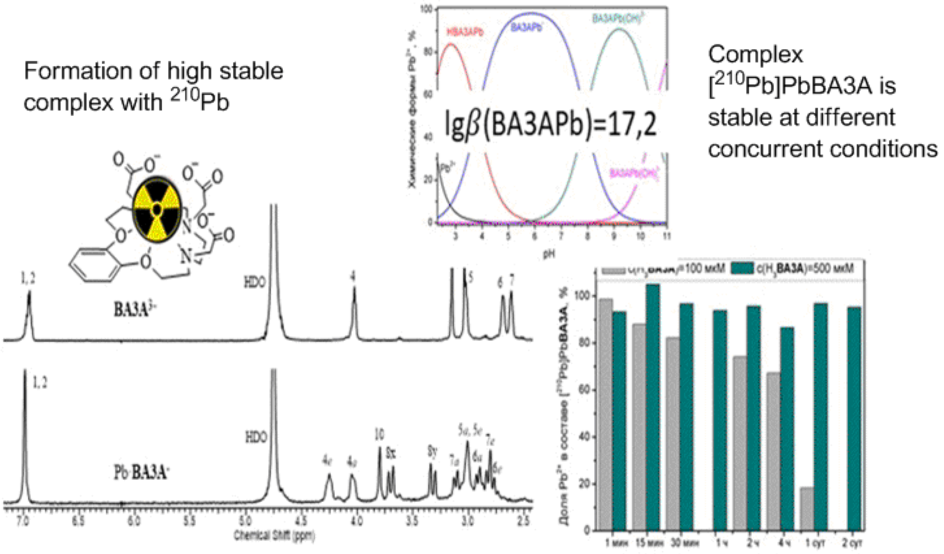

Figure 1. Complex formation between ligand BA3A and ^{210}Pb

Acknowledgements
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Organometallic compounds of transition metals: bright stars of Universe of molecular emitters

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Organometallic compounds (OMCs) of transition metals play a critical role in modern chemical science and are used for fundamental research as well as for many practical applications. It is impossible to imagine today the most part of catalytic processes without OMCs, and using of OMCs as catalysts is a wild field of application, but is not limited by it.

Luminescent OMCs of transition metals are in the heart of molecular emitters' Universe and they can be designed for many applications that exploited triplet photoluminescence.

This talk will discuss complexes of Au(I),[1–3] Au(III), Pt(II),[4] Re(I)[5] and Ir(III)[6] with typical ligands (alkynyl C≡C, carbonyl C=O and cyclometalating C^N) as phosphors based on OMCs of transition metals. The central role of ligand environment in the control of photophysical properties of OMCs of transition metals will be also illuminated.

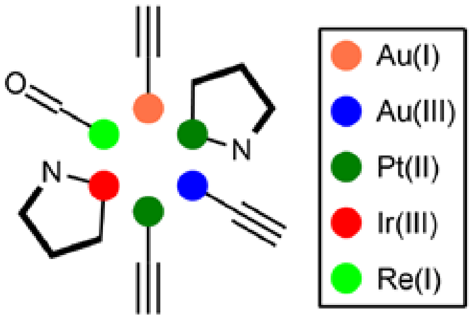

Figure 1. Typical metallofragments for luminescent OMCs of transition metals construction.

Acknowledgements
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Metal Complexes in the Synthesis of Biodegradable Polymers: New Challenges

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Biodegradable polymers based on cyclic ester monomers such as polylactide (PLA), poly(ε-caprolactone) (PCL), and polyglycolide (PGA) during last three decades have become an attractive alternative to classic polyolefins in several fields of technology. Their ability to decompose relatively quickly both in the environment and in living organisms determines two main directions of their use: these are various types of packaging and medical applications, such as, for example, suture material, controlled drug delivery system, tissue-engineering scaffolds, formation of artificial organs, nerve regeneration and wound healing etc. Catalytic ring-opening polymerization (ROP) of cyclic lactones is used usually in industry for the synthesis of said polymers. The ROP requires an appropriate catalyst to proceed in reasonable conditions and to afford polymers with controlled properties, and metal-based catalytic systems remain and are likely to remain for a long time to come as the most suitable ROP initiators. Tin(II) bis-2-ethylhexanoic acid (tin octoate) is now usually preferred as an industrially used initiator because it provides satisfactory reaction and conversion rate, high molecular weights, even under rather mild polymerization conditions.

At the same time, several important challenges remain in the synthesis of biodegradable polymers. First of all, the search for more active and less toxic initiators based on biocompatible metals is still an urgent task, which is especially important for preparation of such polymers for biomedical applications. The second problem is related to the fact that the aforementioned polymers have a number of disadvantages. For example, drawbacks of the PLA are well-known, including: brittleness, poor elasticity, low thermal stability. Some of these shortcomings can be eliminated by using statistical copolymer with ε-caprolactone, which is also obtained by the ROP method (ROCOP - Ring-Opening COPolymerization). At the same time the copolymerization of LA and ε-CL, in most cases, results in the formation of block, poly(LA-block-CL), or gradient poly(LA-grad-CL), copolymers due to the different rate of propagation these monomers on the most of studied initiators. Thus, the search for novel suitable initiators for ROCOP is still an urgent task. As well as the synthesis of novel initiators which are suitable for preparation of biodegradable polymers based on new monomers containing various functional groups.

Obviously, the ligand structure is the main factor determining the catalytic activity of of metal complex. The steric and electronic properties of substituents, the nature of donor atoms in the ligand framework and size of the chelate formed with the metal atom determines the geometry and coordination mode adopted by metal complexes, as well as the electronic properties of metal center¸ which ultimately determines the effectiveness of concrete compound in catalysis. This report will analyze recent results of this author as well as the results of other colleagues from different scientific groups aimed at the synthesis of new initiators that can solve the above mentioned problems.

Acknowledgements
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Specific Features of Metallocene Molecular and Electronic Structures Unveiled by Threshold Ionization Spectroscopy and DFT Calculations

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Metallocenes represent one of the most important classes of sandwich organometallics with wide prospects for practical use in various fields of chemistry, materials science, molecular electronics, and biomedicine. 50 years ago, the Nobel Prize in Chemistry was awarded to E.O. Fischer and G. Wilkinson "for their pioneering work… on the chemistry of the organometallic, so called sandwich compounds." Many applications of these intriguing metal complexes are based on their ability to form stable or reactive molecular ions. The details of ionization processes in sandwich molecules are, therefore, crucial for understanding their reactivity.

Unprecedented opportunities for comprehensive studies of the electronic structure features related to the formation of sandwich ions appeared as the high-resolution methods of laser spectroscopy have been developed. Extremely accurate ionization energies (IEs) of neutral species and vibrational frequencies of free molecular ions can be obtained by mass-analysed threshold ionization (MATI) techniques. These experimental data provide a reliable basis for verification of quantum chemical calculations. Unique and precise information about sandwich electronic structures can be obtained using a combination of DFT and MATI methods. In particular, intriguing new features of substituent effects in bisarene systems have been reported.[1] Compared to bisarene complexes, metallocenes have been little investigated by laser spectroscopy.

In this work, we report the first MATI / DFT study of methylated cobaltocenes, $(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)Co$ (**1**) and $(\eta^5\text{-}C_5H_4Me)_2Co$ (**2**). Experimental high-resolution adiabatic ionization energies (IEs) of **1** and **2** are 5.2097(6) and 5.0966(10) eV, respectively. The introduction of one and two methyl groups to the rings of unsubstituted cobaltocene[2] decreases the IE value by 0.1178 and 0.2309 eV, respectively. This effect appears to be 37% stronger than in chromium bisarene complexes. DFT calculations reproduce nicely vibronic structures of the MATI spectra. This makes it possible to analyze fine structural transformations accompanying the ionization of metallocenes. Cobaltocene derivatives are especially interesting because their geometries are distorted as a result of vibronic interactions. The study of charge distribution in the neutral and ionic complexes reveals the main paths of the electron density relaxation after the electron detachment. They are compared with the results recently obtained for decamethylmanganocene.[3]

Acknowledgements

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Chiral NNO Type Cu(II) and Ni(II) Complexes in Asymmetric Reactions

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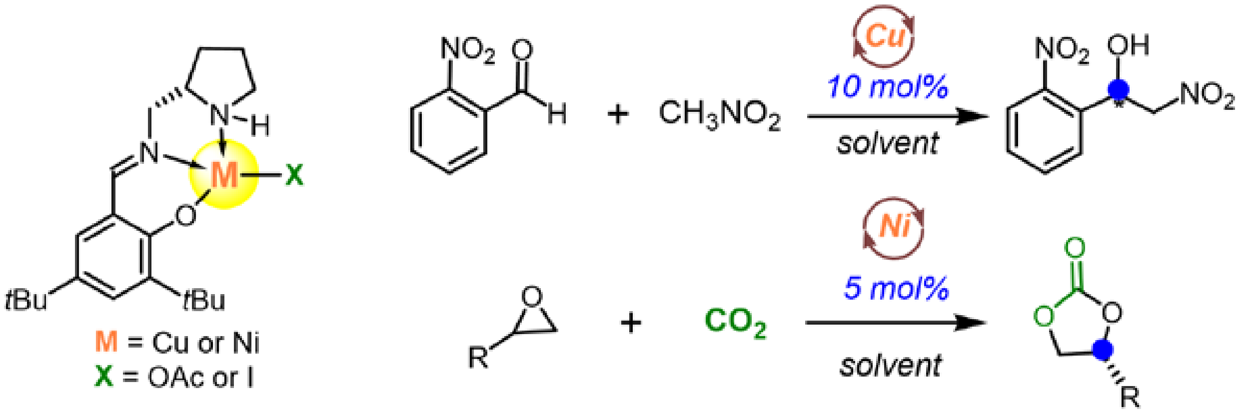
To date, the chiral copper(II) and nickel(II) complexes are very attractive class of enantioselective homogeneous catalysts.

Herein we wish to report the synthesis and characterization of chiral Cu(II) and Ni(II) complexes based on Schiff base of (*S*)-2-aminomethylpyrrolidine and salicylaldehyde derivatives including both Lewis and Brønsted acid/basic functionalities (Figure).[1] In addition, their application as enantioselective catalysts in the Henry reaction and in the kinetic resolution of epoxides with CO_2 was detailed (Figure).[2,3] It was demonstrated that the water molecules play a crucial role in the reactivity of the Cu(II) complex in the asymmetric Henry reaction with up to 82% *ee*. The mechanism of the reaction was kinetically studied. The bridging OAc-ion functioned as the basic group, deprotonating nitromethane molecules. It was shown that water presence may become a crucial feature of the catalysis by copper(II) complexes.[2]

In the kinetic resolution of epoxides, the Ni(II) complex with iodide-anion in the combination with co-catalyst could provide the desired carbonates with the selectivity factor up to 10.[3]



Scheme. Cu(II) and Ni(II) complexes in asymmetric reactions

Acknowledgements
This work was supported by the Russian Science Foundation (RSF grant No. 20-13-00155).

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Rare-Earth-Catalyzed Selective Hydrosilylation

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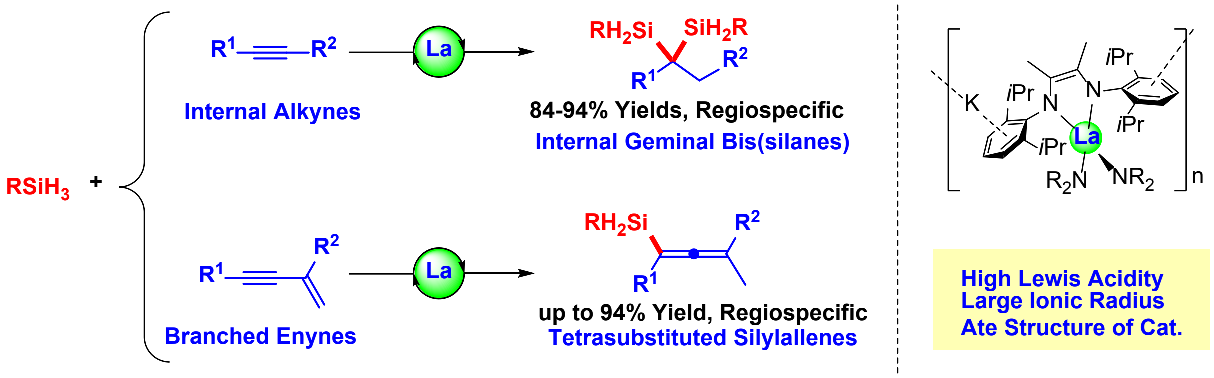
One of the most active research areas for f-elements is the field of catalytic hydroelementation of unsaturated bonds.[1] Due to the large electropositivity and inaccessibility of oxidative-addition process, rare-earth catalysts are often complementary to late transition metal catalysts in selectivity and substrate scope. Catalytic hydrosilylation of alkenes and alkynes represent the most powerful and atom-economic methods for the synthesis of organosilanes. Recently, we report the synthesis and characterization of the rare-earth amide, alkyl and hydride complexes and their application for catalytic hydrosilylation of unsaturated substrates. Remarkably, the ene-diamido samarium alkyl enabled highly regioselective hydrosilylation of a range of internal alkenes with primary silanes in high yields, even in the presence of bulky groups on alkenes.[2] Moreover, we have recently shown that ene-diamido lanthanum ate complex enabled the highly regioselective dihydrosilylation of alkynes and the hydrosilylation of alkenes and enynes. In addition, the σ-bond metathesis of Ln–E (Ln = Sm, La; E = C, N) with hydrosilanes cleanly yielded the corresponding hydrides Sm–H and La–H, providing convincible evidences for the hydride intermediate as the catalytically active species.



Acknowledgements

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Indenyl rhodium complexes: from synthesis to asymmetric catalysis

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Since their discovery in 1965, indenyl rhodium complexes have attracted much attention, due to their high efficiency in many catalytic processes. The indenyl effect, which is expressed in the facilitation of auxiliary ligand substitution as a result of η^5–η^3 isomerization of indenyl ligand, allows to formation of an addition vacant coordination site. However, most catalytic applications have been done with a narrow range of complexes, which are often limited to olefin or carbonyl rhodium(I) derivatives.[1] The rhodium (III) indenyl complexes as well as their catalytic applications are still rare, which can be caused by the low stability of the complexes and intermediates due to the indenyl effect.

Herein, we report general approaches to rhodium(III) indenyl complexes. The rational ligand design made it possible to use these complexes as catalysts for diverse organic transformations, including the C-H activation of aromatic compounds and the reductive amination of aldehydes and ketones (Fig. 1).[2-5] In contrast to cyclopentadienyl ligands, the indenyl derivatives have a fused benzene ring, which can provide additional steric shielding for enantioselective catalytic reactions.

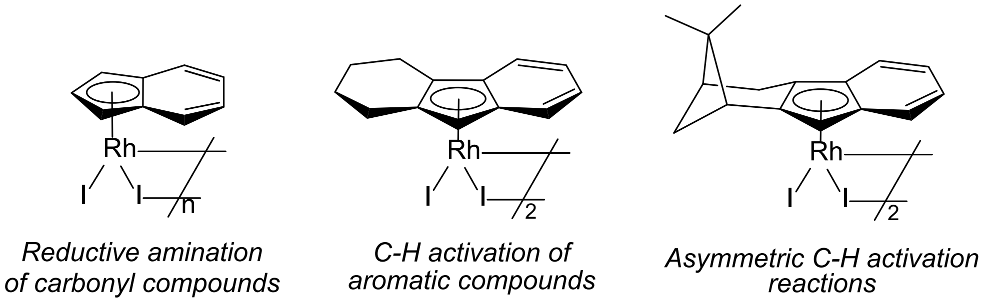

Figure 1. Catalytically active indenyl rhodium (III) complexes.

The special role of the indenyl ligand in catalytic reaction pathways will be also discussed.

Acknowledgements

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The field of metal-based drugs in medicinal chemistry

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We resolved the strategic problem of developing a new approach to low molecular weight synthetic targeted hybrid metal-based molecules. This approach is based on medicinal chemistry approach combining organic drug and metal containing fragment (Sn, Ru, Pt, Au) for selective binding of pharmacologically relevant intracellular structures (targets) (Fig. 1). We synthesized the agents containing the various pharmacophore groups. Multifactorial testing of hybrid complexes containing an antioxidant phenol fragment showed a dose dependent manner of the effect. Tin complexes were more potent than the respective Au complexes. For the tin conjugate we suggested a non-trivial mechanism of action on tubulin, that is, de novo microtubule formation instead of inhibition of depolymerization. For construction of new multitargeted substances we synthesized several organotin compounds combined with non-steroidal anti-inflammatory drugs. Results of ^{1}H, ^{13}C, ^{119}Sn NMR, IR, ESI-MS DPPH, CUPRAC, NBT, LOX, and MTT methods demonstrated that the combinations of metal compounds with non-steroid anti-inflammatory agents are a perspective road to new antitumor strategies. For two lead tin compounds preclinical testing on B16 melanoma and Lewis carcinoma bearing mice was performed. Neither compound evoked heart or liver toxicity at doses that caused an anti-metastatic efficacy. Both compounds are classes III/IV general toxicity.

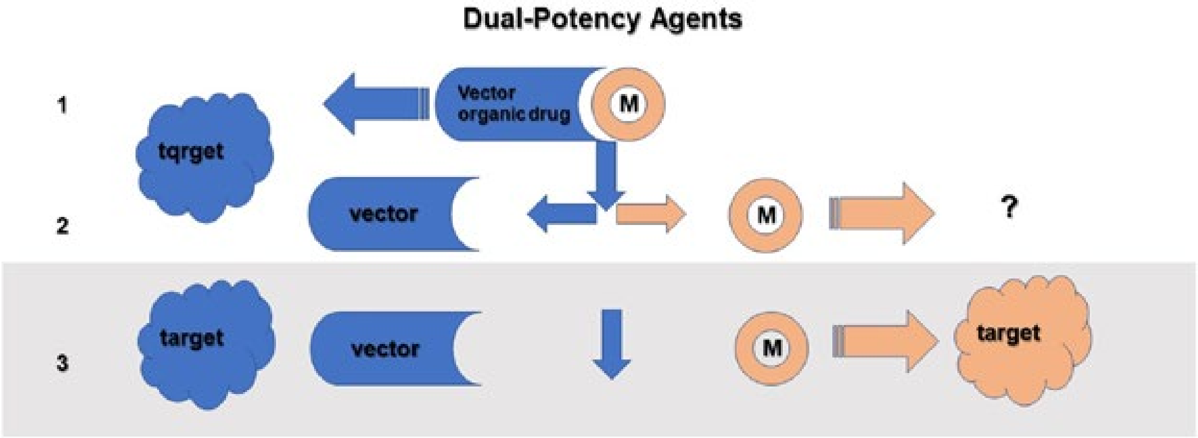

Figure 1.

Acknowledgements

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Dichlorodiazadienes – new versatile building blocks

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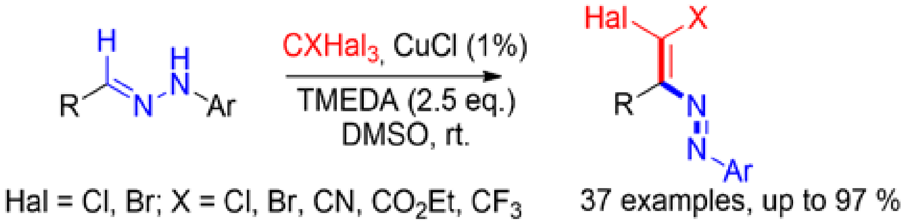
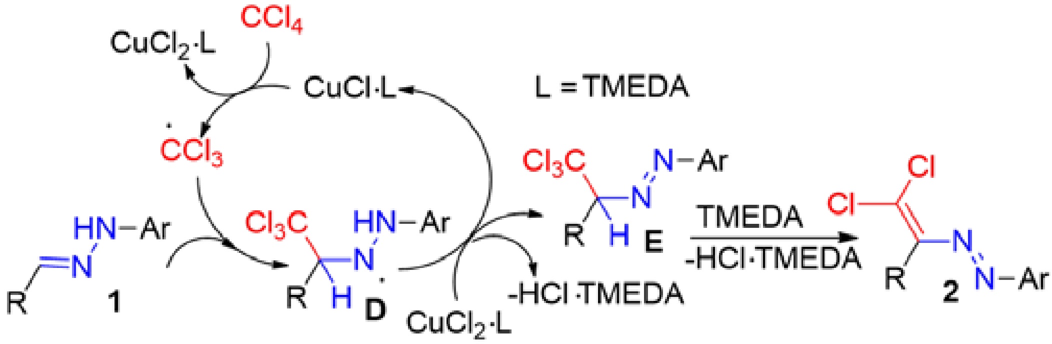
It was shown that the reaction with hydrazones catalyzed by copper salts is of a more general nature, and N-substituted hydrazones can also be involved in it. As a result, we have developed a new reaction for the formation of carbon-carbon bonds of N-monosubstituted hydrazones with polyhaloalkanes with the formation of 1,2-diazabut-1,3-dienes. This highly efficient copper-catalyzed conversion has broad synthetic capabilities and enables the process to be carried out in a much more convenient one-pot mode, starting with readily available aldehydes and hydrazines.



The synthetic importance of the obtained halogenated azadienes was demonstrated in their reactions with O-, N-, S- and C-nucleophiles, which opened access to a number of valuable acyclic and heterocyclic products.Mechanistic studies have shown that this copper-catalyzed conversion takes place in a radical way. At present, our laboratory is conducting further research into synthetic applications of the obtained halogenated azadienes.



C-H Activation/annulation (hetero)arenes with functionalized alkynes

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An efficient and highly selective method for the preparation of various nitrogen-containing heteroaromatic compounds modified with α-CF_3-α-amino acid residues has been developed based on rhodium(III)-catalyzed C-H activation/annulation of (het)aryl hydroxamates with functionalized acetylenes.[1-3] This strategy has been successfully utilized for the construction of new D-A type polyheteroaromatics with great potential to be applied in optoelectronic devices.[4,5]

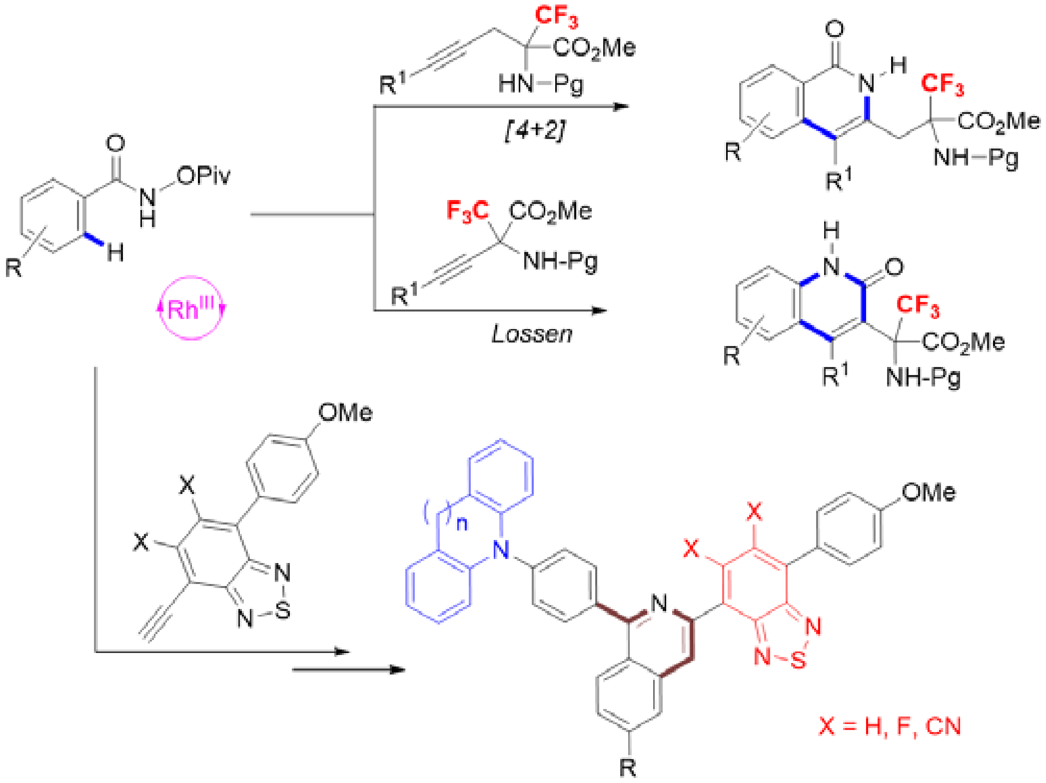

Figure 1.

Acknowledgements
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Noble metals vs Earth-abundant metals in C-H activation catalysis: unexpected results of cost analysis

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One of the clear trends in academic research of catalytic reactions in the 21st century is the intention to replace noble metal catalysts by their 3d metal analogs. The need for such replacement is commonly justified by the high cost of the noble metals. We carried out the cost analysis of the syntheses of isoquinolone heterocycles by various C-H activation methods and demonstrated that many organic substrates and sophisticated reagents are in fact more expensive than catalytic amounts of the noble metals. Therefore, in contrast to popular opinion, the use of 3d metals in catalysis may have no economic benefits. This is especially true for the small-scale, late-stage functionalization reactions, which are popular among academic researchers.

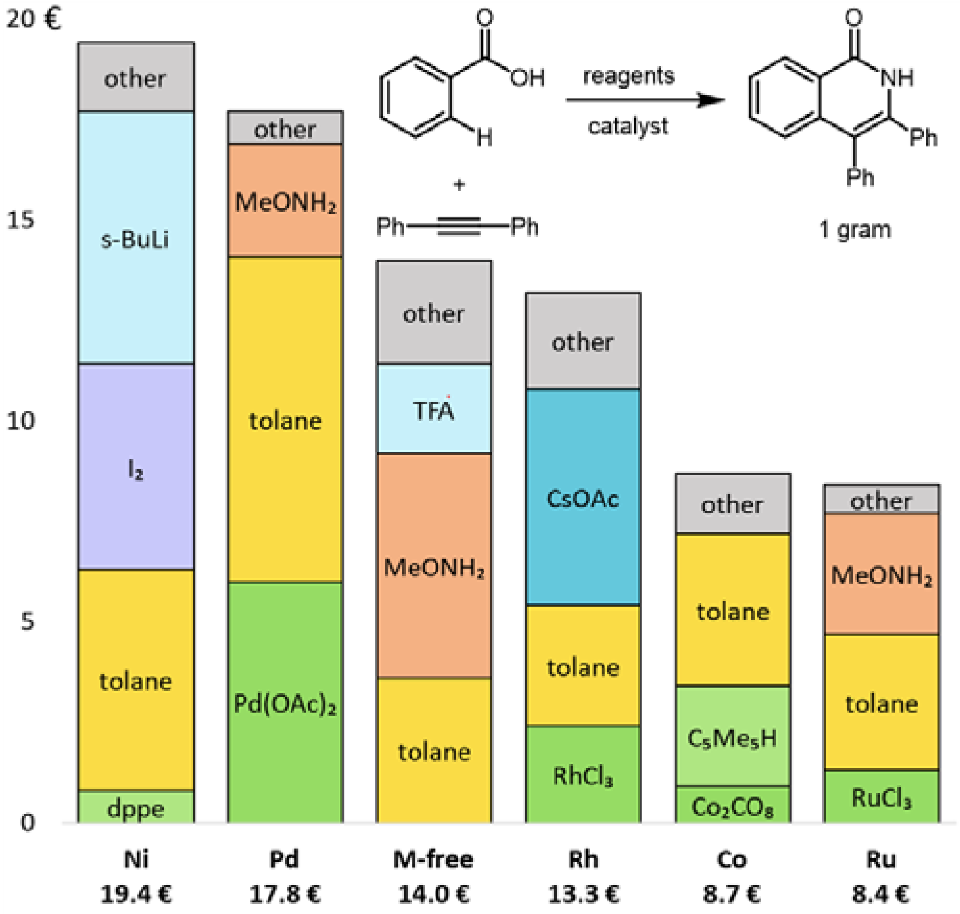

Figure 1. Price (in €) of 1 gram of diphenyl-isoquinolone obtained from benzoic acid and tolane by 6 different methods.

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Design and tuning of electronic properties for LL’CT metal complexes

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Originating in ancient time as a household craft, dyes chemistry has received well-deserved recognition and the widest industrial application, working on the diverse demands of society and making our life unthinkable without an existence of colorants (textile, food, cosmetics, paint and varnish manufacturing, etc.). At the present time, a search of new effective colorants (otherwise dyes or chromophoric systems), corresponding to newly emerging challenges, remains one of the most demanded chemical fields, which involves a row of different technologies to generate and design a huge set of chromophoric compounds and materials.

The presented report discusses aspects of the molecular design of metal complexes containing donor catecholate and acceptor diimine ligands to prepare LL’CT chromophores. The possibilities of fine-tuning the charge transfer energy during the adjustment of the electronic properties of the donor and acceptor are shown. The problems of replacing platinum group metals as complexing agents with other transition or non-transition elements are discussed.

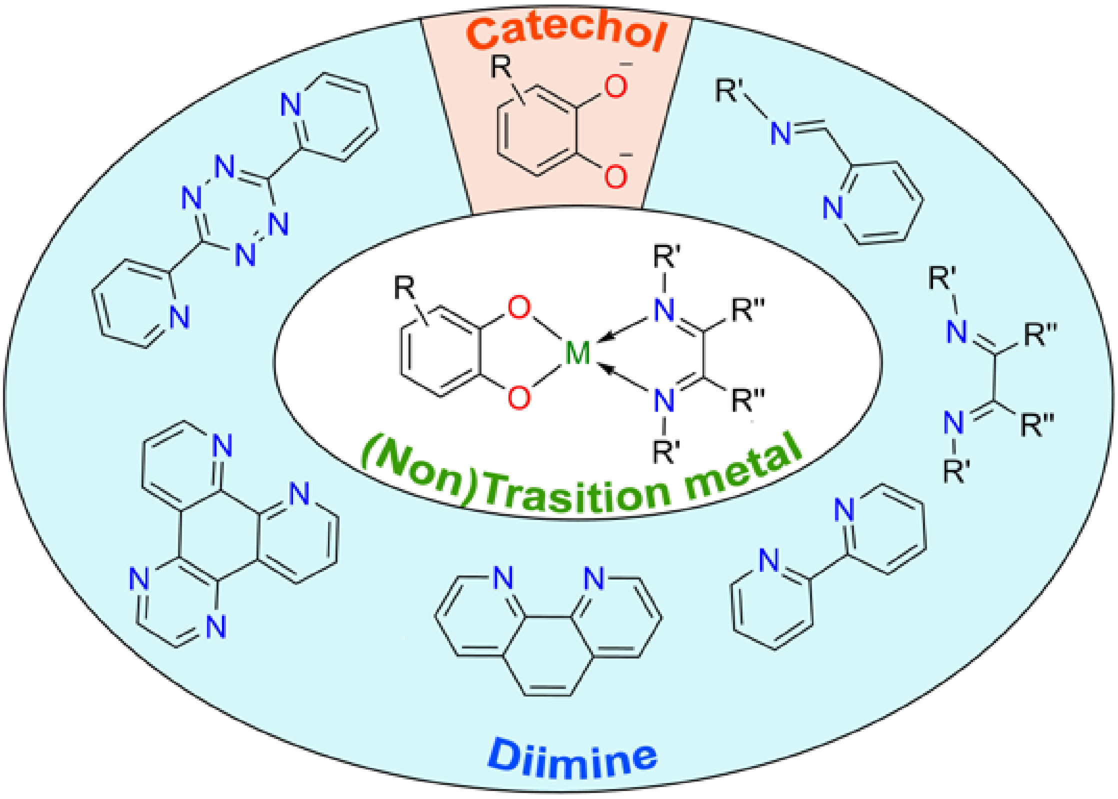

Figure 1. LL’CT-chromophores based on metal complexes.

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Aggregation induced emission in Pt(II) complexes: from molecular systems to nanoaggregates and metallopolymers

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Square-planar platinum(II) complexes with sterically undemanding π-conjugated ligands are prone to demonstrate aggregation induced emission (AIE), driven by intermolecular Pt···Pt and/or π···π interactions. Our approach to AIE generation is based on the use of platinum(II) complexes containing nonsymmetric cyclometallating tri- (N^N^C) and tetradentate (C^N*N^C′) ligands and application of specific chemistries to facilitate stacking of platinum metallocentres and formation of Pt···Pt bond the aggregates. The first method includes spontaneous formation of nanoaggregates in mixed solvents and their stabilization in solution using block copolymer micelles. The second involves copolymerization of mononuclear platinum complexes with terminal double bond in the phosphine ligand with polyvinylpyrrolidone to afford block copolymers containing a polynuclear metal fragments as one of the blocks.

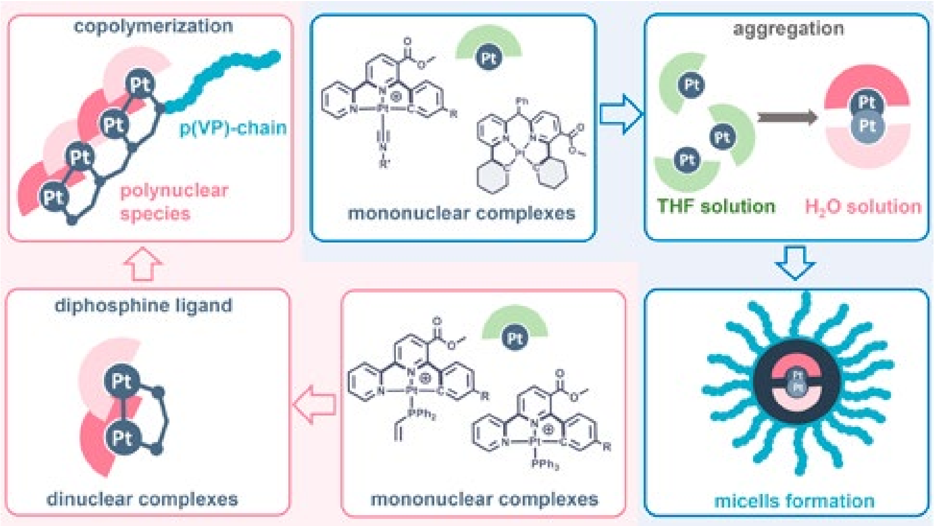

Figure 1. Schematic presentation of approaches to induce aggregation of Pt(II) complexes.

The formation of Pt···Pt contacts in the nanospecies and metal containing polymers dramatically changes the emission characteristics in all cases, giving a bathochromic shift of absorption and emission into the window of transparency down to 600 nm and 850 nm, respectively, that is extremely promising from the viewpoint of applications bioimaging and experimental medicine.

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Magnetic Resonance Imaging Contrast Agents and their Applications for Tumor Theranostics

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To surmount the major concerns of commercial small molecule Gd chelates and reported Gd-based contrast agents (GBCAs) for magnetic resonance imaging (MRI), we propose a new concept of organogadolinium macrochelates (OGMCs) constructed from the coordination between Gd^{3+} and macromolecules. A library of macromolecules were screened for Gd3+ coordination and two candidates [i.e., poly(acrylic acid) (PAA), and poly(aspartic acid) (PASP)] succeeded in OGMC formation. Under optimized synthesis conditions, both Gd-PAA12 and Gd-PASP11 are outstanding T1-weighted CAs owing to their superhigh r1 values (> 50 mM^{-1} s^{-1}, 3.0 T) and ultralow r2/r1 ratios (< 1.6, 3.0 T).[1]

Hollow mesoporous organosilica nanoparticles (HMONs) are widely considered as a promising drug nanocarrier, but the loaded drugs can easily leak from HMON, resulting in the considerably decreased drug loading capacity and increased biosafety risk. We reports the smart use of core/shell Fe_3O_4/Gd_2O_3 (FG) hybrid nanoparticles as a gatekeeper to block the pores of HMON, which can yield an unreported large loading content (up to 20.4%) of DOX.[2]

A prevalent problem of MRI CAs for drug loading applications is easy aggregation. The major concern of HMON is hard control of untimely drug leakage. To overcome both problems, we propose a new strategy of limited-space controlled aggregation for generic enhancement of drug loading capability. Typically, MRI CAs of exceedingly small gadolinium oxide nanoparticle (GO) and Gd poly(acrylic acid) macrochelate (GP) was exploited to load doxorubicin (D) in HMON hollow core. The GO@D@HMON and GP@D@HMON without precipitation formation display very high drug loading contents (33.0 ± 4.9 %, 39.6 ± 4.0 %).[3]

Ferroptosis therapy (FT) of the colorectal cancer (CRC) is usually restricted by the relatively slow rate of Fenton reaction due to the limited concentration of intracellular H_2O_2 and the high-level of endogenous H_2S with strong reducibility. To develop an unprecedented strategy for precise targeted CRC theranostics, we propose a new concept of cycloacceleration of ferroptosis and calcicoptosis for the MRI-guided CRC therapy. The developed FGNPs@TA-Fe3/Ca4 nanoparticles have an ideal hydrodynamic diameter of 16.5 ± 2.2 nm and relatively high loading contents of Fe^{3+}/Ca^{2+} (15.6 ± 3.4 % and 32.1 ± 1.9 %).[4]

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Substituted *nido*-Carboranes and Metallacarboranes Thereoff. Various Aspects.

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The discovery of a nucleophile-assisted removal of one boron atom from the icosahedral *ortho*-carborane to form an 11-vertex open *nido*-carborane in the mid-1960s set one of the main directions in the development of carborane chemistry for many years. Metallacarboranes based on the dicarbollide ligand $[7,8\text{-}C_2B_9H_{11}]^{2-}$, which is formed upon the deprotonation of *nido*-carborane with strong bases, resemble the well-known transition metal cyclopentadienyl complexes. However, the dicarbollide ligand differs significantly from the cyclopentadienyl ligand. In addition to its 3D character, the dicarbollide ligand has a double charge and is a significantly stronger donor than the cyclopentadienyl one.[1] The donor nature of the dicarbollide ligand can be substantially tuned by introducing substituents of various natures, whereas the charge can be partially compensated by introducing the so-called charge-compensating substituents of an onium nature.[2,3] Another group of substituents in *nido*-carborane and metallacarboranes based on them includes substituents with different donor atoms. Such substituents can participate in the coordination of both the metal that is a part of the metallacarborane cluster [4-6] and with external metal ions,[7-11] which opens up broad perspectives for the design of various metallacarborane-based functional materials. In some cases, a substituent may have a directing effect on the complexation of the dicarbollide ligands with transition metals.[12]

The synthesis of various substituted derivatives of nido-carborane and metallacarboranes based thereoff will be considered.

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Coordination of organometallic units to polyoxometals – a rational way to organometallic oxides

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Organometallic oxides represent a unique family of organometallic compounds with relevance to catalysis and materials chemistry. A rational design of organometallic oxide systems involves coordination of polyoxometalates (POM), as inorganic metal-oxide ligands, with a suitable organometallic precursor. Stable semi-sandwich fragments $\{Cp^*M\}^{2+}$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$, M = Rh, Ir) and $\{(arene)Ru\}^{2+}$ are particularly suitable for coordination to POM. In many cases unique oxo complexes with coordinated organometallic fragments are formed as a result of a cascade of self-assembly reactions.

In this contribution we discuss coordination of $\{Cp^*M\}^{2+}$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$, M = Rh, Ir) and $\{(C_6H_6)Ru\}^{2+}$ to Lindquist-type anions $[M_6O_{19}]^{8-}$ (M = Nb, Ta). This coordination leads to grafting of one or two organometallic units to the POM. In some cases it is followed by condensation of $[M_6O_{19}]^{8-}$ into dimeric moieties $[(M_6O_{18})_2O]^{14-}$, which do not exist in non-coordinated state. High-charged Keggin-type $[VNb_{12}O_{40}]^{15-}$ is capable of coordination up to 5 $\{(C_6H_6)Ru\}^{2+}$ units with the formation of $[\{(C_6H_6)Ru\}_5VNb_{12}O_{40}]^{5-}$.[1]

Self-assembly reaction between $(C_6H_6)RuCl_2$ and Na_2WO_4 yields $[\{(C_6H_6)Ru\}_2W_8O_{30}(OH)_2]^{6-}$. Stepwise acidification of the reaction solution leads to further protonation of the anion. The degree of protonation governs the packing effects in the crystal structure, including π–π stacking interactions between the benzene rings.[2]

Molecular and crystal structures and solution behavior of the complexes will be discussed.

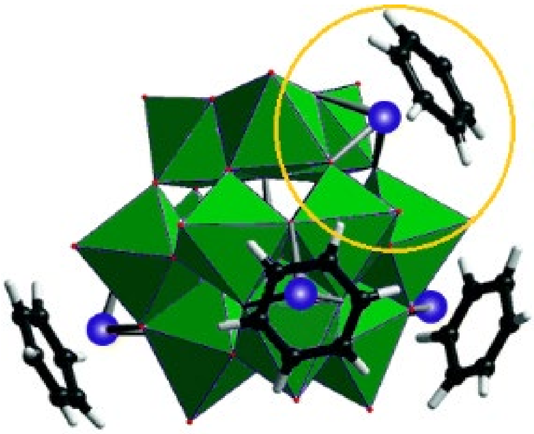

Figure 1. View of $[\{(C_6H_6)Ru\}_4VNb_{12}O_{40}]^{7-}$.

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Structures and stability of group 13-14-15 hydrides stabilized by Lewis bases and Lewis acids

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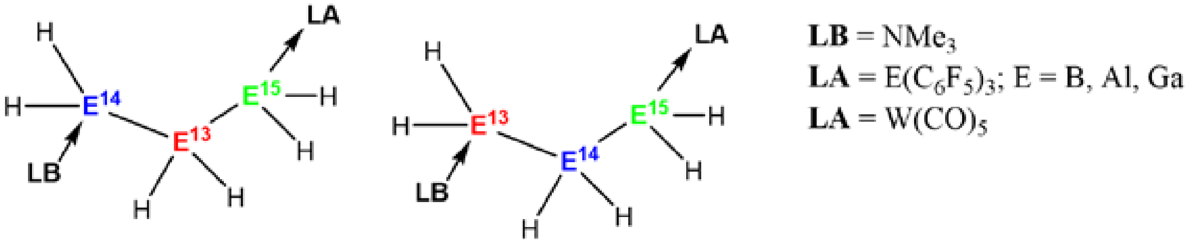
Main group inorganic hydrides based on group 13-14-15 elements are isoelectronic to hydrocarbons and are promising single source precursors for the fabrication of semiconductor and composite materials. Monomeric parent compounds are unstable with respect to polymerization and hydrogen loss, but can be stabilized using complex formation with Lewis acids (LA) and Lewis bases (LB).[1] Results of DFT computational studies at B3LYP-D3/def2-TZVP level of theory on the structures and stability of $LA\cdot E^{15}H_2E^{13}H_2E^{14}H^{2}\cdot LB$ compounds (E^{13} = B, Al, Ga; E^{14} = C, Si, Ge, Sn; E^{15} = P, As, Sb) will be presented and discussed in comparison with donor-acceptor stabilized group 13-15 hydrides[2,3] $LA\cdot E^{15}H_2E^{13}H_2\cdot LB$ and compounds, stabilized by only LB or only LA. Two isomers of group 13-14-15 hydrides were considered (Figure 1). It was demonstrated that the isomer in which the atom of group 14 element occupies the middle position is the most stable for all combinations of group 13-14-15 elements. For the selected systems, transition states for the isomerization were optimized. The key feature of TS is the shift of the LB from E^{14} to E^{13} element with simultaneous formation of the E^{14}-E^{15} bond. Depending on the nature of group 13-14-15 elements and the presence/absence of the stabilizing LB/LA, the energy barriers for the isomerization are in range 42-151 kJ mol^{-1}.

On the basis of DFT computations, possible synthetic approaches towards the most stable isomers of 13-14-15 hydrides were proposed.



LB = NMe_3
LA = $E(C_6F_5)_3$; E = B, Al, Ga
LA = $W(CO)_5$

Figure 1. Schematic representation of the considered isomers of DA stabilized group 13-14-15 hydrides.

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Organonickel sigma-complexes: synthesis, structure and catalytic activity in ethylene oligomerization process

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The search for new ecologically friendly and resource saving methods and approaches for the preparation of new high effective catalysts for industrial processes of ethylene oligo- and polymerization is a key priority in modern synthetic organometallic chemistry and catalysis.[1,2] Organonickel complexes represent most important industrial catalysts based on transition metal complexes and organoelement compounds. Generally, these systems require to use co-called co-catalysts, which are represented by highly flammable organoaluminium, organomagnesium or organolithium reagents, capable to activate a pre-form of the used transition metal complex to generate a catalytically active specie. Main chemical role of these activators is to form a potentially catalytically active M-H or M-C bond and to create a free coordination site at the metal center for coordination of the monomer molecule (ethylene, *etc.*).

We have found that the combination of classical chemical synthesis and electrochemical techniques allows to elaborate new methods for selective preparation of organonickel catalysts and generation of the catalytically active forms avoiding the use of flammable and ecologically dangerous organometallic reagents (MAO, TEA, DEAC TnHA, TiBA, *etc.*).[1-3] These methods are of high fundamental and practical interest and can be considered as a new powerful tool for preparation of new and modification of known industrial catalysts operated by worldwide chemical companies like Shell, Chevron Phillips Chemical, DuPont, BP, SABIC, Linde, Axens, *etc.*

Herein we report our recent results obtained in the field of synthetic organometallic chemistry applied towards creation of new catalysts for industrial application in ethylene oligomerization process based on organonickel sigma-complexes of type [NiBr(Aryl)(L)], where Aryl – aryl group bearing ortho-substituent, L – 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) or substituted phen. The elaborated methods include the synthesis and generation of catalytically active cationic forms of organonickel sigma-complexes.[3-7] Special attention will be focused on new organonickel catalysts for selective production of industrially important butene-1.[8]

Acknowledgements
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Recent advances in parahydrogen induced hyperpolarization

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The talk is dedicated to the memory of our friend and colleague, Prof. Dr Konstantin L'vovich Ivanov, he passed away on the 05th of March 2021.

One of the major challenges in Nuclear Magnetic Resonance (NMR) spectroscopy application to many problems is the inherent low sensitivity of magnetic resonance, which results from the small energy-differences of the nuclear spin-states. Parahydrogen induced polarization (PHIP) is an efficient and cost-effective hyperpolarization method, creates its signal-enhancements by means of a reversible (SABRE) or irreversible (classic PHIP) chemical reaction between the parahydrogen, a catalyst, and a substrate. I

In the talk, we will give a short overview about parahydrogen-based hyperpolarization techniques and review the recent advances on the method developments and applications of various flavors of the PHIP and SABRE experiments in our laboratory.[2,3,4] Detailed experimental and comprehensive theoretical analysis of singlet–triplet conversion in molecular hydrogen dissolved in a solution together with organometallic complexes used in experiments with parahydrogen gives rise to formation of orthohydrogen is a remarkably efficient process that strongly reduces the resulting NMR (nuclear magnetic resonance) signal enhancement of ^{15}N nuclei polarized at high fields using suitable NMR pulse sequences.[4.5] We make use of a simple improvement of traditional pulse sequences, utilizing a single pulse on the proton channel that gives rise to an additional strong increase of the signal[5].

In addition, the magnetic field sweep was optimized by utilizing the field dependence of the average ^{13}C and ^{15}N polarization. Both the experimental detection and the numerical simulation of this dependence are straightforward, even for complex multi-spin systems. We provide comprehensive survey of PHIP transfer dynamics at ultralow fields for different molecular systems that are relevant for PHIP and proposed the facile optimization routines for adiabatic experiments in complex spin systems undergoing rapid relaxation or chemical exchange.[6]

Acknowledgements
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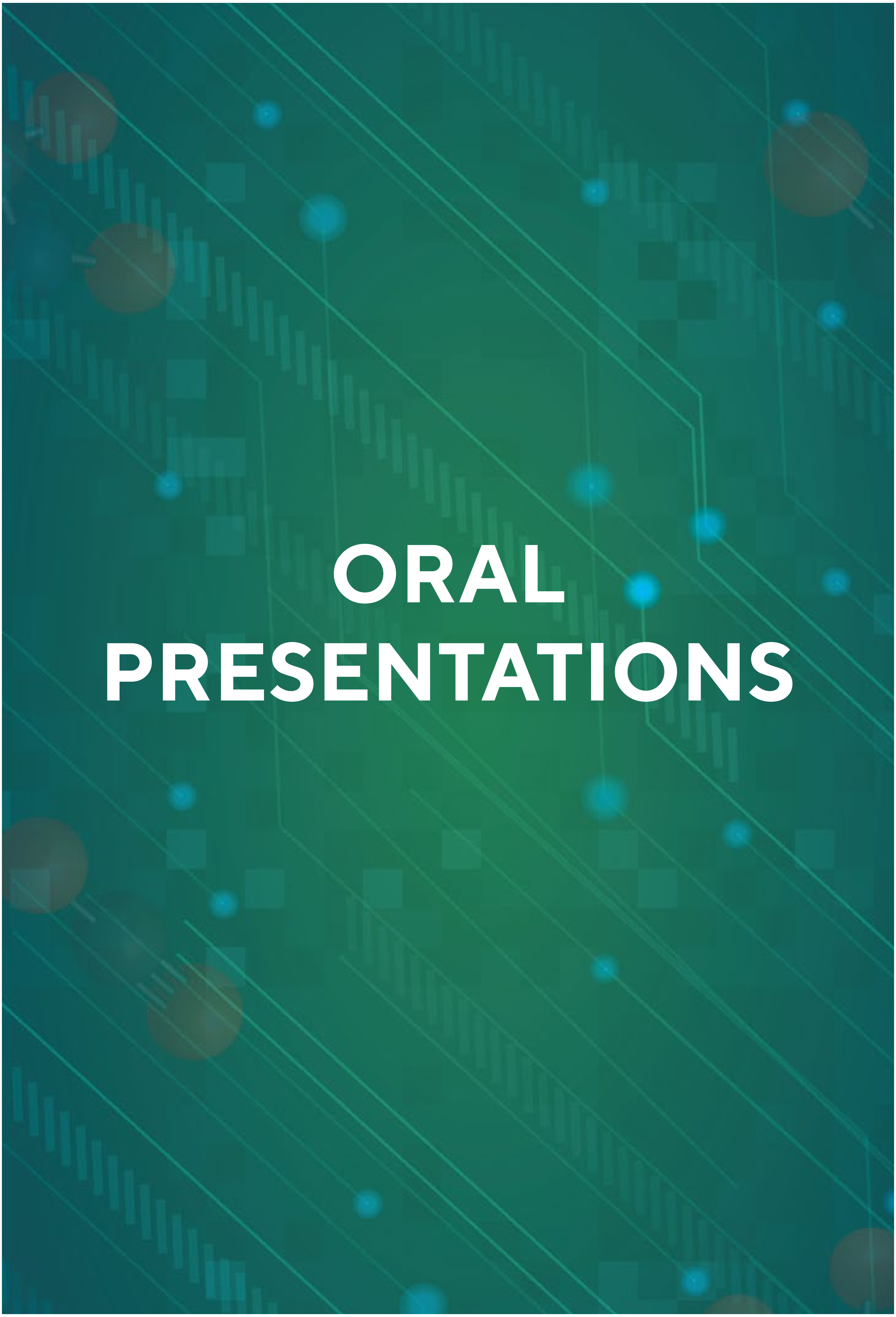

ORAL PRESENTATIONS

Towards the ideal catalyst for the borrowing hydrogen amination

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Borrowing hydrogen amination is a powerful method for the formation of C-N bonds. It is considered as the privileged atom-efficient and green method to synthesize complex amines. Among the hundreds of papers published in this field, several practical questions are still opened:

1. What catalyst better fits to the particular substrate/class of substrates? Is it necessary to use noble metals, or 3d-metal based catalysts are acceptable?
2. What conditions should be used for preparation of the target substrate?
3. Which areas in this field are underinvestigated and which are overinvestigated?

The partial answers for the first two questions could be found in the methodological paper describing the new catalysts for the borrowing hydrogen amination. Authors usually tell that theirs catalyst works well with, for example, aromatic amines, and works poor, for example, with aliphatic amines. However, there is no general view on the field to tell that substrates of type A under the conditions of type B can react with a high efficiency on the catalysts of type C, but does not work with the catalysts of type D.

In this work we present a combined experimental and literature investigation where we attempted to arrange the array of the existing data in a comprehensive and structured manner and determine correlations between the experimental conditions and catalysis outcome both within different groups of catalysts and between the defined groups using the machine analysis.[1] Moreover, we developed a catalyst-free protocol allowed prepare the wide range of classical substrates for the borrowing hydrogen amination under the mild conditions.[2]

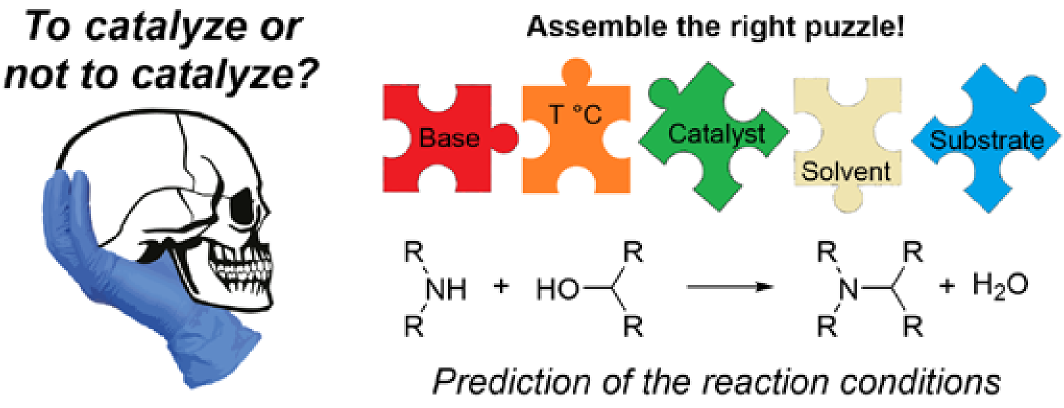

Figure 1. Puzzle of the reaction conditions in the borrowing hydrogen amination

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Synthesis of Isocoumarin-substituted Isoquinolinium Cations by Tandem Rhodium-catalyzed CH Activation/Annulation

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Recently, we have shown that isocoumarins are a promising building block for creating OLED devices due to their high stability and the presence of aggregation-induced emission (AIE)[1]. In the design of donor-acceptor luminophors isocoumarins are usually considered as an acceptor block. On the contrary, in this work, for the first time, we used isocoumarins as a donor group, and positively charged isoquinoline derivatives as an acceptor unit.

Isocoumarin-substituted isoquinolinium cations were synthesized using tandem rhodium-catalyzed C-H activation (Figure 1). The advantage of this approach is the high step economy and easy availability of starting compounds, such as benzaldehydes, aminobenzoic acids, and acetylenes. We also found that the reaction pathway strongly depends on the donor-acceptor properties of substituents in benzaldehydes. For example, in the case of electron-withdrawing substituents, indenone imines or indenyl amines can be formed instead of the isoquinoline cations. The heterocyclic frameworks in the isocoumarin-substituted isoquinolinium cations are orthogonal, which prevents direct conjugation between the donor and acceptor units and leads to a decrease of energy gap between the first triplet and singlet excited states ΔE_{ST}. These structural and electronic features make them potential candidates for the construction of high-performance OLEDs with a TADF effect.

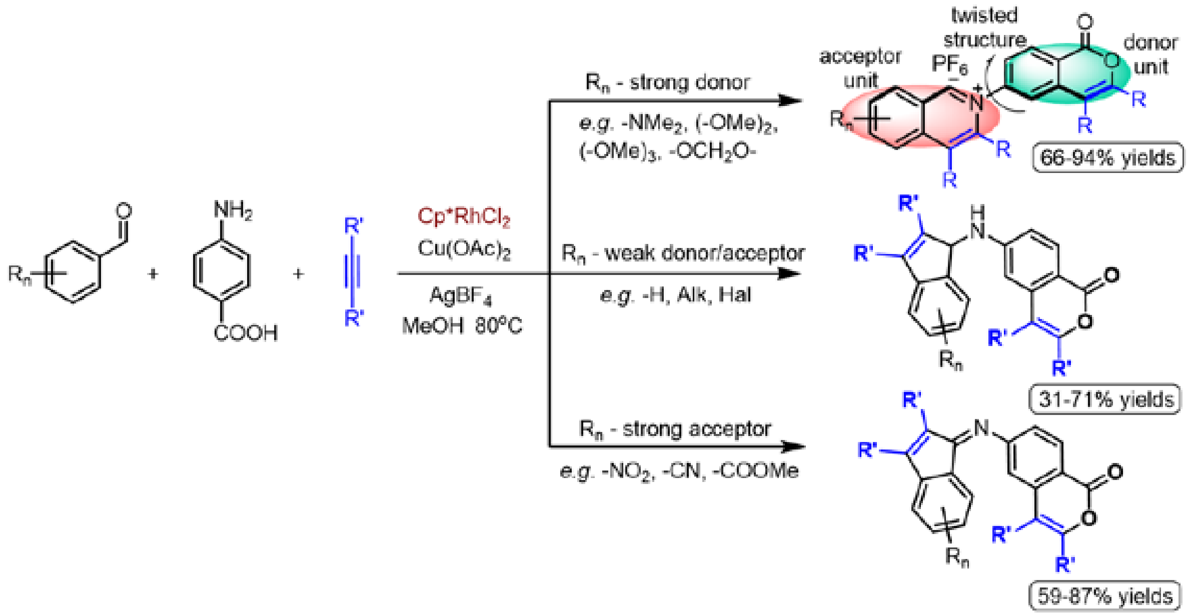

Figure 1. Tandem C-H annulations of benzaldehydes and aminobenzoic acids with acetylenes

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The delocalization of multicentered metal-carbon bonds

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A comprehensive approach to the detection of aromaticity and evaluation of its degree based on modern computational and experimental methods has been developed.[1] A conceptually new type of aromaticity caused by delocalization of multicenter metal-carbon bonds was revealed for 5-membered metallacyclocumulenes,[2,3] allyltetrilenes,[4] and pyramidanes[5,6]. It was found that this type of aromaticity obeys the electron counting rule "4n+2" for planar and three-dimensional systems and "4n" for nonplanar systems. This new type of aromaticity should be common among π-complexes of transition metals.

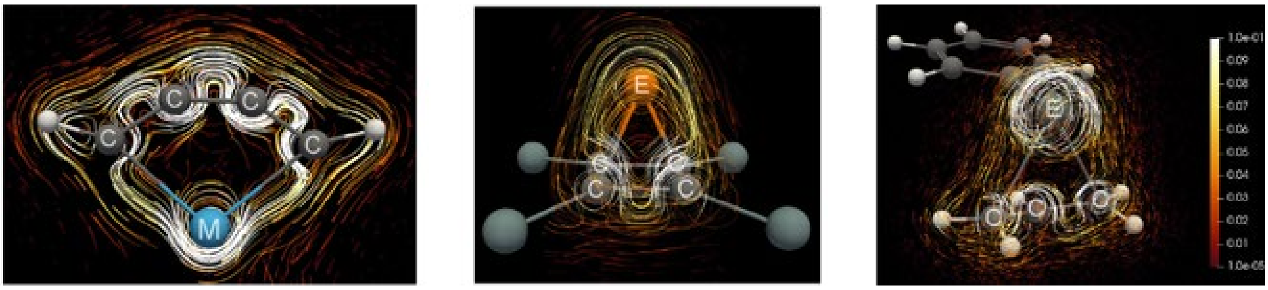

Figure 1. The induced current streamline maps.

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Structure and catalytic properties of $NiCu_{11}X_6$ clusters ($X = S, O$) in dry reforming of methane: active site model

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At the moment, the study of dry reforming of methane mechanism (DRM) and the search for active catalysts of this important process is a hot topic. Possible models of catalytic active sites for methane activation as the first stage of DRM were calculated and studied. The models were based on experimentally obtained and characterized via X-ray analysis copper sulfide cluster $Cu_{12}S_6(PR_2R')_8$ (R = Et, Ph; R' = Et, "Pr, Ph)[1] (Fig. 1). Firstly, structures of $Cu_{12}S_6(PH_3)_8$, $Cu_{12}S_6$, $Cu_{12}O_6(PH_3)_8$, $Cu_{12}O_6$ were calculated. Since it is known[3] that nickel exhibits good catalytic performance in the DRM process, these clusters were doped with a nickel atom, and the structures of all possible isomers of $NiCu_{11}S_6(PH_3)_8$, $NiCu_{11}S_6$, $NiCu_{11}O_6(PH_3)_8$, and $NiCu_{11}O_6$ were studied. Simulation of C-H bond dissociation in CH_4 was carried out on the most energetically stable isomer from each group, energy barriers of this stage were calculated using DFT PBE approach. The smallest barrier in this process is observed for the $NiCu_{11}O_6$ cluster (99 kJ/mol), which gives grounds to consider this model of the active center promising for DRM.

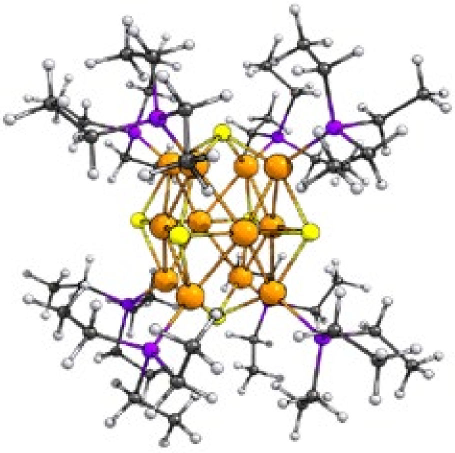

Figure 1. Calculated structure of $Cu_{12}S_6(PEt_3)_8$

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Onium Salts as Noncovalent Organoelement Catalysts

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Today, σ-hole donating species binding to reaction substrates via chalcogen (ChB) or halogen (XB) bonds play an important role in noncovalent organoelement catalysis, as they provide a more directional orientation and a higher electrophilic activation of ligated species compared to traditional hydrogen bond (HB) donating organocatalysts. ChB and XB donors also exhibit very low sensitivity to oxygen and water, thus having advantages over many metal-containing Lewis acids. Considering this, a wide dissemination of ChB and XB donors into the fields yet utilizing traditional HB donating organocatalysts, as well as metal-based Lewis acids, can provide the evolution of sustainable catalysis in the direction of application of efficient and environmentally benign catalytic species.

Recently, it has been shown that cationic chalcogen(IV)- or halogen(III)-derived σ-hole donors (chalconium and halonium salts; **Figure 1**) are remarkably more active than their chalcogen(II)- and halogen(I)-containing analogues. In this report, the latest experimental and computational data on the catalytic activity of the σ-hole donating organoelement catalysts will be discussed.[1-3] Special attention will be paid to the discussion of the solvation effects and importance of binding selectivity during the catalysis.

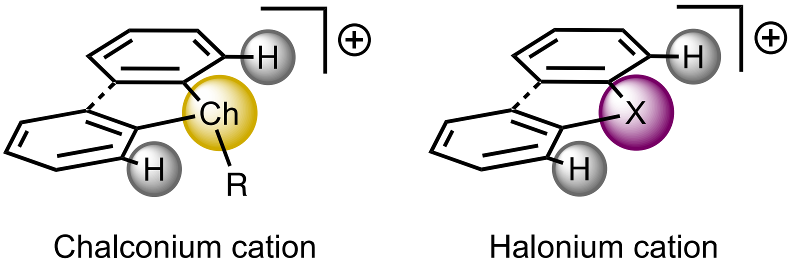

Figure 1. Representative structures of chalconium and halonium cations

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Molecular reorientation motion in plastic crystalline C_{60} under low power laser exposition

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Molecular reorientational mobility and order-disorder phase transition in a C60 plastic crystal were studied on Raman spectroscopy. By changing the irradiating He-Ne laser power in the range of 0.001-1 mW, a new phase transition was detected, in which the reorientational motion of fullerene changes its character from anisotropic to isotropic. Significant differences in the position, half-widths, and contour of the Raman line corresponding to the pinch mode at ~1468 cm–1, as well as the Rayleigh wing are remarkable. The phase transition is reversible and occurs through the formation of a metastable, most likely, glass-crystalline phase in which a set of several states are formed, differing in the character of the molecular rotation. In addition, the process of phase transformation in C60 is characterized by a specific pattern in the broadband «so called» background observed in the Raman spectra (Fig. 1), whose behavior is directly related to the observed phase transformation [1].

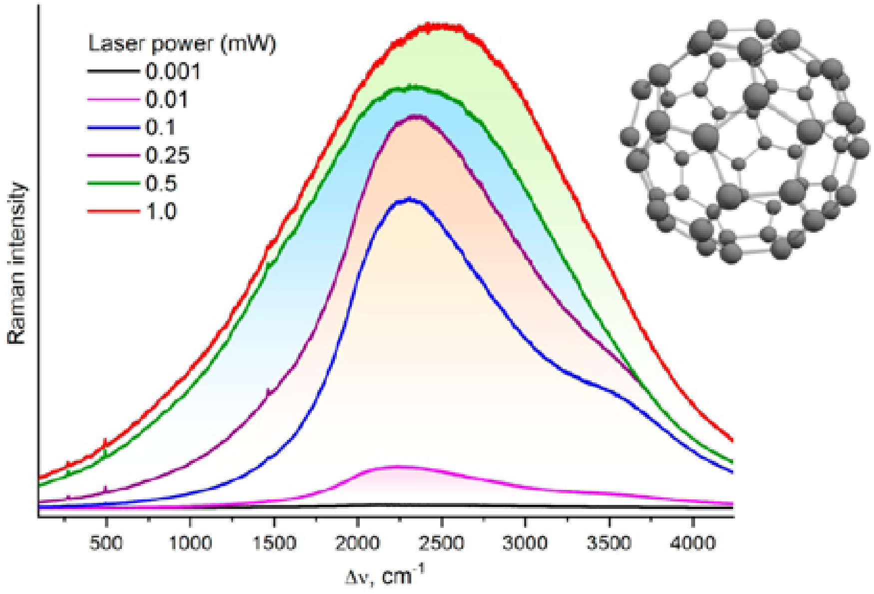

Figure 1. The background change in Raman spectra during the phase transition.

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W-based Silica-Supported Oxo/Imido Heterometathesis Catalysts

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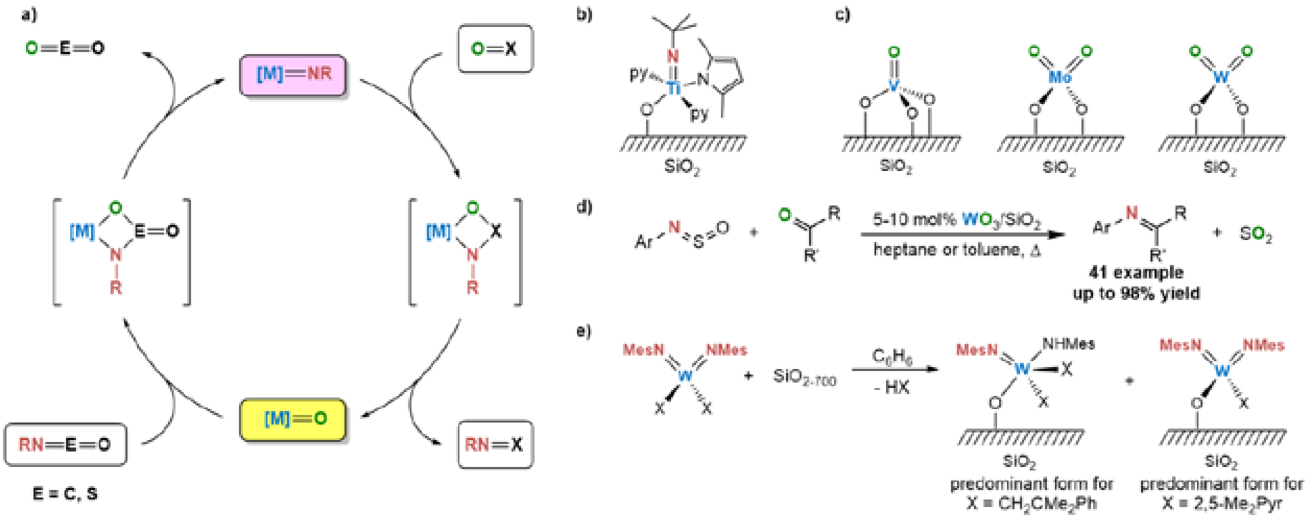
Heterometathesis (*i.e.* metathesis of heteroolefins and/or heteroallenes) is a general methodology for carbon–heteroatom and heteroatom–heteroatom multiple bond construction. Recent works of our group have sufficiently broadened the synthetic possibilities of oxo/imido heterometathesis (Scheme 1a) due to the development of well-defined silica-supported Ti imido catalysts (Scheme 1b) prepared *via* Surface Organometallic Chemistry (SOMC) approach. However, being highly air- and moisture-sensitive, such materials require rigorous inert atmosphere conditions for their preparation and handling, which impedes their widespread application.

We have thus initiated a direct search for the more stable and readily available catalysts. V, Mo and W oxides dispersed on silica were considered as promising candidates due to their availability and presence of terminal M=O surface fragments — key species responsible for catalysis (Scheme 1c). We have shown that these materials can indeed serve as catalysts for oxo/imido heterometathesis between ketones and *N*-sulfinylamines, WO_3/SiO_2 being the most active. Study of the scope of WO_3/SiO_2-catalyzed reaction demonstrated that it provides a high-yielding protocol for obtaining a broad range of imines including those hardly available by classical methods (Scheme 1d). For the further study of the mechanistic aspects of the reaction we were interested to prepare well-defined silica-supported W imides *via* SOMC approach. We have thus investigated grafting of a series of W imido precursors onto the surface of silica partially dehydroxylated at 700°C (SiO_{2-700}), characterized the resulting surface species using physicochemical techniques (solid-state NMR, elemental and mass balance analyses, *etc.*) and compared the activity of the obtained materials with WO_3/SiO_2 system and other previously described catalysts (Scheme 1e).



Scheme 1. a) Catalytic cycle of oxo/imido heterometathesis. b) The most active catalyst. c) Structures of metal sites on the surface for MO_x/SiO_2. d) WO_3/SiO_2-catalyzed synthesis of imines. e) Grafting of tungsten imido complexes on SiO_{2-700}.

Acknowledgements
This work was supported by Russian Science Foundation (Grant No. 19-73-10163).

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Synthesis of C,N-chelated Diaminocarbene Complexes of Palladium and Platinum and Their Application in Catalysis

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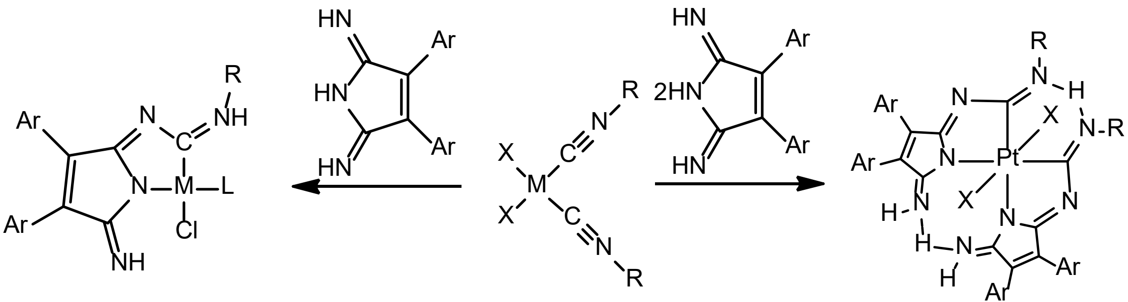
In recent years, metal complexes bearing acyclic diaminocarbenes ([M]ADCs) have emerged as a new family of homogeneous catalysts to be a prominent alternative to well-investigated metal-N-heterocyclic carbene ([M]NHCs) species.[1, 2]

Easy-to-prepare metal-ADCs complexes synthesized by nucleophilic addition of N-nucleophiles to coordinated isocyanides have been successfully investigated as potential catalysts for several organic transformations (cross-coupling, metathesis, cyclization reactions, etc.).[2] In this context, as a continuation of these studies on the application of palladium and platinum complexes as homogeneous catalysts, herein we have presented on the synthesis, characterization, and reactivity of series of acyclic C,N-chelated diaminocarbene complexes of palladium(II), platinum(II) and platinum(IV) (Figure 1) for important organic reactions such as the Suzuki and Sonogashira reactions, and for the hydrosilylation of unsaturated compounds.



M = Pd, Pt;
L = CN-R, Cl

M = Pd, Pt;
X = Cl, Br, I

X = absent, Br, I

Figure 1. Synthesis of C,N-chelated diaminocarbene complexes.

The catalytic activity of ADC-Pd(II) complexes in the Suzuki polycondensation was studied. Also, the prepared ADC-Pt(II) and Pt(IV) complexes can be used as catalysts for the cross-linking of polysiloxanes leading to luminescent silicone rubbers.

Acknowledgements

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Structural significance of weak intermolecular and host-guest interactions for assembly of MoS_2-organic layered compounds

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Molybdenum disulfide is a famous 2D van der Waals solid, considered as one of the most promising post-graphene nanomaterials owing to excellent photothermal, electrocatalytic and conducting properties exhibited by trigonal prismatic (2H) and octahedral (1T) MoS_2 polymorphs. In many application fields, the usage of MoS_2 requires its modification with organic compounds influencing the electronic structure and polymorphic composition and/or providing additional useful effect (for instance, therapeutic one in case of MoS_2-based photothermal agents for medicinal purpose). Profound structural insight into the bonding interactions occurred in such systems is thus a highly topical research field.

In this work, we consider the capability of organic guests containing various aliphatic fragments (the long- and short-chain derivatives of amines, diamines, guanidines) towards self-assembly into two-dimensional nanostructures with MoS_2 sheets produced by liquid-phase exfoliation of molybdenum disulfide crystals. The structures of the resultant organic-inorganic architectures were determined and studied by PXRD technique, DFT calculations and AIM theory topological analysis.[1,2] The obtained structural models elucidated the noncovalent bonding interactions of molecules confined in the two-dimensional spacing between the sulfide sheets and allowed quantification of the energetics of these interactions. It was found that in many cases the most important contribution to hetero-structure stabilization is provided by the weak but numerous host-guest CH…S contacts. Their cumulative effect often prevails over the other contributions including individually much stronger NH…S hydrogen bonds. In case of long-chain amine derivatives as, for instance, quaternary ammonium anticeptic Miramistin (MR), two types of molecule packing were identified in the interlayer space of MoS_2, with different organic layer thicknesses and sets of bonding contacts.[3] In both the MR-MoS_2 structures, apart from dominative CH…S contacts, contributing ~30% and ~50% to the total interaction energy, the hydrophobic intermolecular H…H interactions play an important role, providing additionally approximately one-quarter of that energy. An influence of the noncovalent guest-MoS_2 interactions on the 1T/2H phase ratio is discussed along with photothermal and electrocatalytic properties of the obtained materials.[4,5]

Acknowledgements

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Ruthenacarboranes with chelate ligands: synthesis, isomerism and catalytic application

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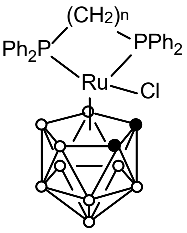
Carborane clusters of transition metals are isolobal analogs of half-sandwich derivatives and thus are capable to replace them in many applications. High donating ability of carborane ligand determines the possibility of formation *exo-nido-*, *closo-* and *pseudocloso-*type clusters expanding the concept of bonding in coordination chemistry.



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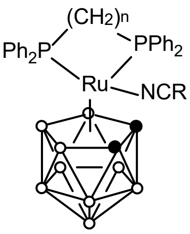

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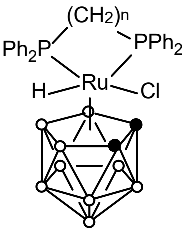

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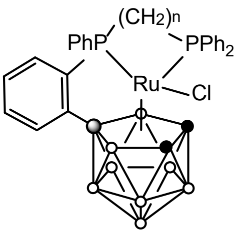

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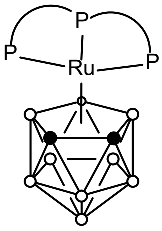

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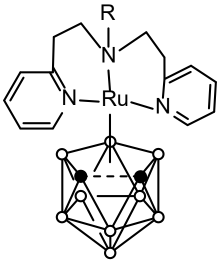

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In a present work the peculiarities of structure and reactivity of carborane clusters of Ru(II)-Ru(IV) with chelate diphosphine and pyridine ligands are discussed. It was shown that complexes of Ru(III) with chelate α,ω-bis(diphenylphosphino)alkanes and POP-ligands (1) may be easily obtained by direct substitution of PPh_3 or through *exo-nido→closo* rearrangement. The obtained Ru(III) species may be reduced by amines in the media of coordinating solvent to form Ru(II) complexes 2. The latter can form Ru(IV) derivatives 3 or initial compounds 1. It was shown that thermolysis of 1 in toluene solution gives compounds 4 with covalent bonding between carborane and diphosphine moieties via *ortho*-cycloboronated fragment. The formation of such boning significantly increases complex stability. It was shown that Ru(II) derivatives with tridentate triphosphine (5) and aminopyridine (6) ligands are characterized by high stability. It was found that complexes 6 exist in so-called *pseudocloso* state with elongated C-C bond in carborane ligand[1].

The performed electrochemical studies have shown that the obtained Ru(III) derivatives undergo reversible Ru(III)-Ru(II) transition. The potential may vary from -0.501 to 0.389 V versus Fc|Fc+ couple depending on the nature of auxiliary phosphine, halogen or nitrile ligand, natural bite angle of κ^2-diphosphine ligand and the presence of alkyl substituents in the carborane cage. The further oxidation towards formal Ru(IV) may be reversible or not depending on complex structure. It was shown that the obtained ruthenacarboranes are capable to catalyze polymerization of methacrylic monomers via ATRP mechanism leading to the well-defined polymers.

Acknowledgements
The work was supported by the Grant of President of Russian Federation (proj. No. MD-1474.2022.1.3).

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Silica-Based Aerogels with Tunable Properties: The Highly Efficient Amphoteric F-containing Catalysts for Aerogels Preparation and Look inside Their Structure

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In recent years, there has been an increased interest in porous materials, which is related to their applicability in different areas of science, medicine and technology. Aerogels, silica aerogels (SA) in particular, have special abilities: (1) high specific surface area and porosity, with a low density; (2) high insulation and soundproof rates; (3) optical transparency; (4) low permittivity; (5) low Young's modulus; (6) thermostability and other.

There are several successive stages that are carried out when obtaining SA (Fig.1): (1) sol-gel synthesis, (2) aging, (3) workup, and (4) drying of gel.

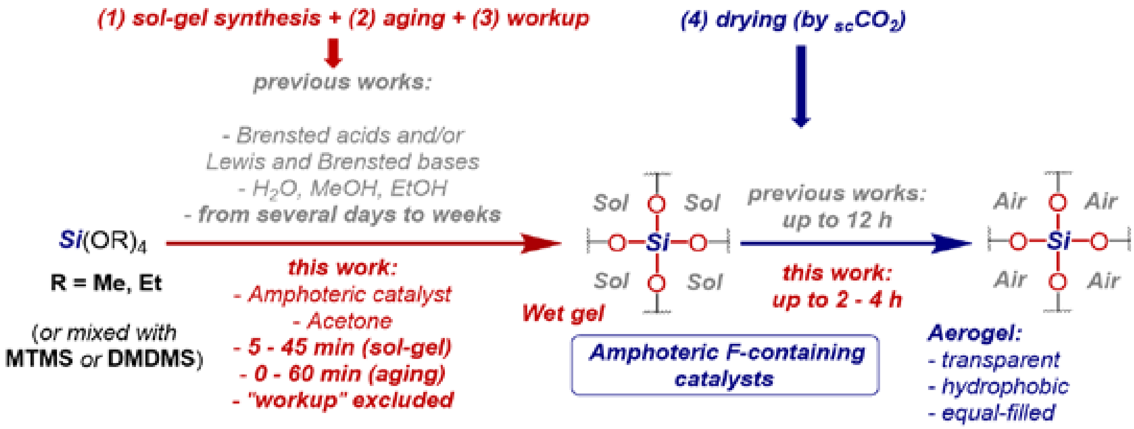

Figure 1. Silica-based aerogels production

This work presents a solution to one of the most fundamentally and practically important challenges in the production of SA, time consumption and expensiveness of these processes, with the main focus on the sol-gel process.[1] We suggested a highly efficient catalyzed by amphoteric F-containing compounds method for the production of aerogels, which allows one to shorten the stage of the formation of a (wet) gel to 5 min, the stage of gel aging to 0, while the stage of gel workup is not required; the duration of these stages, according to the literature, ranges from days to weeks. The process is performed using commercially available, simple, and inexpensive reagents and under mild reaction conditions: amphoteric F-containing compounds as the catalyst, acetone as the solvent, room temperature, and at atmospheric pressure. This approach allows one to quickly obtain both classic opaque and transparent SA from $Si(OMe)_4$ or $Si(OEt)_4$ as well as transparent superhydrophobic ones from their mixtures with $MeSi(OMe)_3$ or $Me_2Si(OMe)_2$. Also, the effect of the method for producing SA on their (supra)molecular structure and morphology was thoroughly studied by a set of physicochemical methods of analysis mostly with using NMR experiments. These findings allow to tune the properties SA depending on the need by choosing the right technique synthesis.

Acknowledgements
This work was supported by a grant of the Russian Science Foundation (RSF grant 19-73-10172-П)

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Unusual ways of using electrochemical data in assessing the properties of organometallic systems

Khrizanforov M.N.,[1,2] **Lazareva A.A.,**[1,2] **Shekurov R.P.,**[1] **Zagidullin A.A.,**[1] **Bezkishko I.A.,**[1]
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There is no doubt that the successful development of organometallic processes depends mainly on the craft of electrochemistry, both in its traditional form and as a technique that interfaces well with complementary methods such as spectroscopy and redox synthesis.

Electrochemical methods sometimes demonstrate possibilities that go far beyond classical voltammetry. In addition to standard redox transitions, it is possible to analyze the size of molecular agglomerates, for example, using potential step chronoamperometric experiments and lattice Boltzmann simulations.[1]

Using differential and integral forms of classical linear and cyclic voltammograms, one can obtain more accurate data related to electron transfer in compounds with complex structures, such as coordination polymers, metal-organic frameworks, nanoparticles, and clusters. In this work, various structures of ferrocene with an included phosphorus atom, as well as other compounds of complex composition, were studied.

The electrochemical, electrocatalytic (CO_2 reduction, HER), chronoamperometric, and other properties of ferrocenyl-*R*-phosphinates, multiferrocenes, and other complex structures are shown. It is demonstrating how the differential analysis allows to estimate and, in some cases, to predict the properties of the synthesized substances. On the example of nanoparticles, chronoamperometric tests were carried out, which showed a direct correlation between current and size. Microscopic measurements were used to confirm the size. The differential method of processing the obtained data makes it possible to obtain the distribution of nanoparticles in the volume of a colloid solution.

Acknowledgements
This work was supported by the grant of the Russian Science Foundation No. 22-73-10203.

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Photo- and Electroluminescence of Platinum Group Metal Complexes with Acyclic Diaminocarbene Ligands

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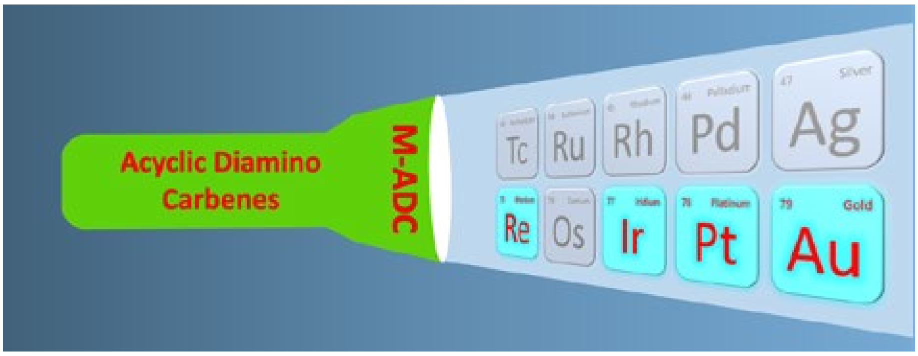
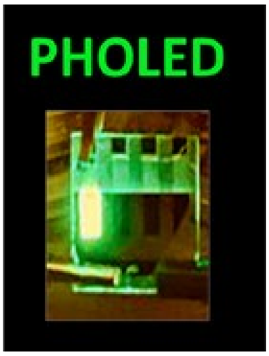
Coordination compounds of platinum group metals with organic ligands exhibit bright and effective fluorescence, phosphorescence, and also thermally activated delayed fluorescence. The presence of these properties makes these compounds attractive objects for their application in various fields of optoelectronics, including the creation of efficient OLEDs. The color of the emission, as well as its efficiency, is largely determined by the type of organic ligand associated with the metal atom. However, for some types of triplet phosphors, harmful photodecomposition processes can occur, proceeding through the dissociation of the ligand after thermal population of higher-lying triplet metal-centred ligand-field excited states. The introduction of strong σ-donor ligands, in particular, diaminocarbenes, into a transition metal-based phosphors leads to destabilize unoccupied d-orbitals and their corresponding metal-centred excited states, and improve the efficiency and stability of phosphorescence. The photophysical properties of diaminocarbene complexes are determined not only by the choice of a suitable metal center, but also by the balance between the donor properties of cyclometallated and auxiliary carbene ligands. Acyclic diaminocarbenes,[1] which are the closest analogues of N-heterocyclic derivatives, have unique, usually higher than NHC, donor properties, while the absence of a cyclic system allows rotation through the nitrogen-carbon bond, leading to significant changes in steric and electronic characteristics of the ligand, which affects the photoemission properties.[2] The report will summarize experimental studies revealing the luminescent properties of complexes of platinum group metals with acyclic diaminocarbene ligands.[3,4]





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The study was supported by the Russian Science Foundation (project no. 21-73-10083). Measurements were performed at the Research Park of St. Petersburg State University.

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Parahydrogen combined with photoisomerization allows persistently hyperpolarize long-lived ^{15}N nuclear spin state of azobenzene

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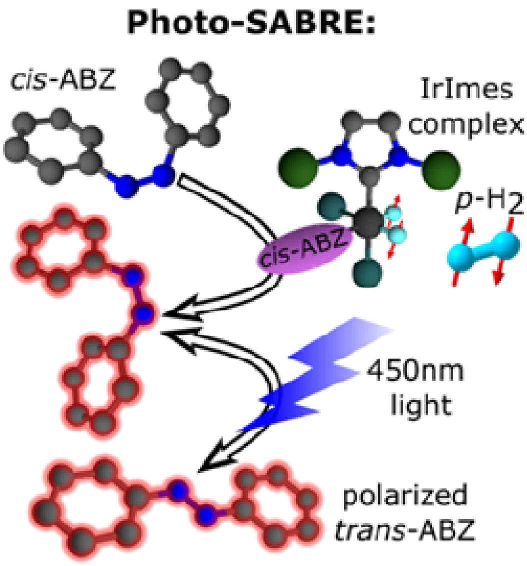

Figure 1. General scheme of polarization transfer to trans-azobenzene via Iridium-Imes catalyst[2]

Over the past decade, azobenzene-based molecular photoswitches have emerged as promising control devices in a range of fields, including chemistry, biology, materials science, physics, energy storage and pharmacology. Previous studies revealed that cis isomer of azobenzene gains strong nonequilibrium polarization (called hyperpolarization) of ^{15}N nuclear spins through interaction with parahydrogen molecules (i.e., a dihydrogen isomer with protons having zero total spin, pH_2) in the reversible exchange with Ir-complex.[1] This technique, known as SABRE (Signal Amplification by Reversible Exchange), enhances inherently weak NMR signals by several orders of magnitude at relatively low operational cost. We demonstrate that performing SABRE in the presence of light irradiation allows to hyperpolarize trans-azobenzene, which direct coordination with the SABRE Ir-complex is sterically hindered. The main process of polarization transfer from the para-hydrogen to the substrate (cis-azobenzene) occurs in the stable dihydride-complex stabilized by the NHC carbene IMes. The optimal polarization transfer process depends on the reaction rates of reversible hydrogen and cis-azobenzene exchange, as well as on the magnetic field and relaxation times. The proposed approach, which we called photo-SABRE, is robust and efficient, as well as non-destructive and reproducible. It combines coherent polarization transfer from pH_2 to cis-azobenzene with the reversible cis-trans-photoisomerization. Continuous irradiation with light during parahydrogen bubbling leads to polarization transfer from cis to trans-azobenzene. Moreover, using photo-SABRE, it is possible to hyperpolarize the long-lived spin order of ^{15}N spin pair in trans-azobenzene, with a lifetime of about 25 minutes, which greatly exceeds the ordinary relaxation times T_1 of its ^{15}N nuclei at high (around 10 s) and low (around 200 s) magnetic fields. [2,3]

Acknowledgements

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An approach to biocompatible sensors based on the Re(I) luminophores

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In recent decade, the utilization of metal-containing chromophores has effectively advanced a range of biomedical applications, such as imaging, sensing, and therapeutic techniques. [1] Due to highly diverse tasks within these fields, the development of novel biocompatible probes with tunable photophysical characteristics and responsive behavior remains a topical interdisciplinary challenge.

Diimine rhenium(I) complexes are among the most fascinating candidates for luminescent materials suitable for biomedical applications, owing to their ability to achieve the desirable water-solubility, stability, sensitivity to the selected biological parameters, and low toxicity. [2]

In order to produce biocompatible organometallic probes, the research presented herein involves the design of emissive Re(I) sensors (Figure 1) comprising pH-sensitive functions or functions for detecting the selected metal cations (**F**) and groups (**P**) suitable for conjugation with non-toxic water-soluble polymers.

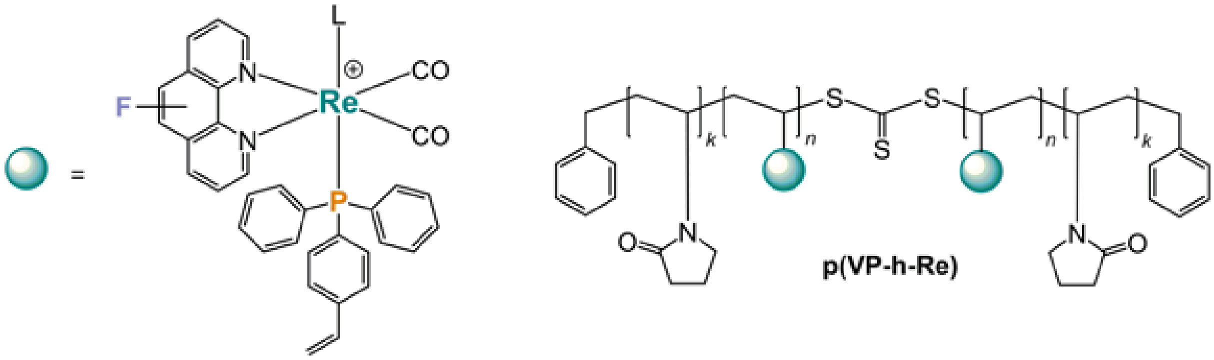

Figure 1. The general scheme of the Re(I)-based sensors.

Direct integration of the Re(I) chromophores into the polymer chain might be implemented through utilization of phosphine ligand with polymerizable styryl fragment, while presence of crown ether groups or N-donor functions might assist in responsive behavior of the target Re(I) compounds.

Acknowledgements

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Transformation of Heteroallenes with Acenaphthene-1,2-diimine Aluminum Compounds

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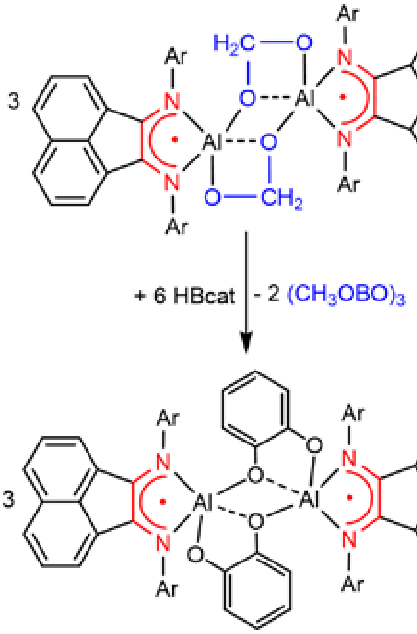
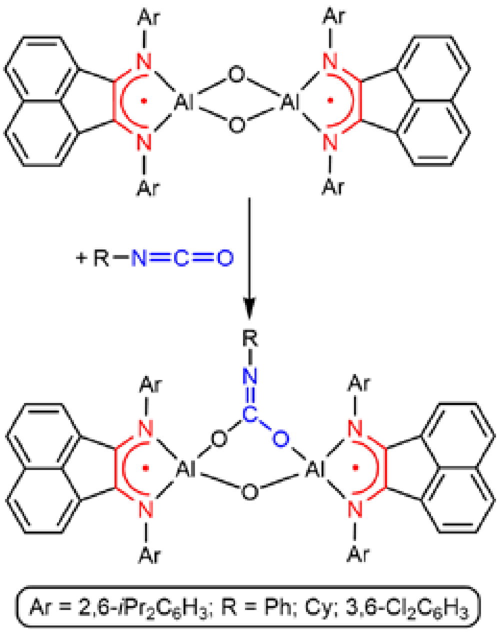
Heteroallenes (carbon dioxide, isocyanates, carbodiimides, etc.) are important reagents in organic synthesis. Whereas isocyanates and carbodiimides are known to be highly reactive, carbon dioxide is an inert molecule, and transformation of CO_2 into valuable chemical materials is one of topical problems in chemistry. Recently we have demonstrated a diverse reactivity of acenaphthene-1,2-diimine aluminum complexes towards carbon dioxide and isocyanates.[1-3] Continuing our study of transformations of heteroallenes we investigated the reactivity of aluminum adduct with CO_2 $[\{(\text{dpp-bian})\text{Al}(\mu\text{-}O_2CH_2)\}_2]$ towards different boranes (Scheme 1)[4] and reactivity of aluminum oxide towards isocyanates with their future catalytic transformation (Scheme 2).



Scheme 1.



Scheme 2.

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Palladium Nanoparticles Entrapped In Hydrogen Bonded Crystalline Organic Salt Matrixes as Selective Heterogeneous Reduction Catalysts

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A new, three-dimensional crystalline organic frameworks (**F-2** and **CF-2**) were obtained, linked by hydrogen bonds and additionally stabilized by the opposite charges of the components (Fig. 1). The materials were proved to be an efficient media for stabilizing metal nanoparticles. For example, **Pd@F2 (A-2)** was simply made by mixing an aqueous solution of tetrasodium salt of tetraphenylmethane-tetrasulphonate (TPSM) and $PdCl_4$ salt of protonated tetrakis(4-aminophenyl)methane under H_2 in water to give the black powder of **A-2**. **Pd@CF2 (A-3)** was obtained by mixing the dipalladium salt of tetraphenylmethane tetrasulfonic acid and a chiral tetraamine hydrochloride in water in a stream of hydrogen.

The materials contained 17-20% of Pd and were not pyrophoric. **A-2** and **A-3** could be used as efficient heterogeneous catalysts of acetylene derivatives reductions with its activity similar to that of Pd/C. **A-2** reduced the aldehyde and epoxide groups very slowly and allowed the reduction of the acetylene groups to be hydrogenated selectively in the presence of the aldehyde groups. The behavior contrasts with that of Pd/C which reduces both aldehyde and acetylene groups simultaneously. A rational for the behaviour was put forward. **A-3** is being used for asymmetric reduction of double C-C bonds.

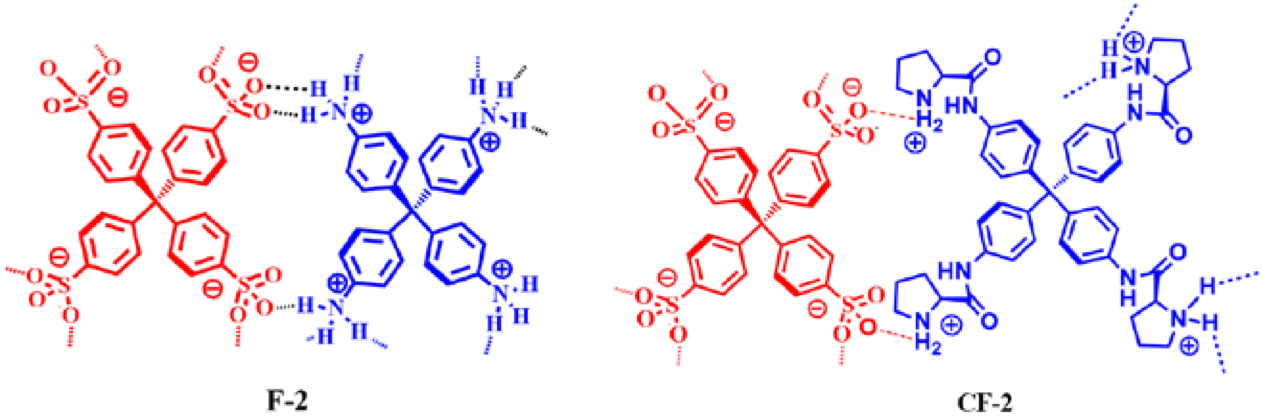

Figure 1. Three-dimensional crystalline organic frameworks (**F-2** and **CF-2**)

Acknowledgements
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Ligand-to-metal charge transfer excited states in organometallics

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Organometallic compounds are an important class of materials in many areas of science and technology. Many classes of organometallic complexes are regarded as rather unstable to air/water and, historically, this fact has drastically hampered development of organometallic photophysics and photochemistry. One of the key problems in photophysics and photochemistry of organometallic complexes is the assignment and characterization of their excited states (e.s.). In this regard, ligand-to-metal charge transfer (LMCT) excited states are rarest and least studied; the state of art in organometallic LMCT e.s. was for the first time generalized in 2022.[1] Perhaps, only early-transition metal complexes in high oxidation states exhibit readily identifiable LMCT excited states. The present contribution will be a reflection of on-going systematic research[2-8] in the field of organometallic LMCT e.s.: the properties of frontier molecular orbitals and the electron transfer paradigm in the case of LMCT e.s. (E_{hn} μ DE_{redox}), the discovery and study of phosphorescent LMCT states based on group 4 metallocenes, triplet-triplet LMCT energy transfer, the relationship between the emission quantum yield and the excited state lifetime, triplet-triplet LMCT absorption, LMCT solvatochromism and estimation of the electric dipole moment of metal complexes (Lippert-Mataga approach and the combined approach based on Bakhshiev, Bilot-Kawski and McRae theories), and so on. The examples to be discussed will illustrate the rich variety of photophysical and photochemical behavior, exhibited by organometallic species in pure LMCT e.s.

The principle objects of study are group 4 metallocene complexes $(\eta^5\text{-RCp})_2MX_2$ (M = Ti, Zr, Hf and Cp - cyclopentadienyl and its derivatives), which have gained special importance as the main components of catalysts for many organic reactions, activation of small molecules, as antitumor drugs, according to our data, have rare LMCT excited states, including unique phosphorescent e.s.: ^{3}LMCT. The properties of the complexes are largely determined by nature and localization of the frontier orbitals (HOMO, LUMO) being a subject of continuous discussions. It is shown that in the case of principal 4 group metallocenes: dichlorides Cp_2MCl_2, dimethyls Cp_2MMe_2 and dicarboranyls $M(\eta^5\text{:}\eta^1\text{-CpCMe}_2CB_{10}H_{10}C)_2$ (M = Ti, Zr, Hf) − first electronic transitions are associated with LMCT. Current state of computational methods available for LMCT spectral assignments of group 4 metallocene complexes and validity of the data obtained will be briefly notified.

Acknowledgements
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Rare-earth anthracenide complexes in ethylene polymerization

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Mononuclear organometallic compounds of rare-earth elements (REEs) with dianions of aromatic hydrocarbons [$X^-Ln^{3+}L^{2-}(solv)_2$] and [$M(solv)_n$]$^+$[$X^-_2Ln^{3+}L^{2-}$] (where L^{2-} is a dianion of naphthalene, anthracene , biphenyl, etc.; X^- is a monoanionic ligand; M^+ is an alkali metal cation) are virtually not studied. Such complexes are of great interest since the Ln^{3+}-L^{2-} bond may have an essentially covalent nature,[1] and their structure mimics that of frustrated Lewis pairs. The latter may indicate an unusual reactivity of the complexes, for example, the ability to activate C-X multiple bonds, and, in particular, C=C. Only a few representatives of mononuclear anthracenide REE complexes are known up to date.[1-5]

In this work, we have developed a convenient method for the synthesis of cyclopentadienyl anthracenide REE complexes of the (η^5-Cp')Ln(η^2-2,6-$R_2C_{14}H_8$) type (Cp' = C_5H_5, 1,3-$Ph_2C_5H_3$, 1,2,4-$Ph_3C_5H_2$; Ln = Y, Nd, Lu; R=H, ^{t}Bu) by reduction of anthracene with KC_8 in the presence of Cp'$LnCl_2$. The ability of dianionic REE complexes to exhibit catalytic activity (without co-catalysts) in the coordination polymerization of ethylene and the copolymerization of ethylene with α-olefins has been demonstrated for the first time. Composition of polymerization products formed under various conditions has been studied by field desorption mass spectrometry to determine end groups. The initiation stage of polymerization has been modeled by a reaction of the complexes with pivalonitrile. Based on mass spectrometry data and crystal structures of key complexes, a plausible mechanism of ethylene polymerization is proposed.

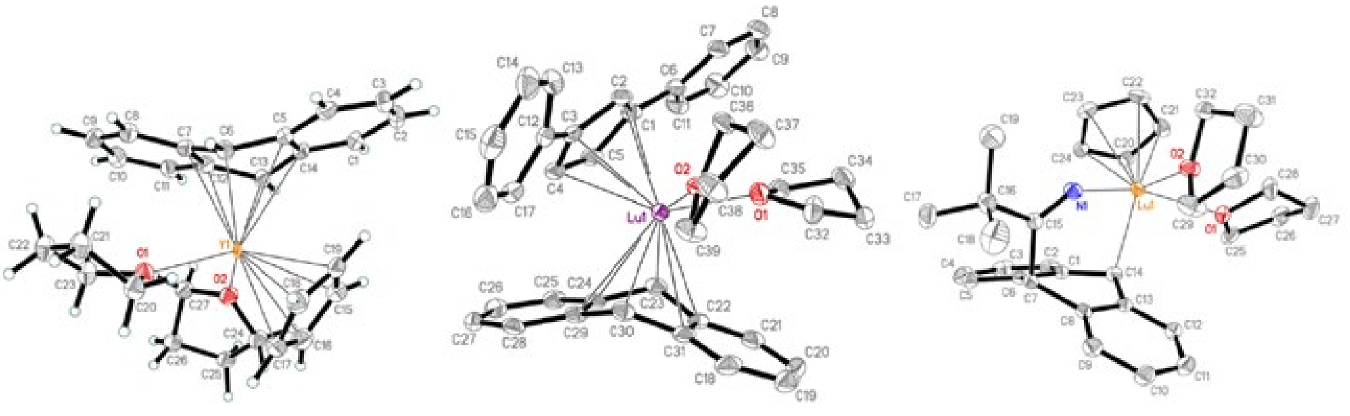

Figure 1. Examples of studied crystal structures (p=50%).

Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 22-23-00711).

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Complexes of 3d and 3d-4f metal carboxylates with N-heterocyclic carbenes as ancillary ligands

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N-heterocyclic carbenes (NHC) are very important ligands in modern coordination and organometallic chemistry. The most of publications describe catalytic activity of NHC complexes whereas other functional properties often remain in shadow. Linear NHC containing complexes of Co(II) recently were found to be single molecule magnets (SMMs) with exclusive efficiency. Despite this fact systematic use of NHC ligands for design of new magnetoactive compounds is not common. On the other hand, carboxylate ligands are uniquely suited for molecular magnetism studies, and they have been widely used for design of new SMMs. At the same time, however, carboxylate complexes with NHCs as ancillary ligands are reported in a limited number of publications.

Recently we have synthesized families of 3d and 3d-4f carboxylates supported by N-heterocyclic carbenes (Fig. 1). The features of synthetic methodology,[1–3] solid state and solution structure as well as magnetic properties (especially in alternating current regime) of selected complexes will be presented and discussed in detail.

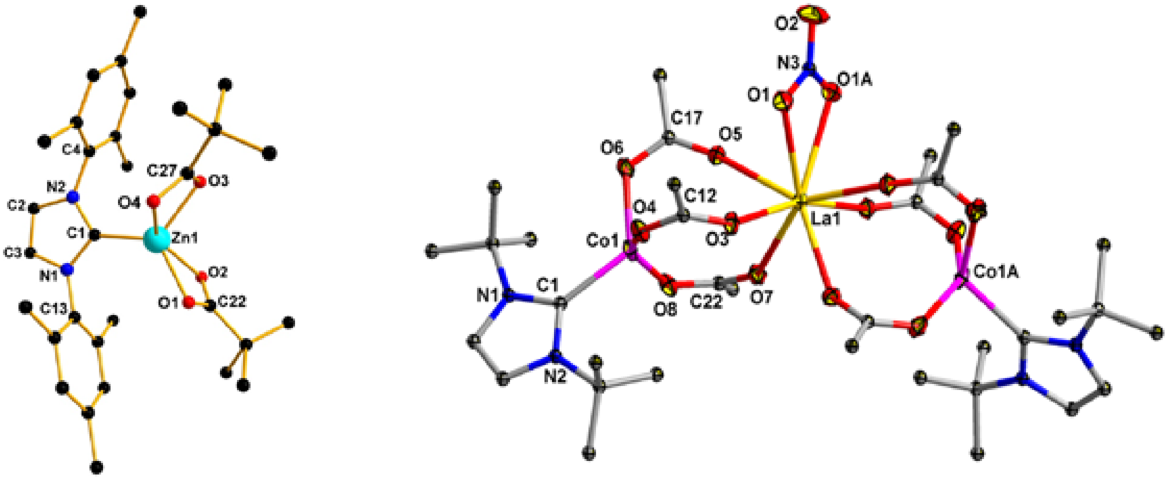

Figure 1. Examples of 3d and 3d-4f metal pivalates supported by NHC ligands

Acknowledgements
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Gold Nanoclusters Protected by Thiolate: Special Structure and Catalytic Properties

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Thiolate-protected gold clusters, $Au_n(SR)_m$, have been attracted interest over the last decade due to unique properties and applications in different fields[1]. Using atomically precise $Au_n(SR)_m$ as a precursor, size-selected and structure-selected nanoparticles with applications in catalysis have been prepared.

The report will present the results of a theoretical study of structure and catalytic properties of $Au_n(SR)_m$ in CO oxidation. $Au_{20}(SR)_{16}$ is considered as a typical protected cluster (as well-known $Au_{25}(SR)_{18}$). The cluster was previously synthesized with 4-tert-butylbenzenethiolate ligands. Au_7 core is surrounded by various staple fragments including an octameric ring ($(AuSR)_8$), one trimeric $-SR(AuSR)_3-$, and two monomeric staple motifs $-SR(AuSR)-$ (Fig. 1).

Different scenarios of reactions between the cluster and oxygen are considered including oxygen photoinitiation, oxidation of the cluster's fragments, oxidation of the cluster after thermal activation, and oxygen adsorption on $Au_{20}(SR)_{16}/CeO_2$. The highest oxygen activation is observed on the cluster lacking three ligands[2]. The active site of O_2 binding is the Au3 fragment. The CO oxidation on $Au_{20}(SCH_3)_{13}/CeO_2$ is simulated proceeding by Langmuir-Hinshelwood or Mars-van Krevelen mechanisms. The active site is near the cluster-support interface. The effect of copper on the catalytic properties of the $Au_{20}(SR)_{16}$ in CO oxidation is studied also.

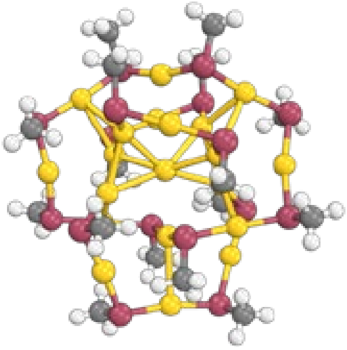

Figure 1. Structure of $Au_{20}(SR)_{16}$ cluster: gold atoms are colored yellow, sulfur atoms are colored burgundy, carbon atoms are colored grey.

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Peroxocomplexes of p-block elements

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Coordination compounds containing various forms of dioxygen ligands (molecular oxygen O_2, superoxide anion O_2^-, hydroperoxide anion OOH^-, peroxide anion O_2^{2-}) are involved in key biological processes, including cellular respiration, signaling and determine cell death. On the other hand, dioxygen complexes of transition metals are intermediate compounds in the selective catalytic oxidation of organic compounds.

Protonated dioxygen ligands exhibit increased activity in catalytic processes. In addition, due to their nucleophilicity, coordinated hydroperoxo groups react with coordination centers with the formation of peroxo bridging structures, releasing a hydrogen peroxide molecule. Apparently, the high reactivity of hydroperoxo complexes complicates their preparation and study. Thus, coordination compounds with hydroperoxoligands remains a relatively poorly studied class of dioxygen complexes: only 20 such compounds have been structurally characterized, which is only about 1% of the structural data on dioxygen complexes.

It was previously shown by J. Mayer that hydrogen peroxide is a poor ligand to main group elements,[1] and hydroperoxo and peroxo complexes are formed only after deprotonation of hydrogen peroxide in the presence of a base.[2–4] The latter can be extended for organic hydroperoxides and they become active ligands only after deprotonation with a base.[5] A number of hydroperoxo complexes of silicon, germanium, tin, antimony, lead were obtained using concentrated hydrogen peroxide and corresponding organoelement halides and hydroxides and structurally characterized for the first time.[6,7] In addition, tin and lead complexes with organic peroxides as ligands were obtained and structurally characterized.[5]

The catalytic activity of obtained organoelement hydroperoxides as a two-electron oxidant for the enantioselective catalytic epoxidation of olefins were studied.[7]

Acknowledgements

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Structural diversity of the rare-earth polyarylcyclopentadienyl complexes

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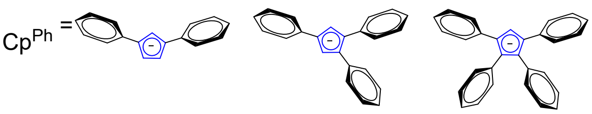
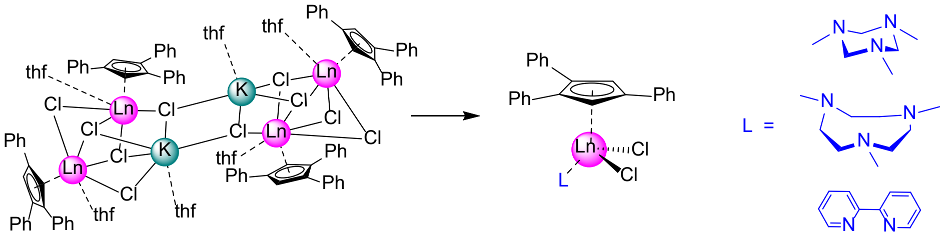
Cyclopentadienyl ligands are widely used in organolanthanide chemistry to stabilize homo- and heteroleptic complexes. We have developed synthetic routes to polyarylsubstituted cyclopentadienyl complexes of the rare earth. A series of di-, tri-, and tetraphenyl-, mono-, bis-, and tris- cyclopentadienyl complexes have been obtained.[1, 2]

$LnCl_3(THF)_3 + Cp^{Ph}K \rightarrow [(Cp^{Ph})_nLnCl_{3-n}(KCl)_x(THF)_y]$, Ln = La, Ce, Pr, Nd, Gd, Tb, Dy



Mono- and bis- cyclopentadienyl complexes of this type are mostly bi- or tetranuclear *ate*-complexes like $[\{Cp^{Phn}Ln(THF)\}_2(\mu\text{-}Cl)_5K(THF)_x]_2$ and $[Cp^{Phn}{}_2Ln(\mu\text{-}Cl)_2K(THF)_x]_2$, or even coordination polymers. Using chelating bi- and tridentate N-donor ligands we have found an efficient route of converting these complexes into mononuclear complexes.[3, 4]



The use of arylsubstituted Cp ligands with bulky arylsubstituted Cp-ligands allowed us to obtain new structural types of complexes.[1, 5] Synthesis, structural diversity and photophysical properties of polyaryl-substituted cyclopentadienyl complexes of Pr, Nd, Gd, Tb and Dy will be discussed in the presentation.

Acknowledgements

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Cationic Palladium Cyclopentadienyl and Acetylacetonate Complexes Containing Tertiary Phosphines: Synthesis, Structure and Catalytic Properties

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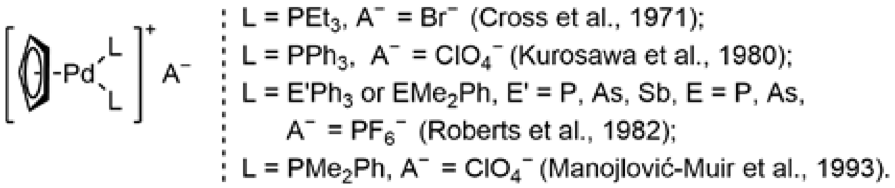
Cyclopentadienyl-containing transition metal compounds are among the most studied organometallic complexes. In the last three decades, they have played a significant role in the development and understanding of the concepts of homogeneous catalysis, especially in such an important area of catalysis as the polymerization of olefins [1]. Despite the wide application and the presence of a number of studies of cyclopentadienyl complexes of various transition metals, cyclopentadienyl palladium complexes have been studied to a lesser extent. Most of these are neutral palladium(II) species. Cationic palladium complexes containing η^5-cyclopentadienyl ligand are rare (see e.g. Figure 1, [2–5]). This is largely due to the lack of convenient approaches to the synthesis of such compounds. The main reagent for the preparation of palladium cyclopentadienyl complexes is TlCp [6], a highly toxic compound often used in syntheses in a large molar excesses.



$L = PEt_3$, $A^- = Br^-$ (Cross et al., 1971);
$L = PPh_3$, $A^- = ClO_4^-$ (Kurosawa et al., 1980);
$L = E'Ph_3$ or EMe_2Ph, $E' = P, As, Sb$, $E = P, As$,
$A^- = PF_6^-$ (Roberts et al., 1982);
$L = PMe_2Ph$, $A^- = ClO_4^-$ (Manojlović-Muir et al., 1993).

Figure 1. Examples of the reported cationic η^5-cyclopentadienyl Pd-complexes with phosphine ligands

The report presents the results of research on the development of a novel route for the synthesis and preparation of new cationic cyclopentadienyl complexes of palladium with organophosphorus ligands of the general formula $[CpPd(L)_n]BF_4$ (where, for example, n = 1: L = dppp, dppb, dppf, etc., n = 2: L = PPh_3, PPh_2Cy, $P(o\text{-}CH_3OC_6H_4)_3$, etc.) based on cationic palladium acetylacetonate complexes as precursors. Their spectroscopic (NMR, UV and IR) and structural properties (XRD- and DFT-based) are discussed. We also disclose our findings on the catalytic activity of the novel complexes in the addition polymerization of norbornene, phenylacetylene and telomerization of butadiene with methanol (mostly compared to their cationic acetylacetonate analogues).

Acknowledgements
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Cymantrenylalkylptalimides as photo- and electroactive compoumds

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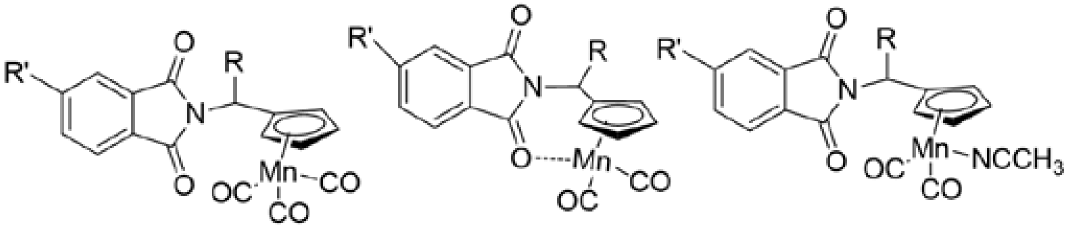
At present, multiparametric smart materials with variable properties are actively developed. One of these classes of compounds is phthalimides, which possess pronounced optical and electrochemical properties. The phthalimide fragment is used as an optically active group, which, when incorporated into a matrix system, allows fine tuning of the absorption and/or emission color.1 The introduction of a phthalimide group as a copolymer into organic semiconductor materials makes it possible to obtain conjugates with the required electronic parameters.2 Exchange an organic substituent at the nitrogen atom with a photo- and electroactive organometallic cymantrenylalkyl fragment can make it possible to create a new class of acceptor materials. In this work, the optical and electrochemical properties of tri- and dicarbonyl complexes 1-9 (Figure 1) were studied in order to establish the influence of substituents both in the 1 position of the side chain of the Cp-ring, and in the 4 position of the phenyl ring of the phthalimide fragment, as well as the ligand environment of manganese on the ability to vary the physicochemical properties of the system.



R = H R' = H	**1**	**4**	**7**
R = CH_3 R' = H	**2**	**5**	**8**
R = CH_3 R' = $COO(CH_2CH_2O)_2CH_2CH_3$	**3**	**6**	**9**

Figure 1. Tri- and dicarbonyl complexes based on cymantrenylalkylphtalimides.

Using IR, NMR, UV-vis spectroscopy and cyclic voltammetry, it was shown that change in the ligand environment of manganese leads to a sharp change in the optical and electrochemical properties of the studied compounds. The introduction of a substituent at position 1 of the side chain changes not only the physicochemical properties, but also the stability of dicarbonyl complexes. The substituent in the 4 position of the phenyl ring of the phthalimide fragment has a significant effect on the interaction of cyclopentadienyl manganese complexes with the solvent. Thus, we can control the properties of the system by changing the structural and electronic parameters of cymantrenylalkylphthalimides.

Acknowledgements

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Insights into the structure-property-activity relationship of zeolitic imidazolate frameworks for cycloaddition of CO_2 to epoxides

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Nowadays, the chemical fixation of carbon dioxide is attracting more and more attention. The CO_2 fixation into cyclic carbonates through the direct cycloaddition of CO_2 to epoxides is the most attracting route to convert the CO_2 into chemicals. Such type processes could be realized in the presence of a catalyst. According to the literature, zeolitic imidazolate frameworks (ZIFs) can be utilized for the coupling reactions of CO_2 with epoxides [1]. Their unique structural and physicochemical properties, such as uniform pores, high surface areas, and open porous framework systems with large accessible pore volumes allow them to demonstrate excellent activities and selectivities providing high product yields. Herein, we present an investigation of the nature of ZIFs in terms of their chemical composition, textural, acid–base, and morphological properties that affect strongly their catalytic performance in the cycloaddition reaction of CO_2 to epoxides (propylene oxide and styrene oxide).

A series of Zn- and Co-containing ZIFs, such as ZIF-8(Zn)/ZIF-67(Co), MAF-5(Zn)/MAF-5(Co), and MAF-6(Zn)/MAF-6(Co) have been prepared. The effect of the chemical composition, textural, structural and physicochemical properties on their activity was investigated. Our examination allowed us to conclude [2]:

1. The activity of Zn-containing materials is higher in comparison with Co-based other type systems. Moreover, the yield of a cyclic carbonates is decreased with increasing Co content in mixed Zn,Co-ZIFs (ZIF-8/ZIF-67) materials that is related to the accessibility of active centers to reagents and the strength of their interaction with CO_2 and epoxide.
2. The number of active sites is tuned by a modulation of the chemical composition and particle size of ZIF catalysts. The strength of basis sites depends on the basicity of imidazolate linkers, and ZIF structure.
3. The catalytic performance of ZIFs is improved by increasing the size of pore aperture contributed to the guest molecule diffusion and accessibility of the active site for reagents.
4. The shape and size of particles should be taken into account because these factors affect textural properties and active site number. Moreover, particle size can provoke problems in the course of cyclic tests and/or isolation of ZIF catalysts from reaction mixtures.

Acknowledgements

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Mixed-ligand metal-organic coordination polymers based on redox-active linkers of the anilate type

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Synthesis of new mixed-ligand metal-organic coordination polymers (MOCP) and study of their properties is one of the actual growing points in supramolecular chemistry. The combination of properties of two types of anionic ligands in one compound makes it possible to synthesize derivatives with unique physical and physico-chemical properties. Anilate-type ligands (derivatives of 2,5-dihydroxy-1,4-benzoquinone) were used as the main organic ligands. Well-studied derivatives of dicarboxylic acids (terephthalic, biphenyl-4,4'-dicarboxylic and furandicarboxylic acids) and various glycols (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol) were used as additional ligands. Heteroleptic MOCP of lanthanides with two types of anionic ligands in the link (anilate and dicarboxylate) have been synthesized. The structure of the link was found to depend on the nature of the metal center as well as the nature of coordination of both types of the ligands (Fig. 1).

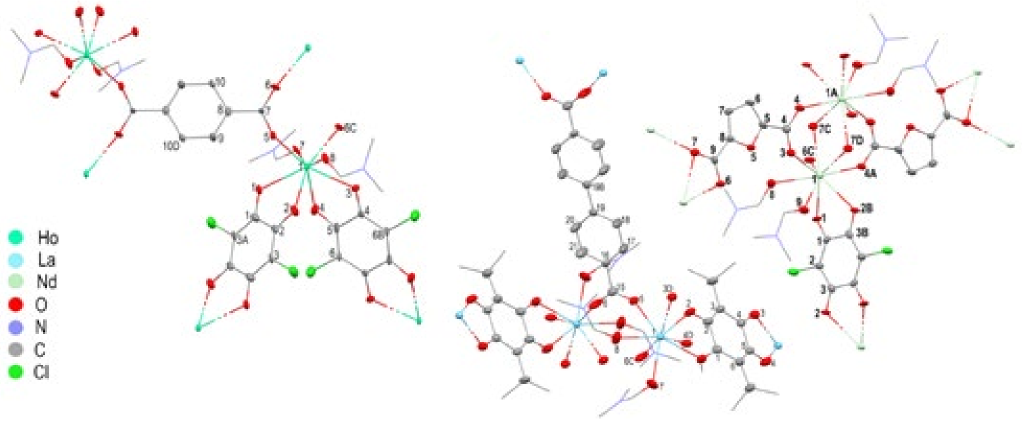

Figure 1. Molecular structures of the MOCP of lanthanides. Thermal ellipsoids are given with a 50% probability. Hydrogen atoms are not depicted.

Zinc and cadmium mixed-ligand derivatives based on anilates and glycols are zigzag-type MOCP and diatomic alcohols are acting as the coordination ligands (Fig. 2).

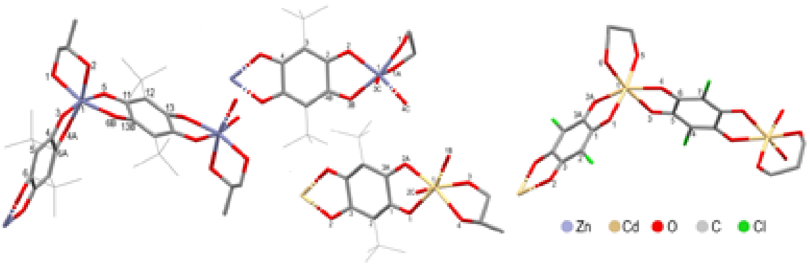

Figure 2. Molecular structures of the MOCP of zinc and cadmium. Hydrogen atoms are not depicted.

Acknowledgements

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Oxidative C-H functionalizations for synthesis of metallocene ligand systems and pharmacologically active compounds

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Since its discovery in 1951, the research towards ferrocene-containing compounds has received a lot of attention. Nowadays, ferrocene is an applicable organometallic scaffold for the preparation of functional derivatives in catalysis, material science and biomedical chemistry. P,N, P-O, P-P-ferrocenyl ligands have found a widespread use in asymmetric catalysis. However, despite the impressive progress in this area, the design of chiral ligands for a particular application remains a formidable task.

Enantiomerically enriched derivatives of ferrocenes **L1**, **L2** were obtained using two general synthetic approaches. The first one exploits the Pd-catalyzed cross-coupling, the second method involves the direct oxidative C-H functionalizations of (hetero)arenes. The ligands demonstrated high enantioselectivity in the reaction of asymmetric synthesis (Figure 1).

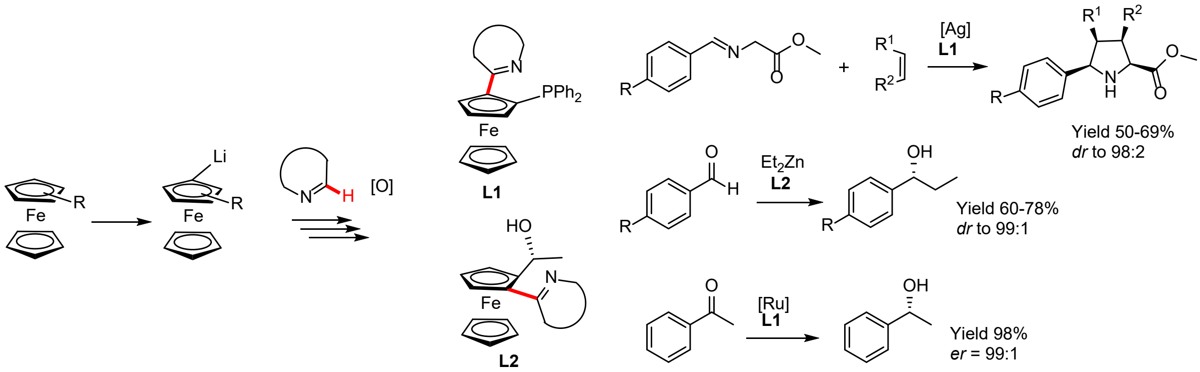

Figure 1

In addition, the developed synthetic approaches were used to obtain asymmetric 1,1’-disubstituted azinyl containing vinylferrocenes **L3** (Figure 2). It was found that 1-azinyl-1’-vinylferrocenes exhibited extremely high inhibitory activity against butyrylcholinesterase (BChE) and radical-scavenging activity.

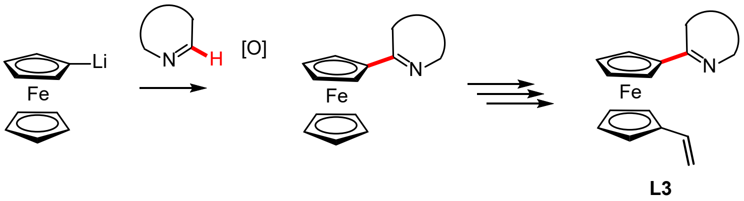

Figure 2

A focused search for cholinesterase inhibitors with neuroprotective and disease-modifying properties is of interest for obtaining potential multitarget drugs for the treatment of neurodegenerative diseases.

Acknowledgements

The research was financially supported by the Russian Science Foundation (Project No. 22-13-00298)

Catalytic and Photocatalytic Activity of TiO_2 Nanoparticles in Polycarbonate Nanocomposites Degradation Reactions

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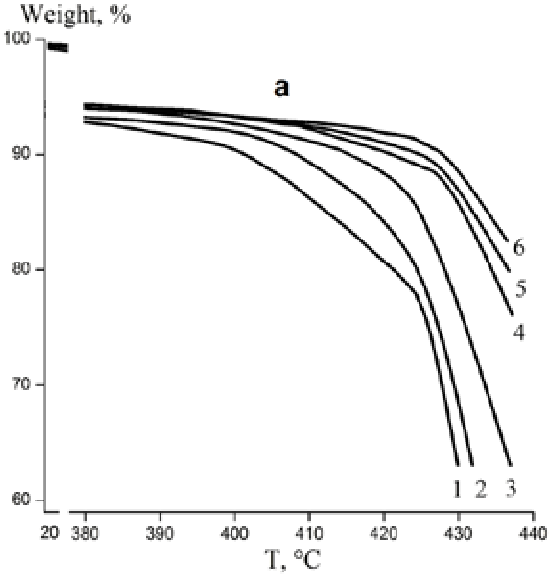
The kinetics of thermal degradation of polycarbonate films containing TiO_2 nanoparticles deposited on polymer films by electron-beam evaporation of TiO_2 powder in vacuum has been studied. The weighted average thickness of the deposited layer was 5–30 Å, which corresponded to ~0.003–0.020 wt. **%**. TiO_2 nanoparticles in the polymer. The forms of pre-deposited TiO_2 nanoparticles are shown in Fig. 1b. The isothermal (T=420°C) and nonisothermal kinetics of the thermal degradation of nanocomposites was studied by TGA method with a heating rate of 3 K/min at a residual pressure of 1.3 Pa using an ATV-14 automatic electronic vacuum balance. To activate the catalytic action of the TiO_2 nanoparticles, the nanocomposite films of 80-100 μm in thickness were irradiated with a DRT-400 mercury lamp (wavelength $\lambda < 390$ nm) for 6 hours.

It was found that the rate of degradation of pre-irradiated samples decreases with increasing concentration of TiO_2, while non-irradiated polycarbonate films containing TiO_2 nanoparticles decompose faster than the original polycarbonate (Fig. 1, a-b).



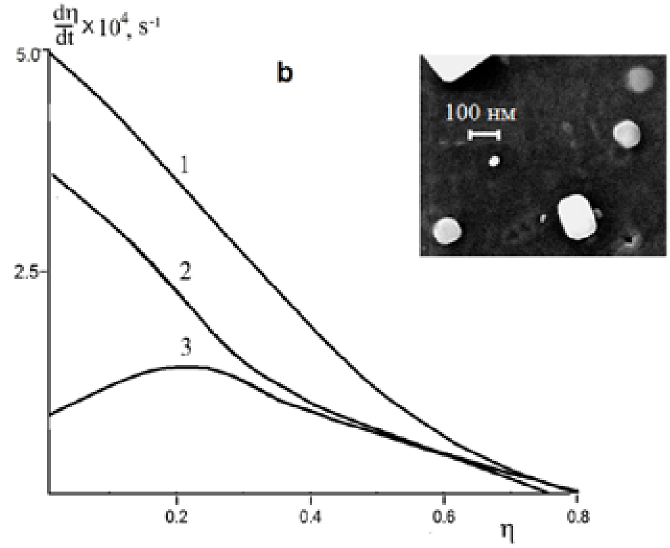


Figure 1a - TGA-curves of the decomposition of the original polycarbonate (3); non-irradiated polycarbonate films containing 0.02 (1); 0.01 (2) wt. % TiO2 nanoparticles and irradiated films containing 0.003 (4); 0.006 (5) and 0.01 (6) wt. % TiO_2 nanoparticles.

Figure 1b - Dependences of the rate of weight reduction on the degree of conversion during thermal degradation of the original polycarbonate (2); non-irradiated (1) and irradiated (3) polycarbonate films containing 0.01 wt. % TiO_2 nanoparticles; T=420°C.

Acknowledgements

This work has been performed in accordance with the state tasks, state registration AAAA-A19-119120690042-9 and AAAA-A19-119032690060-9 using equipment of the Center for Collective Use FRC PCP MC RAS

Recent advances in the chemistry of phosphacyclopentadienide derivatives

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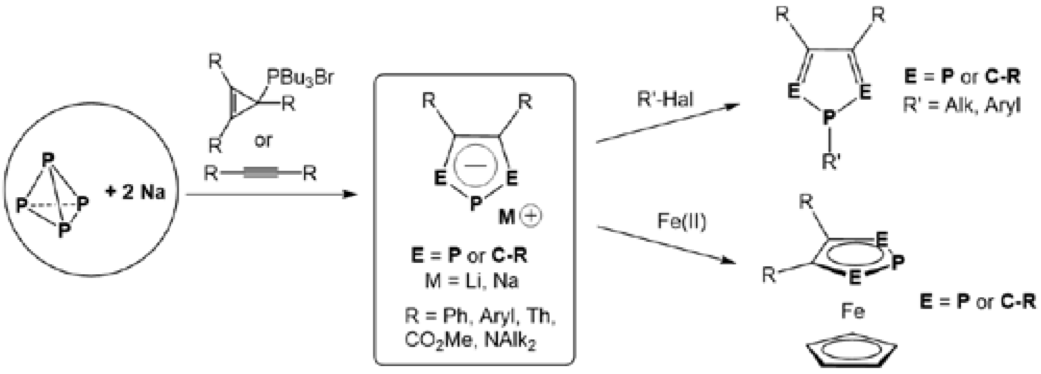
Phosphacyclopentadienide (phospholide) anions and their derivatives are very attractive as building blocks for the construction of versatile organophosphorus molecular materials with useful and interesting catalytic, optical, luminescent, magnetic properties.[1] Therefore, development of convenient methods for straightforward synthesis of these phosphorus heterocycles and their derivatives through functionalization of elemental phosphorus P_4 (bypassing toxic chlorine Cl_2) has a significant interest.[2] This lecture features recent advances on the synthesis of various phosphacyclopentadienide-anions and their chemical behavior toward organic, organoelement substrates, and transition metal complexes.



A rational and highly efficient method to access 1-mono-[3], 1,2-di-[4] and 1,2,3-triphospholide[5] anions in individual forms directly from white phosphorus P_4, alkali metals and small molecules (alkynes and cyclopropenylium halides) have been developed. Interaction with various chiral and non-chiral alkyl halides has allows for formation of novel *P*-heterocycles - 1-mono-, 1,2-di- and 1,2,3-triphospholes. Reaction with Fe(II) complexes was used as a convenient way for efficient synthesis of a number of phosphaferrocenes.[6] First results on application in material science and homogeneous catalysis of phospholide derivatives (phospholes and their [4+2] cycloadducts) was also presented.[7]

Acknowledgements
This work was supported by Russian Science Foundation (project no. 21-73-10204)

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Electrochemical study of new platinum and nickel bis((diphenyl)phosphinoxy)phen pincer complexes

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At present, transition metals pincer complexes have become the subject of intense research as potential electrocatalysts for proton reduction [1]. The catalytic activity of these compounds depends on the metal and ligand environment. In this work, the redox properties of new platinum and nickel bis((diphenyl)phosphineoxy)phenyl pincer complexes with different terminal ligands: $[C_6H_3\text{-}1,3\text{-}(OPPh_2)_2]M\text{-}X$ [M = Pt, X = C≡C-(4-$C_6H_3N_2S$) (**1**), Cl (**2**), Br (**3**), I (**4**); CN (**5**), C≡C-Ph (**6**); M = Ni, X = C≡C-(4-$C_6H_3N_2S$) (**7**); CH_3COO (**8**)], were studied using dc polarography at a dropping mercury electrode (DME), cyclic voltammetry at platinum (Pt) or glassy carbon (GC) and controlled-potential electrolysis on Pt electrode in acetonitrile solution in the absence and presence of proton donors.

It was showed that different redox-centers are involved in the electrochemical reactions of **1-8**: a metal center during oxidation, and a ligand upon reduction. Thus, the oxidation potentials values of **1-8** on Pt and GC electrodes depend significantly on the nature of the metal atom. Platinum complexes **1-6** are oxidized to the one two-electron stage, while nickel compounds **7, 8** - one-electron stage, which can be assigned to a Pt(II)/Pt(IV) and Ni(II)/Ni(III) couple. The reduction of **1-8** on DME and GC electrodes depends on the nature of the terminal ligands X and proceeds through different mechanisms. Complexes **2-6, 8** with X = Cl, Br, I, CN, C≡C-Ph and CH_3COO ligands are reduced in one irreversible two-electron step with the elimination of the X- anion and the formation of $[(C_6H_3\text{-}1,3\text{-}(OPPh_2)_2)M]^-$. The one-electron quasi-reversible reduction of compounds **1, 7** with alkynyl C≡C-(4-$C_6H_3N_2S$) ligand results in a radical anion, the further two-electron reduction that leads to the elimination of the alkynyl ligand.

The study of the ability of complexes **1-8** to catalyzed electrochemical reduction of protons has showed that these compounds are ineffective in these processes. Probably, the reduction of **1-8** in the presence of proton donors results in the elimination of the terminal ligand with the formation of anionic metal-containing $[(C_6H_3\text{-}1,3\text{-}(OPPh_2)_2)M]^-$-fragments.

Acknowledgements

This work was conducted within the framework of the budget project FWES-2021-0012 (registration number in EGISU 121031500209-6) for Institute of Chemistry and Chemical Technology SB RAS and Krasnoyarsk Region Science and Technology Support Fund (on participation of students, graduate students and young scientists in conferences, scientific events and internships)

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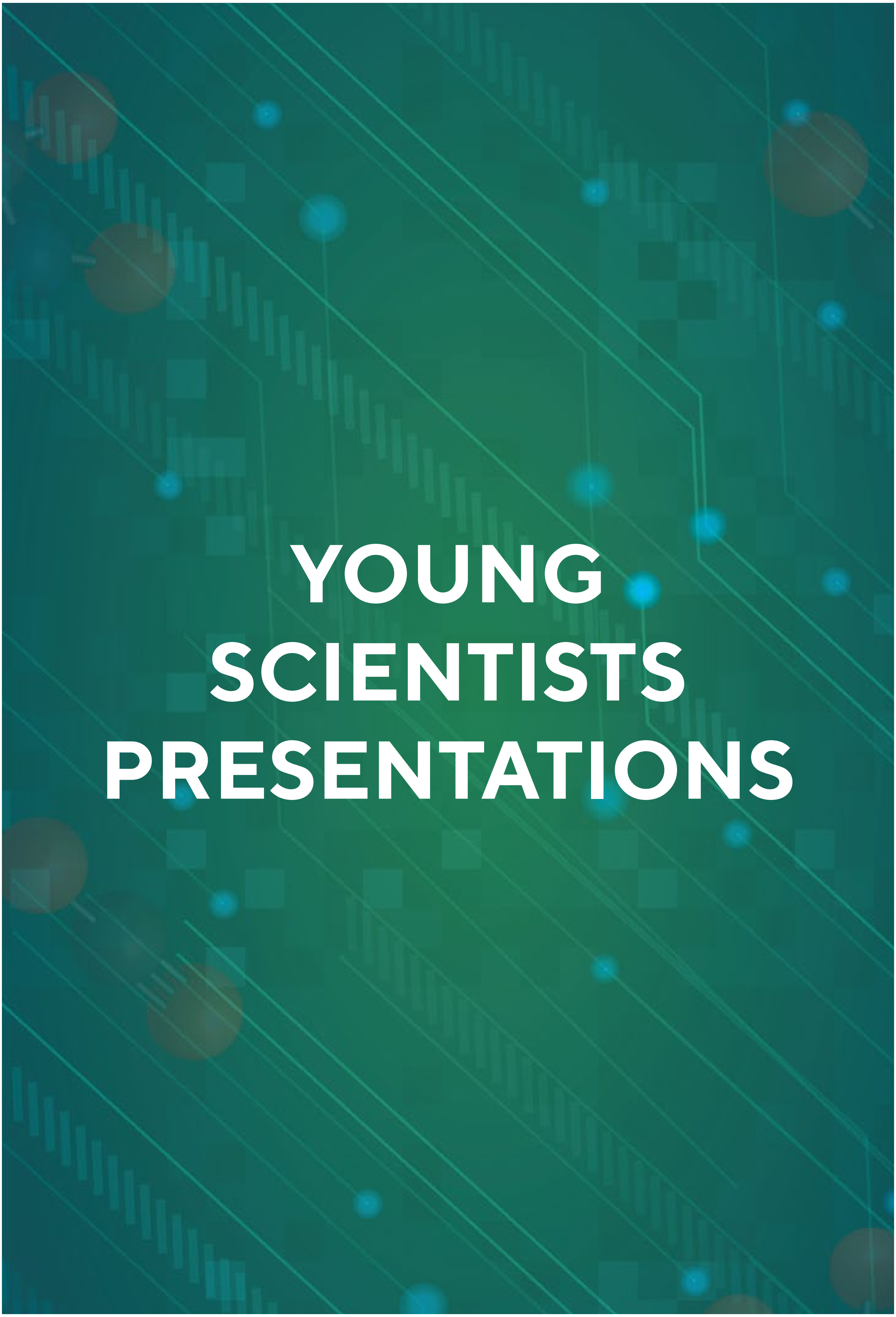

YOUNG SCIENTISTS PRESENTATIONS

CHIRAL FERROCENYLPHOSPHINATES: STRUCTURAL FEATURES AND PHYSICO-CHEMICAL PROPERTIES

Akhmatkhanova F.F.,[1] **Zagidullin A.A.**,[1] **Khrizanforov M.N.**,[1,2] **Miluykov V.A.**[1]

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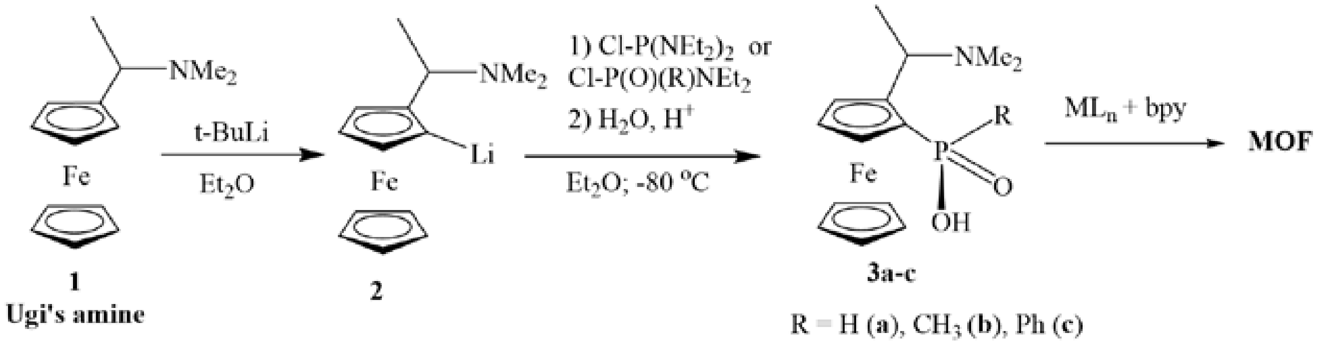
Ferrocene, a “privileged” scaffold for chiral ligands and catalysts, plays an outstanding role in asymmetric organic synthesis both in academia and industry. Ferrocene-containing phosphine acids are promising ligands for the construction of coordination compounds and metal-organic frameworks (MOFs) due to their structural and coordination properties. Racemic and enantiopure ferrocene-based *P*-chiral amidophosphinates **3a-c** have been simply and stereoselectively synthesized by *ortho*-lithiation of *rac*- or (*R*)-Ugi’s amine **1** and further reaction with diamidochlorophosphine $ClP(NEt_2)_2$ [1], amidochloromethylphosphinate $Cl\text{-}P(O)(Me)NEt_2$ or amidochlorophenylphosphinate $Cl\text{-}P(O)(Ph)NEt_2$ [2]. The structures of *rac*- and (*R*)-Ugi’s amine ferrocenyl(phenyl)phosphinic acids **3a-c** have been extensively studied experimentally by NMR, X-ray analysis and electrochemistry.



Scheme. Synthesis of phosphinic acids 3a-c and MOF’s based on them

Utilization of 2-(*N,N*-dimethyl-α-aminoethyl)ferrocenylphosphinic acid (L, 3a) as a ligand along with 4,4`-bipyridine (bpy) facilitated the synthesis of the coordination polymer based on Ugi’s amine with the composition $Ni(bpy)_2L_2$ and $Co(bpy)_2L_2$. These are the first examples of use of Ugi’s amine as a platform for the construction of chiral coordination polymers. When studying the electrochemical properties of this polymer, it was found that the cathodic shift of the oxidation potential of the ferrocene fragment in the polymer in comparison to free acid demonstrates a strong interaction of iron and nickel within the coordination polymer structure [1]. The structural features and electrochemical properties of new Ugi’s amine based chiral coordination polymers were studied, as well as its electrocatalytic properties in CO_2 reduction.

Acknowledgements

This work was supported by the grant of the Russian Science Foundation, No. 22-73-10203.

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Polymorph-Dependent Phosphorescence of Platinum(II) Complexes

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The luminescent properties of platinum(II) complexes are closely associated with their molecular conformations and, at the same time, with crystal packing determined in particular by intermolecular interactions; thus, different polymorphs of the same compound could exhibit different photophysical properties. The control over the formation of polymorphs is challenging because of the complexity of multiple molecule–molecule and molecule–solvent interactions that occurred on crystallization.

In this study,1 we prepared four new cyclometalated platinum(II) complexes [(ppy)PtCl(CNR)] (R = C_6H_4-2-I 1, C_6H_4-4-I 2, C_6H_3-2-F-4-I 3, C_6H_3-2,4-I2 4) whose solid-state luminescence depends on the aggregation motifs. Complex 2, which was crystallized in two polymorphic forms 2^{I} and 2^{II}, shows green and orange phosphorescence, respectively. The other studied solid luminophores, namely, 1, $3^{I–II}$, 4, and $4\cdot CHCl_3$, exhibit green luminescence. All yellow crystals (1, 2^{I}, 3^{I}, 3^{II}, 4, and $4\cdot CHCl_3$) demonstrated a reversible mechanochromic green-to-orange color change achieved by mechanical grinding (green-to-orange) and solvent adsorption (orange-to-green).

The most interesting finding of this work is that orange polymorph 2^{II} exhibits a significantly higher emission quantum yield of luminescence (12%), while 2^{I} is a very weak emitter (0.5%). One of most significant differences in the structure-determining non-covalent interactions between the two polymorphs, that is 2^{I} and 2^{II}, is seen in the availability of Pt···Pt interactions in 2II and absence of these metallophilic contacts in 2^{I}. We hypothesized that the 24-fold difference in the phosphorescence emission quantum yield between polymorphs 2^{I} and 2^{II} could be related to the presence and absence of Pt···Pt interactions; these metallophilic interactions are accompanied by the reduction of vibrational relaxation due to the formation of a rigid supramolecular structure.

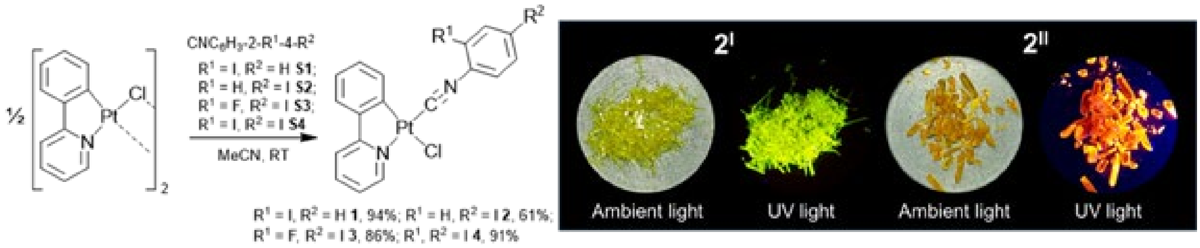

Figure 1. Synthesis of 1–4 (left). Image of crystals of 2^{I} and 2^{II} under ambient and ultraviolet light.

Acknowledgements
The study was supported by the Russian Science Foundation (project no. 21-73-10083). Measurements were performed at the Research Park of St. Petersburg State University.

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Ferrocene Containing Sterically Hindered Phosphonium Salts

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The promising applications of ionic liquids is electrical engineering and smart materials design.[1] The unique combination of physical and chemical properties of ionic liquids such as high ionic conductivity, wide electrochemical potential window, low melting point and incredible possibility of functionalization led to their wide implementation in the design of efficient lithium-ion batteries and supercapacitors, fuel cells, new stimulus-responsive materials.[2]

Phosphonium salts based on tri-tret-butyl(n-alkyl)phosphonium found their application as a binding agent in creating a paste electrode to study the electrochemical properties of insoluble compounds.[3] In addition, our laboratory synthesized ferrocene-containing phosphonium salts with sterically hindered cation.[4]

The obtained compounds were characterized by physical and chemical methods and electrochemical properties were studied. As a result, solutions of the obtained compounds could change their optical properties when a certain potential is applied to them.

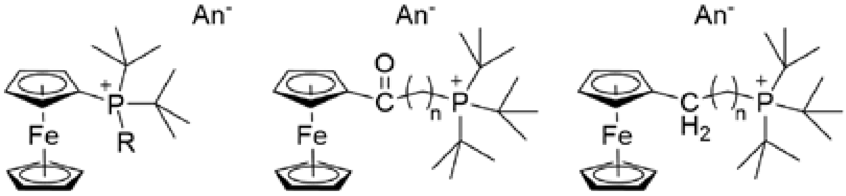

Figure 1. Objects under investigation

Acknowledgements

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A new method for the synthesis of five-membered metallacyclocumulenes. Protolysis of the zirconacyclocumulene complex and its reaction with ketones

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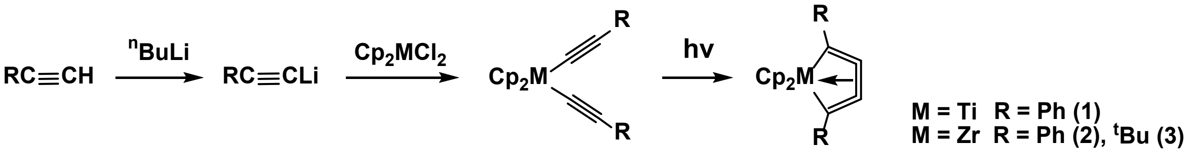
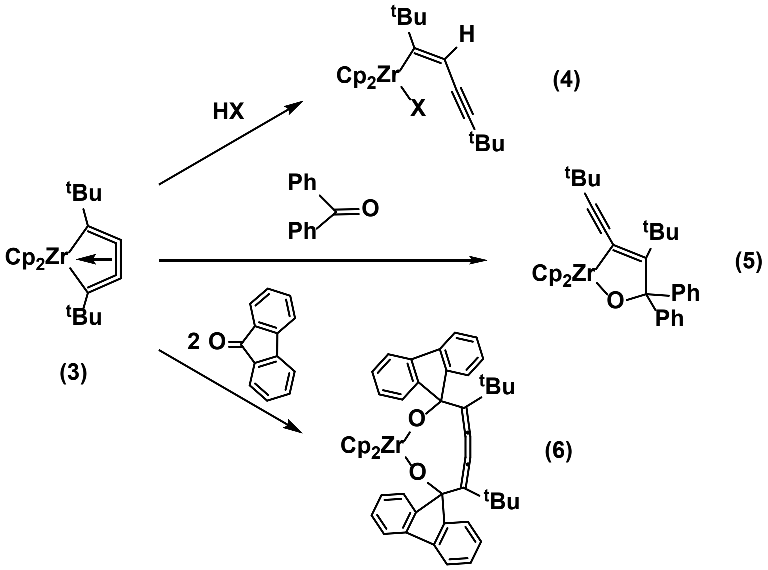
In recent decades, a new direction in organoelement chemistry has emerged - the chemistry of strained metallacyclic systems. One of the brightest representatives in this field are five-membered metallacyclocumulene complexes of Group 4 metals. Despite the presence of three cumulated double bonds in the cycle of these compounds suggesting an unusual structure and unique reactivity the methods of their synthesis and chemical properties have not yet been sufficiently studied.

Most methods for the synthesis of five-membered metallacyclocumulenes are based on the interaction of active forms of metallocenes with expensive diacetylenes. We have developed a simple and inexpensive method for the synthesis of five-membe-red metallacyclocumulenes $Cp_2M(\eta^4\text{-}RC_4R)$ (**1**-**3**) starting from Cp_2MCl_2 and terminal acetylenes by exposure to light of diacetylides of titano- and zirconocenes.



We investigated some of the chemical properties of the resulting metalla-cyclumulenes. In particular, the interaction of complex **3** with one equivalent of HCl gave σ-alkenyl complex (**4**). The reaction of **3** with benzophenone leads to the formation of a five-membered zirconadihydrofuran metallacycle (**5**), while the addition of 9-fluorenone to **3** results in a nine-membered dioxazirconacycle (**6**) which contains the conjugated cumulene fragment. These and other reactions will be presented in the report.



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Structure and catalytic properties of Au_4 cluster protected by bis(dimethylphosphinomethyl) and phenylacetylide ligands

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Over the past few decades, gold clusters protected by phosphine ligands, $[L_sAu_nX_m]^q$, have been extensively studied due to their applications in different fields including catalysis [1]. For example, $Au_{55}(PR_3)_{12}Cl_6$ cluster is a main component of Nanogold@ reagent which is often used as a precursor for supported gold nanoparticles [2]. The clusters have core-shell structure, where Au_n core is anchored by electronwithdrawing X ligands (i.e., thiolate, halogen) and L ligands (phosphine) weakly bound to the core.

The aim of this work was to evaluate of the effect X ligands (–C≡CH, $–CH_3$, $–SCH_3$, –F, –Cl, –Br, –I) on the structure, stability and reactivity gold cluster in scalar-relativistic DFT/PBE approach. $[Au_4(dmmp)_2(C{\equiv}CCH_3)_2]^{2+}$ (fig. 1) protected by bis(dimethylphosphinomethyl) and phenylacetylide ligands was chosen as model for studying decomposition and ligand exchange reactions. The calculations were performed in Priroda program [3].

It was found that in general, the type of the X ligand weakly affects the cluster structure but determines the electronic properties of the clusters [4]. Reactivity of the cluster towards CO and O_2 were also studied. The cluster is inert to CO binding and activation, while it reacts with O_2 and forms peroxide $[O_2Au_4(dmmp)_2(C \equiv CCH_3)_2]^{2+}$ complexes [5].

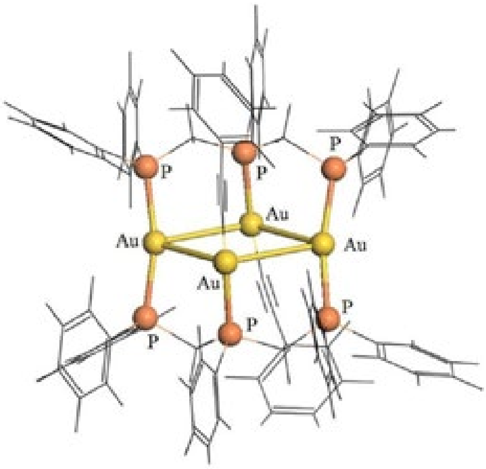

Figure 1. Optimized structures of $[Au_4(dmmp)_2(C \equiv CCH_3)_2]^{2+}$

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[M]-/Organo-Catalyzed Aerobic Oxidation as the Green Way for the Preparation of Functionalized Organosilicon Compounds

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Organosilicon derivatives are widespread organoelement compounds produced industrially. However, to date, only limited range of functionalized organosilicon products are commercially available. In this regard, their potential is not yet fully recognized. This is partially due to the limitations during their synthesis derived from poor stability of Si–C, Si–O- and Si–Cl-bonds in harsh conditions, non-neutral media and in the presence of strong oxidants.

On the other hand, aerobic oxidation utilizing oxygen from air is one of the most attractive functionalization techniques. A great improvement in this field gained in the past decades allowed wide range of functional groups to be introduced into organic molecules. However, aerobic oxidation is still understudied for the functionalization of organosilicon compounds.

In this research, we proposed tandem [M]-/organo-catalytic system for mild liquid-phase oxidation of organosilicon using molecular oxygen. This approach showed to be viable for the synthesis of silanols[1,2] and carboxyphenylsilanes,[3] containing organo-, siloxy- and alkoxy-groups (figure 1), showing the high selectivity of the suggested catalytic system.

Applicability of the synthesized silanols in further synthesis of dumbbell-shaped and graft siloxane polymers was also studied.[4] Polyfunctional carboxyphenylsiloxanes were used in synthesis of siloxane-containing esters and amides,[5] as well as were used as building blocks for hybrid porous (HOF, MOF) polymers.

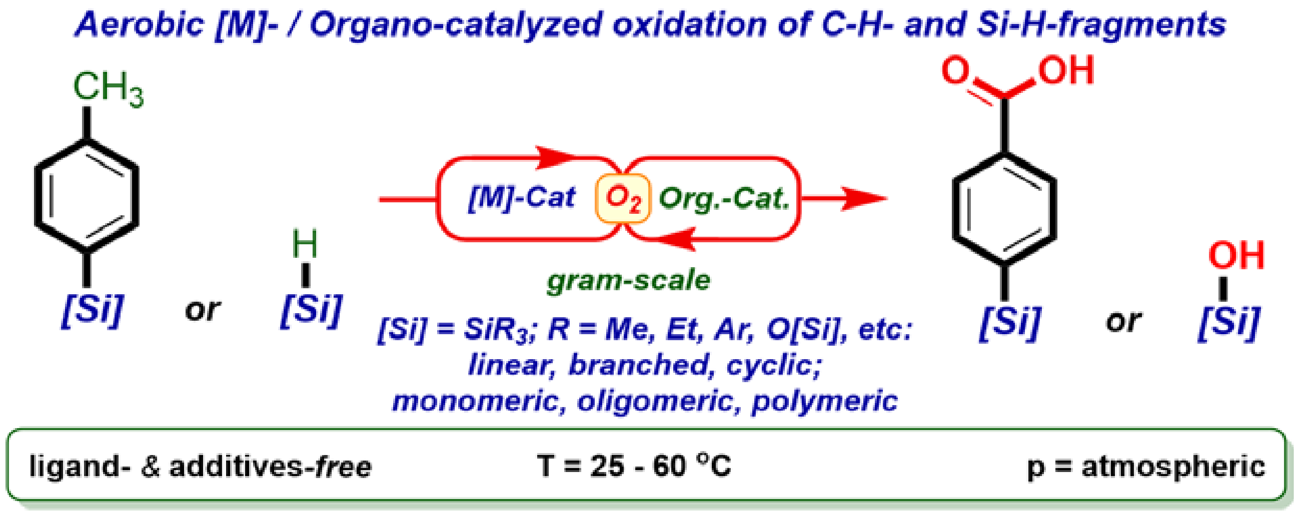

Figure 1.

Acknowledgements

This work was supported by a grant of the Russian Science Foundation (RSF grant 19-73-10172-П)

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Triphenylcyclopentadienyl rhodium complexes: synthesis and application for catalytic C-H annulations

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Nowadays, rhodium complexes are widely used in homogeneous catalysis.[1] Most of them are based on the cyclopentadienyl ligand, which supports rhodium atom in a catalytic cycle. Changing substituents in the cyclopentadienyl ring leads to changes in the reaction rate, regioselectivity and pathway.[2] Although a large number of rhodium cyclopentadienyl complexes are known, the complexes with phenyl-substituted cyclopentadienyls (Figure 1) have not been studied sufficiently. Herein we report the synthesis and catalytic activity of triphenylcyclopentadienyl rhodium complexes.[3]

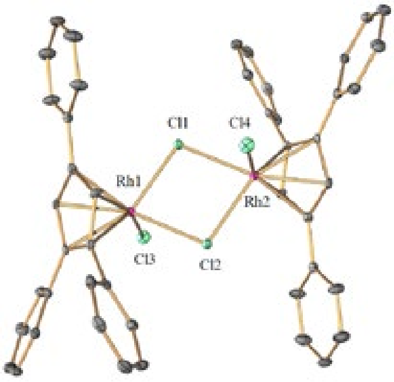

Figure 1. Molecular structure of the triphenylcyclopentadienyl rhodium dichloride.

The complexes proved to be effective catalysts in the construction of isocoumarin, naphthalene, isoquinoline, and dibenzo[*a*,*f*]quinolizine frameworks via C−H activation reactions (Figure 2). The reactions provide full compatibility with a range of functional groups, for example, hydroxy, ether, and thioether substituents.

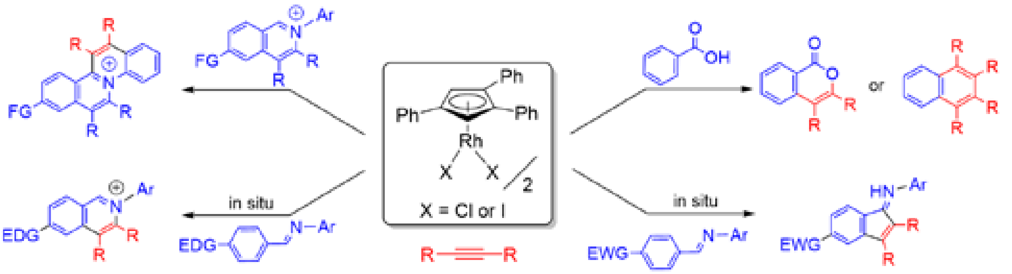

Figure 2. Organic reactions catalyzed by the triphenylcyclopentadienyl rhodium complexes.

To highlight the versatility of these protocols, we also demonstrated their utility in the synthesis of naturally occurring compounds.

Acknowledgements
This work was supported by the Russian Science Foundation (Grant No. 17-73-30036).

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Synthesis and coordination properties of 2,3,4,5-tetraaryl-1-mono- phosphaferrocenes

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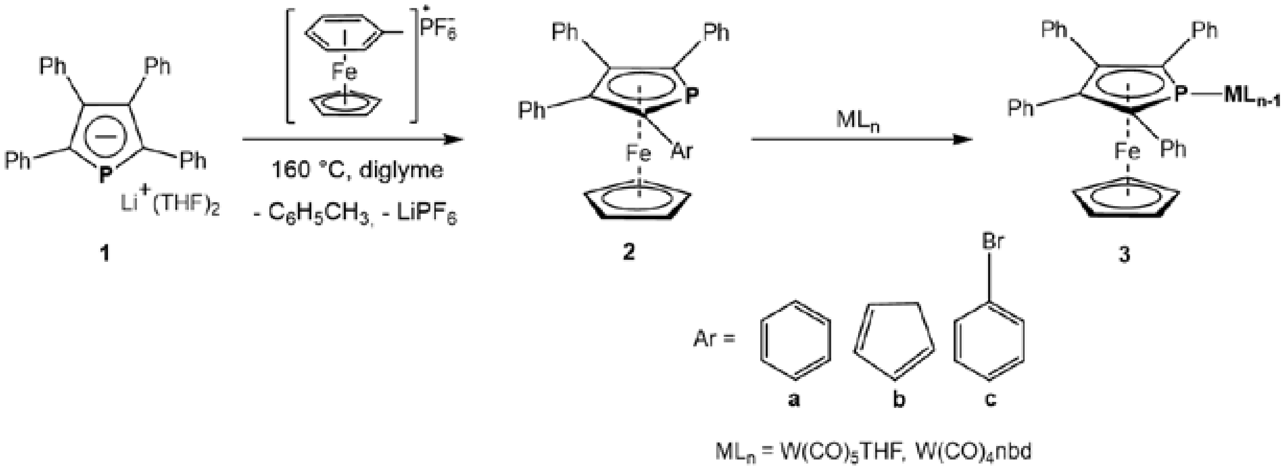
Phosphaferrocenes are ferrocene derivatives in which one or more than one carbon atoms (CH-fragment) in the cyclopentadienyl ring is replaced by a phosphorus atom (P-fragment). Most of the known monophosphaferrocenes have predominantly alkyl substituents (Et, ^{t}Bu) at the carbon atoms, while the aryl-substituted phosphaferrocenes remain poorly studied.[1] The 1-monophosphaferrocenes **2** were prepared from 2,3,4,5-tetraaryl-1-monophosphacyclopentadienide **1** and (toluene)cyclopentadienedienyl-iron (II) hexafluorophosphate salt $[FeCp(\eta^6\text{-}C_6H_5CH_3)]^+[PF_6]^-$ with good yields 54-62%. The coordination properties of new 2,3,4,5-tetraphenyl-1-monophosphaferrocene (**2a**) towards tungsten carbonyl complexes ($W(CO)_5$THF, $W(CO)_4$nbd) were investigated. The structure of new compounds **1-3** was proved by ^{31}P, ^{1}H, ^{13}C NMR spectroscopy and the single-crystal X-ray diffraction.[2]



Electrochemical properties of 2,3,4,5-tetraphenyl-1-monophosphaferrocene (2a) and its tungsten carbonyl complexes 3 were investigated by cyclic voltammetry. It was shown that 2,3,4,5-tetraphenyl-1-monophosphaferrocene has a quasi-reversible oxidation wave, while in the case of $W(CO)_5L$ complexes 3 this quasi-reversibility is disappeared.[2]

Acknowledgements
This work was supported by the grant from the Russian Science Foundation, No. 21-73-10204.

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Catalytic imidation of lactones via oxo/imido heterometathesis

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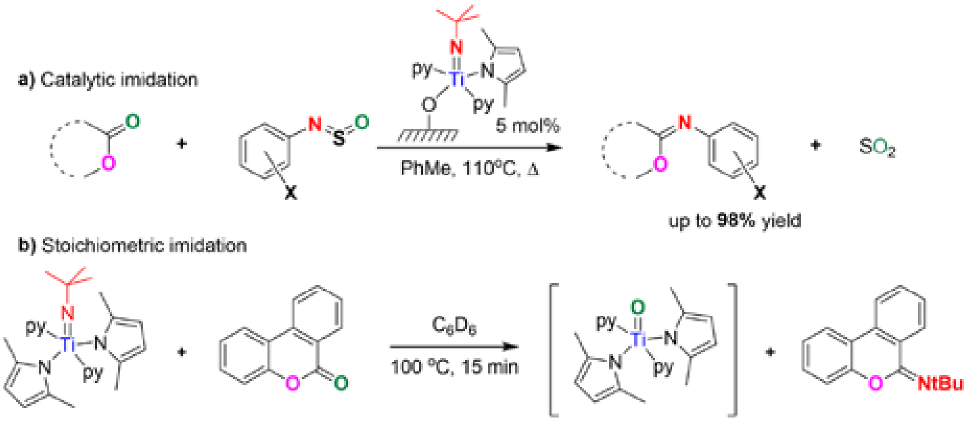
Catalytic oxo/imido heterometathesis[1] (i.e. metathesis of multiple bonds between heteroatoms) is a novel synthetic methodology that takes advantage of the high reactivity of early transition metal imido complexes and ultimately aims at the development of a general protocol that would allow transforming any X=O unit (organic carbonyl and carboxyl functionality, nitro and nitroso compounds, isocyanates, CO_2, etc.) into the corresponding imino derivative (X=NR).

The most active currently developed oxo/imido heterometathesis catalysts are based on well-defined silica-supported Ti imido complexes prepared via the Surface Organometallic Chemistry approach, where the attachment of the metal center to the surface appeared to be a key to prevent the dimerization of the highly reactive transient oxo intermediate ($L_nTi=O$). These catalysts allow for straightforward imidation of a broad range of carbonyl derivatives and catalyze self-condensation of isocyanates and Nsulfinylamines into carbodiimides and sulfurdiimines, respectively.[2]

In this work we report the first examples of catalytic imidation of carboxylic acid derivatives (lactones) with N-sulfinylamines giving corresponding cyclic imidates (Scheme 1a).[3] The range of substrates have been tested and the effect of ring size and structural parameters of lactones as well as electronic and steric properties of Nsulfinylamines on the reaction rate have been evaluated. As a preliminary mechanistic study we have investigated a stoichiometric interaction of the molecular precursor of the catalyst with 1 equiv. of 3,4benzocoumarin (Scheme 1b).



Scheme 1. Catalytic and stoichiometric lactone imidation.

Acknowledgements
This work was financially supported by the Russian Science Foundation (Grant No. 19-73-10163).

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NMR and UV-Vis studies of the oxotransfer reaction's mechanism involving a tungsten enzymes' model

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Tungsten-containing enzymes are involved in oxotransfer reactions, i.e., the transfer of an oxygen atom from a substrate-donor to an acceptor. Model complexes are widely used for studying the action of tungsten enzymes' active centers[1]. Tungsten complex with maleonitriledithiolate (mnt^{2-}) as a ligand is one the of such model complexes. Kinetic characteristics of oxotransfer reactions between the complex and substituted phosphines have already been studied[2]. The reaction mechanism through the formation of $[WO(mnt)_2]^{2-}$ is suggested.

In the present work the reaction between oxidized complex $[Bu_4N]_2[WO_2(mnt)_2]$ and PPh_3 in acetonitrile solution was studied. The UV-Vis spectrum for the solution was registered after the end of the reaction. Comparison of the reaction mixture UV-Vis spectrum with the spectra of individual forms $[WO_2(mnt)_2]^{2-}$ and $[WO(mnt)_2]^{2-}$ was made. it can be concluded that the oxidized form, i.e. the reagent, was present in the reaction mixture. We assume that the catalytic cycle is realized, rather than an oxotransfer reaction only. The cycle represents the oxidation of PPh_3 by oxygen dissolved in acetonitrile. The tungsten complex $[WO_2(mnt)_2]^{2-}$ acts as a catalyst.

^{31}P NMR measurements were carried out to confirm this hypothesis. Data were obtained for the reaction mixture in CH_3CN-D_2O (10:1). Two peaks (31.21 ppm and 44.38 ppm) are observed in the spectra. The first of them corresponds to the product triphenylphosphine oxide $OPPh_3$. The second pick belongs to the intermediate. We suppose the intermediate is a tungsten complex with coordinated PPh_3.

Thus, NMR measurements confirm the reaction proceeded by a complicated mechanism with the formation of an intermediate and $OPPh_3$ as a product. However, the formation of the reduced form $[WO(mnt)_2]^{2-}$ was not observed, which contravenes the proposed mechanism by Tucci et al.[2] An alternative reaction mechanism will be suggested by us in the further study of this process.

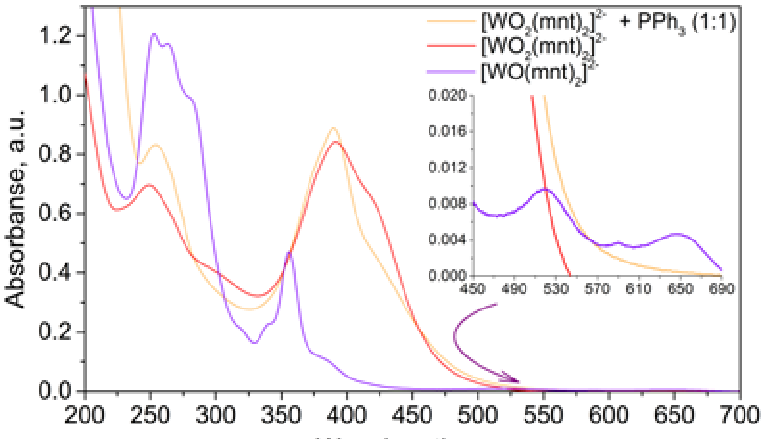

Figure 1. UV-Vis spectrum of the mixture after reaction and the spectra of the individual forms.

Acknowledgements

The NMR and UV-Vis measurements have been carried out in the Center for Magnetic Resonance and Chemical Analysis and Materials Research Centre of Research Park of St. Petersburg State University.

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Polynuclear and polymeric lanthanide carboxylates - self-assembly, structure and application for catalysis

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Coordination compounds of 3d and 4f elements are of high interest for various fields of application – as precursors for the synthesis of inorganic nanomaterials, as materials for luminescent devices, as magnetic materials, catalysts, etc. In recent years, the rational design of porous metal-organic frameworks (MOF) with polynuclear metal-containing secondary building units has been actively developed. Formation of polynuclear species with bridging OH- groups occurs in solution due to partial hydrolysis of metal salts. In the present work we have developed a self-controlled hydrolysis process which allow one to reproducible synthesize polynuclear lanthanide hydroxocarboxylates with different topology of $\{Ln_xO_y\}$ core.

Self-assembly of complexes with $\{Ln_xO_y\}$ core in solution in a presence of aliphatic amines have been monitored by total X-ray scattering techniques with pair distribution function (PDF) analysis[1]. It has been revealed, that *in situ* formed lanthanide hydroxytrifluouroacetates promotes the absorption of CO_2 by diethylenetriamine and stabilize the resulting diethylenetriamine dicarbamate in a form of chelating ligand within the complex cationic species $[Ln_4(OH)_4(tfa)_3(deta)_4(detadcH)_2]^{3+}$. The later ones have been isolated in a form of single crystals and their X-ray crystal structures have been revealed[2].

Pre-synthesized polynuclear species with $\{Ce_xO_y\}$ core have been also applied for tailored synthesis of a novel Ce-based MOF and its composite with nano-CeO_2. It has been shown that aliphatic amines play a key role in formation of a MOF with a certain composition, while the Ce-containing precursors determine the morphology of MOF. In oxidative conditions MOF prepared from hydroxocaroxylates are readly transformed to MOF-derived nano-CeO2 which has been tested as catalyst for CO oxidation.

Molecular species with $\{Ce_6O_8\}$ core have been also applied as precursors for nano-CeO2 formation via further hydrolysis in mild conditions at 120ºC. As a result particles with an average size of ca. 3 nm have been reproducibly obtained. The later has been applied as a carier for Pd-cluster deposition by chemical routed and the resulting material have been tested as the selective heterogeneous catalyst for hydrogenation of phenylacetlene.

Acknowledgements

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POSTER PRESENTATIONS

Ru-assisted synthesis of graft copolymers based on 5-succinylcyclooctene

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Olefin metathesis is one of the most important chemical reactions. Its prospects and potential applications are largely determined by the catalytic systems available today. The commercially produced metal-carbene Ru-complexes, known as the Grubbs catalysts, are currently considered to be among the most advanced ones.

Amphiphilic block copolymers and functional materials based on them are attracting more and more attention. By combining hydrophilic and hydrophobic segments in a controlled manner, one can use such copolymers as emulsifiers, nanoparticle stabilizers, nanoreservoirs, membranes, and coatings [1-3]. At the same time, methods for the preparation of amphiphilic copolymers based on linear cycloolefins with C=C double bonds in the main chain have not been practically developed.

We develop a facile route toward block (including multiblock) and graft copolymers with various functional groups based on the reactions of ring-opening metathesis polymerization and macromolecular cross-metathesis. The presence of unsaturated C=C bonds in the main chain of the copolymers opens the way for their further modification.

In this study a number of 5-substituted cyclooctenes with ester groups are synthesized and then polymerized to obtain novel graft copolymers with a hydrophobic backbone and hydrophilic pending groups. Ru-carbene complexes of Grubbs of I, II, and III generations are used as the initiators of the metathesis reaction. A discussion on the influence of the catalyst and substituent types on the solubility, chain structure, and thermal and surface characteristics of the obtained copolymers is presented. Water contact angle decreased from 97 for polyoctenamer to 45 for tetraPEG-substituted one.

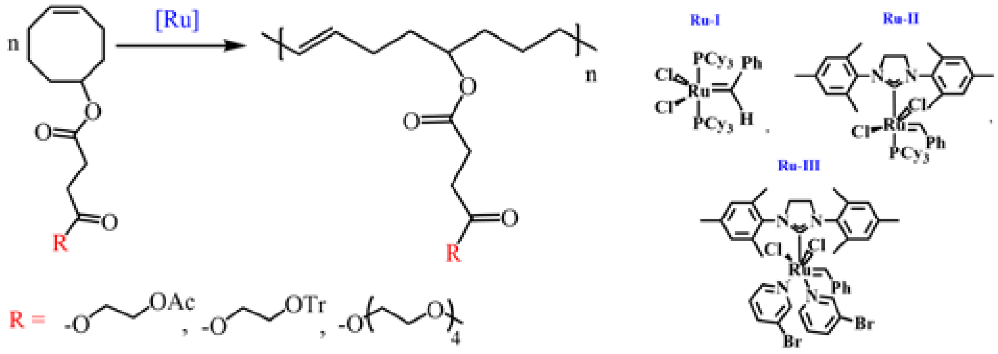

Figure 1. Synthesis of new graft copolymers based on 5-succinylcyclooctene

Acknowledgements
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Reactions of Five-Membered Metallacyclocumulene Complexes of Zirconocene and Hafnocene with Acetonitrile

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The first seven-membered zirconacyclocumulene complex was synthesized in 1993 by Buchwald[1] and a year later five-membered zirconacyclocumulene[2] was obtained. Despite the deviation of the butatriene moiety from linearity, these complexes turned out to be extremely stable at room temperature for an indefinite period of time, in contrast to organic cumulenes. Interest in such compounds is also due to their ability to catalyze the formation of pyrimidines in the coupling reactions of diacetylenes with nitriles[3].

During our study we have found that heating five-membered metallacyclocumulenes with two equivalents of acetonitrile leads to the formation of dimeric metallaazacyclopentadienes (**2**), bicyclic amidines (**4**), and tricyclic complexes (**5**)[4].

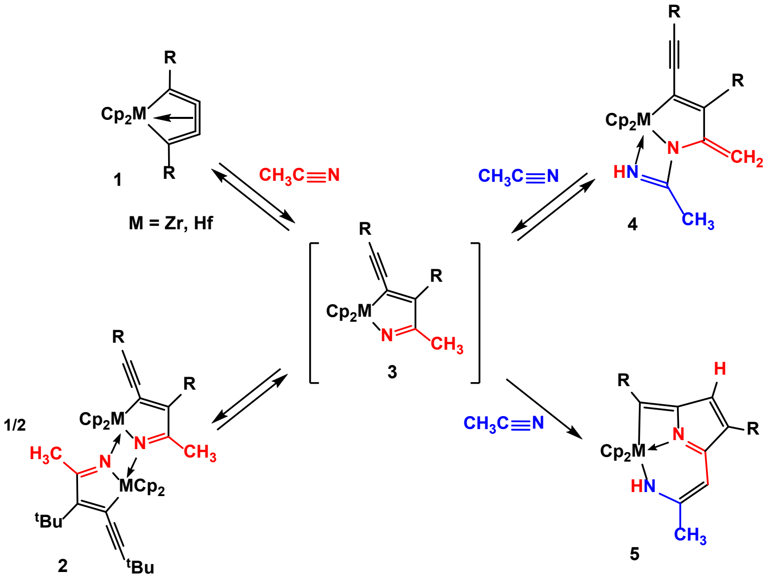

Figure 1. Interaction of five-membered metallacyclocumulenes with acetonitrile

The found transformations are studied in detail, a mechanism is proposed in which compound **2** can be considered as a kinetic but **4** and **5** as thermodynamic reaction products.

Acknowledgements
This work was supported by the Russian Science Foundation (Project 22-73-00326).

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Investigation study of nitrogen dioxide capture by metal-organic frameworks

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Nitrogen oxide NO_2 is a toxic gas that is produced in large quantities by human industrial activity. It is also the main cause of photochemical smog and acid rains. The search for materials capable of repeatedly sorbing nitrogen dioxide without losing sorption capacity is an essential goal, because reducing NO_2 pollution is an important and challenging problem, due to its strong oxidizing and corrosive properties.

Various types of materials (such as zeolites[1], metal oxides[2] and activated carbons[3]) have been proposed for this purpose, but they all have such drawbacks as low sorption capacity and irreversible chemical interaction because of the high reactivity of NO_2 which often leads to oxidation and degradation of sorbents.

During the last several decades, metal-organic frameworks (MOFs) have attracted attention due to their structural diversity and the number of promising applications. A large amount of research has been devoted to these compounds because of their almost unlimited possibility to vary their properties by changing a metal center and organic linkers. The wide numder of synthesized materials could be of interest in a pull of applications such as gas separation and storage, catalysis and liquid-phase separation. For example, MOFs are solid adsorbents that show promise in the sorption of harmful gases such as CO_2, NO_2 and others[4,5].

Metal-organic frameworks exhibiting high structural stability are particularly interesting for adsorption of chemically active gases, considering that many of the already synthesized MOF materials are often unstable. Zirconium MOFs are particularly notable for showing the highest structural stability due to strong Zr-O bonds.

Therefore, in this work, the interest has been focused on the zirconium MOFs and their aluminum counterparts with various organic linkers (fumaric acid and terephthalic acid). They were considered as NO_2 sorbents and their sorption capacity was evaluated. A spectrum of immobilized NO_2 at room temperature was obtained for the first time. The sorption mechanisms were studied by a set of different physicochemical methods (EPR spectroscopy, infrared spectroscopy and powder X-ray diffraction).

Acknowledgements
This work was supported by Russian Science Foundation (22-73-10239).

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Supramolecular materials based on amidopyridine pillar[5] arene derivatives and Cu(II) and Pd(II) cations as efficient sorbents and electrochemical sensors

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At the present time organometallic polymers based on polyfunctional macrocyclic platforms are being studied and used as unique components of new smart nanomaterials with the properties of protective coatings, sensor films, and chips. The presence of a metal in the structure of the material provides unique physicochemical properties (redox, photophysical, magnetic, etc.), and the macrocyclic ligand contributes to complex spatial organization and the possibility of forming a host-guest complex with small molecules (gases, pollutants, pharmaceuticals).

In this study, per-functionalised pillar[5]arenes containing amidopyridine fragments were obtained, which were acted as macrocyclic ligands in the presence of Cu^{2+} and Pd^{2+} ions for the formation of metal-supramolecular polymers. The structure and composition of all the synthesized macrocycles were confirmed by the following research methods: ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, MALDI-TOF mass spectrometry and elemental analysis.

Then we established the formation of a complex between pillar[5]arene **1** containing the 4-amidopyridine fragment and Cu^{2+} and Pd^{2+} cations with association constants $K_{2:1}(\mathbf{1}/Pd^{2+})=9827072$ M^{-1}, $K_{2:1}(\mathbf{1}/Cu^{2+})=1133170$ M^{-1}. Increasing the concentration of a mixture of **1**/Cu^{2+} and **1**/Pd^{2+} (2:1) to 10^{-2} M promotes the formation of gels of metal-supramolecular polymers.

The morphology of the resulting metal-supramolecular polymers is a reticulated polymer with a thread diameter of about 20 nm in the case of the **1**/Cu^{2+} system and 30 nm for the **1**/Pd^{2+}. Supramolecular gels using sol-gel technology were converted into amorphous powders, which proved to be components of electrochemical detection sensors and sorbents of nitrophenol derivatives. The efficiency of extraction of nitrophenol derivatives was 44-46%.

Thus, the preparation of ligands based on new persubstituted amidopyridine derivatives of pillar[5]arenes capable of assembling into metal-supramolecular polymers with Cu^{2+}, Pd^{2+} cations opens up the opportunity of creating effective sorbents for electrochemical sensors for the detection of nitrophenol pollutants in water.

Acknowledgements
This work was supported by the Russian Science Foundation (project № 22-73-10166), https://rscf.ru/project/22-73-10166/

Influence of the substituent in ferrocenyl acetate on the reaction with 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin

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The development of effective ferrocene-containing porphyrins is a modern area for effective drugs researching. Recent studies[1] revealed an cytotoxic activity of ferrocene-modified porphyrins under sonication in vitro, making them potential sonosensitizers for sonodynamic therapy. Here, a method developed for obtaining ferroceneporphyrins by a nucleophilic substitution of an acetate group in ferrocenylcarbinols with the 5-(p-aminophenyl)-10,15,20-triphenylporphyrin (H_2TPP-NH_2). Available ferrocenylcarbinols chosen as starting compounds, the OH group of which was replaced by an acetate one under acylation with acetic anhydride in anhydrous pyridine. Hybrid ferrocene-porphyrins 3a-d obtained by the interaction of ferrocenyl(alkyl/aryl)acetates 1a-d with H_2TPP-NH_2 2 in toluene with the addition of K_2CO_3. The dependence of the reaction progress on the substituent in the initial ferrocene derivative was revealed (Fig.1). Thus, in the case of ferrocenylmethanol acetate, bis-ferrocenyl derivative of porphyrin was isolated as the main product, the reaction with methyl and isopropyl substituents gives the target ferrocene-porphyrins, when using ferrocenyl(phenyl)acetate bis-ferrocenylphenyl, ether was isolated as the main product. Further biological studies are planned.

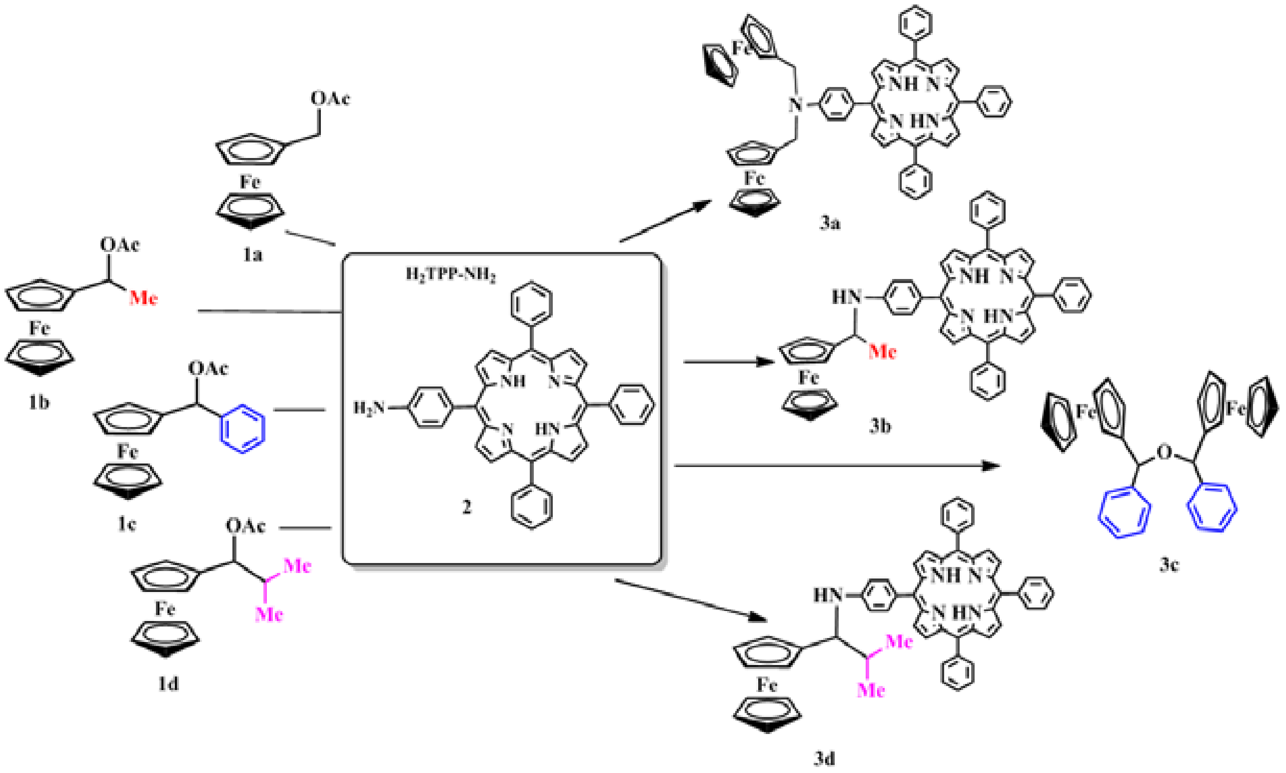

Figure 1. Influence of substituent in ferrocenyl acetate on the reaction with H_2TPP-NH_2

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Ligand-to-ligand charge transfer state in polyphenylcyclopentadienyl-bipyridine lanthanide complexes

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Most lanthanide ions are luminescent with characteristic narrow line emission, however the luminescence intensity is low as the f-f transitions are parity-forbidden. Indirect excitation via σ-bonded organic chromophores is frequently used to sensitize lanthanide luminescence ("antenna"-effect). Our group recently proposed the use of polyphenylcyclopentadienyl ligands as π-bonded "antenna"-ligands[1]. In this project our aim was to investigte the luminescence of lanthanide complexes containing both types of "antenna"-ligands: the conventional σ-bonded bipyridine and the novel π-bonded polyphenylcyclopentadiene.

Heteroleptic cyclopentadienyl-bipyridine complexes were obtained with a convinient one-pot procedure (Fig. 1). Their crystal structures were determined by X-ray diffraction method. In all complexes studied phenyl substituents of polyphenylcyclopentadienyl ligands form short intramolecular contacts with bipyridine moiety. Such mutual disposition of ligands results in generation of a cyclopentadiene-to-bipyridine ligand-to-ligand charge transfer (LLCT) excited state. Energy of the LLCT state is close to the energy of terbium $^5D_4$ excited level, which leads to efficient back energy transfer from the Tb^{3+} ion to the LLCT state and quenching of terbium luminescence. Resonance level energy of the Nd^{3+} ion is remarkably lower than that of the Tb^{3+} ion, so metal-centered luminescence is observed in neodymium derivatives.

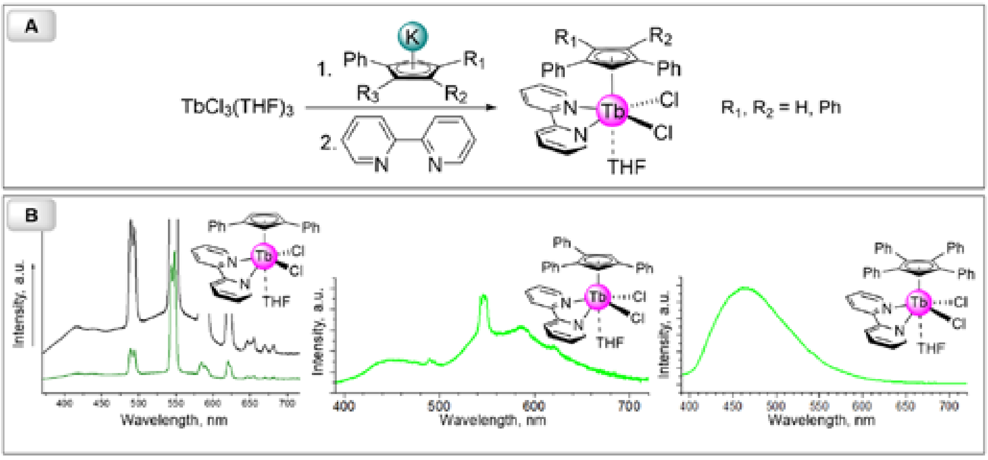

Figure 1. Synthesis of cyclopentadienyl-bipyridine terbium complexes (A).
Luminescence spectra of di-, tri-, tetraphenylcyclopentadienyl-bipyridine terbium complexes (B).

Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 22-23-00711).

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1D coordination polymers of europium and ytterbium

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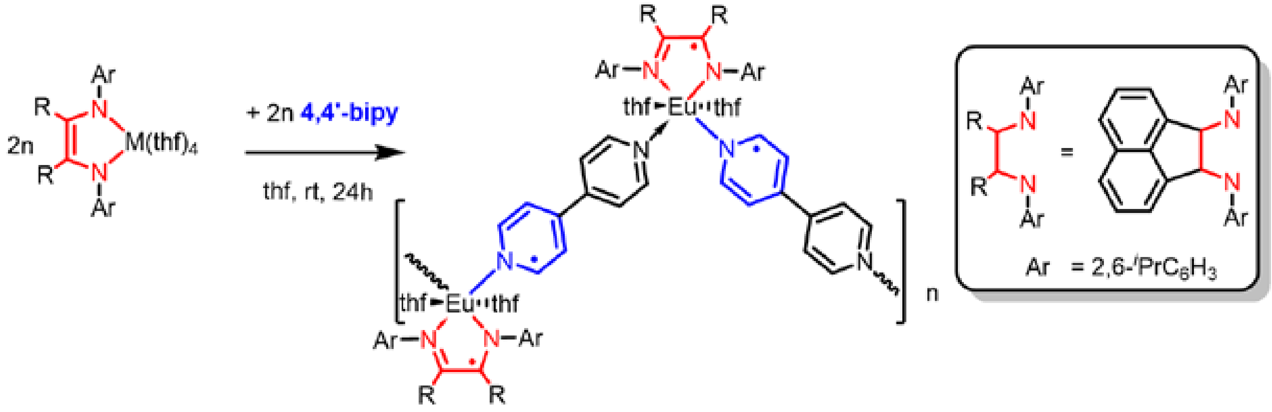
In recent years, crystalline materials are called metal-organic frameworks (MOFs), in which molecules of coordination compounds are linked into infinite chains (1D), networks (2D), or frameworks (3D), have attracted great interest. Combinations of lanthanide ions and redox-active organic ligands (bridging and terminal) are promising for the preparation of innovative materials, for example, materials that respond to external stimuli to change the redox state of their structuring elements and, as a consequence, the spectroscopic and magnetic characteristics.

In this work we synthesized 1D ytterbium coordination polymer with not redox-active ligand 1,3-di(4-pyridyl)propane (bpp) and 1D europium coordination polymer with redox-active 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) and 4,4´-bipyridine (4,4´-bipy) ligands. The reaction of $[(\text{dpp-bian})\text{YbI}(\text{DME})]_2$ with 1,3-di(4-pyridyl)propane in THF leads to the formation of 1D coordination polymer $[\text{YbI}_2(\text{Bpp})_2{\bullet}2(\text{THF})]_n$. Unfortunately, the redox-active dpp-bian was replaced of bpp in this reaction. The reaction of $[(\text{dpp-bian})\text{Eu}(\text{THF})_4]$ with 4,4´-bipyridine leads to the partial replacement of coordinated tetrahydrofuran molecules by 4,4´-bipyridine. The coordination of 4,4´-bipy to the europium atom is accompanied by the electron transfer from the dpp-bian dianion to neutral 4,4´-bipy to form 1D coordination polymer. The spectroscopic and structural data demonstrate that the monomer unit of $[(\text{dpp-bian})^{1-}\text{Eu}^{2+}(4,4'\text{-bipy})^{1-}(\text{THF})_2{\bullet}4(\text{THF})]_n$ contains three paramagnetic centers, namely, $(\text{dpp-bian})^{\bullet-}$ ($S = 1/2$), $(4,4'\text{-bipy})^{\bullet-}$ ($S = 1/2$), and Eu^{2+} ($S = 7/2$), which undergo magnetic ordering at low temperature due apparently to the determinism of the mutual arrangement of the paramagnetic centers in the polymer chain.[1]



Acknowledgements
The study was financially supported by the Russian Science Foundation (Project No. 19-13-00336-П).

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Electrocatalytic Transformations of Isomeric Butanethiols and Hexene-1 in the Presence of Metal Complexes

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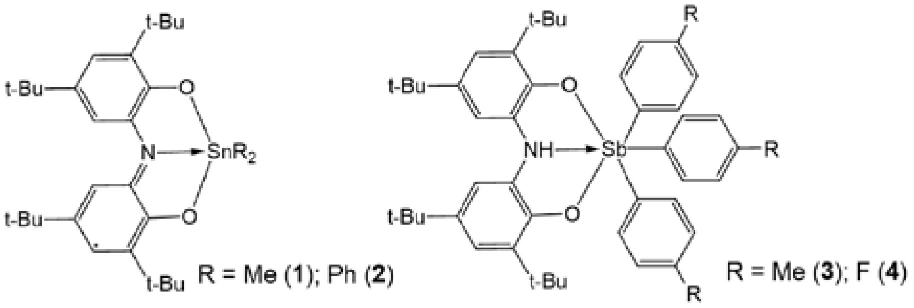
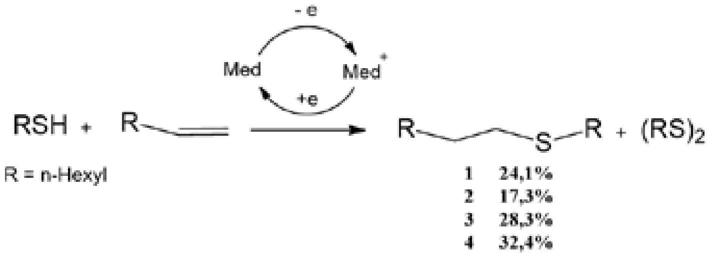
At present, the ability of metal complexes to catalyze organic reactions is considered as one of the powerful tools necessary and available for the development of new synthetic routes that are environmentally safe and economically beneficial.[1] At the same time, much attention is paid to the prospects of using metal complexes as redox catalysts for indirect organic electrosynthesis.[2] Previously, we studied tin(IV) and antimony(V) complexes with redox-active ligand as mediators (Med) of alkanethiol oxidation to disulfides with a significant decrease in anodic overvoltage compared to direct electrosynthesis.[3]

In this work, the electrocatalytic synthesis of sulfides based on hexene-1 and hexanethiol (1.8 V) in CH_3CN (Pt, Ag/AgCl) using complexes **1–4** was carried out, which made it possible to reduce the anodic overvoltage of the process by 0.4–1.0 V.



Along with sulfide, a disulfide was found in the mixture of reaction products with a comparable yield.



Thus, tin(IV) and antimony(V) complexes with a redox-active ligand are effective as electromediators in the oxidation of thiols to disulfides and in reactions with unsaturated hydrocarbons at 298 K. The highest activity was demonstrated by the Sb(V) complex containing 4-fluoro-substituted phenyl groups. However, the degree of regeneration of tin(IV) complexes turned out to be higher. The use of Sb(V), Sn(IV) complexes with redox-active ligand proved to be expedient due to the energy efficiency of this environmentally friendly method compared to direct electrosynthesis of mono- and disulfides.

Acknowledgements
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Organotin (IV) complexes with thio-Schiff bases bearing phenol fragment: synthesis, spectral and electrochemical properties

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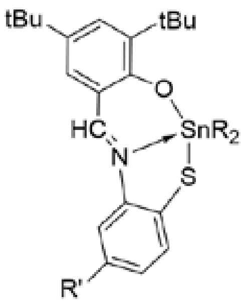
Complexes of transition and non-transition metals with O,N,O'-, O,N,N'- or O,N,S-ligands are characterized by unusual electrical and photophysical properties.[1,2] In this work, new tin(IV) complexes **1-9** with redox-active tridentate O,N,S-donor Schiff bases were synthesized in 57-75% yield (Figure 1). Electrochemical transformations of **1-9** were studied by cyclic voltammetry. A comparative assessment of spectral properties and luminescent activity of synthesized complexes in the UV-visible range of the spectrum (300-600 nm) was carried out.



1: R = Et, R' = H (65%)
2: R = tBu, R' = H (75%)
3: R = Ph, R' = H (64%)
4: R = Et, R' = CF_3 (70%)
5: R = tBu, R' = CF_3 (67%)
6: R = Ph, R' = CF_3 (63%)
7: R = Et, R' = Cl (57%)
8: R = tBu, R' = Cl (61%)
9: R = Ph, R' = Cl (63%)

Figure 1. Organotin (IV) complexes 1-9 with thio-Schiff bases.

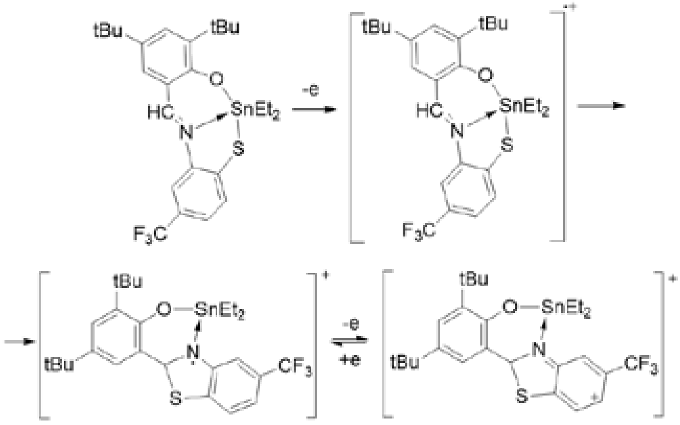


Figure 2. Mechanism of the electrooxidation of 4.

A feature of the electrochemical transformations of **1-5**, **7-9** is the cyclization of the ligand to the benzothiazoline form during the anodic process (Figure 2). The energy gaps calculated from electrochemical data for **1-9** are observed in a narrow range of 2.62–2.85 eV and are comparable with the results of spectral studies (2.67-2.77 eV). Fluorescent activity (λ_{ex} = 340 nm) was discovered only for compounds **4**, **6**, and **7** with emission bands at 546 and 580 nm (**4**), 554 and 582 nm (**6**), and 602 nm (**7**). The relative quantum yield does not exceed 7.2% and depends on the nature of the substituents in the ligand or organic groups bonding with the tin atom.

Acknowledgements
This research was funded by Russian Science Foundation, grant number 22-13-00118.

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Preparation of new iron(II) phthalocyaninatoclathrochelates and their functionalization giving the carboranyl-containing polytopic derivatives

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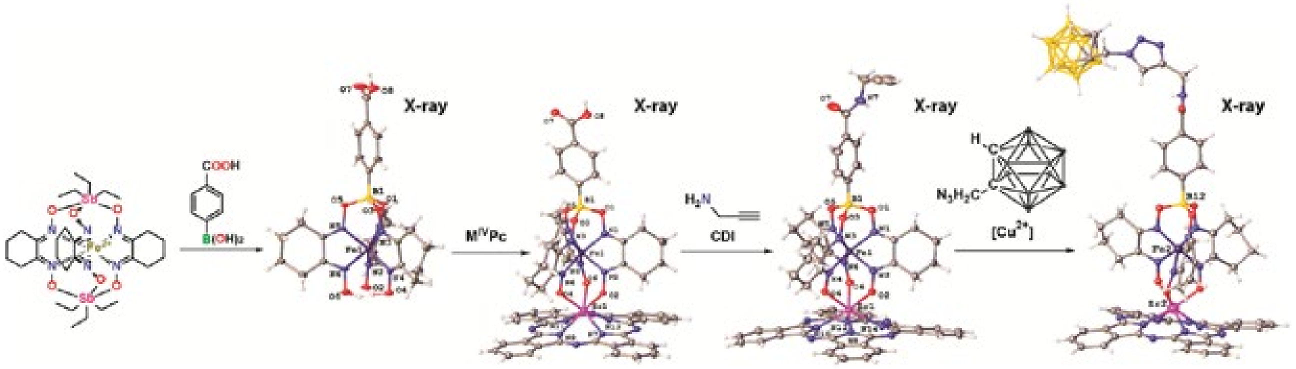
Cage metal complexes (clathrochelates) with terminal reactive, donor or biologically relevant group(s) are prospective and chemically robust three-dimensional molecular platforms and macrobicyclic building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs as well.[1]

A multistep general synthetic strategy towards polytopic carboranyl-containing phthalocyaninatoclathrochelate metal complexes, based on the template synthesis, transmetallation, amide condensation and 1,3-dipolar cycloaddition reactions as well is shown in Scheme 1.[2]

The obtained new complexes were characterized using elemental analysis, MALDI-TOF mass spectrometry, multinuclear NMR and UV-vis spectroscopies, and by the single crystal X-ray diffraction experiments for all of them (Scheme 1).



Scheme 1.

Acknowledgements
This work was supported by the Russian Science Foundation (project 22-23-00765)

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Pt(II) complexes with NNC pincer ligands capable of aggregation-induced emission (AIE). Study of the effect of substituents on their photophysical properties

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The increased interest in Pt (II) phosphorescent complexes is due to their potential use as agents for visualizing biological objects and sensing physiological parameters, as well as in the creation of optoelectronic devices[1].

These applications require a high concentration of emitters, which makes the development of AIE-active emitters reasonable. Moreover, the ability of phosphorescent molecules to AIE additionally increases the efficiency of emission and the depth of its penetration into biological samples[2].

Planar Pt (II) complexes with NNC pincer ligands and alkynyl monodentate ligands have already proven to be effective emitters[3]. Their planar architecture explains the ability of complexes to aggregate in the ground or excited states.

As part of this work, flat phosphorescent Pt (II) complexes with different substituents in the cyclometallated fragment were synthesized with the aim of creating biocompatible micelles based on them (**Figure 1**).

The final compounds were fully characterized using ESI-MS, 1D (1H) and 2D (1H-1H-COSY) NMR spectroscopy, and the [Pt(NNC)Me-Me] complex was studied using X-ray diffraction. The luminescent properties of all complexes were studied in acetonitrile solution and water-organic solutions. The influence of substituents (Me, Cl, OMe) in the cyclometallated fragment and aggregation processes on the photophysical properties of the obtained complexes was studied.

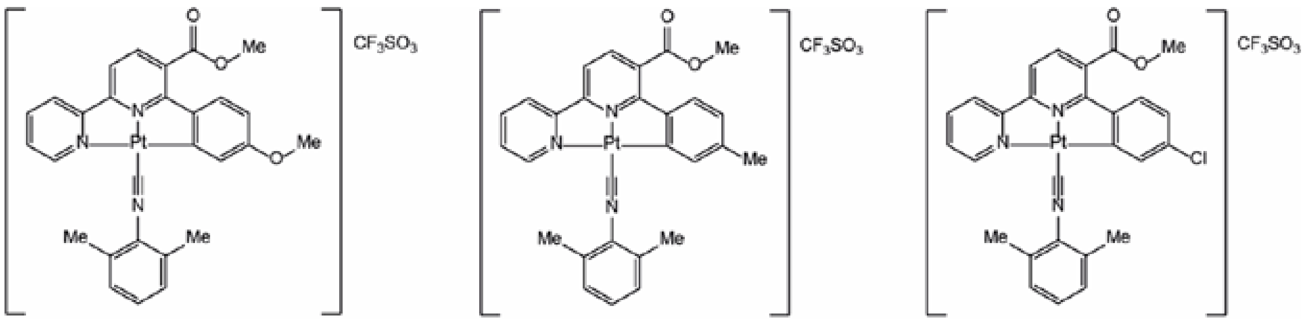

Figure 1. New Pt (II) compounds

Acknowledgements
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Diastereomeric Co(III) Complexes with Two Types of Chirality: Synthesis and Application in Catalysis

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Previously, we have obtained the first congener (or sample) of a new generation of metal-templated ionic catalyst with a hydrogen bond donor functionality *PhDA*-**1**. It is an octahedral, coordinatively saturated, stereochemically inert Co(III) complex. Despite the achiral ligands, the resulting complex still has chirality at the metal center. Due to the high ability of the coordinated with the metal ion N–H groups to form hydrogen bonds, this complex demonstrated a high catalytic activity as a bifunctional catalyst in the epoxide opening reactions with CO_2 (10 bar) at 20°C (51-95% yields).[1]

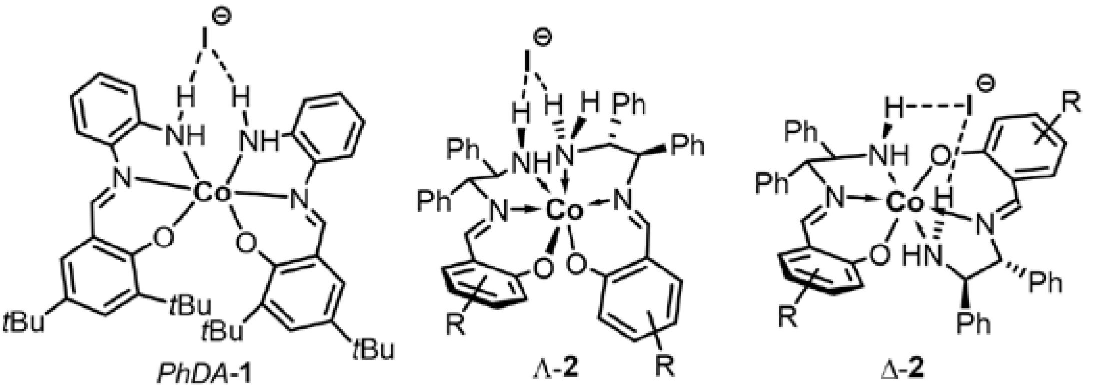

Fig. 1. Structures of octahedral Co(III) complexes.

We were able to isolate two diastereomeric complexes (Λ and Δ-forms) in pure form for the first time by the modifying of the ligand sphere by a replacing of the achiral phenylenediamine fragment with chiral (1*R*,2*R*)-diphenylethylenediamine. The complex Λ-**2** demonstrated a high catalytic activity (63-91% yields) in the model styrene epoxide cycloaddition with CO_2 at 1 atm and 25°C, while Δ-**2** catalyzed the reaction only at 10 atm CO_2 and 60 °C.[2]

In the kinetic resolution of chalcone oxide, the diastereomeric complexes Λ-**2** and Δ-**2** act as "*pseudo*-enantiomers", providing the desired carbonates with the opposite configuration (conv. 33%, *ee* 40%, *s*=2.8 and conv. 8%, *ee* -38%, *s*=2.3, respectively).[3]

Acknowledgements
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Synthesis of new tungsten carbonyl complexes with thioether carboranyl ligands

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Metallacarboranes are of considerable scientific interest because of their unusual spatial and electronic structure (three-dimensional aromaticity) as well as their diverse reactivity. In particular, the discovery and study of such compounds led to the proposal of the fundamental theory of cluster structure. It should be noted that in most of the complexes described in the literature the carboranyl ligands are π-type coordinated with the metal atom[1,2], while σ-metallacarboranes remain relatively underexplored. Thus the synthesis of σ-metallacarborane complexes seems to be very promising[3].

The aim of this work was to synthesis and characterization of novel σ-complexes of closo/nido-carborane thioesters with tungsten carbonyl and DFT-calculations the dependence of the stability of it’s on the nature of carbonyl ligand.

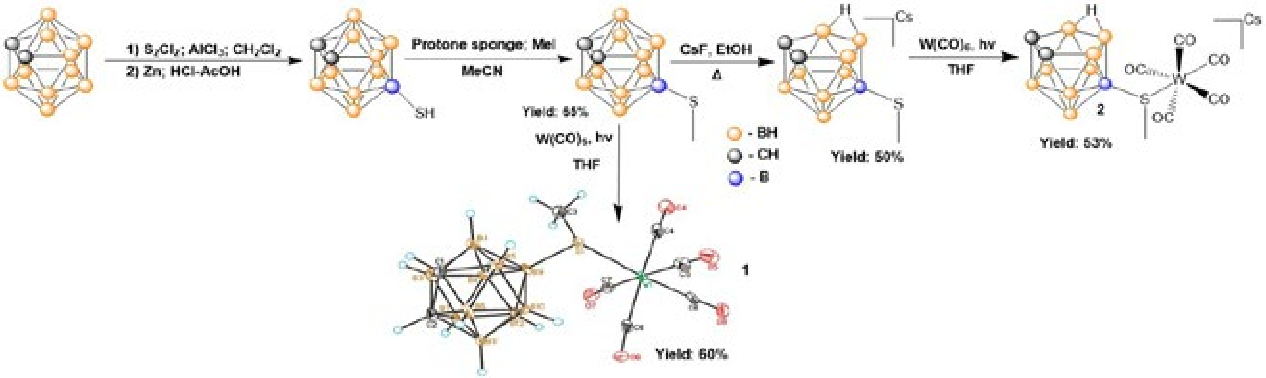

Figure 1. Synthesis of thioether ligands and complexes based on them

New σ-complexes of closo/nido-carborane thioesters with tungsten carbonyl were synthesized. All of them were isolated and fully characterized by ^1H NMR, ^{11}B NMR, ^{13}C NMR spectroscopy and IR spectroscopy. The structure of complex **1** was confirmed by SCXRD. Quantum-chemical calculations using density functional theory revealed that previously supposed difference in the electronic density distribution in the closo- and nido-ligands is not significant and the difference in the stability of the complexes is probably due not to thermodynamic but to kinetic reasons.

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Synthesis, structure and electrochemical transformations of diphenylgermanium (IV) catecholate complexes

Fokin V.A.,[1] **Burmistrova D.A.**,[1] **Voronina Yu.K.**,[2] **Smolyaninov I.V.**,[1] **Berberova N.T.**,[1] **Eremenko I.L.**[2]

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In this work, new diphenylgermanium(IV) catecholate complexes **1-6** (**Ph_2GeCat**) were synthesized via an exchange reaction between Ph_2GeCl_2 and sterically hindered catechols (Figure 1). The yield of target compounds varied from 42 to 76%. Compounds **1-6** have been characterized by means of ^{1}H and ^{13}C NMR-, IR-spectroscopy, and elemental analysis. The molecular structure of **2**, **4** and **6** was confirmed by X-ray diffraction. Electrochemical transformations of **1-6** were studied by cyclic voltammetry (CV).

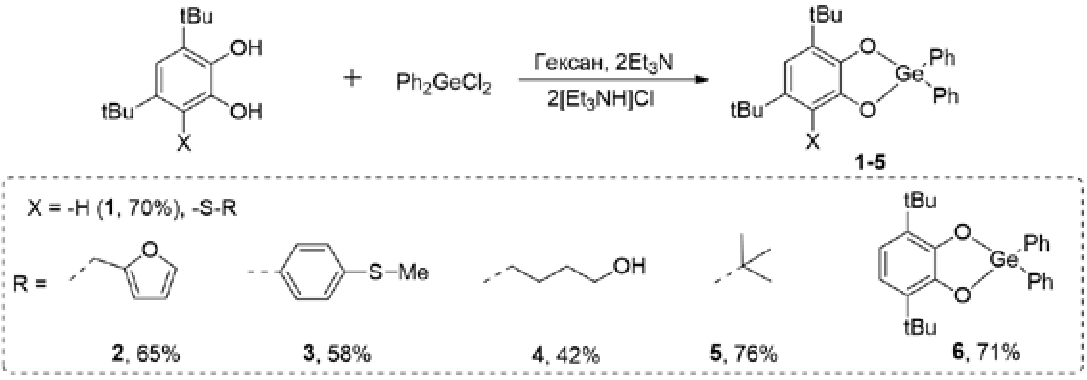

Figure 1. Synthesis of diphenylgermanium (IV) catecholate complexes **1-6**.

The electrochemical oxidations of complexes **1-6** in CH_2Cl_2 proceed as two successive stages leading to the formation of mono- and dicationic forms (Figure 2). The first one-electron stage of the electrooxidation of the studied compounds is in the range of potentials 1.08-1.28 V, the second signal appears from 1.36 to 1.50 V (GC-electrode, CH_2Cl_2, Ad/AgCl) The anodic peak at 1.70-1.82 V is characterized the oxidation of the thioether linker in **2-5**.

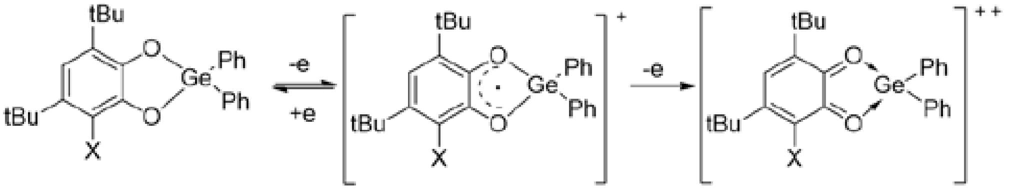

Figure 2. Electrochemical oxidation of **Ph_2GeCat**.

The interaction **1** or **6** with different nucleophiles (DMAP, DABCO, tetraalkyl(aryl)ammonium halides) was studied under electroanalytical control. A new peak in the range of 0.38–0.73 V is displayed on the oxidation CV, which corresponds to the catecholate ligand oxidation in formed *in situ* five-coordination Ge(IV) complex, similar to the previously considered transformations of antimony(IV) catecholates.

Acknowledgements
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Preparation of Chiral β-Aminoalanine Derivatives via Michael Addition of Amides, Imides and Isatins to a Dehydroalanine Ni(II) Complex

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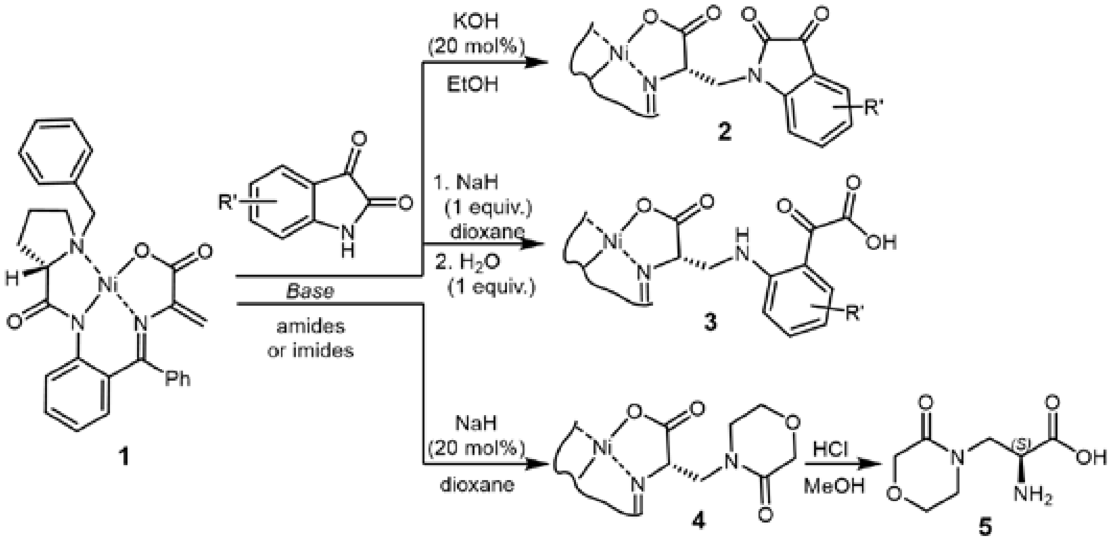
Chiral α-amino acids (AAs) are the most important bioactive molecules which widely used in synthetic chemistry, biochemistry, catalysis and for the development of new drugs.[1,2]

We have developed a new method for the synthesis of enantiopure β-aminoalanine derivatives starting from a chiral (*S*)-BPB-Ni-Δ-Ala complex **1** and various amides, imides and isatins (Scheme). The reactions were carried out in the presence of a catalytic amount of base and led to the formation of products with 70–96% yields and *dr* >20:1. The enantiopure AA **5**, which may be of interest as potentially biologically active compound, was isolated by acidic decomposition of the obtained Ni(II) complex **4**. The complexes **2-4**, obtained from isatin and amide, were isolated and characterized by X-ray analysis.[3]



Scheme. Michael addition of various amides, imides and isatins to a chiral Ni(II) complex 1

Acknowledgements
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A series of new photoluminescent materials based on lead(II) halide complexes with N,N'-dimethylthiourea

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0D organic-inorganic halides of ns^2 metal ions (Pb^{2+}, Sn^{2+}, Sb^{3+}) have recently gained attention as highly efficient broadband light emitters[1,2]. In these ionically bonded materials the photoluminescence (PL) are mainly centered at metal halide anions while the role of organic cations consists in the isolation of the ns^2 metal ions.

A new luminescent series *trans*-Pb(DMTU)$_4$X$_2$ (DMTU = N,N′-dimethylthiourea, X = F, Cl, Br, I) was obtained by direct grinding of PbX$_2$ with N,N'-dimethylthiourea, as well as by the hydrothermal method. The structures were determined by single crystal X-Ray diffraction and FTIR. Their absorption, excitation and photoluminescence spectra and thermal stability have been studied. The samples *trans*-Pb(DMTU)$_4$X$_2$ under UV-light excitation exhibit a bright broadband emission with a high PLQY (**Fig. 1**). When heated in air, the compounds first melt without decomposition, and then undergo thermal decomposition at 187-197 °C.

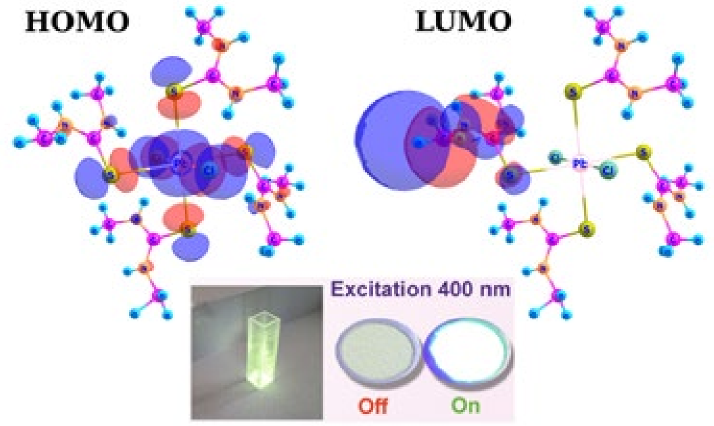

Figure 1. HOMO and LUMO molecular orbitals and photoluminescence of Pb(DMTU)$_4$Cl$_2$

We noted a close dependence between emission properties and halide nature of complexes. The high PLQY of complexes can be explained by the formation of strong hydrogen bonds N−H···Cl and N−H···Br, which impart rigidity to the structure. The broad peak, large Stokes shift and long lifetime of PL suggest that the PL of *trans*-Pb(DMTU)$_4$X$_2$ samples should originate from self-trapped exciton $^3P_i \rightarrow {}^1S_0$ transition. This suggested by the quantum-chemistry calculations by RHF/B3LYP/LANL2DZdp.

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Synthesis, Redox study, and DFT calculations of ferrocene-containing betulonic acid conjugate

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Plant pentacyclic triterpenoids of the betulin series are an important and widely studied class of phytocompounds.1, 2 It is an almost inexhaustible source of beneficial properties, such as anticeptical, antibacterial, anti-inflammatory, antimicrobial, antitumor, hepatoprotective, antiviral properties, including anti-COVID, and many others.

Ferrocene-modification of natural bio-active compounds is considered as a promising approach to polyfunctional drugs.3 On the basis of betulonic acid, a conjugate with ferrocene through a piperazine linker was synthesized in good yield (Fig. 1)

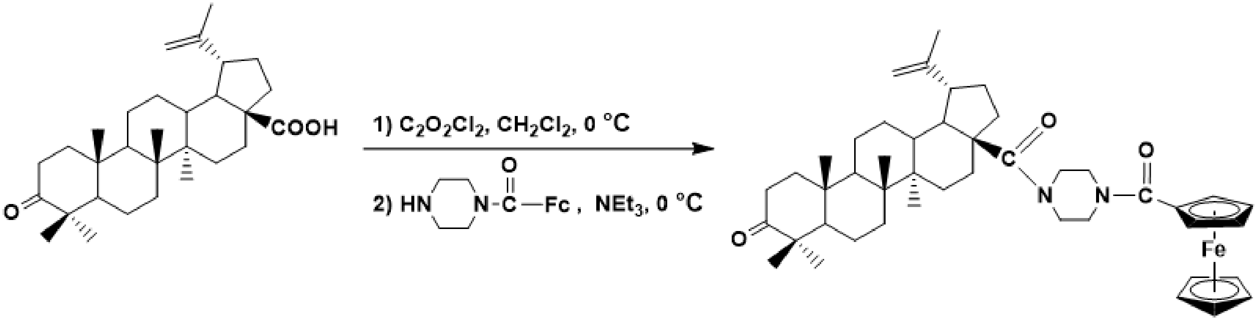

Figure 1. Synthesis of ferrocene-betulonic acid conjugate

This conjugate was studied by spectroscopic methods, including the method of circular dichroism (CD) and cyclic voltammetry (Fig. 2). CD spectra of the studied compounds were simulated using DFT calculations. A high correlation between experimental data and DFT calculation results was obtained.

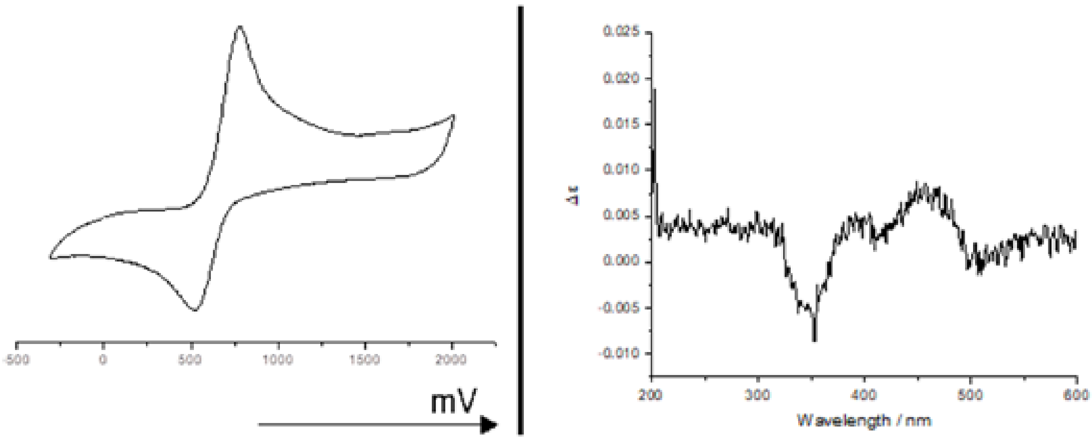

Figure 2. Cyclic voltammogram of ferrocene-betulin conjugate (left) and experimental CD spectrum (right)

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Direct Modification of Chiral-at-Metal Co(III) “Organocatalysts in Disguise” by Suzuki-Miyaura Cross-Coupling Reaction

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Significant progress in the field of asymmetric catalysis has been achieved through a steadily updated library of chiral catalysts that provide a high level of enantioselectivity control of reactions. Despite the many effective chiral organocatalysts and metal complex catalysts with chiral ligands, asymmetric catalysis in organic synthesis being a hot topic remains to develop new universal catalytic systems. In this research, we focused on the preparation of new octahedral chiral-at-metal Co(III) complexes based on NNO-donor ligands and on the methods for their post-synthetic modification in order to obtain an efficient and multifunctional enantioselective catalytic system. The configurations at the metal center are designated according to the mutual arrangement of tridentate ligands around the cobalt ion: Λ (a left-handed propeller) and Δ (a right-handed propeller) configurations.

The process of the formation of diastereomeric Co(III) complexes has been fundamentally studied. It was experimentally shown that the ratio of Λ- and Δ-forms is affected by both the nature of the chiral diamine and substituents in the salicylaldehyde. Next, in order to expand the family of chiral-at-metal Co(III) catalysts we have developed a straightforward method for post-complexation derivatizations of diastereo- and enantiomerically pure Co(III) complexes by Suzuki-Miyaura cross-coupling reaction.[1]

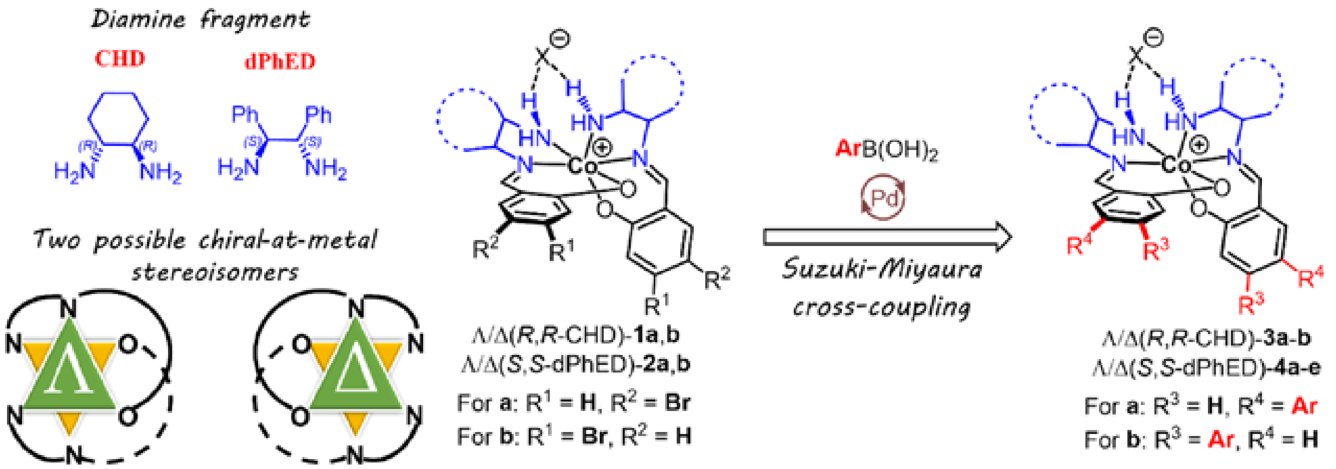

Figure. Representation of Λ- and Δ-configured octahedral chiral-at-metal complexes featuring two chiral symmetrical tridentate ligands and their post-modification through Suzuki-Miyaura CCR

Acknowledgements

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The interaction of the Zn complex tetra(4-pyridyl)porphyrin with sodium hexamolybdenonickelate in aqua-organic medium

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Currently, more attention is being paid to modeling and determining the structure of heteropolycompounds (HPC), describing their synthesis, characteristics and studying the physico-chemical properties of new materials and hybrid systems based on HPC, as well as opening up new areas of research and synthesis of multifunctional materials which properties can be a symbiosis of magnetic, electrical and optical parameters of solids. It is also necessary to study the reactions of HPC with inorganic and organic compounds, to identify patterns of “composition - structure - physico-chemical properties”, on the basis of which it would be possible to predict the behavior of compounds under various conditions.

In this work new hybrid structures based on Zn complex tetra(4-pyridyl)porphyrin and HPC of sodium hexamolibdenonickelate has been synthesized, and the interaction of Zn complex tetra(4-pyridyl)porphyrin and hexamolybdenonickelate anions in aqua-organic medium has been studied by electron absorption spectroscopy and spectrofluorimetry. The idea of obtaining such hybrid organo - inorganic complex is of interest because the formation of these structures will allow solubilizing porphyrins in an aqueous medium. Moreover, in such complexes, porphyrin turns out to be the part of nanoscale particles and it gives new opportunities for their delivery to biological cells of the body in normal and pathological conditions. In addition, in this case, it is possible to combine the biological activity of individual HPC and porphyrin, as well as the manifestations of newly emerging physicochemical and biological properties in the hybrid system.

The data obtained have shown that the presence of HPC in the system makes it possible to stabilize porphyrin metal complexes in an aqueous medium, which, possibly, is associated with the formation of hybrid organo-inorganic structures.

Acknowledgements

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Hybrid structures based on hemin and sodium hexamolibdenonickelate

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Spectroscopy of porphyrins and their complexes with metals due to their wide distribution in nature and great practical significance is an actual section of the chemical physics of tetrapyrrole compounds. Modification of porphyrins makes it possible to obtain durable systems used as drugs for photodynamic therapy, light energy converters, electro- and photo-catalysts. The development of compounds with high antibacterial activity is also a very urgent task.

In this work new hybrid structures based on hemin and heteropolycompound of sodium hexamolibdenonickelate has been synthesized, and the interaction of hemin and hexamolybdenonickelate anions in an aqueous and aqua-organic media has been studied by electron absorption spectroscopy and spectrofluorimetry. In the electronic absorption spectra a transformation of the hemin characteristic bands is demonstrated, new bands are found, indicating the formation of hybrid organo-inorganic complexes. The role of the structural features of hemin in the course of their interaction with heteropolyanions is traced.

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This work was supported by government funding within the framework of the scientific project “45.9 Theoretical and experimental studies of new materials and hybrid structures, including polyconjugate systems, nanostructures, composite materials and systems of reduced dimension” (FFEG-2019-0001) and the project “Research on the problems of recycling waste of natural origin for the practical use of the products obtained” (122122600056-9).

Synthesis of hybrid nanostructures based on monoamino acids derivatives of fullerene C60 and vitamin B_{12}

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A significant place among modern nanomaterials is occupied by nanocarbon structures, including fullerenes and their derivatives. It is shown that water-soluble monoaminoacids C60 show antioxidant, membrane, neuroprotective, antiviral, antibacterial and antitumor properties, play the role of effective compounds for the delivery of drugs to targets of various diseases.1

According to the idea expressed by academician M.E. Vol'pin, catalytic sources of active forms of oxygen (AFO) that can selectively accumulate into tumors can actively suppress the growth of malignant cells. The results of our studies confirmed that the catalytic systems generating AFO based on cobalt complexes with corrin ligands and L-ascorbic acid can be very effective as antitumor and related agents.2 Therefore, it was assumed that the introduction of a pharmacophore fullerene fragment in the molecule of a catalytically active vitamin B12 derivatives will significantly improve the effectiveness of the antitumor action of the complexes, as well as to obtain compounds with a new set of biological properties.

Based on this, methods of the synthesis of new hybrid nanostructures were developed (fig. 1). The results obtained in L-ascorbic acid oxidation in the presence of synthesized hybrid nanostructures are comparable to data for the compounds not modified by derivatives of vitamin B12. This fact confirmed the prospects of further study of the obtained hybrid nanostructures as biologically active substances.

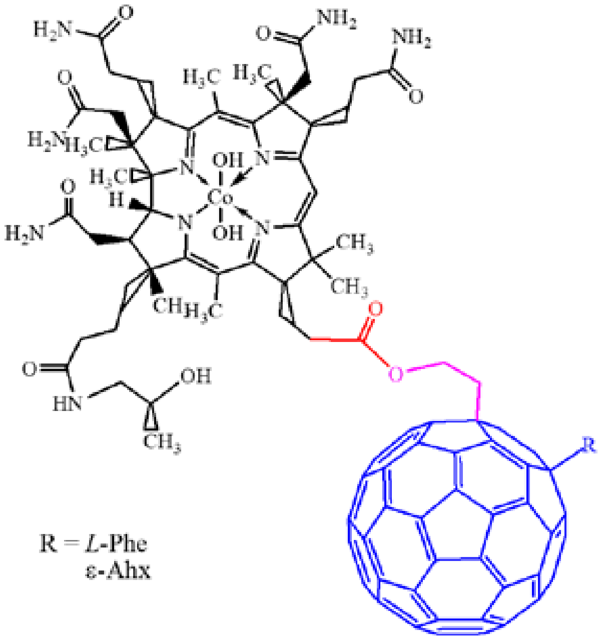

Figure 1. Obtained hybride nanostructures.

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Investigation of the nature of metal-ligand interaction in pincer complexes based on Ni(II) by quantum chemistry methods

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Among the numerous polydentate ligands obtained over the past decades, pincer (claw-shaped) ligands are becoming increasingly important due to their special characteristics and the ability to "tune" the electronic properties of the complexes formed by them. Despite such a wide interest in pincer complexes, the question of the influence of the ligand environment on their catalytic properties remains open[1,2]. This effect cannot be estimated without a detailed study of the electronic structure of the compounds.

Based on this, we set a goal to study the nature of the interaction of nickel (II) with a pincer ligand of the POCOP type and an alkyl substituent of 2,1,3-benzothiadiazole by methods of theoretical chemistry: QTAIM and NBO.

All quantum chemical calculations were performed using the Gaussian09 software package. The analysis of the electronic structure was carried out by the programs NBO7 and Multiwfn. Optimization of the studied structures was performed by the density functional method with the correlation-exchange functional TPSSh.

Using the NBO and QTAIM methods, it was possible to establish that charge transfer occurs from the orbitals of the POCOP-ligand and 2,1,3-benzothiadiazole to the Ni(II) metal center. The values of the charge transfer in the opposite direction are much smaller therefore, it is possible to exclude the possibility of back donating. Also using these methods, it was determined that the interaction of ligands with Ni(II) is ion-covalent in nature with relatively identical contributions.

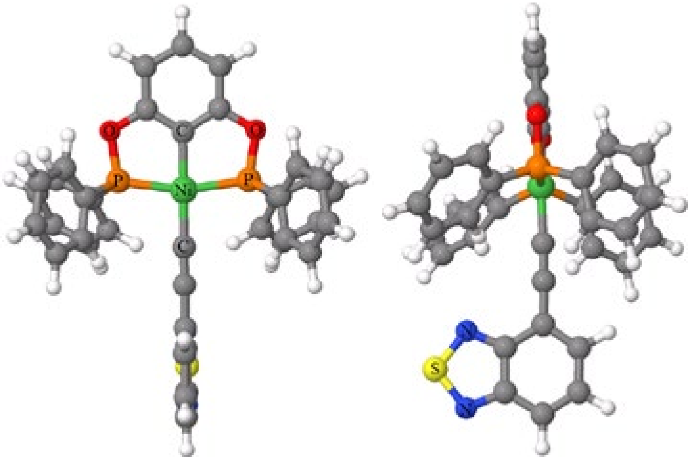

Figure 1. The structural formula of a complex compound $[C_6H_3\text{-}1,3\text{-}(OPPh_2)_2]Ni\text{-}C{\equiv}C\text{-}(4\text{-}C_6H_3N_2S)$.

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Catalytic activity of novel Ln cymantrenecarboxylate complexes with ferrocene phosphine oxido ligand in polymerization of vinyl monomers

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It is known that cymantrene (CymH = (η^5-C_5H_5)Mn(CO)$_3$) derivatives can serve as polymerization catalysts.[1] At the same time, carboxylate complexes of the lanthanides can influence the stereoregularity of this process.[2]

Earlier we have shown that cymantrenecarboxylate complex of neodymium [$Nd_2(CymCO_2)_6(DMSO)_4$] can be the catalyst of stereoregular polymerization of 2,3-dimethyl-1,3-butadiene.[3] Continuing our research in the field of organometallic carboxylates, we obtained a new series of heteroleptic organometallic *3d-3d´-4f*-complexes [$Ln(CymCO_2)_2(DppfO_2)_2$]Cl·*Solv* (Ln = Nd (**1**), Dy (**2**), Ho (**3**), and Er (**4**); $DppfO_2$ is the Fe(η^5-C_5H_4P(O)$Ph_2)_2$ ligand; *Solv* are the lattice solvent molecules). Both kinds of organometallic ligands in the unique bulky cations [$Ln(CymCO_2)_2(DppfO_2)_2$]$^+$ are bidentate (Fig.1, left).

All the constituents of the obtained complexes can potentially affect the polymerization processes. Activities of complexes **1** and **3** in the processes of polymerization of methyl methacrylate and styrene in the presence of benzoyl peroxide, as well as under UV-light or thermal activation in the presence of CCl_4, are studied and discussed.

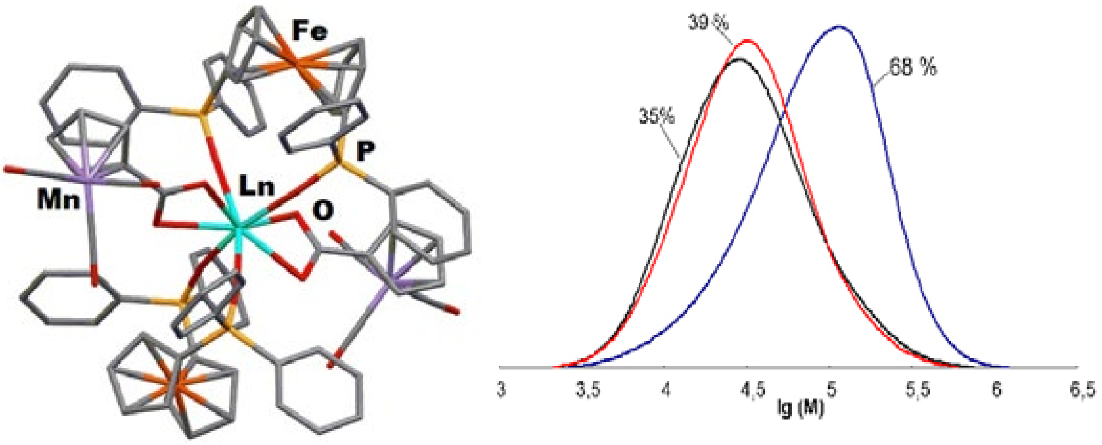

Figure 1. Structures of bulky cations in compounds 1-4 (left) and the curves of the molecular weight distribution of polystyrene samples synthesized in the presence of 1 (0.05 mol.%) and CCl_4 (0.25 mol.%) at 110°C; the yields are given in percent values (right).

Acknowledgements

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Parahydrogen induced hyperpolarization of insensitive nuclei at ultralow magnetic fields

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Parahydrogen induced polarization (PHIP) provides a powerful tool to enhance inherently weak NMR signals, particularly in biologically relevant compounds. Conventional method of PHIP creation exploits the homogeneous catalytical hydrogenation of unsaturated C-C bond of the substrate molecule with parahydrogen, i.e., dihydrogen where the two protons make up a singlet spin state. Subsequent conversion of PHIP spin order into net magnetization of magnetic heteronuclei, e.g., ^{13}C, provides one of the most efficient ways to exploit PHIP. We propose a facile route to increase the performance of PHIP transfer in experiments with adiabatic sweeps of the ultralow magnetic field. To date this technique yields the highest efficiency of PHIP transfer, yet it has been mostly utilized with linear field sweeps, which does not consider the underlying spin dynamics, resulting in sub-optimal polarization. This issue was previously addressed by using the “constant” adiabaticity method, which, however, requires extensive calculations for large spin systems. In this work, the field sweep is optimized by utilizing the field dependence of the average ^{13}C polarization. This work provides a comprehensive survey of PHIP transfer dynamics at ultralow field for two molecular systems that are relevant for PHIP, namely, maleic acid and allyl pyruvate. We test the maximum achievable ^{13}C polarization in various experimental protocols, including continuous hydrogenation at ultra-low magnetic field, coherent PHIP transfer induced by sudden field variations, and adiabatic transfer via magnetic field sweeps. Such direct comparisons of different methods highlight the efficiency and robustness of adiabatic transfer compared to other methods. The proposed optimization allowed us to increase the resulting ^{13}C polarization in ^{13}C-allyl pyruvate from 6.8% with a linear profile to 8.7% with an “optimal” profile.[1] Such facile optimization routines are valuable for adiabatic experiments in complex spin systems undergoing rapid relaxation or chemical exchange

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Experimental-theoretical investigation of the topology of electron density in mercaptobenzothiazolate complexes of Nd^{3+} and TB^{3+}

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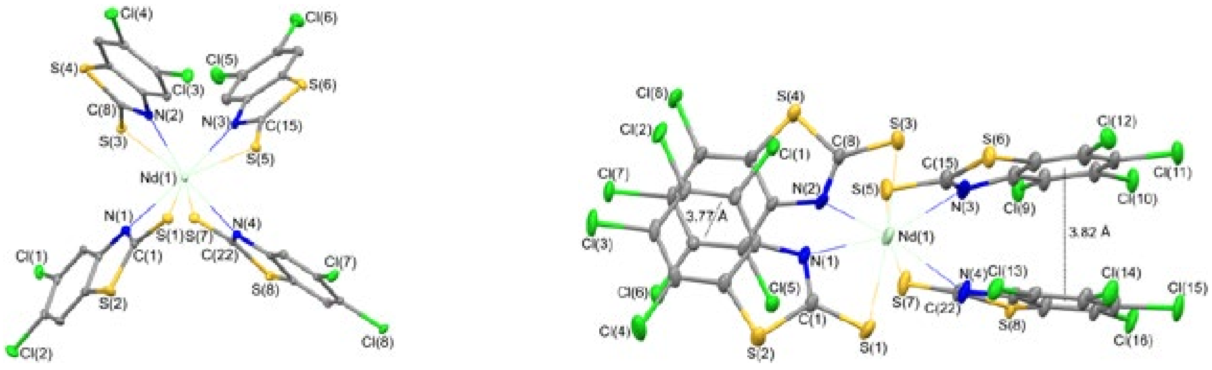
Trivalent lanthanide ions are known for their narrowband luminescence which intensity can be multiplied in complexes by orders of magnitude if suitable organic ligands are bonded to the ion. [1, 2] The design of near infrared (NIR) emitting lanthanide complexes with “antenna” ligands is a challenging task in modern material and synthetic chemistry. [3, 4] NIR emission is in demand in various advanced technologies including lasers, amplifiers, telecommunication organic light-emitting diodes and bioimaging systems. The X-ray diffraction analysis of neodymium and terbium complexes with di- and tetrachloro-substituted 2-mercaptobenzothiazolate (mbt) complexes has shown a significant difference in the mutual arrangement of ligands in the coordination sphere of lanthanides (Fig.1). To investigate this phenomenon and its relation to properties, we carried out a study of the experimental-theoretical topology of electron density based on an asymmetric unit-cell aspherical scattering factor (a crystal invariom). [5,6]



a b

Fig. 1. Molecular structures of Nd^{3+} complexes with polychlorinated mbt-ligands. Only the anionic part of complexes is shown whereas the cationic part ($[Na(DME)_3]^+$) is omitted for clarity.

Acknowledgements
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Influence of the length of the hydrocarbon spacer between silicon and sulfur on the reactivity of sulfur-containing silanes in the hydrosilylation reaction

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One of the main ways to modify organosilicon compounds is the catalytic hydrosilylation of substituted olefins [1]. Also in recent decades, the click reaction of radical hydrothyolation has been increasingly used in organosilicon chemistry [2]. Previously, we showed that under the conditions of this reaction on hydride-containing substrates, the Si-H group is not affected [3], and at the next step of this study, we performed sequential hydrothyolation and hydrosilylation on a wide range of substrates [4].

However, during the development of the method, it was found that vinyldimethylsilane, being hydrothiolated with decyl- or phenylthiol cannot be hydrosilylated. But if the length of the hydrocarbon spacer between sulfur and silicon is changed, the reaction proceeds at different rates [4].

It is well-known that sulfur in the composition of various sulfides is able to coordinate with platinum, forming a donor–acceptor bond [5]. Based on this fact it was suggested that the length of the spacer affects the stability of the corresponding intermediates (Figure 1).

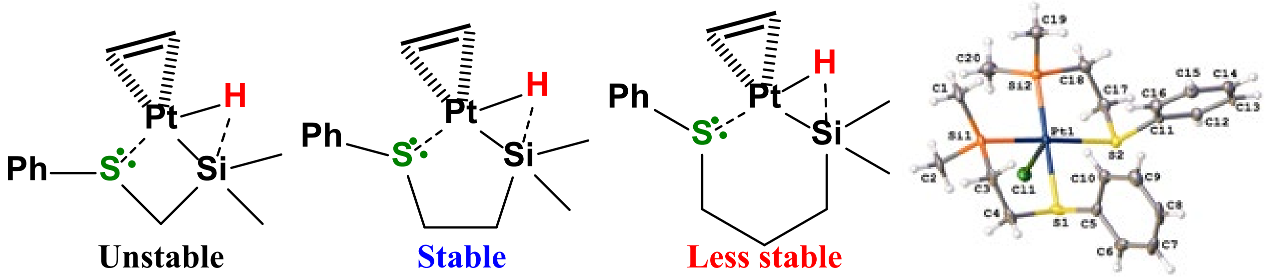

Figure 1. Structural motifs of the intermediates formed with different spacers [4].

This assumption was proved by a number of experiments and quantum chemical calculations. Thus, in this work, we demonstrate a previously unknown effect of platinum chelation with silanes containing sulfur in the γ-position from silicon.

Acknowledgements
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Overcoming mycobacterial resistance to isoniazid

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Isoniazid (isonicotinic acid hydrazide, INH) is one of the most active anti-TB drugs. However, the effectiveness of its use is decreasing due to the increasing spread of resistant strains of the pathogen (*Mycobacterium tuberculosis*). The vast majority of resistance cases are associated with mutations of two pathogen proteins: KatG and InhA.[1] KatG mutations prevent the transformation of the prodrug INH into the active metabolite isonicotinoyl-NAD. InhA mutations decrease the affinity of this enzyme for activated isoniazid and the completeness of its blocking.

The failure of activation can be overcome by a variation of the base carrying the isonicotinoyl fragment. In this case, activation can occur on a different enzyme from KatG or parametabolically. The parametabolically activated substance should quite easily eliminate the isonicotinoyl radical in the pathogen cellular environment. This effect can be achieved, for example, by combining a labile isonicotinoyl and a redox-active fragment, such as ferrocene, in the molecule. Ferrocene in this case is also useful due to its high lipophilicity that can facilitate the substance penetration through mycolic membranes of the pathogen. We have shown that resistance of Mycobacterium rubrum to isoniazid is overcome by modification of isoniazid hydrazones with a ferrocenoic fragment (Fig. 1, **1**).[2] We also found the possibility of easy elimination of the isonicotinoyl from ferrocene-containing derivatives of N-isonicotinoylpyrazoles in acid medium and studied the dependence of the process rate on the nature of the substituents. N-isonicotinoyl-4(5)-ferrocenyl-1H-pyrazoles (Fig. 1, **2**) with electron-donor substituents are promising leaders for further research in this field.

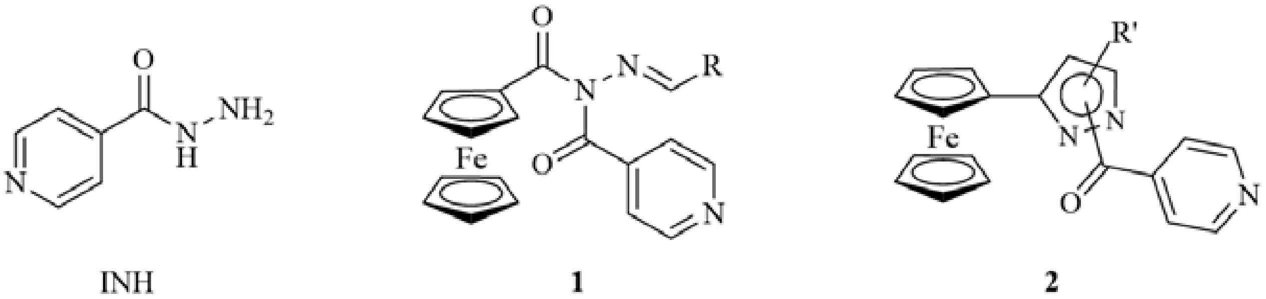

Figure 1. Isoniazid and its synthesized derivatives

Acknowledgements
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Interaction of Zirconacyclopentadiene Complexes of Zirconocene with Dicarbonyl Compounds

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Nowadays, the chemical properties of metallacyclic derivatives of the Group 4 using the reactions with various unsaturated compounds have been well studied. However, the reactivity towards dicarbonyl compounds has not been practically examined. Our recently study, the reactivity of a seven-membered zirconacyclocumulene complex (**1**) with acenaphthoquinone showed the formation of metallacrown (**2**) and tetrasubstituted cyclobutadiene, which then dimerizes to octasubstituted cyclooctatetraene (**3**)[1].

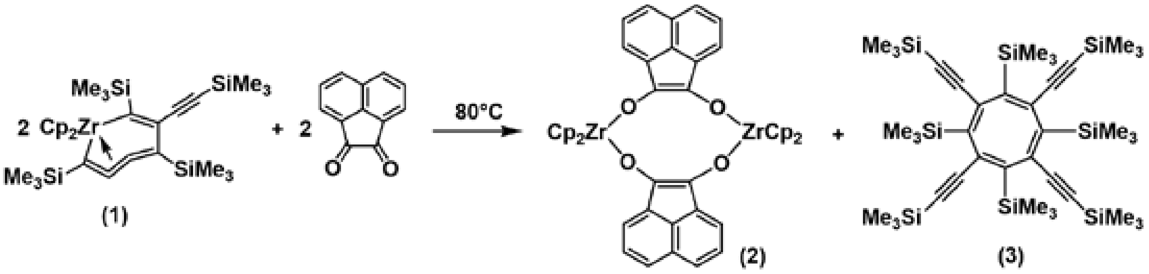

Figure 1. Reaction of complex 1 with acenaphthoquinone

In continuation of this work, we studied in detail the reactions of various complexes of zirconacyclopentadiene (**4-7**) with acenaphthoquinone and benzyl. It was found there are two main directions of the reactions: the insertion of dicarbonyl into the Zr–C bond with a ring enlargement; the elimination of the organic part from the zirconocene moiety (**8-11**), with the formation of metallacrowns **2** and (**12**).

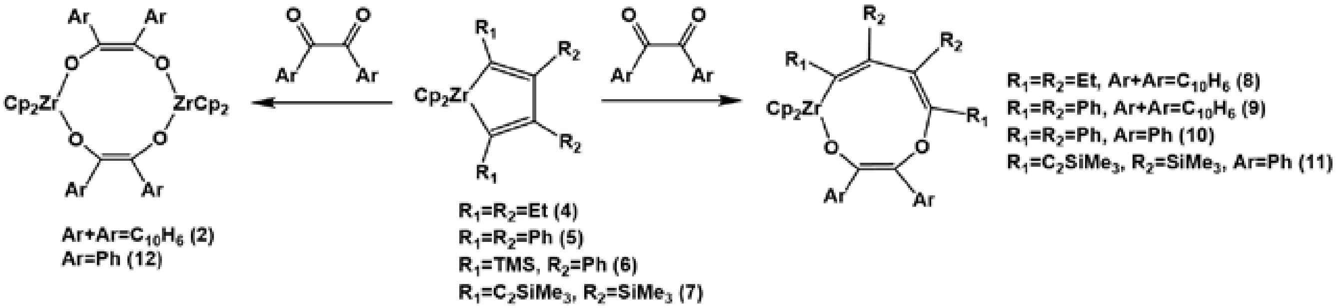

Figure 2. Obtaining complexes 2, 8-12

Acknowledgements
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A role of N,N'-linker in the solvothermal synthesis of MOFs based on ferrocenyl-*R*-phosphinates

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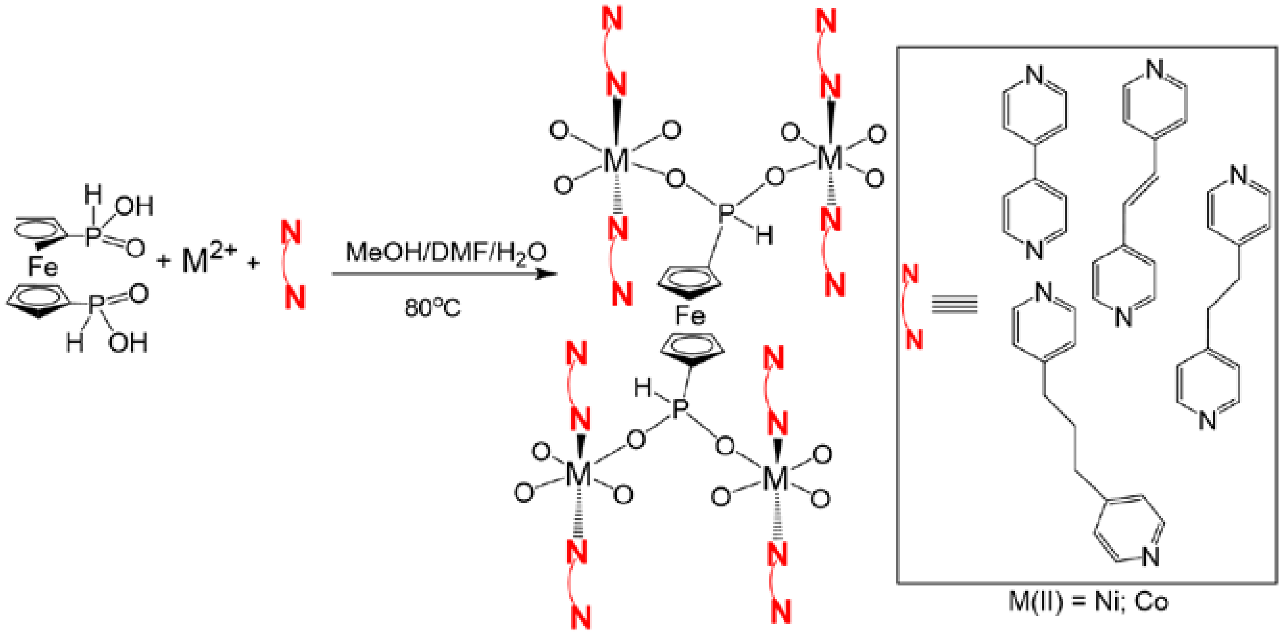
Due to their unique properties, including ultra-high surface area, adjustable pore sizes, and well-defined porosity, metal-organic frameworks (MOFs, as well as porous coordinate polymers, PCPs), a new class of porous materials that are composed of metal ions or cluster centers and organic ligands have been applied in many areas. In order to meet various specific requirements, the original MOFs usually need further functionalization, which could preserve the original topology structures, allowing the modified MOFs to exhibit outstanding performance in adsorption, wastewater treatment, energy storage and conversion, catalysis, sensors, and biomedicine.



Within the framework of this research, the behavior of ferrocenyl-*R*-phosphinates and the role of substituents in MOF formation with d-metals in the presence of additional neutral linkers were studied. The physico-chemical properties of the obtained polymers were also studied, including electrocatalytic (CO_2 reduction reaction and others)

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Effective computational route to unravel geometry of d^0 titanocene with promising photo-, tribo-, and mechanoluminescent properties

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The diverse titanium complexes represent a major class of compounds widely used in many fields of modern molecular science.[1] The present contribution systematically evaluates ability of quantum-chemical methods at different levels of theory to correctly simulate geometry of a structurally sophisticated organometallic species. Notably, theoretical treatment of metal complexes remains a sophisticated problem due to near-degeneracy of their electronic states and relativistic effects. Moreover, accurate benchmarking of theoretical methods with small molecules does not always reflect special structural and electronic features of medium and large-size metal complexes utilized in practical applications.

The performance of DFT and Hartree-Fock (HF) methods for computing geometry of the room-temperature emissive d^0-titanocene dicarboranyl $Ti(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ as a reference model is analyzed. An extensive systematic series of different methods was applied to establish the best methodology for studying organometallics of this type. We demonstrate that the right selection of the density functional and the basis set has a critical significance for the reliable assessment of geometric data of the complex organometallics. The HF methods and most of the applied DFT are shown to reproduce the crystal structure with appropriate accuracy. In addition, it is found that conformational transitions (small structural changes with a change in the point group, for example: $C_1 \leftrightarrow C_2$) in $Ti(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ are almost barrier-free and lead to a significant change in the electric dipole moment: $\Delta\mu = 0.1 - 0.2$ Debye and to shifts of the ligand-to-metal charge transfer (LMCT) bands in the excitation (absorption) spectra by several nm (calculated by a set of TDDFT methods in good agreement with experiment), which, in the general case, explains the nature of band broadening in the electronic spectra of bent sandwich complexes. This sensitivity of the position and shape of electronic bands to very weak conformational changes in metal-complex chromophores has not been previously reported in the literature. Note that a characteristic feature of this class of molecules is very small solvatochromic shifts of the LMCT bands in the spectra[1-3].

Changes in the geometry of the metal complex upon the transition from the ground electronic state to ^{1}LMCT state are evaluated. In the S_1 state, the coordination of stable Cp-ligands (spectator ligands) is weakened; thus, the π-bonds are activated. The titanocene dipole moment in the S_1 state increases ($\Delta\mu > 0.5$ Debye), thereby confirming the formation of a charge-transfer excited state.

Acknowledgements
The study was carried according to the state contract 0089-2019-0003 (AAAA-A19-119070790003-7).

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Ligand-to-metal charge transfer excited states based on group 4 bent metallocenes

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Molecular electronically-excited states are of great fundamental and technological importance. Ligand-to-metal charge transfer (LMCT) excited states are rarest and less studied. We have conducted a lasting study[1-5] on molecular photonics of group 4 bent metallocenes, having rare ^{3}LMCT excited states. Some results are summarized below:

Photo properties	d^0 metallocenes						
	Cp_2MMe_2	Cp_2MCl_2			$M(CpCMe_2CB_{10}H_{10}C)_2$		
		Ti	Zr	Hf	Ti	Zr	Hf
LMCT absorption: $S_0 \rightarrow S_1$	Me → M	Cp → M			Cp → M		
λ_{max} / nm		517	335	307	466	334	316
phosphorescence:	no $(T_1 \rightsquigarrow S_0)$						
λ_{00} / nm		595	408	377	525.5	386	373
λ_{max} / nm		649	459	424.5	602	441	419

In the principle series Cp_2MMe_2, Cp_2MCl_2, and $M(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$ (M = Ti, Zr, Hf), the first electronic transitions are associated with LMCT. A good agreement of the results of some theoretical (TD DFT)[5] and photophysical studies is obtained, accounting for the unusual change in the nature of LMCT states and the dipole moment of $(\eta^5\text{-}RCp)_2MX_2$ when replacing σ-ligands.

Notably, simulation of charge-transfer bands is problematic even in case of much simpler organics. According to our systematic study performed using popular TD DFT methods (the functionals: CAM-B3LYP, B3LYP, M06, M06-2X, M11, PBE0, TPSSh, etc., and the basis sets: QZVP, aug-cc-pVTZ, 6-311++G**, TZVP, 6-311G**, 6-31G**, DGDZVP, CEP-121G, SDD, 3-21G, and LANL2DZ), choice of a computing method for d^0 metallocenes depends on the metal nature, while there are no optimal computing methods. Conventional DFT and TD DFT calculations at high levels of theory make it possible to obtain more or less reliable data on electronic-structural and orbital characteristics of organic d^0-metal complexes and LMCT transitions. Nevertheless, their rigorous verification in series of similar compounds is necessary with the involvement of other calculations and the maximum amount of experimental data (X-ray data, redox potentials and electrochemical processes, absorption and luminescence spectra, etc.).

Acknowledgements

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1D coordination polymer dysprosium based dpp-bian

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Design and preparation of the metal-organic coordination polymers (MOCPs) is a rapidly developing field of coordination chemistry. The 2D and 3D metal-organic frameworks (MOFs) often display advanced properties that may be useful in catalysis, gas storage, magnetism, *etc*. The combination of transition metal atoms and redox-active ligands (bridging and terminal) makes it possible to give these compounds new unusual properties, both spectral and magnetic, due to the appearance of the ability to electron transfer from metal to ligand[1]. As is known lanthanide complexes are appealing candidates for single-molecule magnets (SMMs) because of their large unquenched orbital angular momentum and strong magnetic anisotropy.[2] Thus, the combination, on the one hand, of the rigid structure of MOFs and, on the other hand, of lanthanide ions can lead to obtaining interesting magnetic properties materials. We have previously prepared the 1D coordination polymers with europium,[1] as well as zinc,[3] gallium,[3] and alkali metals[4] - 1D and 2D architectures based on the dpp-bian ligand (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene).

Here we report of an synthesis and characterization of the dysprosium complex [(Ar^{BIG}-bian)DyICp*][K(dme)$_4$] (Ar^{BIG}-bian = 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)–imino]acenaphthene) and 1D dysprosium coordination polymer [(dpp-bian)DyIKCp*]$_n$. According to X-ray diffraction analysis, the complex based on more sterically hindered Ar^{BIG}-bian ligand has a monomeric structure while [(dpp-bian)DyIKCp*]$_n$ represents 1D-polymer chain which is built from alternating ions of dysprosium(III), potassium and iodine. Acenaphthene-1,2-diimine dpp-bian acts as a terminal chelating dianion ligand. The newly prepared compounds were characterized by IR spectroscopy and elemental analysis. The molecular structures of compounds have been established by single crystal X-ray analysis. For complex [(Ar^{BIG}-bian)DyICp*][K(dme)$_4$] magnetic measurements were carried out.

Acknowledgements
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Photophysical parameters of micelles loaded with the cyclometalated Ir(III) diimine phosphorescent complex

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Nanoscale biosensors based on phosphorescent emitters are currently in great demand in the field of biomedical research, as they are a promising approach for determining the level of oxygen in cells.[1]

In this work, we synthesized an iridium(III) complex with two cyclometalating N^C ligands and one diimine N^N ligand with a long alkyl chain (Fig. 1). This type of complex was chosen because analogous iridium compounds in general have low toxicity,[2] and their emission is quite sensitive to oxygen. Next, a series of micelles was prepared, based on poly(ε-caprolactone-*block*-ethylene glycol), with different mass concentrations of the complex. Synthesis of block copolymer micelles was carried out under the same conditions.

The synthesized Ir(III) complex was characterized by 1D (^{1}H) and 2D (^{1}H-^{1}H COSY, NOESY) NMR spectroscopy and ESI+ mass spectrometry. For the complex and micelles, their photophysical properties were measured: the absorption and emission spectra and the lifetimes of excited states were taken both in aerated and in the degassed solution.

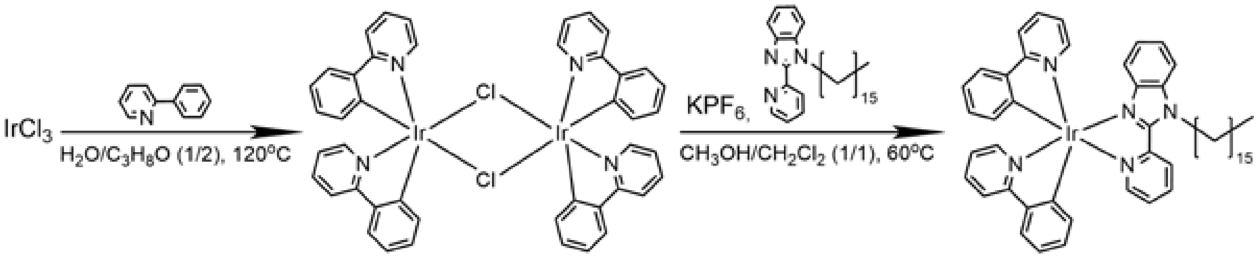

Figure 1. Scheme for the synthesis of the cyclometalated Ir(III) diamine phosphorescent complex.

Acknowledgements

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SABRE hyperpolarization of 15N nuclei at high magnetic fields based on adiabatically modulated radiofrequency magnetic fields

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Parahydrogen Induced Polarization (PHIP) is an efficient technique to enhance NMR-signals, being otherwise tremendously weak. PHIP stems from the rational usage of parahydrogen, pH2, which is a H2 molecule in its nuclear singlet spin state. There are two general choices of such reaction - catalytic hydrogenation of the unsaturated precursor with pH2 (hydrogenative PHIP) and reversible interaction of pH2 with metalorganic complexes (non-hydrogenative PHIP). The second method, termed Signal Amplification By Reversible Exchange (SABRE) exploits simultaneous binding of pH2 and to-be-polarized substrate with Ir-complex, in which the substrate acquires polarization. At low and ultralow magnetic fields this polarization transfer runs in a spontaneous fashion, while at high fields it requires applying radiofrequency (RF) excitation.

In this work, we analyze SABRE pulse-sequences with adiabatic RF-amplitude modulation aimed to enhance 15N NMR-signals at high magnetic field and provide a simple method to optimize RF-amplitude switching profile. Such an optimization procedure is simple and based on considering 15N SABRE-polarization induced by constant-amplitude RF-pulses. Moreover, it can be performed based either on interpolation of experimental data or exploiting calculated one which takes into account SABRE chemical dynamics. In order to support our approach, we conducted a set of adiabatic double-frequency (1H and 15N nuclear channels) SABRE-experiments at identical conditions with different amplitude-modulated profiles: linear, constant-adiabaticity and “optimal” one. Finally, we report both experimental and theoretical studies of adiabatic SABRE transfer at high magnetic field to give a detailed algorithm for RF-amplitude modulation profile optimization.

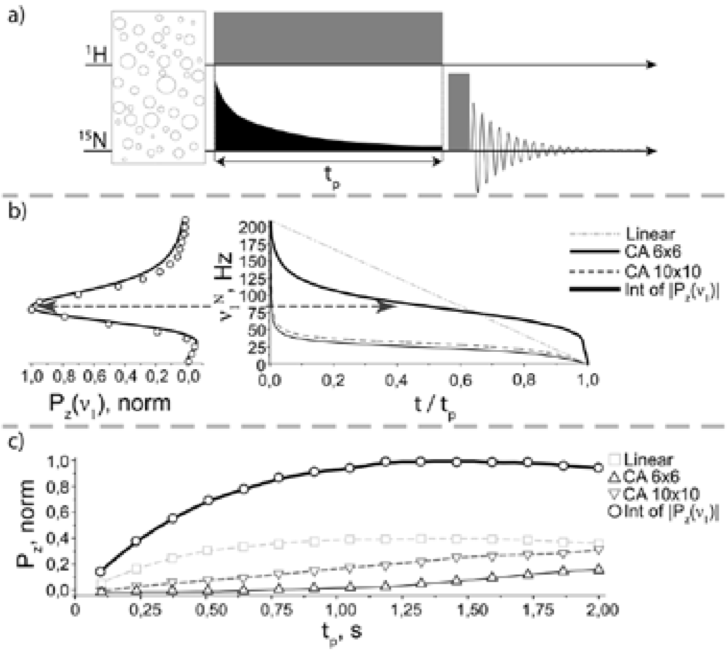

Figure 1. a) High-field SABRE pulse sequence with adiabatic 15N RF-modulation;
b) 15N RF-modulation profiles under consideration: linear, constant-adiabaticity, and “optimal”;
c) 15N polarization dependance on the full time of RF-switching

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Unexpected Coordination of the Nitronyl Nitroxide Radical to the Au (I) Atom: A Crystallographic Study

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Nitroxide radicals and their complexes have been intensively studied for many years, leading to key discoveries in the field of molecular magnetism, such as the preparation of pure organic ferromagnets and ferrimagnets, complexes of transition metals with nitroxides showing magnetic ordering effects, and copper–nitroxide complexes with unusual spin-crossover behavior. This situation has stimulated the subsequent active developments in the chemistry of this class of paramagnetic compounds with an emphasis on the synthesis of their polyfunctional derivatives. Although, to date, a huge number of different nitroxides have been successfully obtained, there are still poorly studied but interesting types of organic radicals within this class [1].

Until now, there is not enough research on the coordination compounds of Au(I) with nitroxide radicals. In this study, the crystal structure of new compounds of this series is considered, a comparison with a model compound described in the literature is made, and an analysis of the crystal packing and non-covalent interactions is carried out.

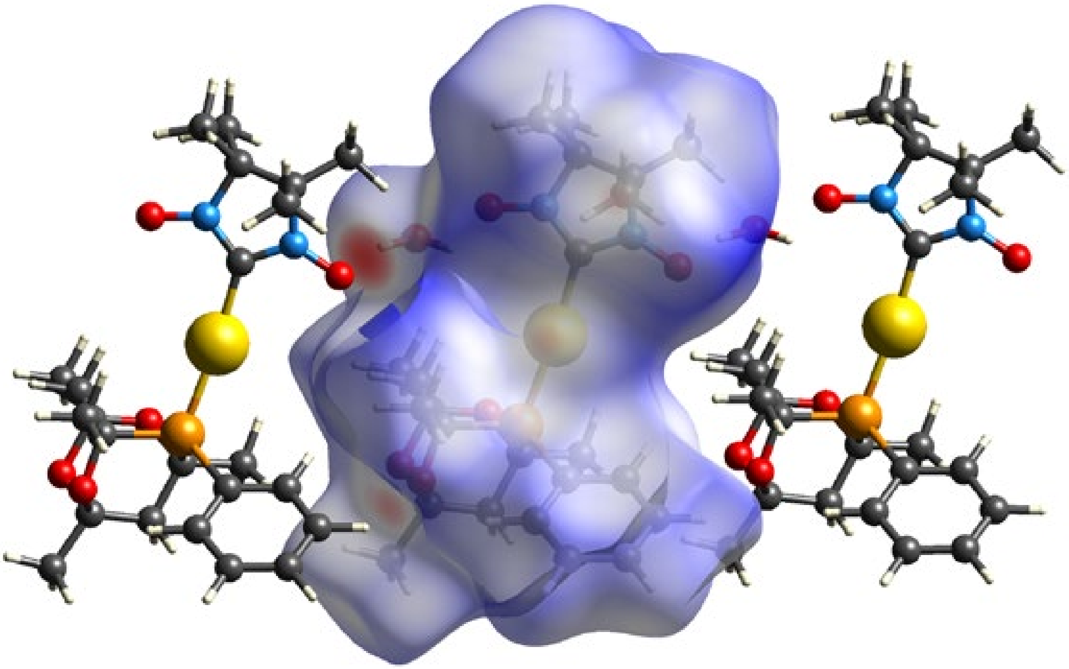

Figure 1.

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Complexation of trinuclear silver(I) pyrazolates with pyridine-chalcones

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Group 11 metal pyrazolate complexes attract the interest of researchers by their ability to form supramolecular systems with a wide range of bases and photophysical properties.[1] Based on the ability of trinuclear metal pyrazolates $[MPz]_3$ to form complexes with compounds possessing carbonyl groups and basic nitrogen atoms, the pyridine-containing chalcones were chosen as agents for the complexation with silver(I) trinuclear macrocycle.[2]

The investigation of the interaction of cyclic trinuclear silver(I) pyrazolate $[AgPz]_3$ (Pz = 3,5-bis(trifluoromethyl)pyrazolate) with pyridine-containing chalcones (E/Z-3-(anthracen-9-yl)-1-(pyridin-2-yl)prop-2-en-1-one(E-1, Z-1), E-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one(E-2)) have been performed by IR-, UV-vis, and NMR spectroscopy. The carbonyl group is one center of coordination in all cases. The *cis-trans* isomerization of the C=C double bond significantly influences the complexes formation.[3] E-form of chalcones in seek to planar structure in the complexes with trinuclear pyrazolate adduct $[AgPz]_3$ via multiple π-π/M-π. Carbonyl and pyridine fragments also take place in coordination with the $[AgPz]_3$ also via π-π/M-π interactions. In contrast, Z-1 of anthracene-containing chalcone, the preferable formation of complex possessing with desired chelating coordination of O- and N atoms to silver atoms is observed.

The complexation in the case of anthracene-containing chalcones allows switching of the emission nature from charge-transfer to ligand-centered at 77 K.

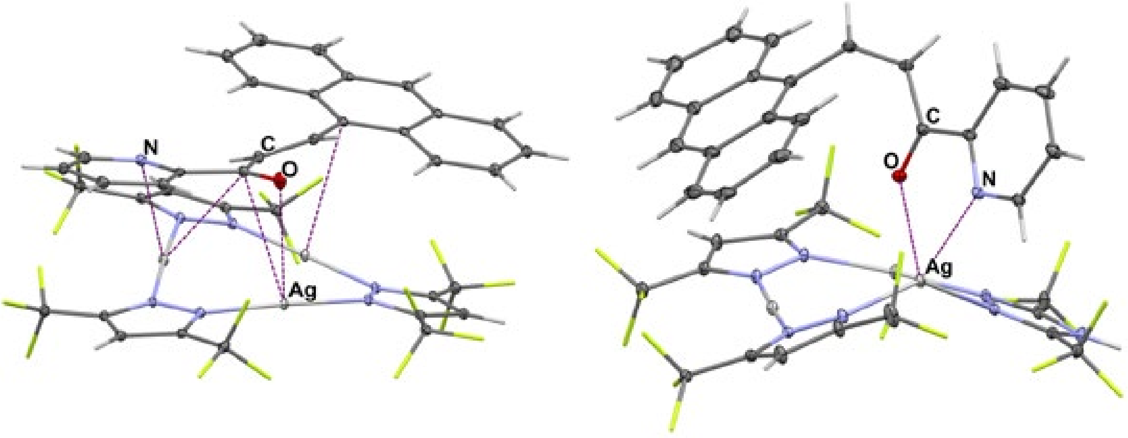

Figure 1. XRD structure of complex E-1 with $[AgPz]_3$ (left) and Z-1 with $[AgPz]_3$ (right).

Acknowledgements

This work was financially supported by the Russian Science Foundation (project № 19-73-20262)

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Copper-catalyzed cross-coupling of a monoterpenyl derivatives with benzyl Grignard reagents

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Active juvenoids, which are environmentally friendly insecticides, were found among terpenylbenzyl compounds[1]. The key stage of synthesis was the copper-mediated reaction between a terpenyl electrophiles such as chlorides 2a,2b, ammonium salts 3a,b, carbonate 4 and benzyl Grignard reagents 6-7 in the presence of copper salts 8,8a,9 (Figure 1). This kind of coupling reactions involves the formation of an organocopper intermediate from a transmetalation reaction. An important issue in this reaction is the control of regiochemistry, i.e., whether the leaving group is displaced α- or γ- by the organometallic reagent[2].Depending on the reaction conditions and the reagents used, we were able to achieve a high α-regioselectivity (products 10 a-d) of the reaction (94-98%).

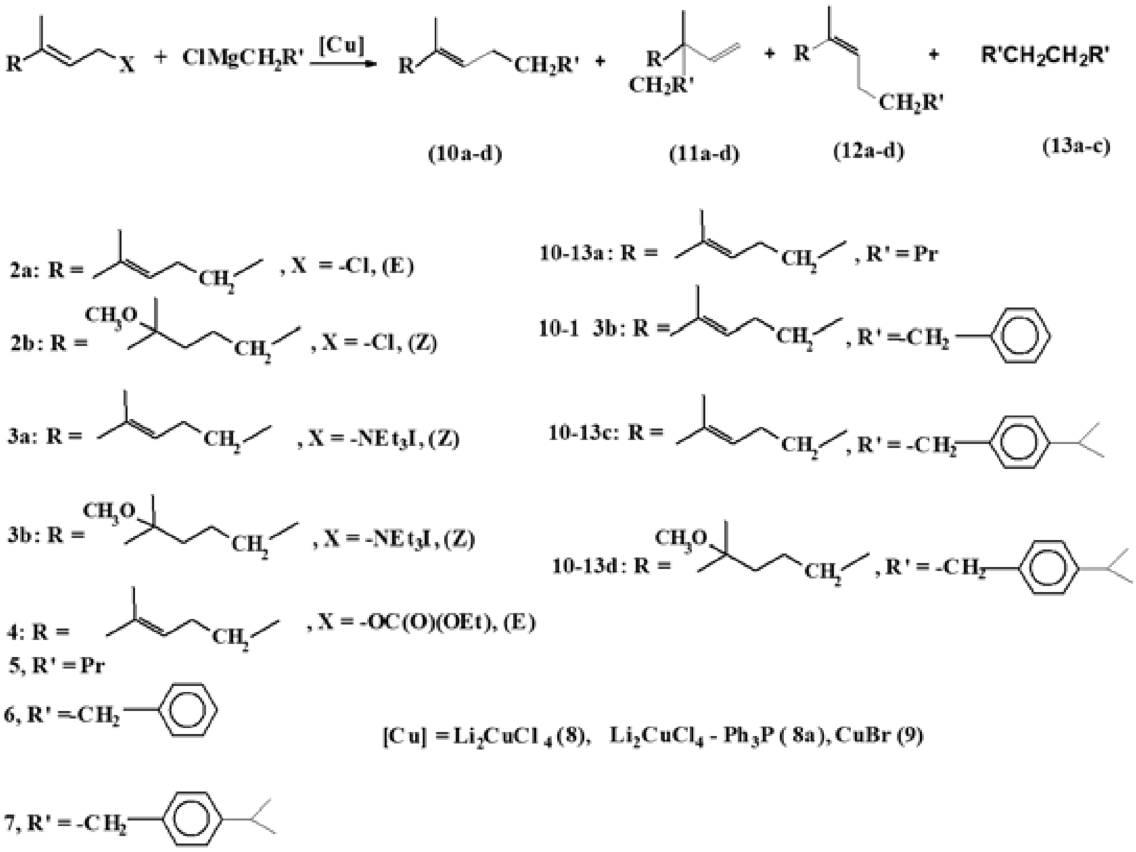

Figure 1. The reaction between a terpenyl derivatives and benzyl Grignard reagents in the presence of copper salts.

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Phosphorescent O_2-sensors Based on Ir(III) Complexes for Bioimaging Applications

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Design, synthesis and investigation of new molecular oxygen sensors for bioimaging, based on phosphorescent transition metal complexes, are among the topical problems of modern chemistry and advanced bioimaging. Three new iridium [Ir(N^C)2(N^N)]+ complexes with cyclometallating 4-(pyridin-2-yl)-benzoic acid derivative and different diimine chelate ligands have been synthesized and characterized by using mass-spectrometry and NMR spectroscopy (Figure 1). The periphery of these complexes is decorated with three relatively small “double-tail” oligo(ethylene glycol) fragments. All these complexes exhibit phosphorescence, their photophysical properties have been thoroughly studied, and quantum chemical calculations of their photophysical properties were also performed. It turned out that the changes in the nature of the diimine ligand greatly affect the character of the electronic transitions responsible for their emission. Two complexes of this series show the desired photophysical characteristics; they demonstrate appreciable quantum yield (14–15% in degassed aqueous solutions) and strong response to the changes in oxygen concentration, ca. 3-fold increase in emission intensity and excited state lifetime upon deaeration of aqueous solution. The study of their photophysical properties in model biological systems (buffer solutions containing fetal bovine serum - FBS) and cytotoxicity assays (MTT) showed that these complexes satisfy the requirements of application in bioimaging experiments.

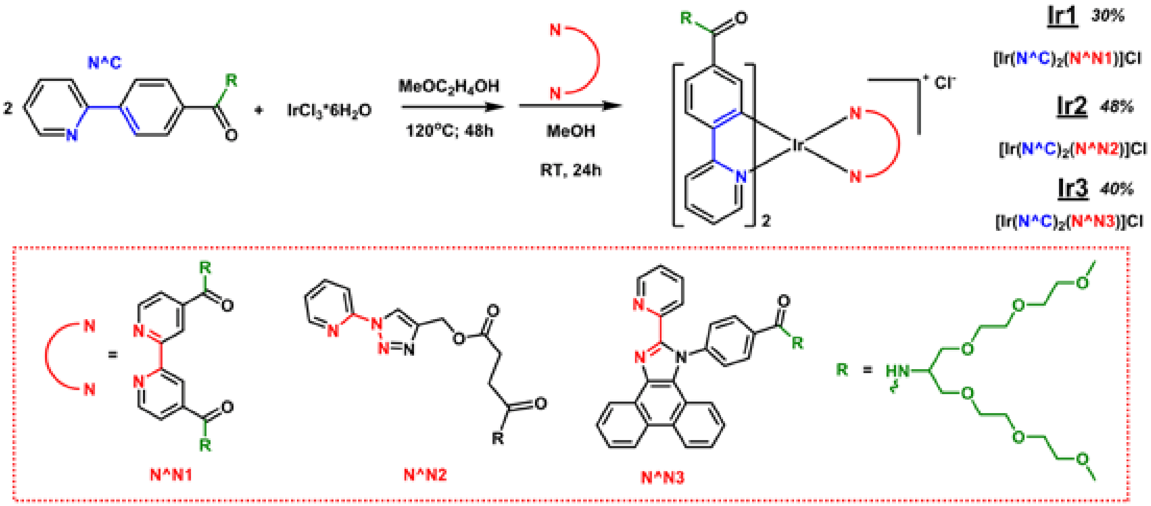

Figure 1. Scheme of synthesis of new Ir(III) dimer $[Ir_2(N^{\wedge}C)_4Cl_2]$ and new complexes Ir1-Ir3.

Acknowledgements

This research was funded by the Russian Science Foundation, grant number 18-73-10021. This work was performed using the equipment of the Centers for Magnetic Resonance, for Optical and Laser Materials Research, for Chemical Analysis and Materials Research, Computing Centre and Cryogenic Centre of Research Park of St. Petersburg State University.

Synthesis and Structure Study of Copper(I) Complexes Bearing 1,2,4-Oxadiazolate Ligands With Dibenzohalolium(III) Stabilizing Counterion

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Hypervalent iodine compounds are capable to form halogen bonds simultaneously with several nucleophiles due to the presence of two σ-holes on iodine(III) atom. Huber et al. showed that the formation of cyclic supramolecular assemblies between dibenzoiodolium cation and bidentate nucleophiles leads to the increasing stability of these systems.[1]

We obtained a number of copper(I) complexes consisting of [CuL2] anion (L – 1,2,4-oxadiazolate ligand) and dibenzohalolium cation (Figure 1). In solid structures of these compounds, we found halogen bonds between X+ atom (X = I, Br) and two exocyclic O atoms of 1,2,4-oxadiazolate ligands. Computational studies have demonstrated the key role of these noncovalent interactions in the stabilization of the complexes obtained. Notably, when ligands being in syn-conformation the dibenzoiodolium cation forms the copper(I) involved chelate metallacycle.

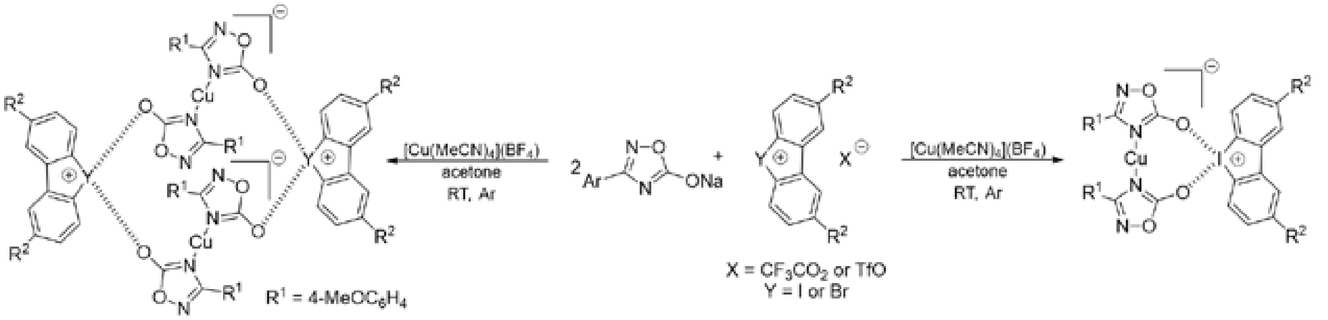

Figure 1. Synthesis of complex stabilized by I···O,O halogen bonds in *syn*- and *anti*-conformations

Acknowledgements

This study was supported by the Russian Science Foundation (project No 22-73-10031) and the Ministry of Science and Higher Education of Russian Federation in framework of the “Mega-grant” program (project No 075-15-2021-585). Physicochemical studies were performed at the Center for X-ray Diffraction Studies, Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, and Thermogravimetric and Calorimetric Research Center (all belonging to Saint Petersburg State University).

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ESTER SYNTHESIS FROM SECONDARY ALCOHOLS AND CO IN THE PRESENCE OF PALLADIUM-PHOSPHINE CATALYTIC SYSTEMS

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Alkene alkoxycarbonylation with alcohols and CO leads to the formation of esters. CO, as a rule, is obtained from synthesis gas, which, in turn, can be obtained not only from oil and natural gas, but also from alternative raw materials – coal, characterized by large reserves, and biomass waste – a renewable raw source. When using homogeneous Pd-catalysts under mild conditions, esters of linear structure are mainly formed. However, in some cases alcohols are more accessible reagents compared to the corresponding alkenes. Esters can also be obtained by alcohol carbonylation, for which homogeneous rhodium and iridium catalysts with additives of iodide compounds are most preferred. It is not the alcohol that is directly carbonylated, but the corresponding alkyl iodide. These processes are inferior to alkoxycarbonylation, since they are carried out under more stringent conditions[1].

This study is devoted to the development of a combined process of the secondary alcohols dehydration and alkoxycarbonylation of the resulting alkenes in the presence of catalytic systems Pd-precursor / organophosphine / HA (strong acid). HA is the catalyst of dehydration and the co-catalyst of alkoxycarbonylation. The ^{1}H and ^{13}C NMR spectroscopy and GC were used to analyze the products. In all samples of the reaction mass taken during the experiments, alkenes were present as products of alcohol dehydration catalyzed by HA. $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(acac)_2$ ($acac^-$ – acetylacetonate ion), and $Pd_2(dba)_3$ (dba – tris(dibenzylidenacetone)) were tested as catalytic precursors in the model combined process with cyclohexanol and CO. In this process, PPh_3 and a number of diphosphines were tested as promoters, while CH_3SO_3H, CF_3SO_3H, $C_6H_5SO_3H$, p-$CH_3C_6H_5SO_3H$, CF_3COOH, and H_2SO_4 were tested as HA. To bind the water formed as a result of the cyclohexanol dehydration, additives of sodium and potassium salts of HA were used. Hydrolysis of these salts led to the generation of additional amounts of acids. In the model combined process leading to the formation of cyclohexyl cyclohexanecarboxylate, the $Pd(PPh_3)_2Cl_2$ – XantPhos – CH_3SO_3H catalytic system with the addition of CH_3SO_3Na showed the greatest activity. Using this system, the influence of various process parameters on the rate of formation of the target product was studied. Under optimized conditions (110 °C and CO pressure of 2 MPa), the yield of the target product reached 95%. At 115 °C and CO pressure of 3 MPa, combined processes using 2-hexanol and 2-heptanol were carried out in order to obtain esters $C_6H_{13}COOC_6H_{13}$ and $C_7H_{15}COOC_7H_{15}$, respectively. The total yield of $C_6H_{13}COOC_6H_{13}$ isomeric esters was 56% in 8 h and selectivity for 2-hexyl heptanoate was 59% (GC). The total yield of $C_7H_{15}COOC_7H_{15}$ esters was 45% in 8 h and the selectivity for the 2-heptyl octanoate was 55% (GC). Apparently, the predominant formation of an ester with a linear carboxyl component was provided by the use of the Pd-XantPhos system, which is able to catalyze the migration of the internal bond C=C to the terminal position[2].

Acknowledgements

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Platinum(II) Block Copolymer Based on Polyvinylpyrrolidone

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In recent years, luminescent platinum(II) complexes are in the research focus due to their high potential of application in bioimaging, OLED technologies and photocatalysis. The crucial advantage of platinum complexes with pincer ligands is provided by the easy tuning of their photophysical properties varying the substituent in the cyclometalating ligand.

This year, a new strategy for turning luminescent Re(I) complexes into water-soluble and biocompatible sensors for bioimaging was suggested by our colleages.[1] In present work we applied this method to a platinum(II) complex. Thus, we synthesized a novel platinum(II) complex with a N^N^C-type pincer ligand and ancillary phosphine ligand containing vinyl group. We also obtained a copolymer of the complex and polyvinylpyrrolidone (p(VP)), which was characterized using NMR spectroscopy, gel permeation chromatography and dynamic light scattering. Photophysical properties of the polymer were studied in water and acetonitrile solutions under different temperatures and at different concentrations. It was found that the copolymer aggregates into micelles in water solution generating a new absorption band at 600 nm.

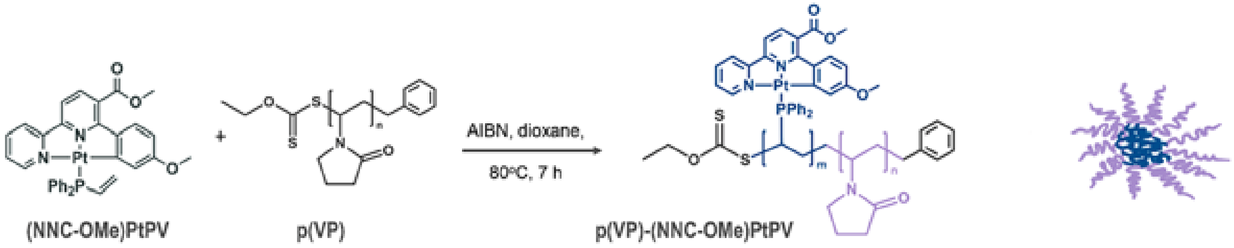

Figure 1. Synthesis of the platinum(II) block copolymer

Acknowledgements
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π-Expanded porphyrins - a promising platform for new photosensitizers

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Porphyrins are a class of macroheterocyclic compounds possessing unique electronic and chemical properties. Their capability of energy or electron transfer under photoexcitation determined their intensive investigation as photocatalysts for organic reactions. Modification of the periphery of the tetrapyrrole macrocycle enables the precise tuning of its optical and redox properties, which consequently affects the catalytic perfomance of the resulting derivatives. Recently we have demonstrated the high catalytic activity of pyrazine-appended porphyrins in sulfide oxidation at low catalyst loading (10^{-3} mol.%) [1]. In this regard, further expansion of the aromatic system is expected to increase the catalytic activity of such photosensitizers.

Our reported procedure was followed to synthesize the heterocycle-fused porphyrins **Ni-3 – Ni-6**, involving the generation of labile 2,3-diaminoporphyrins and their reaction with aromatic carbonyl compounds (Figure 1) [2]. Demetallation of **Ni-3 – Ni-6** resulted in the formation of the corresponding free-bases **2H-3 – 2H-6** for the application as photosensitizers. A bathochromic shift of bands (6-26 nm) in UV-vis spectra of pyrazinoporphyrins **2H-3 – 2H-7** with respect to the parent porphyrin was found to correlate with the gradual expansion of the aromatic system.

The photocatalytic activity of the obtained porphyrins was studied in the oxidation of thioanisole, showing that even at low catalyst loading (10^{-2} mol.%) complete conversion of the substrate could be achieved in 16 hours with high selectivity (up to 99%) (TON up to 10000). Phenanthrene-appended porphyrin **2H-6** turned out to be the most efficient catalyst. Introduction of functional groups to the periphery of this molecule opens up prospects for further obtaining new hybrid catalytic materials based on π-expanded porphyrins. Functionalization by introduction of phosphonate groups made it possible to achieve complete conversion of thioanisole at a catalyst loading of 10^{-3} mol.%.

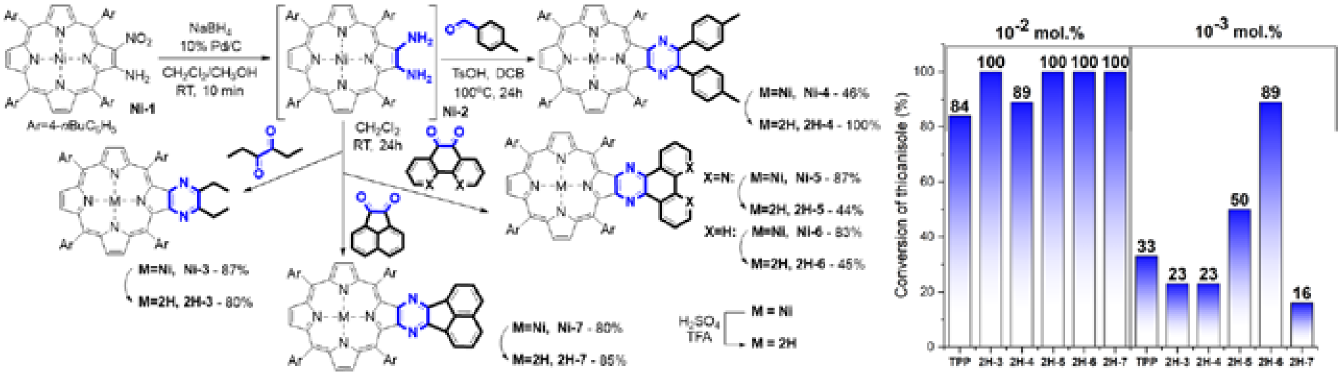

Figure 1. Synthesis of Ni-3 – Ni-7 and 2H-3 – 2H-7 (left) and the photocatalysis data (right).

The research was supported by RSF (project No. 23-23-00542)

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Singlet-triplet conversion in molecular hydrogen on a homogeneous catalyst in parahydrogen induced polarization experiments

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SABRE (Signal amplification by reversible exchange) belongs to the family of methods for induced hydrogen-parahydrogen polarization of nuclei. Pure parahydrogen potentially contains a huge stock of nonequilibrium polarization, and it can be stored for up to several weeks. One of the problems in PHIP applications is the singlet-triplet conversion in the H_2 molecule (similar to singlet-triplet transitions in radical pairs), which reduces the lifetime of the singlet spin order of H_2 in solution. In the presence of a catalyst, this conversion is significantly accelerated (up to several seconds), which negatively affects the enhancement of NMR signals. The study of this process will make it possible to estimate the lifetime of the singlet spin order H_2 in the systems used in PHIP experiments, and, ultimately, to increase the gain of NMR signals obtained.

Field dependences of the ortho-para conversion rate and free hydrogen signal amplification factor were experimentally obtained for the IrImes catalyst. To investigate the influence of different factors on the behavior of the hydrogen conversion rate, we also performed numerical calculations of parahydrogen induced polarization experiments.

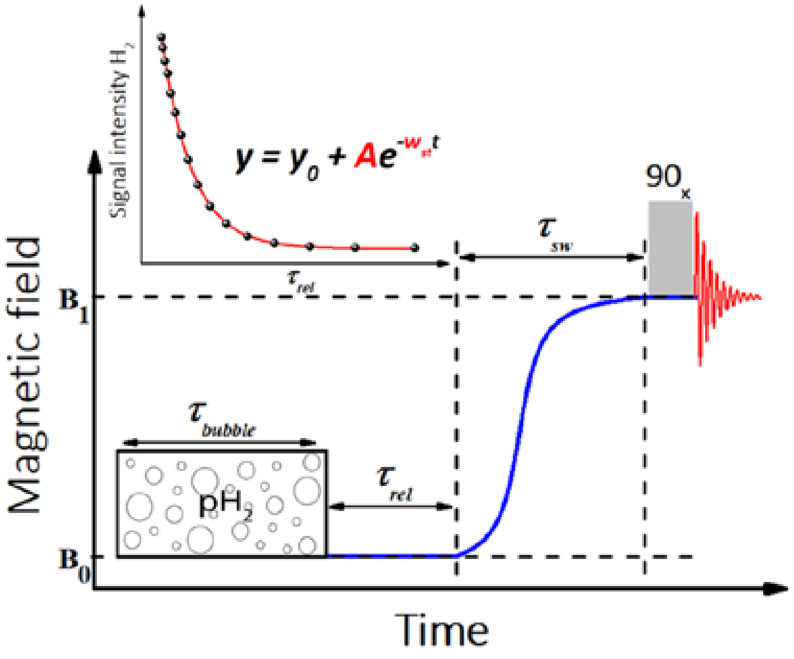

Figure 1. Schematic of experiments to measure the field dependences. τ_{bubble} – time of sample bubbling with parahydrogen (10 s), τ_{rel} – time of varying delay

Acknowledgements
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Rh(III)-catalyzed Coupling of Aryl Hydroxamates with Chiral Ni(II) Complexes: Access to α-Amino Acids with an Isoquinolone Core

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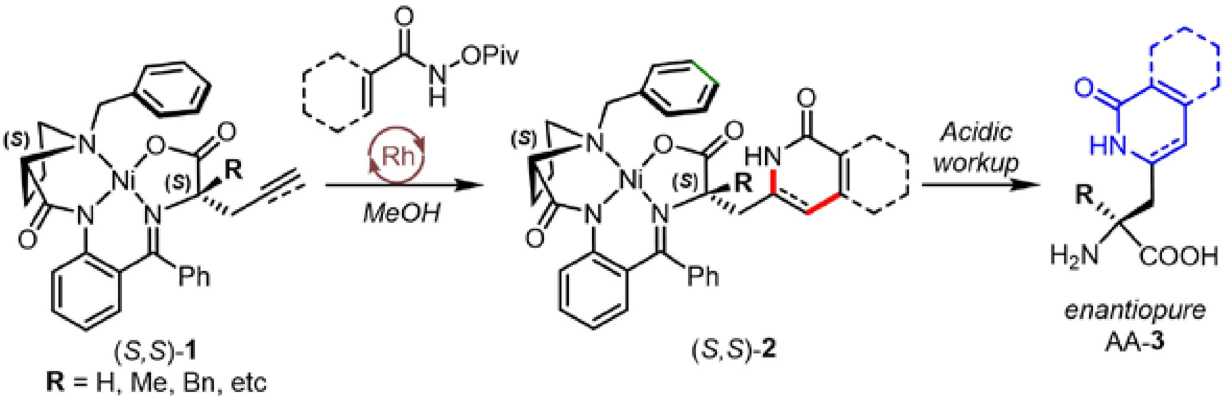
Enantiopure α-and α,α-disubstituted amino acids (AAs) with an isoquinolone core are a promising class of compounds in terms of their biological activity. Isoquinolone motif is widely presented in medicinal drugs, agrochemicals and many natural products.[1] The most efficient and straightforward approach for the synthesis of isoquinolone skeleton is Rh(III)-catalyzed C–H activation/annulation of various readily available aryl hydroxamates with alkynes or alkenes.

We report a general and efficient asymmetric route to artificial AAs with an isoquinolone core through a Rh(III)-catalyzed reaction of aryl hydroxamates with a series of chiral Ni(II) complexes **1** (Gly, Ala and Phe derivatives) featuring propargylic and/or allylic groups (Scheme).[2] Moreover, we showed for the first time that a combination of both the substrate structure and the bulky catalyst controls the formation of an unfavorable 4-substituted isoquinolone core. The target enantiopure AAs featuring an isoquinolone fragment were isolated by an acidic decomposition of the obtained Ni(II) complexes.[2]



(*S*,*S*)-**1**
R = H, Me, Bn, etc

(*S*,*S*)-**2**

AA-**3**

Scheme. Asymmetric route to artificial AAs with an isoquinolone core

Acknowledgements
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Regiodivergent Addition of CF_3-containing Azomethine Ylides to a Chiral Dehydroalanine Ni(II) Complex

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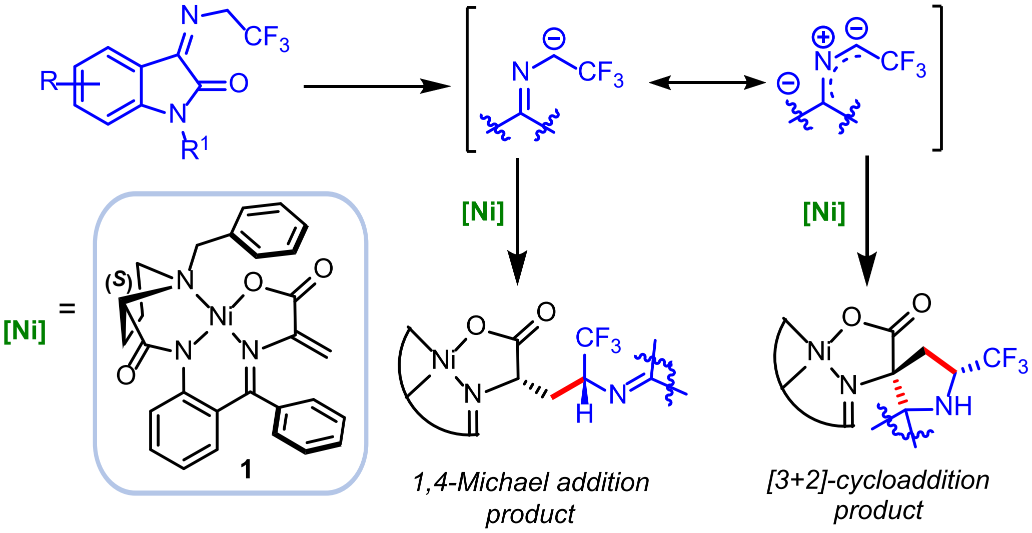
Currently, about 20% of commercial medicines contain fluorinated motifs in their structure due to the fact that fluorine-containing molecules have a wide range of biological activities.[1,2] In this context, chiral unnatural α-amino acids (AA) featuring fluorine atom are used as intermediates in synthetic chemistry, biochemistry and pharmaceuticals.[3] We elaborated a general protocol for the asymmetric synthesis of arduous non-proteinogenic AAs containing a trifluoromethyl group via the reaction of a chiral dehydroalanine Ni(II) complex **1** with CF_3-containing azomethine-ylides of isatins (Scheme). Depending on the nature of base, either [3+2]-cycloaddition or 1,4-Michael addition products were obtained. Moreover, the structures of the obtained complexes were confirmed by X-ray analysis.[4]



Scheme. Conjugate addition of CF_3-containing azomethine-ylides of isatin to a chiral Ni(II) complex 1

Acknowledgements
This work was supported by the Russian Science Foundation (RSF grant No. 22-23-00050).

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4. Manuscript in preparation.

Synthesis of fluorinated aluminum alkoxides and magnesium alkoxyaluminates

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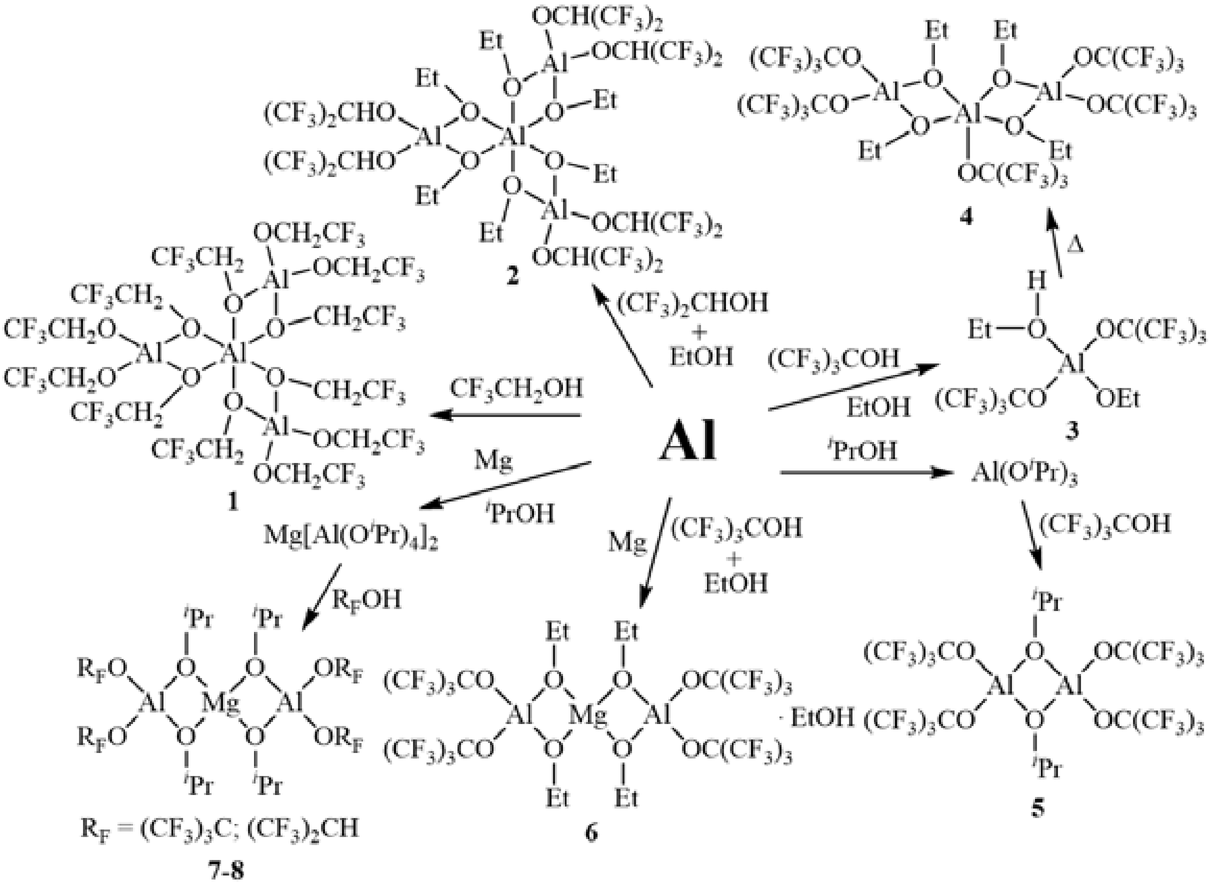
Preparative methods have been developed for the synthesis of new fluorine-containing aluminum alkoxides and magnesium alkoxyaluminates, which are of interest as intermediates for the preparation of catalysts and ceramic materials, as well as liquid electrolytes. During the research, it was found that when passing a direct electric current with a voltage of 200V through CF_3CH_2OH using Al as an anode material and an SS cathode, Al is activated and its reaction with CF_3CH_2OH is induced, which then occurs in the absence of an electric current to give aluminum alkoxide **1**. Attempts to carry out a similar reaction between Al and $(CF_3)_2CHOH$ or $(CF_3)_3COH$ failed. However, an electric current induces reactions of Al with a 1:1 (mol.%) mixture of $(CF_3)_2CHOH$ or $(CF_3)_3COH$ and ethanol to afford a mixed aluminum alkoxide **2** and an ansolvate acid **3**. In contrast, Al shows no reaction with similar mixtures in isopropyl alcohol. Therefore, to produce a mixed O^iPr-substituted aluminum alkoxide **5**, a two-step approach should be used comprising the initial preparation of $Al(O^iPr)_3$ and its further alcoholysis with $(CF_3)_3COH$, which is easily carried out at room temperature. Combinations of these two approaches can also open access to mixed magnesium aluminates **6-8**, solutions of which have a high electrical conductivity of about 9 mS/cm and can be used as electrolytes for magnesium batteries. The use of direct electric current to activate Al makes it possible to synthesize high-purity compounds **1-8**.



Ferrocene-modified pyrimidines as anticancer drugs

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The use of ferrocene-containing compounds for medical purposes has long been considered as a promising way to develop anticancer drugs due to their low toxicity, significant stability, lipophilicity, easy modification and unique electrochemical properties[1,2]. In particular, the combination of ferrocenyl and pyrimidine fragments makes it possible to obtain substrates with potentially better inhibitory activity against cancer cells than widely used drugs.

In this work, a number of pyrimidine analogs of “Ferrocerone” were synthesized by the condensation of enamine (1) with substituted amidines and ureas. Subsequent hydrolysis gave sodium salts, the structures of which were confirmed by NMR, ESI-MS, X-ray diffraction analysis and elemental analyses. The resulting salts were tested for antitumor activity against certain cancer cell lines.

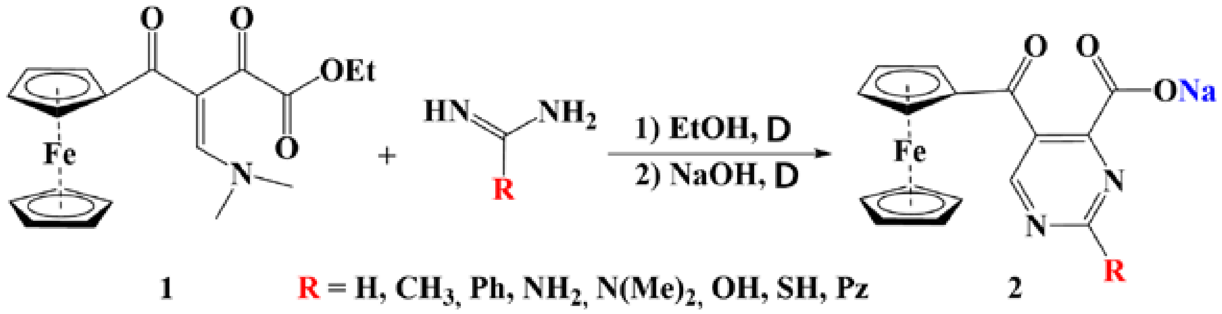

Figure 1. Synthesis of ferrocene pyrimidine derivatives

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Encapsulation of halide anions with biphenylene four-mercury anticrown

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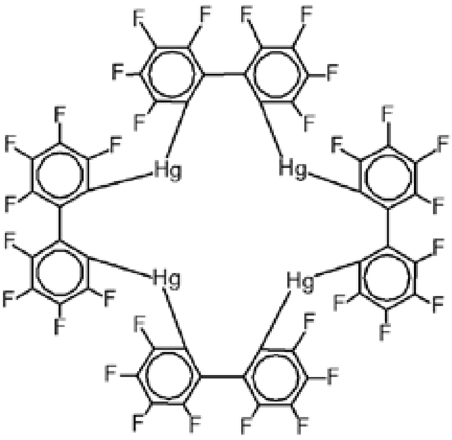
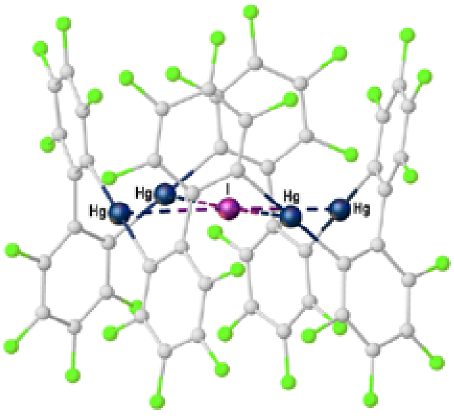
One of the important trends in supramolecular chemistry is the development of receptors, including Lewis acids, capable of selectively binding small anions, for example, by including them into their cavity. One of such receptors are anticrowns, some of them we have already studied. Recently we started research on a new example of anticrowns – non-planar biphenylene four-mercury macrocycle (o,o'-$C_6F_4C_6F_4Hg)_4$ (**1**)[1]. In the course of our research it was shown that **1** is able to bind fluoride, bromide and even iodide anions with the formation of 1 : 1 complexes. There we report on syntheses and structures of unusual complexes of anticrown **1**, $\{[(o,o'\text{-}C_6F_4C_6F_4Hg)_4](\eta^4\text{-}X^-)\}$ (X = F, Br, I), obtained by the interaction of **1** with various onium halides ($[Bu_4N]F{\cdot}3H_2O$, [PyH]Br and $[PPh_4]I$).

$(o,o'\text{-}C_6F_4C_6F_4Hg)_4{+}X^-$ $\{[(o,o'\text{-}C_6F_4C_6F_4Hg)_4](\eta^4\text{-}X^-)\}$ X = F, Br, I

These obtained halide complexes have a discrete structures where the anion is included inside the anticrown cavity and near symmetrically bound to all four Hg atoms of **1**. It should be noted that the coordinated anions are located virtually in the mean plane of four mercury atoms of anticrown.



(1)



1·I⁻

It was previously shown that macrocycle **1** also has the ability to complexate the chloride anion.[2]

Acknowledgements
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Synthetic approaches to the M-C bond formation in the σ-alkynyl complexes of iron, nickel and platinum

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Acetylide transition metal complexes have shown great potential as attractive building blocks for the production of materials in molecular electronics and nonlinear optics, as well as precursors of catalysts for the electrochemical reduction of protons to hydrogen.[1,2] There are many approaches to the synthesis of these compounds. However, many of these synthetic approaches have limitations due to their insufficient selectivity in reactions or the difficulties in obtaining the initial compounds.[3]

The most promising and convenient method for obtaining σ-alkynyl complexes is cross-coupling catalytic reactions between transition metal halides and terminal alkynes, in which the target M-C bonds are formed due to metal-alkynyl ligand coupling in catalytic cycles. However, such reactions are poorly understood. Previously, we have studied Pd/Cu- and Pd-catalyzed reactions of $Cp(CO)_2FeI$ with pyridylacetylenes and 4-ethyl-2,1,3-benzothiadiazole. Eventually, synthetic approaches to the corresponding σ-ethinyl iron complexes $Cp(CO)_2Fe\text{-}C\equiv C\text{-}R$ have been developed.[4] In the present work, we have found that similar reactions of pincer bis((diphenyl)phosphinoxy)phenyl halides of platinum or nickel with terminal alkynes occur under the Cu-catalysis to lead to the corresponding acetylenide complexes with the 83-97% yields. Apparently, these reactions proceed through the formation of intermediate σ-acetylide complexes of copper.

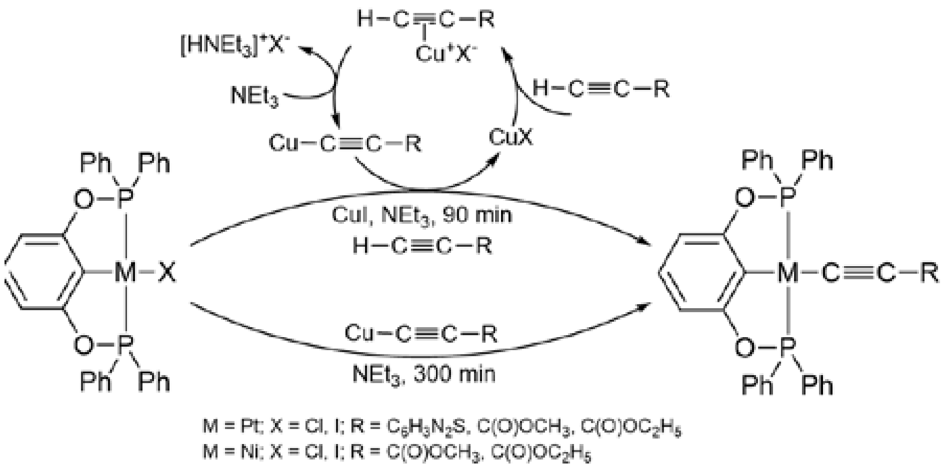

Figure 1. Formation of a metal-carbon bond in σ-alkynyl complexes

Acknowledgements

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Tetranuclear Cu(I) and Ag(I) Pyrazolate Complexes with bibenzimidazole: Synthesis, Structures and Photoluminescence

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The interaction of cyclic trinuclear copper(I) or silver(I) pyrazolate complex ($[\mathrm{MPz}]_3$, M = Cu, Ag) with chelating diimine ligands in different ratios leads to the formation of new structurally diverse complexes capable of exhibiting fluorescence and phosphorescence.[1, 2]

Complexation of $[\mathrm{CuPz}]_3$ and $[\mathrm{AgPz}]_3$ with 1,1′-dimethyl-2,2’-bibenzimidazole **L** leads to the formation of tetranuclear adducts containing one or two molecules of a diimine ligand **L**, depending on thereagents ratios. The diimine ligands are twisted in these complexes with dihedral angles of ca. 50–60°. TD-DFT analysis demonstrated the preference of a triplet state for the twisted **L** and a singlet state for the planar geometry in free **L**. All obtained complexes exhibit blue fluorescence of the ligand-centered (LC) nature typical for free diimine in a solution. In contrast, a temperature decrease to 77 K activated the triplet states, leading to green phosphorescence at ca. 500 nm. The silver-containing complex $[\mathrm{AgPz}]_4\mathrm{L}$ exhibited dual emission from both the singlet and triplet states, even at room temperature.[3]

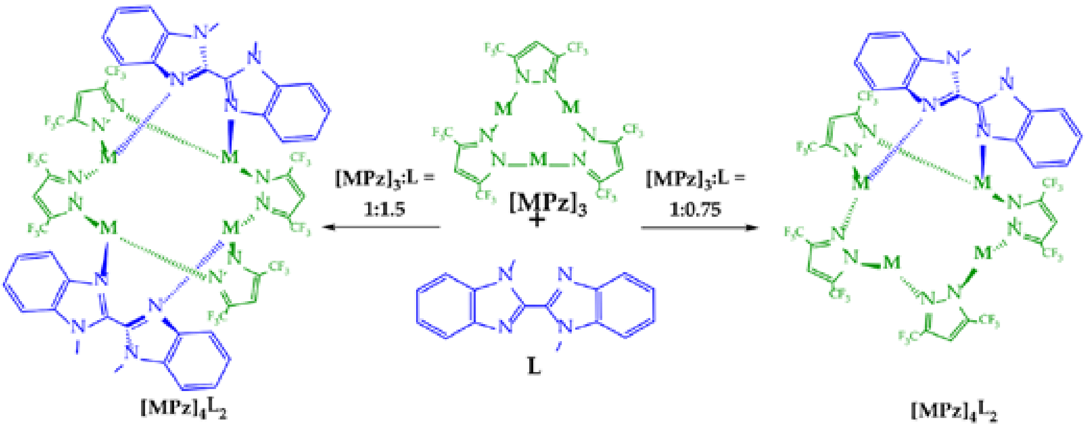

Figure 1. Synthesis and chemical structures of complexes

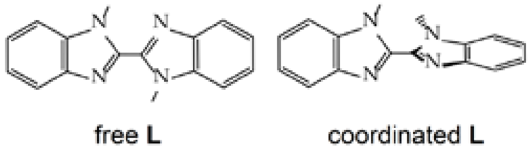

Figure 2. Free and coordinated L

Acknowledgements
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