Organometallic Chemistry Around the World

(7th Razuvaev Lectures)

Russian-Chinese Workshop on Coordination and Supramolecular Chemistry

September 16-21, 2019, Nizhny Novgorod, Russia

Cluster of International Conferences

Topical Problems of Modern Chemistry

Organometallic Chemistry Around the World
(7th Razuvaev Lectures)

18th International Conference on Chemistry and Physical Chemistry of Oligomers

Russian-Chinese Workshop on Coordination and Supramolecular Chemistry

Nizhny Novgorod, September 16–21, 2019

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Organometallic Chemistry Around the World

(7th Razuvaev Lectures)

Oral Presentations

HALOGEN-RICH COMPLEXES OF 15 AND 16 GROUP ELEMENTS

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Halide complexes of p-block elements attract an interest due to their optical properties and possible applications in photovoltaics. During our studies of bromobismuthates (III), we have found that reactions of general scheme "$[BiBr_6]^{3-}$ + Br_2 +(cation)Br_x" in HBr solutions may result in anionic polybromide Bi(III) complexes where $\{Br_2\}$ units are connected with bromide lidands of Bi(III) coordination sphere via halogen bonding, yielding in $\{Br_x\}_y$-type polymeric ligands. In some cases, there also form tribromide $\{Br_3\}^-$ ligands coordinated to bismuth atoms. The structure of anionic part strongly depends on the nature of cation used in reaction. Mixed-halide complexes – polybromide-chlorobismuthates and polyodide-bromobismuthates – may be obtained by similar straightforward synthetic approach. Related polybromide- or polyidodide-bromotellurates (IV) can be obtained as well; in all cases, those consist of mononuclear $[TeBr_6]^{2-}$ and $\{X_2\}$ (X = Br, I) dihalogen building blocks. For antimony, similar reactions in presence of Br_2 proceed in more sophisticated way, usually resulting in formation of bromoantimonates (V), sometimes accompanied by polybromide units (Figure 1).

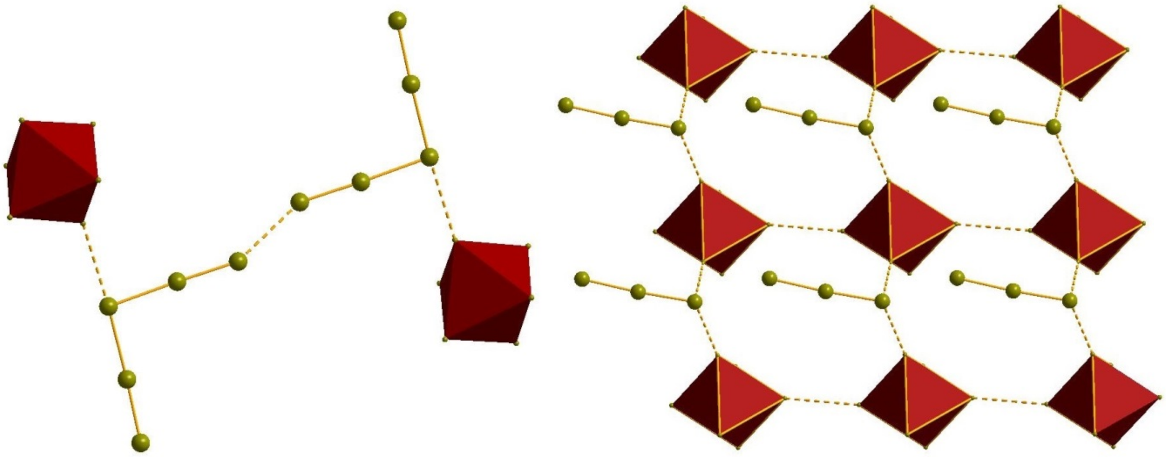

Figure 1. Polybromide-bromoantimonates (V): $\{[SbBr_6]\{Br_{10}\}]^{4-}$ (left) and $[SbBr_6]\{Br_3\}]^{2-}$ (right)

In presence of I_2, there form polyiodo-bromoantimonates (III), revealing several additional structural types, including those where Sb atom is 5-coordinated (pyramidal environment).

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FROM ALKYNE ORIGAMI TO ELECTRON UPCONVERSION: OVERCOMING BARRIERS IN THE DESIGN OF CYCLIZATION REACTIONS

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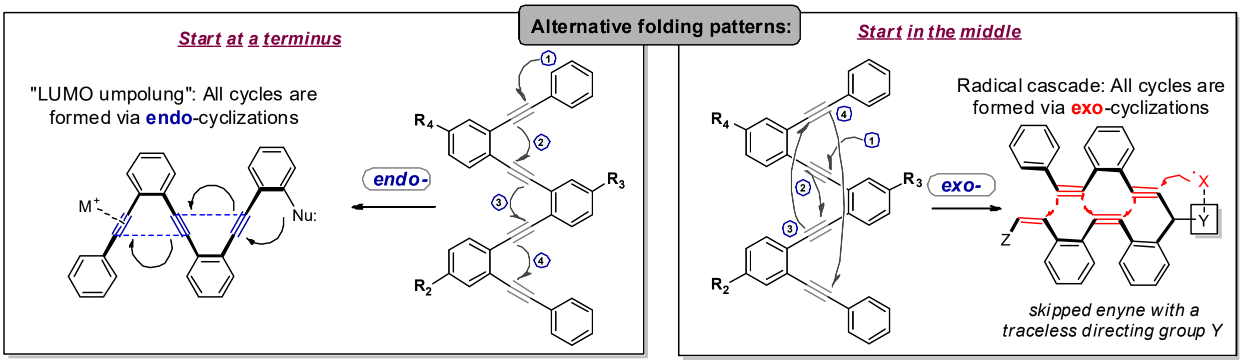
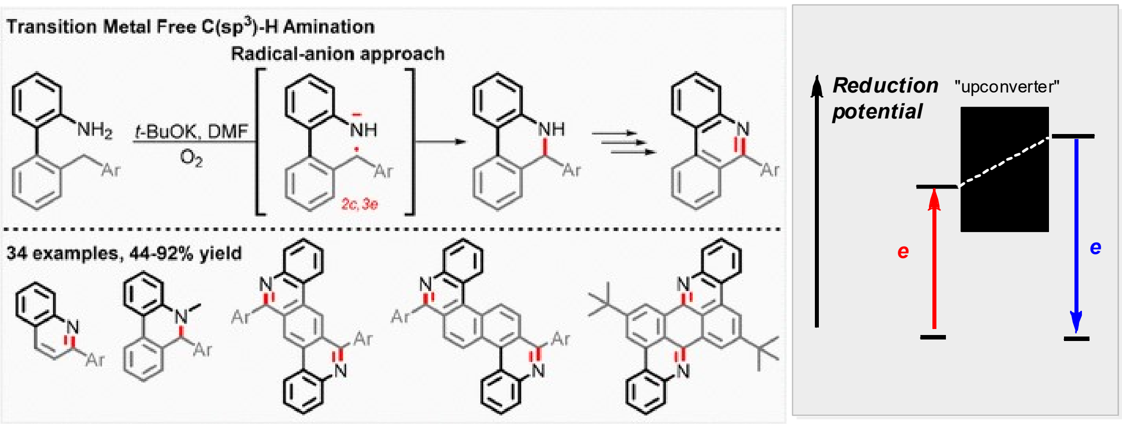
In the 1st part, I will discuss the advantages of alkynes as high-energy carbon-rich precursors for extended polyaromatics, the two general patterns of oligoalkyne folding into an aromatic ribbon, and the use of supramolecular effects in the design of traceless directing groups for radical reactions.[1]



In the 2nd part, I will present a mild method for oxidative C(sp3)–H amination from unprotected anilines and C(sp3)–H bonds. In this process, basic, radical, and oxidizing species work together in a coordinated sequence of deprotonation, H-atom transfer and electron transfer that forges a new C–N bond.[2] I will also use this cascade transformation to illustrate how reductant upconversion, a new concept in catalysis, can be used for preventing the premature activation of oxidants.[3]



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SPIN TRANSITION CHARACTERISTICS OF MOLECULAR SOLVATES OF Cu^{II} COMPLEXES WITH NITROXIDES

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and V. Ovcharenko

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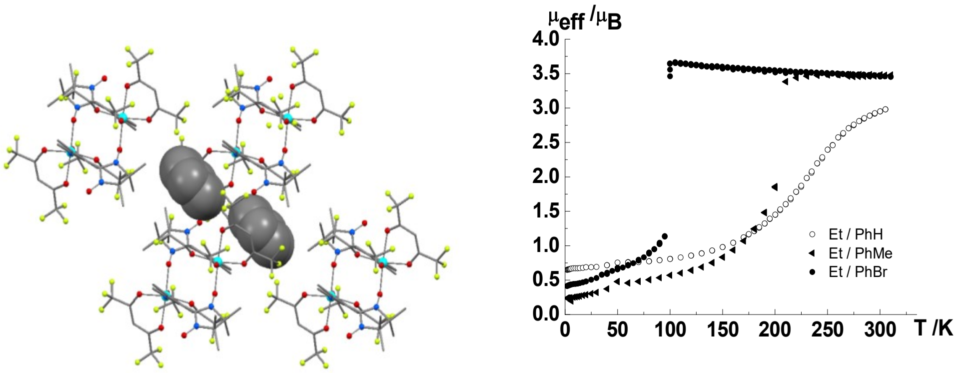
The solid phases of heterospin complexes based on *bis*(hexafluoracetylacetonato)copper(II) [Cu(hfac)$_2$] with nitronyl nitroxide radicals attract interest of the researches due to the fact that they can undergo structural transformations accompanied by spin transition under the action of external factors.

We synthesized a few series of solvates of dinuclear heterospin complexes of [Cu(hfac)$_2$] with the nitroxyl nitroxide radicals L^{Me} and L^{Et} of the composition [Cu(hfac)$_2$L^R]·Solv [1]. Temperature changes induced significant structure transformations of these complexes, leading to considerable changes (from 2.321 to 1.974 Å) in the distances between the paramagnetic centres, *viz*., Cu^{2+} ions and nitroxide O atoms, which is responsible for the appearance of the future anomalies of the $\mu_{eff}(T)$ dependence.



Molecular structure of [Cu(hfac)$_2$L^{Et}]·PhH and $\mu_{eff}(T)$ dependences of [Cu(hfac)$_2$L^{Et}]·PhH, [Cu(hfac)$_2$L^{Et}]·PhMe and [Cu(hfac)$_2$L^{Et}]·PhBr

Comparing the results obtained in this study of molecular solvates with the data obtained earlier for chain polymer solvate complexes [2], mention may be made, that the $\mu_{eff}(T)$ dependences for the heterospin chains are much more sensitive to the type and even orientation of the solvate molecules in the interchain space. In fact, heterospin chains can act as sensor for particular type of solvent molecules, whereas in molecular crystals the magnetic properties of multispin compounds are sensitive to the changes in the parking type rather than the nature of the solvate molecules.

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CONJUGATED DONOR ACCEPTOR BASED SEMICONDUCTORS

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After starting from benzothiadiazole (BTZ) in donor acceptor copolymers, we concluded to strengthen the acceptor part upon introducing thiadiazoloquinoxalines (TQ) leading to a lowering of the LUMO levels and more suited ambipolar character.[1-3] Upon condensation of the diamino benzothiadiazoles with benzodithiophene-dione the acceptor part could be further strengthened and open a variety of new copolymers as PBDTTQ-2 and small molecule acceptor structures.[4,5]

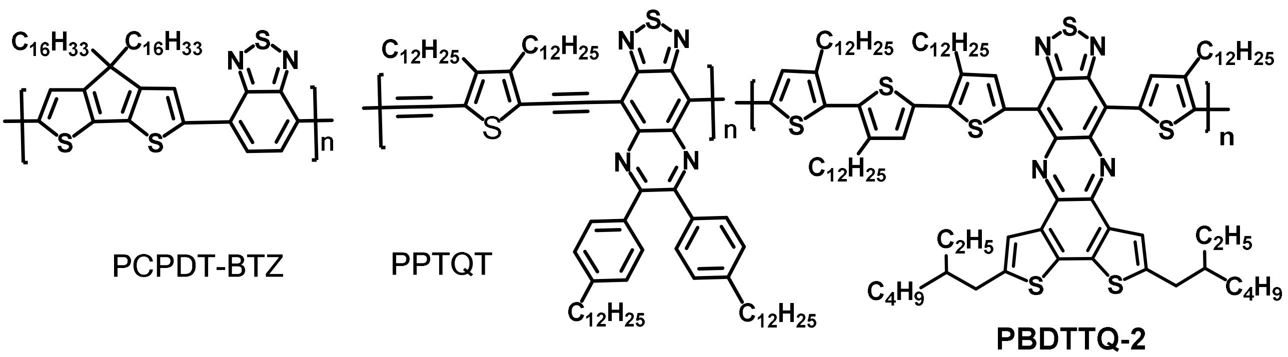

Fig. 1: Development of polymers for ambipolar transistors

We further went into devoloping extended N-heteroacene structures in linear and 2D-3D extensions, keeping the strong TQ acceptors as end cap units.[6,7]

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SPIN IN ORGANICS

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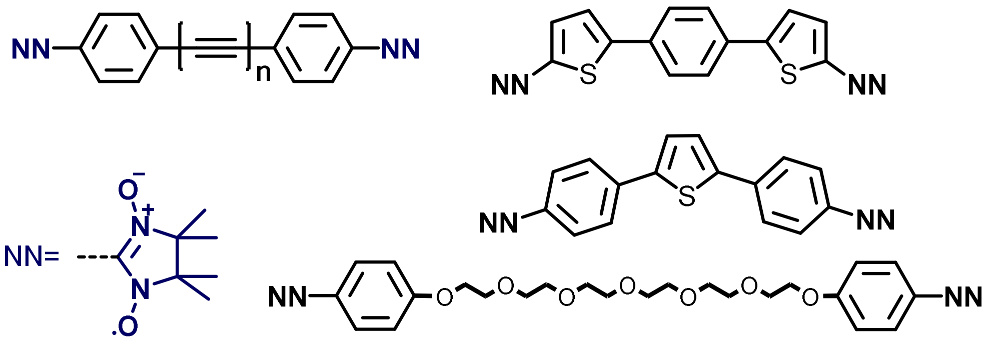
The magnetic exchange interactions in anti-ferromagnetically coupled biradicals depend on the distance and type of the radical moiety as well as the π-conjugated system. Thus we can tune for high spin ground state or low spin ground state and influence the size of exchange interaction. Herein we present the systematic tuning of the exchange interactions by varying the conjugated bridge and the radical moieties. Thereby we found magnetic field induced 2D and 3D ordered phases at low temperatures in AC susceptibility.[1-3] Further a flexible bridged bis(nitronyl nitroxide) was studied to evaluate the thermodynamic parameters from temperature dependent EPR studies in different solvents.



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FLUORINATED FUNCTIONALIZED DIKETONATES IN THE SYNTHESIS OF LANTHANIDE COMPLEXES

D. N. Bazhin, Yu. S. Kudyakova, Ya. V. Burgart and V. I. Saloutin

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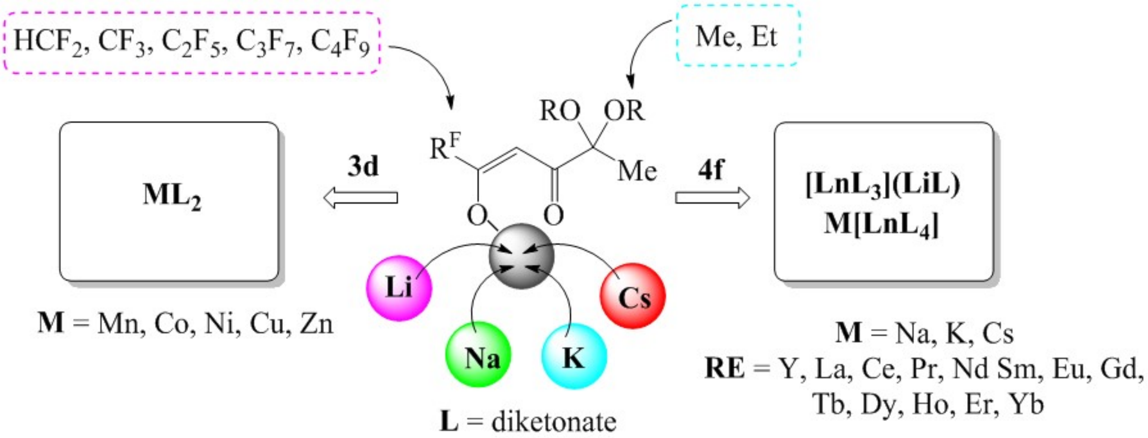
β-Diketones are among the most used tools in the coordination chemistry providing the wide diversity of metal-organic architectures such as homo- and heterometallic complexes, clusters of various nuclearities, MOFs, nanoparticles, thin metal films. The applicability and efficiency of these ligands in the design and synthesis of advanced materials with optical, magnetic and catalytic properties is well documented.

The employment of non-symmetrical 1,3-diketones in coordination with lanthanides should also be stressed as challenging approach to fine-tuning of magnetic and luminescent properties. Moreover, the additional functional groups in dicarbonyl fragment enable the fulfilling of metal ion coordination sphere without extra-ligands (e.g. aza-coligands). We have therefore endeavored to investigate the potential of such β-diketonates for the synthesis of multifunctional lanthanide complexes.

Recently, we have elaborated the preparation of a novel lithium fluorinated β-diketonates bearing acetal fragment [1,2]. Using trifluoromethyl-containing lithium diketonate we have obtained a number of 3d and 4f metal complexes [3,4]. Some of heteronuclear [LnL_3][LiL] complexes exhibited strong packing-controlled mechanoluminescence [4]. In this work, synthetic routes to fluorinated β-diketonates with variable substituents or alkali metals and their use in the preparation of lanthanide complexes will be discussed (Figure).



Figure

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NEW TRENDS IN CATALYSIS OF ORGANIC REACTIONS

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New results in Pd- and Cu-catalyzed reactions of substitution and addition will be considered.

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BIFUNCTIONAL TRANSITION METAL COMPLEXES IN CATALYTIC PRODUCTION OF H_2

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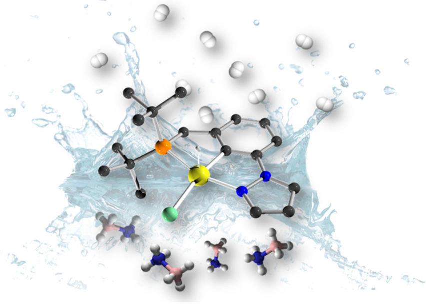
The processes of catalytic hydrogenation of multiple bonds and the dehydrogenation/dehydrocoupling of alcohols, amine boranes, etc., make it possible to obtain a variety of products that are important from fundamental and practical points of view. Since the beginning of this century, the so-called "cooperative" non-innocent ligands have been developed that are involved in reversible transformations of the catalyst molecule during the catalytic process. An alternative and still underestimated approach is to create catalytic systems in which two or more metal centers either interact at key stages of bond breaking/formation.

The homogeneously-catalyzed dehydrogenation/hydrolysis of tetrahydroborate salts (BH_4^-) and ammonia-borane (NH_3BH_3) is the effective chemical path to exploit them as hydrogen storage materials. Coordination compounds containing boron hydride ligands possess many other practically valuable properties and may be used as selective reducing agents, precursors for the production of molecular or nanostructured borides, hydrides and other inorganic materials, and also as discrete catalysts for carrying out important industrial processes. In this talk we present our recent results on the mechanisms of amineboranes dehydrogenation to produce H_2 utilizing both bifunctional iridium complexes[1-3] and bimetallic transition metal systems in which two sites (metal and ligand, or two metals) have different properties (Lewis acids and bases). These studies showed the importance of relatively weak metal-ligand and substrate-ligand interactions for keeping the active conformation of catalyst or for its activation.



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MIXED METAL LANTHANIDE TRIAZOLEDICARBOXYLATES FOR LUMINESCENT SENSING

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Lanthanide containing metal organic frameworks (Ln-MOFs) are in the focus of attention of researchers due to the unique combination of sorption and luminescence properties, promising for chemical sensing tasks. Sensory material must meet a number of requirements - high stability, low solubility, the minimum amount of CH,NH and OH quenchers. Triazole-dicarboxylic acid (H_3TDA) based Ln-MOFs meet all these criteria. The intensity ratio of the radiative transitions of terbium ($^5D_4$-$^7F_5$) and europium ($^5D_0$-$^7F_2$) was chosen as the analytical signal (***S***).

Depending on the conditions of solvothermal synthesis, two types of complex 1,2,3-triazole-4,5-dicarboxylates of lanthanides can be obtained, namely $\{[Ln(TDA)(H_2O)_2](H_2O)_3\}$ and $\{(NMe_2H_2)[Ln(TDA)(HCOO)]\}$, Ln = Eu, Tb, Gd. A series of both types of complexes containing various amounts of terbium and europium was synthesized. It was shown that in such systems the excitation energy is transferred along the pathway ligand$\rightarrow$$Tb^{3+}$$\rightarrow$$Eu^{3+}$. The compounds were tested as sensor materials for the determination of water traces in aprotic organic solvents and D_2O. In addition, they show sensory activity for transition metal cations - Zn^{2+} and Co^{2+}.

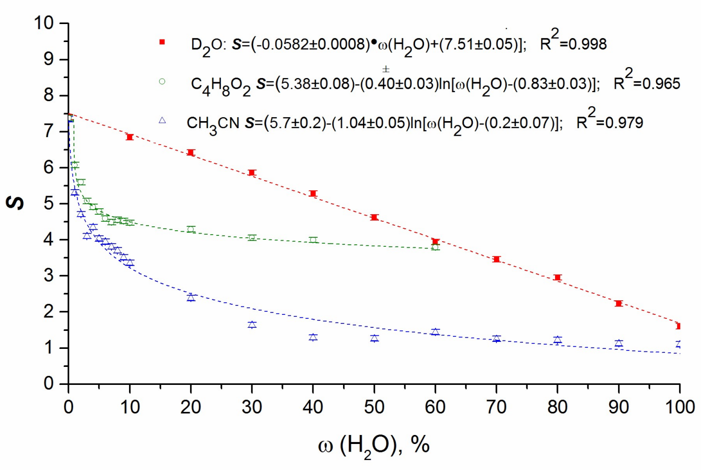

Figure 1. Calibration charts for the H_2O-D_2O (red squares), H_2O-dioxane (green circles) and H_2O-CH_3CN (blue triangles) systems.

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HETEROLIGAND METALLACOMPLEXES BASED ON SESQUIOXANE UNITS. SYNTHESIS, STRUCTURE AND PROPERTIES

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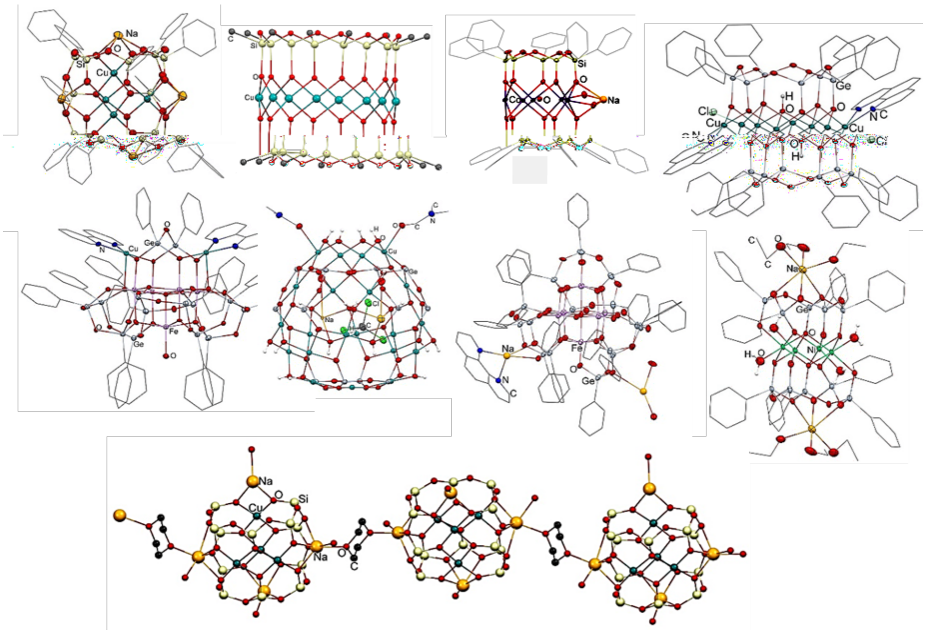
Cagelike metallasesquioxanes (CMSs) based on silicon and germanium centers [1-3] attract significant attention of scientific teams worldwide due to extraordinary molecular geometry and wide potential of further application. Recently an alternative approach to CMSs (via participation of additional N- [4] or P-ligands [5]) was suggested. In turn, an isolation of unusual high clusters (up to record level of $Cu_{42}Ge_{24}Na_4$ [6]) was described. Features of CMSs' synthesis, catalytic/magnetic behaviour, as well as CMSs' transformation into 1D-3D coordination polymer assemblies will be discussed in detail.



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NOVEL METAL-MEDIATED *O*-FUNCTIONALIZATION OF OXIMES

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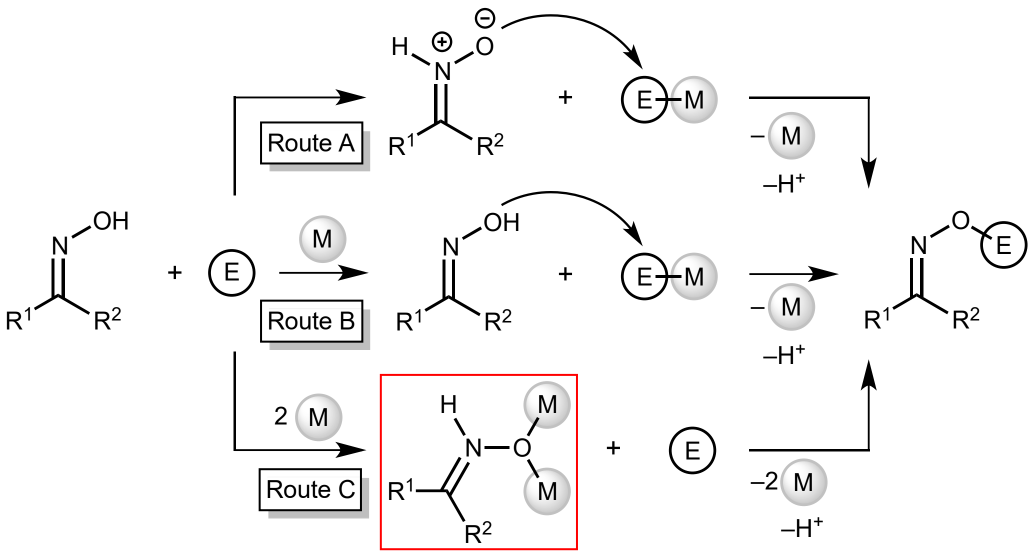
Oximes are important class of organic substrates applied in industry as precursors of caprolactam and also in pharmacology. They also are important compounds in coordination and organic chemistry acting as precursors for preparation of wide variety of acyclic and heterocyclic organic and organometallic compounds [1, 2]. General part of transformations of oxime species is metal-mediated reactions, which typically utilize *O*-substituted oximes or start from initial *O*-functionalization of unsubstituted oxime species [1]. In the *O*-functionalization of oximes, a metal center plays a role of electrophilic activator of E toward nucleophilic attack of the O atom of an oxime (**Route B**).

A, B: Electrophilic Activation of E



C: Nucleophilic Activation of Oxime

In our studies, we demonstrated that in the *O*-functionalization of oximes, active form of oximes is their tautomeric nitrone form (**Route A**) [3] and general reactivity of oxime species is determined by oxime–nitrone energy gap [4]. Based upon this observation, we found a novel route of metal-mediated functionalizations comprising of stabilization of the nitrone form of oxime by two zinc(II) centers (**Route C**) [5].

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RECENT ADVANCES IN THE CHEMISTRY OF COBALT AND IRON BIS(DICARBOLLIDES)

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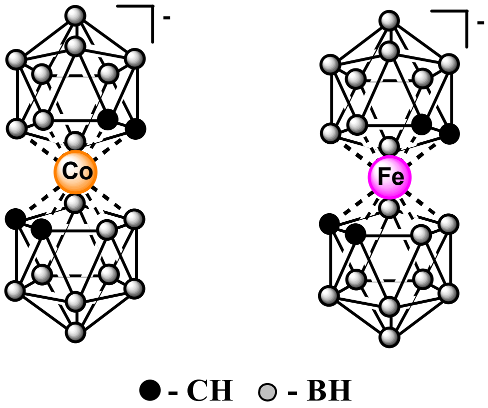
From the time of discovery of metallacarboranes by M.F.Hawthorne in 1964, they are of increased interest for many aspects of fundamental and applied chemistry. Cobalt bis(1,2-dicarbollide) anion is the most investigated representative of this class of boron compounds. The subject of this lecture is our recent results in the chemistry of cobalt[1] and iron[2] bis(dicarbollide) anions $[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_2]^-$ and their potential applications.



Conjugates of cobalt and iron bis(dicarbollide) anions $[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_2]^-$ with chlorine e_6 were prepared and their accumulation in human lung adenocarcinoma A549 cells and biodistribution in mice with transplanted CT26 murine colon carcinoma as potential BNCT agents were studied [3]. Synthesis, structure and electrical conductivity of fulvalenium salts of cobalt and iron bis(dicarbollides) were discussed [4, 5]. Development of these investigations [1-5] will be presented.

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SYNTHESIS AND STRUCTURE OF SUBSTITUTED ZINC(II) AND MANGANESE(II) MALONATES WITH PHOTOSENSITIVE AND PHOTOINERT N-DONOR LIGANDS

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A.A. Sidorov[a], and I.L. Eremenko[a,b].

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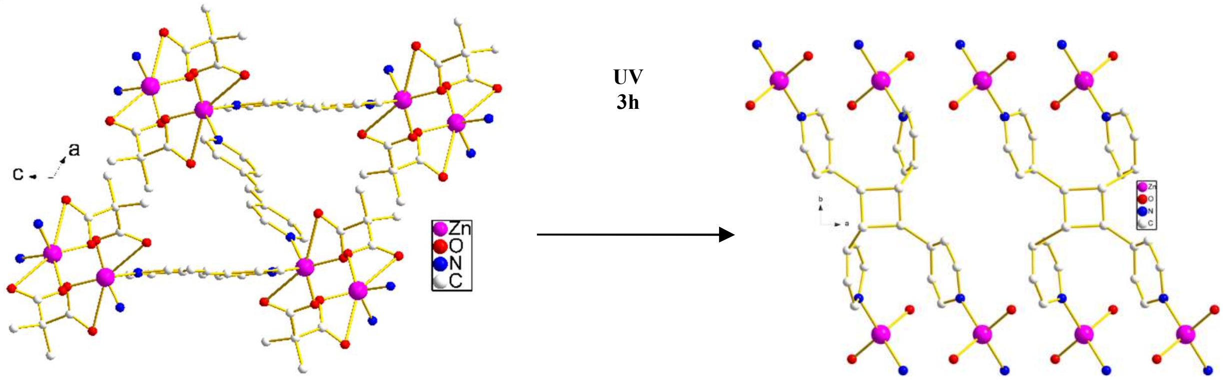
Nowadays the synthesis of coordination polymers is one of the rapidly evolved part of the coordination chemistry, because of their potential applications in many areas including heterogeneous catalysis, separation and storage of gases and many others [**1**]. The use of photosensitive ligands allows the preparation of polymers that can participate in the reactions of [2+2]-cyclophotoaddiction. The study of the cyclophotoaddiction reactions is important from the point of view of studying such natural phenomena as photosynthesis and phototaxis, and, in addition, it makes it possible to obtain materials for optical recording and information storage systems [**2**].



$\{[Zn(bpa)(Me_2mal)]\cdot H_2O\}_n$ **$\{Zn(bpe)(Me_2Mal)]_2[Zn_2(tpcb)(Me_2Mal)_2]\cdot H_2O\}_n$**

We synthesized a series of new zinc(II) and manganese(II) compounds with different structure with anions of substituted malonic acids and bridged N-donor ligands: from molecular $[Zn(H_2O)_4(bpe)_2](HEt_2Mal)_2$ (1) to framework coordination polymers such as $[Zn_2(H_2O)_2(bipy)(Me_2Mal)_2]_n$ (2) or $\{[Zn(bpa)(Et_2Mal)]\cdot 0.38H_2O\}_n$ (3) (where Et_2Mal^{2-} are dianion of diethylmalonic acid, Me_2Mal^{2-} is dianion of dimethylmalonic acid). The greatest attention is attracted to compounds containing 1,2-bis(4-pyridyl)ethylene, since in these systems the [2+2]-cyclophotoaddition reaction is possible, which was demonstrated in the case of our compounds [**3**,**4**].

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REAR EARTH COMPLEXES FOR CATALYTIC HYDROELEMENT ADDITION REACTIONS

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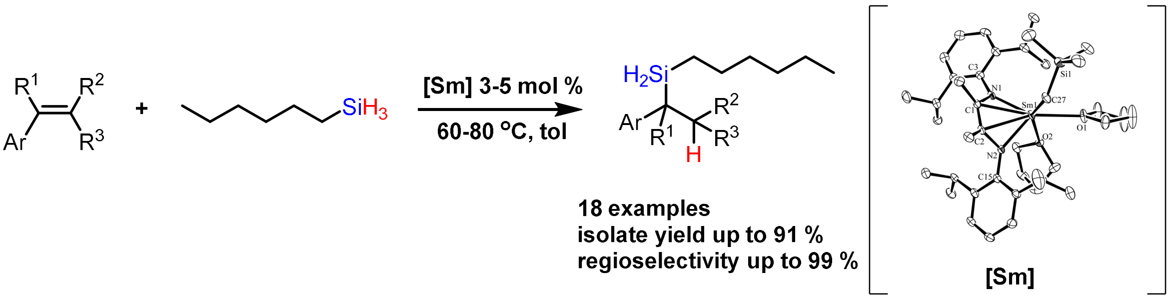
Well-defined rare earth complexes have emerged as powerful catalysts for some important transformations because of their unique selectivity and mechanistic distinctions derived from the high electrophicility of rare earth metal ions.[1] Herein, we report the synthesis and characterization of rare-earth complexes supported by ene-didamido, NHC and silaimine ligands and their applications in selective catalytic hydrosilylation, hydrophosphination and polymerization of styrenes. These complexes exhibit high regioselectivity and stereoselectvity for these important transformations. The ene-diamido rare earth complexes appeared to be the most selective catalyst for hydrosilylation of both styrenes and non-activated alkenes reported so far. In addition, polymerization of styrene led to the formation of silyl-capped, highly syndiotactic polystyrene. The experiments and density functional theory (DFT) calculations disclosed the highly selective formation of the samarium hydride intermediates, which, in combination with the electronic and steric factors of the ligand, is responsible for the high regio- and stereoselectivity. In addition, the corresponding alkyl complexes enabled highly regioselective hydrosilylation of internal alkenes and double hydrosilylation of alkynes.



18 examples
isolate yield up to 91 %
regioselectivity up to 99 %

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COMBINING N-HETEROCYCLIC CARBENES (NHCS) WITH CHEAP AND EARTH-ABUNDANT ZINC(II) AND ALUMINUM(III) CENTERS: FUNDAMENTAL REACTIVITY AND USE IN HOMOGENEOUS CATALYSIS

D. Specklin[a], C. Fliedel[a], C. Gourlaouen[a], J.-C. Bruyere[a] and S. Dagorne[a]

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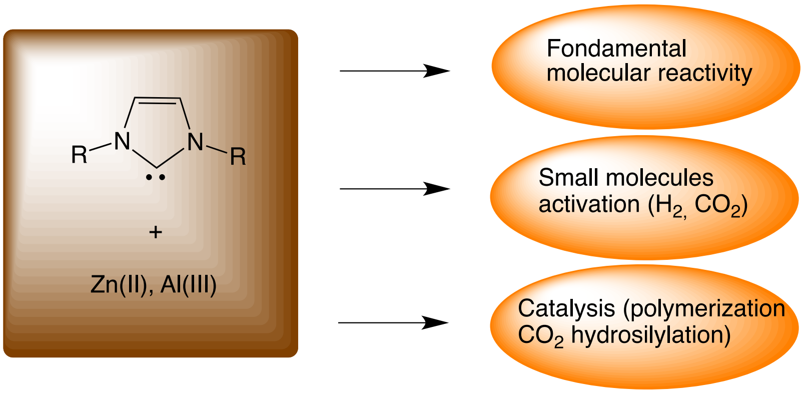
Over the past twenty years, N-heterocyclic carbenes (NHCs) have become an ubiquitous class of supporting ligands in coordination chemistry with countless successful applications of the derived NHC metal complexes in various areas. Due to their exceptional σ-donating properties and steric tunability, NHC-bonded metal complexes usually exhibit an inert NHC-M bond yielding enhanced stability. This has opened the way to the development of robust NHC-incorporating metal compounds that often feature an increased activity/selectivity in catalysis and may exhibit novel fundamental reactivity. Though less investigated thus far, combining NHCs with main group elements and/or oxophilic metal centers may also be the source of unusual reactivity and/or unprecedented activation chemistry.

We are interested in the NHC coordination chemistry of oxophilic and high-oxidation state metal centers (which are typically cheap metal sources) for fundamental reactivity/activation studies and the use of the derived complexes in homogeneous catalysis. In the present seminar, discrete NHC-Zn(II) and NHC-M(III) (M = Al, Ga, In) species are described along with their reactivity trends. Such simple coordination complexes are shown to be of rather broad interest since they may be involved in various chemical transformations ranging from unusual fundamental reactivity (rearrangement processes), small molecules activation (H_2, CO_2) and homogeneous catalysis (cyclic esters/carbonates polymerization, CO_2 hydrosilylation catalysis). All these aspects will be discussed.



Selected references: *Chem. Eur. J.* **2019**, *in press (doi.org/ 10.1002/chem.201900961)*; *Synthesis* **2018**, *50*, 3662; *Chem. Eur. J.* **2017**, 23, 15908; *Chem. Eur. J.* **2017**, 23, 5509; *Chem. Eur. J.* **2015**, 21, 17959; *ChemCatChem* **2014**, 6, 1357.

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LOW-COORDINATE ZERO-VALENT 3D METAL COMPLEXES WITH NHC AND ALKENE LIGATION

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The knowledge on the formation, structure, and reactivity of low-coordinate 3d metal species is important for developing transition-metal-catalyzed transformations and also for understanding the mysterious mechanisms of various small molecule activation reactions mediated by transition-metals. Aiming to deepen our knowledge on this type of reactive metal species, over the past years we have been working on the chemistry of low-coordinate low-valent cobalt, iron and manganese complexes with N-heterocyclic carbene (NHC) and olefin ligation. This ligand set is found effective to stabilize three-coordinate cobalt(0), iron(0), and manganese(0) complexes in the forms of (NHC)M(olefin) and $(NHC)_2M(olefin)$ (Figure 1). [1-6] In this presentation, the synthesis and electronic structure of the three-coordinate zero-valent metal complexes, as well as their reactivity toward dinitrogen, *C*-nitroso compounds, hydrosilanes, and hydrophosphines will be discussed.

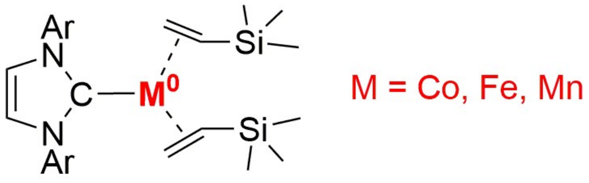

Figure 1. Three-Coordinate M(0) Complexes

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CATALYTIC C-H BOND CROSS-COUPLINGS AND MODIFICATIONS OF P & N LIGANDS

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Ruthenium(II) catalysts associated to a carboxylate or a phosphate partner are able to promote the selective sp^2 C-H bond activation, via C-H bond deprotonation., of functional arenes and heterocycles to selectively lead to cross-couplings with hetero(aryl) halides [1,2]
It is possible now to perform such processes in water as renewable solvent without surfactant and with higher catalyst activity.[3,4]

The lecture will present several new aspects based on these activation principles.

- Catalytic sp^2 C-H bond activation in water solvent can be directed to produce polyheterocycles and Hexa(Hetero)arylbenzenes[5]
- Ruthenium-catalyzed selective C-H bond alkylations with alkenes of arylphosphine oxides can directed and give access to bifunctional phosphines with carboxylic group.[6]
- $C(sp^3)$-H bond amination of cycloalkanes can be favoured by copper-catalyzed oxidative dehydrogenative using NH-heterocycles as amine sources[7]
- $C(sp^3)$-H bond functionalization of alkyl goups linked to heterocycles can be selectively achieved using simple copper catalysts and in situ generated radicals [8]
-

New perspectives of C-H bond functionalisations will be pointed out as discussed in our 2018 feature article on Late Stage Modifications of P-Containing Ligands using Transition-Metal-Catalysed C–H Bond Functionalisation[9], and in our review "Photoredox Catalysis for Building C−C Bonds from C(sp2)−H Bonds" [10]

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PINCER TYPE NICKEL (II) COMPLEXES: SYNTHESIS AND CATALYTIC ACTIVITY

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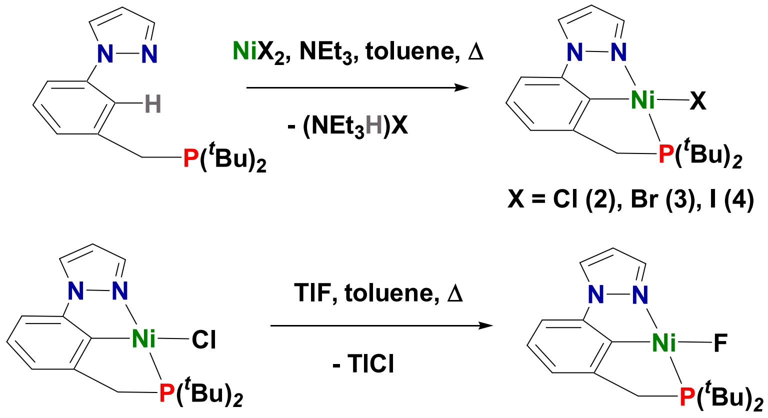
Asymmetric NCP and other chelating ligands are used as ligands, which in the combination with transition metals such as palladium or nickel exhibit high catalytic activity in catalytic reactions of the cross- and homo-coupling of organic halides and in the process of oligomerization of ethylene [1].

In this work we present four metal halides of the ($^{t\mathrm{Bu}}$PCN)NiX family [X=F(**1**), Cl (**2**), Br (**3**), or I (**4**); PCN = 1-[3-[(di-tertbutylphosphino)methyl]phenyl]-1H-pyrazole], which have been prepared through a direct reaction of the corresponding anhydrous NiX_2 salts and the unsymmetrical PCN pincer ligand (Scheme 1). Structural information from single-crystal X-ray data, ^{19}F solution nuclear magnetic resonance, and combined electrochemical results [cyclic voltammetry (CV) and in situ electron paramagnetic resonance spectroelectrochemistry] reveal that the fluoride complex **1** is different from the other halides **2**−**4** in terms of electro-oxidation behaviour (presence of three anodic peaks instead of one in the CV profile) [2]. The complex **3** has shown high catalytic activity in the ethylene oligomerization process.



2 **1**

Scheme 1. Synthesis of complexes **1-4**.

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CHEMISTRY OF NITRIC OXIDE (NO) WITH RUTHENIUM ORGANOMETALLICS: PHOTOLABILITY OF COORDINATED NO FOR TARGET SPECIFIC DELIVERY

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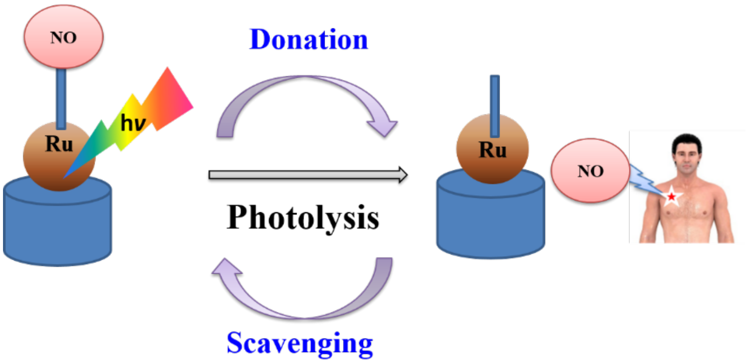
Nitric oxide (NO) is highly reactive and paramagnetic diatomic radical species andNO has been found to be an important signaling molecule involvedin several physiological processes namely, blood pressure regulation, immune and endocrine response,neurotransmission, immune response, and cellular apoptosis in different cells and tissues.[1] NO is produced in human bodybynitric oxide synthase (NOS) enzyme from L-arginine[2]and NO exhibit concentration dependent biological activities. Hence,NO scavenging as well as NO delivery to a particular site are important events in human cells.[3]We have been working with designed organometallic ruthenium(III) complexes and their chemistry with NO. Organometallic ruthenium nitrosyls were utilized for target specific and ondemand delivery of NO.[4]Anti-proliferation activity of NO was investigated where NO was obtained from organometallic ruthenium complexes.



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"MISSIONS IMPOSSIBLE" IN RUTHENIUM CATALYZED OLEFIN METATHESIS

Karol Grela[a,b]
[a] *Organometallic Synthesis Laboratory, Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Warsaw, Poland*
[b] *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland*

Ruthenium-catalyzed olefin metathesis reactions represent an attractive and powerful transformation for the formation of new carbon-carbon double bonds [1]. This area is now quite familiar to most chemists as numerous air and moisture stable ruthenium catalysts are available that enable a plethora of olefin metathesis reactions [1]. However, formation of substituted and crowded double bonds, decreasing the loading and then the trace amount of a catalyst in products, selectivity issues during self-CM and ethenolysis, etc. still remain a challenge, making industrial applications of this methodology difficult. These limitations can be solved by designing new, more selective and stable catalysts and catalysts that can be easier removed or recycled. New catalysts can even make a metathesis based macrocyclisation at high concentration possible for the first time.

Fig. 1. Ruthenium impression [2] © www.fb.com/effe.fineart

During the lecture a number of representative examples will be presented.

References (if necessary)

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This work (Fig. 1) was supported by FNP TEAM-TECH «Catalysis for the Twenty-First Century Chemical Industry» Grant.

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RUTHENIUM (II) CARBORANE CLUSTERS WITH CHELATE LIGANDS: SYNTHESIS, STRUCTURE AND APPLICATIONS

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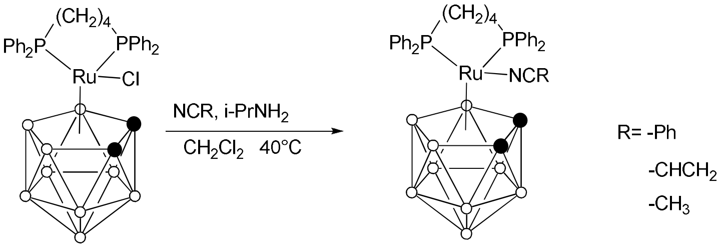
Lobachevsky state university of Nizhny Novgorod, Nizhny Novgorod, RUSSIA

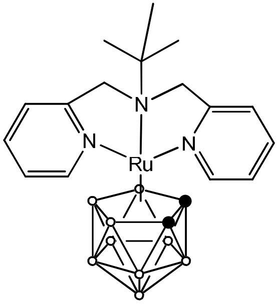
Carborane complexes of transition metals are of a great interest due to its unique structure and the presence of nonclassical bonding in the boron cage as well as because of possible implementation in catalysis of various processes. In spite of carborane clusters of ruthenium (III) and (IV) with chelate diphosphine ligands are well-known and vastly explored, the chemistry of its divalent analogues obtained recently remains unknown.

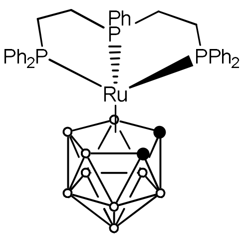
This work is devoted to the synthesis of novel carborane clusters of ruthenium (II) with chelate bi- and tridentate ligands and investigation of its properties.

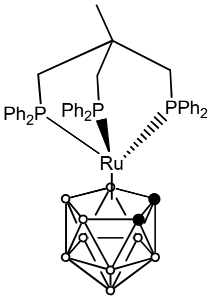
It was shown that the interaction of paramagnetic chlorine-containing Ru(III) derivatives with aliphatic amines in the presence of phosphine or nitrile as stabilizing ligand leads to the formation of the corresponding Ru(II) complexes. It was shown that the interaction of the obtained complexes with carbon tetrachloride of hydrochloric acid results in chloride addition and formation of initial Ru(III) species.

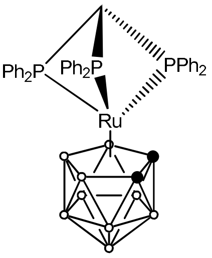


The further experiments allowed us to obtain carborane clusters with tridentate chelate phosporous and nirogen ligands. It was shown that stability of the corresponding complexes and its structure dramatically depends on the ligand structure. The increase of the methylene chain in the ligand structure leads to the increase of complex stability due to the decrease of angle strain. The performed RCA studies have shown that the exchange of phosphorous atom by its nitrogen based analogues results in the change of the complex structure from closo- to pseudocloso type.









The performed cyclic voltammetry studies showed the reversibility of Ru(II)-Ru(III) oxidation for the obtained complexes showing the possibility of its implementation in catalysis of radical polymerization via ATRP mechanism.

Acknowledgements - The work was supported by Russian Science Foundation (proj. 18-73-10092)

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SYNTHESIS, STRUCTURAL PROPERTIES AND REACTIVITY OF RUTHENOCENE-BASED PINCER Pd(II) TETRAHYDROBORATE

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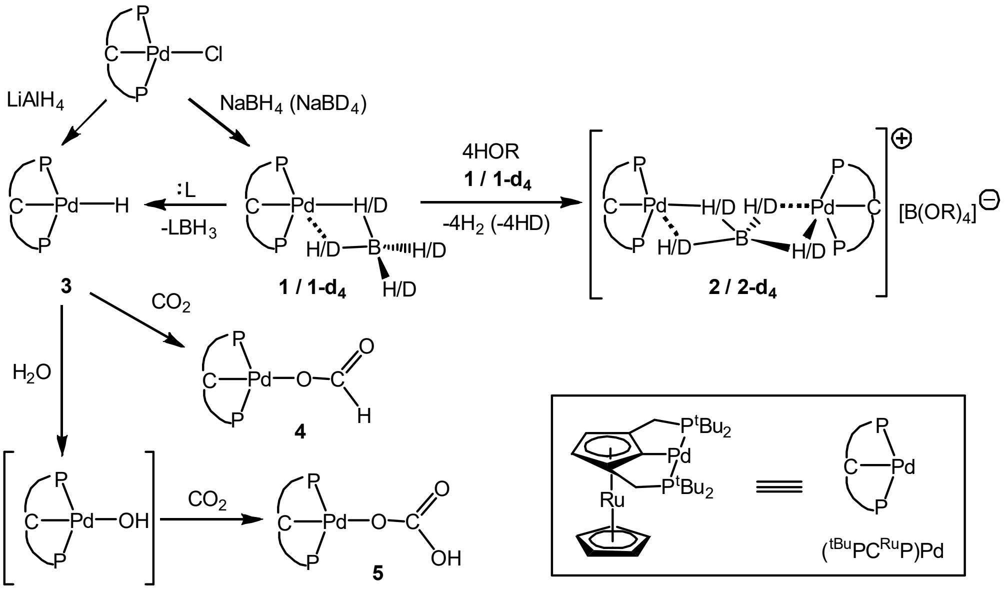
The two novel ruthenocene-based pincer palladium tetrahydroborates were synthesized and characterized by X-ray, NMR and FTIR. The alcoholysis of Pd(II) tetrahydroborate $LPd(BH_4)$ ($L= \kappa^3$-$[\{2,5\text{-}(^tBu_2PCH_2)_2C_5H_2\}Ru(C_5H_5)]$) is shown to yield the dinuclear cationic Pd(II) tetrahydroborate with bridging BH_4^- ligand $[(LPd)_2(\mu,\eta^{1,2}:\eta^{1,2}\text{-}BH_4)]^+$. The bifurcate dihydrogen-bonded complexes were found to be the active intermediates of the first proton transfer in the step-wise alcoholysis of $LPd(BH_4)$ yielding eventually $[(LPd)_2(\mu,\eta^{1,2}:\eta^{1,2}\text{-}BH_4)]^+$. According to the X-ray DFT/M06 geometry analysis, BH_4^- ligand in both palladium tetrahydroborates has mixed coordination mode $\eta^{1,2}$.

The possibility of BH_3-group abstraction from $LPd(BH_4)$ by an excess of organic base (THF, Py) with the formation of hydride $LPd^{II}H$ is shown. This Pd(II) hydride is very reactive compound able to rapidly activate CO_2 (ca. 15 min) converting into formiate complex $LPd^{II}(\eta^1\text{-}OC(O)H)$. Hydrolysis of LPdH with the subsequent CO_2 yields hydrocarbonate complex $LPd^{II}(\eta^1\text{-}OC(O)OH)$. Hydrocarbonate complex forms hydrogen-bonded dimers in the crystal due to the hydrogen bond between the -OC(O)OH fragments.



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RECENT ADVANCES IN ORGANO RARE EARTH CATALYSIS FOR ORGANIC SYNTHESIS AND OLEFIN POLYMERIZATION

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Rare-earth metals possess unique chemical and physical properties that are different from those of main-group and late-transition metals. By taking the advantage of these unique properties, we have designed and synthesized a series of rare-earth-based catalysts for organic synthesis and olefin polymerization.[1] By combining the strong Lewis acidity and heteroatom affinity of the rare-earth metal ions with the high C=C insertion activity and basicity (C–H activation ability) of the rare-earth metal alkyl species in a half-sandwich-type ligand environment, we have achieved the regioselective C–H addition of various heteroatom-containing organic compounds such as anisoles, pyridines, amines, and sulfides to a wide range of alkenes and styrenes, thereby constituting a 100% atom-efficient route for C–H alkylation.[2] By using chiral cyclopentadienyl ligands, we have synthesized a series of chiral half-sandwich rare-earth alkyl complexes that show high activity and excellent enantioselectivity in various transformations such as asymmetric C−H addition of pyridines to alkenes, enantioselective intermolecular hydroamination of cyclopropenes with amines, diastereodivergent asymmetric carboamination/annulation of cyclopropenes with aminoalkenes, and enantioselective construction of silicon-stereogenic silanes through the intermolecular asymmetric hydrosilylation of alkenes with dihydrosilanes.[3]

Based on our findings on rare-earth-catalyzed C−H addition to C=C bonds, we have achieved the C−H polyaddition of dimethoxyarenes to unconjugated dienes and simultaneous chain-growth and step-growth polymerization of methoxystyrene via C−H activation, which offered a unique route for the construction of novel macromolecular architectures difficult to make by other means.[4a,b] By using the unique interaction between rare-earth metal atom and heteroatom, we have synthesized for the first time a series of heteroatom (O, S, Se, N, and P)-functionalized polyolefins with high molecular weights and controllable functional monomer contents through the copolymerization of ethylene with heteroatom-containing α-olefins. This protocol has recently led to the successful synthesis of a series of novel olefin-based self-healing materials.[4c,d]

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CURRENT ADVANCES AND FUTURE PERSPECTIVES IN RATIONAL DESIGN OF NEW AQUA METALLAMACROCYCLIC 15-MC-5 COMPLEXES

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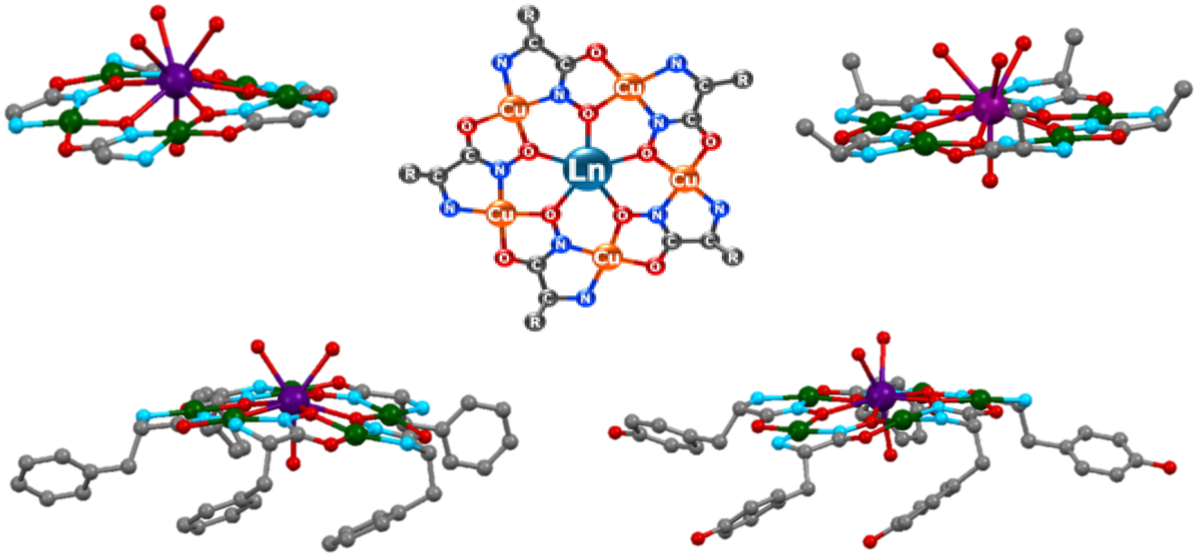
In recent years, growing interest has been focused on the synthesis of water-soluble lanthanide complexes due to their potential biomedical applications. Developing the aqua lanthanide complexes with desired organic ligands, however, is not an easy task. In this work we present the rationale we have followed in the syntheses as well as in the experimental and theoretical studies of aqua metallamacrocyclic aminohydroximate Ln(III)-Cu(II) 15-MC-5 complexes, while putting this in perspective with the advances made by other metallacrown researchers. The water-soluble Ln(III)-Cu(II) 15-MC-5 metallacrowns form an exceptional class of polynuclear metalllamacrocyclic complexes with unique structures and properties. In these systems the planar metallamacrocycle consists of five [Cu(II)-N-O] repeat units with five hydroximate oxygen atoms surrounding the lanthanide central ion which can coordinate additional species. These well-defined stable structures make it possible to increase the number of the Ln(III) inner-sphere water molecules up to four, providing new opportunities for potential applications.



Acknowledgements
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PROBING MOLECULAR ORBITALS OF SANDWICH COMPOUNDS BY DFT-SUPPORTED LASER SPECTROSCOPY

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The first chromium bisarene systems were synthesized a century ago by Hein [1] but until the middle of 20th century these compounds were believed to represent phenyl σ-complexes. The sandwich structures of ferrocene and bis(benzene)chromium were discovered in 1950's [2-4]. Since then, sandwich complexes have played key roles in both pure and applied organometallic chemistry. Metallocenes, bisarene derivatives and mixed sandwiches serve as model organometallics for studying the nature and properties of the metal-ligand delocalized interactions. On the other hand, these complexes have attracted considerable chemical interest during last decades because of their relevance to catalysis, organic synthesis, supramolecular chemistry, metal-containing polymers, biomedicine, nanoelectronics and material science.

Sandwich compounds possess specific MO structures due to the presence of an essentially non-bonding metal d_z2 orbital which is involved into the electronic excitation and ionization processes responsible for the unique spectroscopic and redox properties of these organometallics. The transitions of the d_z2 electron to Rydberg levels appear to give laser photoionization spectra of extremely high resolution. The modern laser ionization techniques such as resonance-enhanced multiphoton ionization (REMPI) and mass-analyzed threshold ionization (MATI) provide unprecedented accuracy in determination of ionization energies of neutral species and vibrational frequencies of free ions so qualitatively new opportunities become available for investigations of sandwich electronic structures [5-10]. Laser ionization spectroscopy in combination with DFT calculations represents a powerful instrument for analysis of fine ligand effects on the orbital properties. Recent surprising experimental and theoretical results concerning the carbocycle influence on the intramolecular interactions in sandwich complexes are reported in our presentation.

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FLUORENE COMPLEXES OF 9 GROUP METALS: SYNTHESIS AND CATALYTIC APPLICATION

V. Kharitonov[a,b] and D. Loginov[a]

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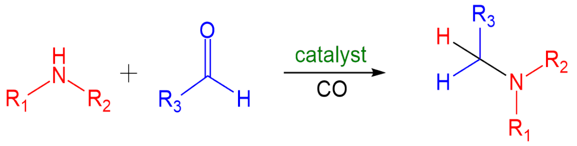
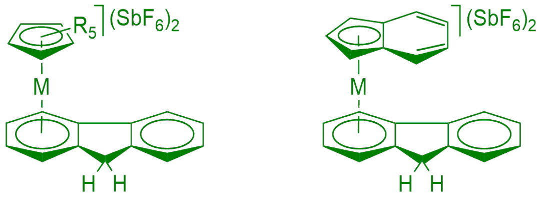
[b] *Dmitry Mendeleev University of Chemical Technology of Russia, Moscow, RUSSIA*

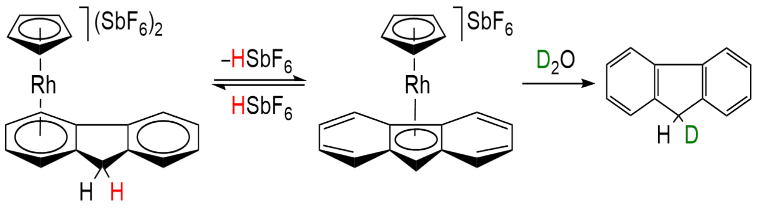
The catalytic applications of arene complexes of cobalt subgroup metals are well known [1,2]. Elimination of arene ligand results in three vacant coordination sites at the metal atom. Therefore, the catalytic activity is strongly depended on the lability of arene ligand. In the present work, we developed general approaches to η^6-fluorene complexes of 9 group metals with supporting cyclopentadienyl and indenyl ligands from the corresponding halide complexes. We demonstrated their applicability as catalysts for reductive amination of aldehydes or ketones in the presence of carbon monoxide.





M = Co, Rh, Ir; R = H, Me

We found that the η^6-fluorene complexes have higher catalytic activity than benzene analogues. It is in accordance with higher lability of fluorene as compared with benzene that can be explained by easy fluorene deprotonation and following η^6→η^5→η^1 haptotropic rearrangement. In particular, we showed that the rhodium complex undergoes rapidly decomposition by D_2O to give 9-D-fluorene.



Structure of the catalysts as well as mechanisms of catalytic reactions will be also discussed.

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ALKYL COMPLEXES OF ALKALINE AND RARE-EARTH METALS WITH TRIDENTAL DIPHENYLMETHANIDO LIGAND.

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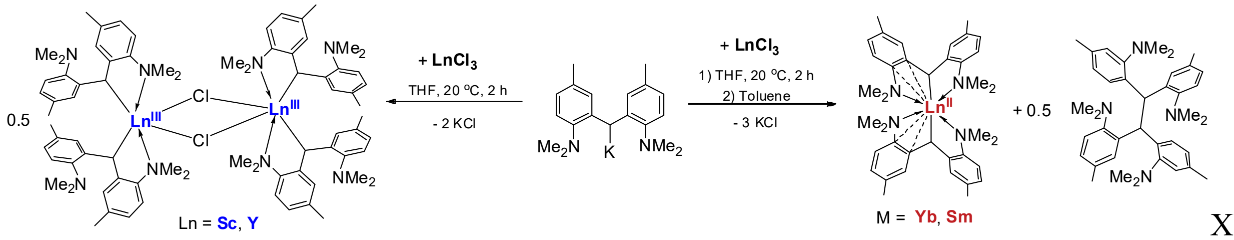
Alkyl complexes of rare-earth metals possess a unique complex of properties and have undoubted interest for catalysis. Studies over the past three decades have vividly demonstrated that the stability and reactivity of alkyl derivatives of rare earth metals are determined by the nature of the auxiliary ligand environment. However, the modification of the coordination environment of the metal center can be achieved not only by replacing the auxiliary ligand (spectator ligand), but also by varying the nature of the alkyl group itself. In our study 2,2'-methylenebis(N,N,4-trimethylaniline) 2,2’-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH$_2$ was used as potentially tridentate alkyl ligand.

A series of alkali metal alkyl complexes containing tridentate diphenylmethanido ligand [2,2’-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]Li(TMEDA) (**1**$^{\mathbf{TMEDA}}$), [2,2’-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]Na(THF)$_3$ (**2**$^{\mathbf{THF}}$), {[2,2’-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]K(THF}$_2$ (**3**$^{\mathbf{THF}}$) and [2,2’-(4-MeC$_6$H$_4$NMe$_2$)$_2$C(SiMe$_3$)]K (**5**) were synthesized and structurally characterized. Smaller Li and Na ions form monomeric complexes **1**$^{\mathbf{TMEDA}}$ and **2**$^{\mathbf{THF}}$ featuring ^{4}-CCCN-coordination of [2,2’-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]$^-$ ligand, while larger K affords dimeric complex **3**$^{\mathbf{THF}}$ in which two different types of metal-ligand bonding μ-η^5-pentadienyl:κ^2-NN and μ-η^3-CNN:η^6-arene are realized.

Further salt metathesis reaction of **1–3** with LnCl$_3$ (M = Sc, Y) lead to the formation of dimeric bis(alkyl) complexes {[2,2’-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH]$_2$Ln(μ^2-Cl)}$_2$ (Ln = Y (**4**), Sc (**5**)). Analogues salt metathesis reactions of **3** with YbCl$_3$ or SmCl$_3$ accompanied by spontaneous reduction of the Ln(III) ions to divalent state giving homoleptic bis(diphenylmethanido) complexes [2,2’-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH]$_2$Ln^{II} (Ln = Yb^{II} (**6**), Sm^{II}(**7**)).



XRD study revealed that in Ln(III) complexes of Y and Sc diphenylmethanido ligands are bidentate (κ^2-C,N), while in case of Ln(II) derivatives diphenimethanido ligands become tridentate and bounded to Ln(II) ions via κ-N-η^4-CCCN coordination mode.

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WELL-DEFINED IRON AND MANGANESE COMPLEXES IN CATALYSIS – HYDROGENATIONS, DEHYDROGENATIONS AND MORE

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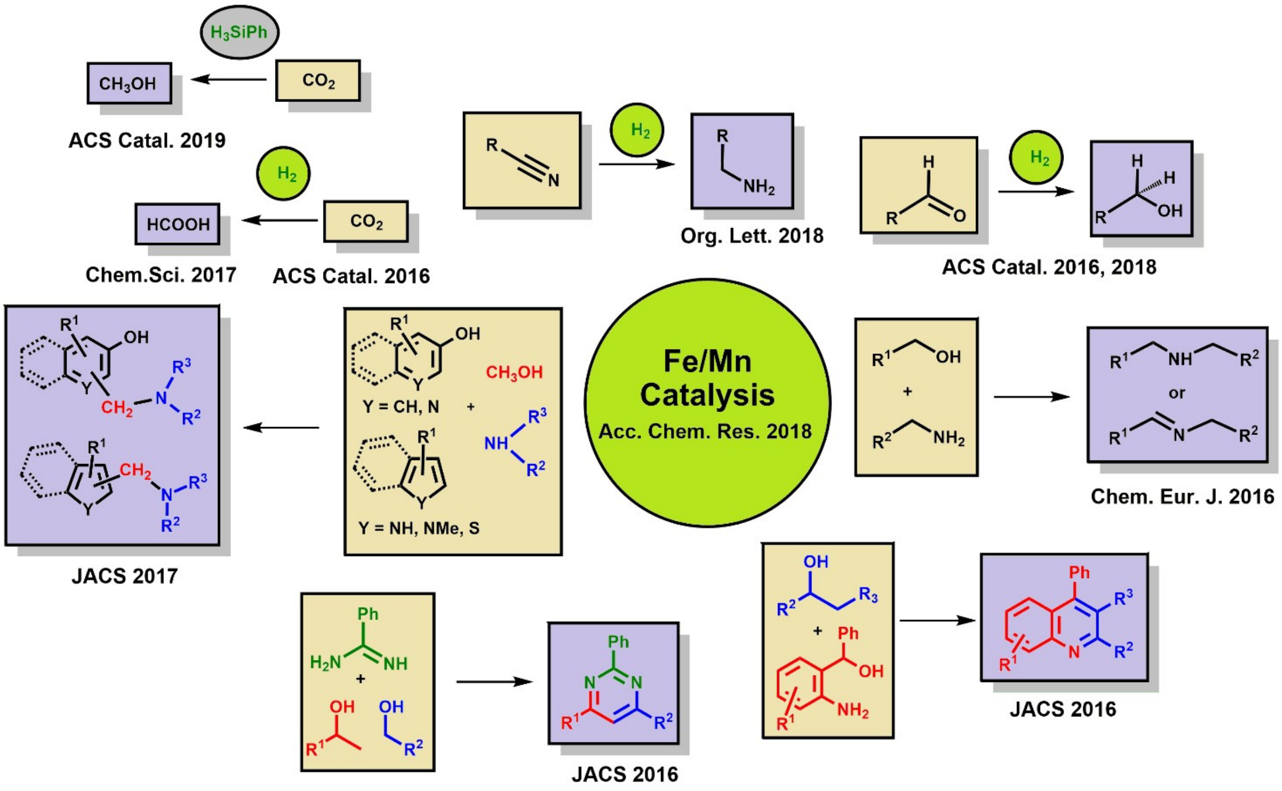
In view of concerns regarding economy, environment and sustainable energy, there is a constant need for the discovery of new catalytic reactions. The limited availability of precious metals, their high price, and their toxicity diminish their attractivness and more economical and environmentally friendly alternatives have to be found. In this respect, the preparation of well-defined non-precious metal-based catalysts of comparable or even higher activity is desirable.

Iron and manganese are one of the most abundant transition metals in the earth crust, ubiquitously available, and thus ideal candidates for catalytic applications. The synthesis, characterization, and reactivity of novel hydride and alkyl Fe(II) and Mn(I) complexes will be described. These compounds are highly active catalysts for the hydrogenation of alkenes, carbonyl compounds, nitriles as well as the dehydrogenation of alcohols [1].



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METAL-ORGANIC ARCHITECTURES FOR CATALYSIS & (BIO)MATERIALS

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This presentation will highlight our recent research on the design, synthesis, characterization, and applications of a wide diversity of functional metal-organic architectures, including metal-organic frameworks (MOFs), coordination polymers (CPs), and multinuclear metal complexes [1−3]. The following main topics will be discussed.

(1) Aqueous medium self-assembly generation, structural diversity and topological features of copper(II) coordination polymers and multinuclear cores driven by aminoalcoholate building blocks and carboxylate linkers. Application of these compounds as efficient bioinspired catalysts in mild oxidative C−H functionalization of hydrocarbons and other substrates.

(2) Hydrothermal synthesis, crystal engineering and structural diversity of MOFs & CPs assembled from multifunctional polycarboxylic acids with biphenyl or phenyl-pyridine cores and various metal nodes (Fe, Co, Cu, Mn, Ni, Zn, Cd, Ln). Examples of functional applications of these compounds and derived materials as recoverable heterogeneous catalysts, selective sensors, adsorbents, or luminescent probes.

(3) Design and self-assembly of bioactive Ag, Cu, and Zn-based metal-organic architectures toward applications as topical antimicrobial agents and antibiofilm materials.

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MODERN METALLOCENE CATALYSTS FOR STEREOSELECTIVE POLYMERIZATION OF OLEFINS

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Our studies are focused on the engineering of new catalytic systems and developing of new polymerization processes for production of industry relevant materials with desired physicochemical and thermo-mechanical properties. Our interests lie in the following areas: (1) development of new industrial catalysts for stereoselective (co)polymerization of α-olefins;[1] (2) mechanistic investigation of polymerization process;[2] (3) establishing structure/reactivity relationships for the catalytic systems.[3]

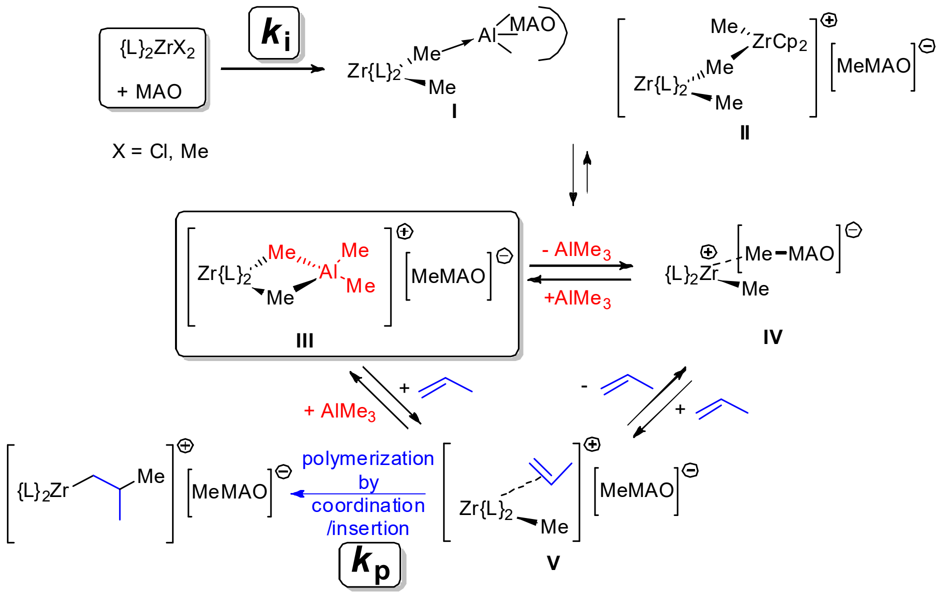

Figure 1. Putative mechanism of activation of zirconocenes with MAO.

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NOVEL SERIES OF CYANO-ARYL PORPHYRAZINES FOR SPECIFICALLY PERSONALIZED MEDICINE: PDT TREATING AND OPTICAL SENSING OF INTRACELLULAR VISCOSITY

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For a long time the idea of separated diagnostic and therapeutic approaches was predominant in the development of new drugs in medicine. However, recently a significant increase has been observed in the trend to create drugs which effectively combine diagnostic and therapeutic approaches. Such the drugs termed the agents of theranostics allow to determine the tumor localization in the body and to provide a therapeutic effect on it. Furthermore, in some cases theranostic agent allows to provide the real time monitoring of individual therapeutic response during the treatment procedure. Recently we reported on the preparation and studies of the photophysical properties of new fluorescent porphyrazine pigments which have been found to be an excellent platform for drugs with the unique combination of various biomedical functions: bimodal (fluorescent/ MRI) diagnostic agents, sensitive optical sensors of intracellular viscosity and highly efficient photosensitizers in photodynamic therapy [1-2], Here we report the new series of aryl-cyano porphyrazine pigments containing condensed aromatics and n-donor heteroatoms in the aryl groups framing the macrocycle. They demonstrate significantly improved photodynamic activity and more high potential for biomedical application as photosensitizers in PDT. Moreover, this series of tetrapyrrols with the alternation of strongly electron withdrawing CN and π-donor aryl groups in the periphery of macrocycle have been found to be novel fluorescent molecular rotor type pigmens. with the desirable feature of intense absorption and emission of red light that can be useful in vivo to enable deep tissue penetration in the 'tissue optical window'. High efficacy of all the series as the fluorescent sensors of local viscosity in a wide viscosity range, had been demonstrated. In addition, we first proposed semi-empirical model describing photophysical behavior of novel porphyrazine series . The model was verified with fluorescence decay investigations for the porphyrazine series.T

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COORDINATION CHEMISTRY OF FUNCTIONALIZED BENZOTHIADIAZOLES AND THEIR ANALOGUES

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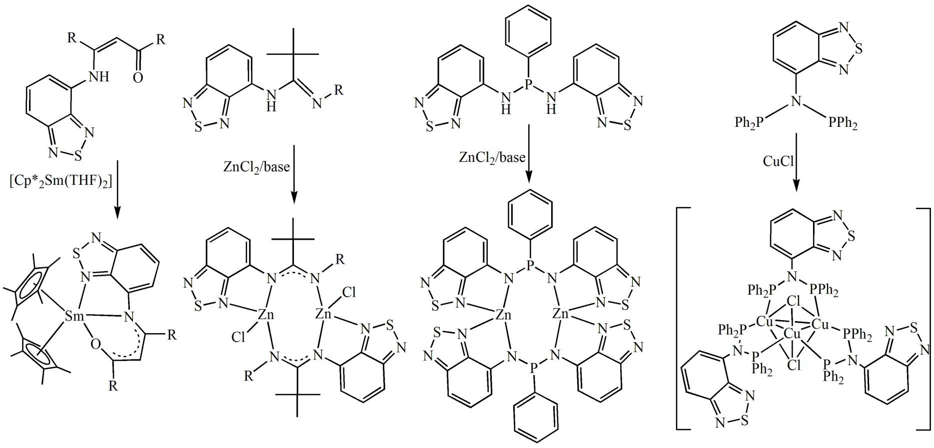
Molecular materials containing a 2.1.3-benzothiadiazole (**btd**) unit attract an attention mainly due to the intensive luminescence. That encourages synthesis of new organic derivatives of **btd**, and study of their photophysical properties. At the same time, coordination chemistry of **btd**-based ligands is still limited with few complexes, containing unsubstituted **btd** or its derivatives with such simple functional groups as $-NH_2$, -OH or -COOH [1-6].
This report is focused on an overview of our ongoing study devoted to the synthesis, complexation and photophysical properties of new **btd**-based ligands containing more advanced functional groups. Some representative examples of the ligands and the complexes obtained are shown in the scheme 1.



Scheme 1. Examples of some functionalized 2.1.3-benzothiadiazoles and the complexes with them.

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ONE OR TWO ELECTRON REDOX OXIDATION INDUCED C-H ACTIVATION AND OXIDATIVE CROSS-COUPLING WITH HYDROGEN EVOLUTION

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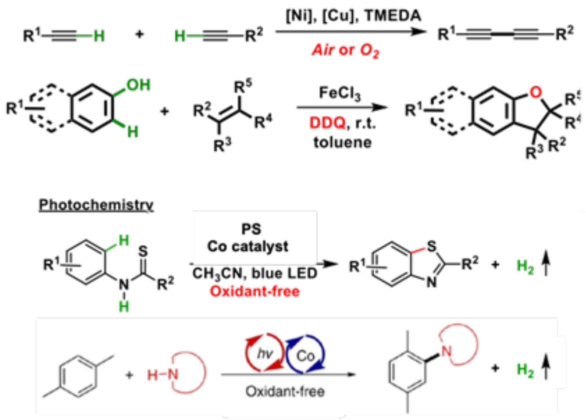
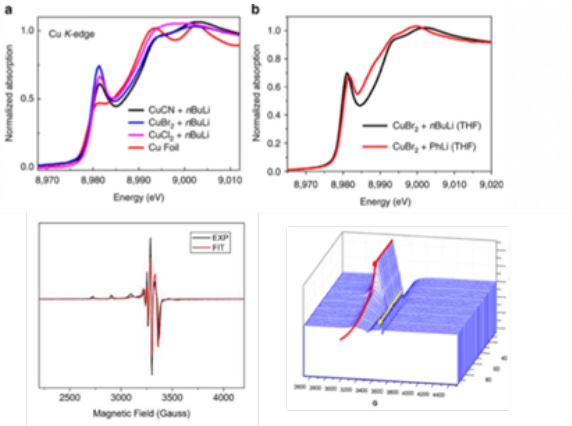
In the last decades, there has been great interest in noble transition metal catalysis system, which have activated several types of C-H bonds and provided a significant stimulus on organic synthesis. Since the urgent demand for green and sustainable chemistry, develop a catalytic system in place of the noble catalyst would be more attractive to scientists. We recently have developed a series of oxidative cross-coupling reactions that employ different kinds of early-transition metal salts as the catalyst. With the addition of suitable oxidants, these inexpensive metal catalysts can economically provide more valuable cross-coupling products. Moreover, by the combination of metal catalyst and photocatalyst, two different R-Hs will be simply constructed a cross-coupling R-R compound without introducing an extra-oxidant. In the meantime, H_2 can also be directly released in this mild condition. Furthermore, we devoted to investigate the key intermediates and mechanism in the oxidative coupling reactions. By using spectroscopical tools, such as XANES, EXAFS, *in situ* IR, Raman, EPR, and NMR spectroscopies, the structure information of organometallic complexes under real (catalytic) reactive conditions would be observed.





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NONCOVALENT INTERACTIONS IN THE 3D STRUCTURE OF METAL COMPLEXES: AN INLUENCE ON THE STEREOSELECTIVITY OF THE REACTIONS AND STABILITY OF THE REDOX FORMS

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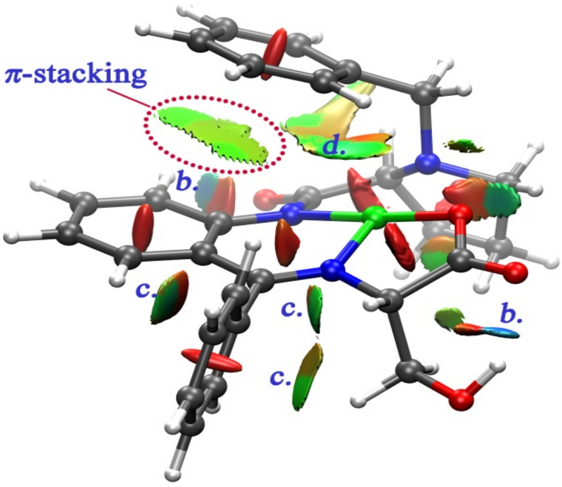
Stereoselective synthesis in a metal coordination environment is highly efficient and widely used approach. Recently, we demonstrated that combination of this approach with the electrochemical activation opens new horizons in stereoselective functionalization of amino acids in the form of Ni-Schiff base complexes. It allows reactivity and selectivity control of the substrates at the molecular level (due to cathodic or anodic activation) thus broadening a scope of available reaction routes (including processes which were not possible in common reaction conditions).

Voltammetric investigation of a series of thus obtained diastereomeric Ni-Schiff-base complexes revealed an interesting phenomenon of the stereodependent redox activity inherent to the derivatives of various types of amino acids. The difference in the redox potential values for the diastereomeric complexes is rather significant opening the route for the electrochemical discrimination of the stereoisomers.

To reveal the origin of the stereodependent redox activity and to shed light on the stereochemical results of the electrosynthesis, a detailed investigation of non-covalent interactions in the metal coordination environment was performed using recently reported method [1]. Though the basic structural network of a molecule is defined by covalent bonding, noncovalent interactions (H-bonding, π-stacking, van der Waals interactions, etc.) may essentially influence electronic properties of a molecule (by switching on/off additional electronic interactions) as well as thermodynamics and/or kinetics of electrochemical processes for either diastereomer creating background for electrochemical recognition.

Thus, chiral Ni(II) Schiff-base complexes constitute interesting examples of electrochemical discrimination in the metal complexes which is not attributed to the distortion of coordination polyhedra of the metal center in one of the stereoisomers, as it has been actualized in the previously reported data. The obtained electrochemical results supported by quantum-chemical calculations clearly demonstrate that even peripheral groups in the metal coordination environment can play an important role influencing the relative impact of different parts of molecule in the frontier orbitals via conformational changes. The examples discussed will be useful for targeted molecular design of new chiral redox active materials for electrochemical enantio recognition.



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SYNTHESIS AND PROPERTY OF N-HETEROCYCLIC SILYLENES (NHSI) COBALT AND IRON COMPLEXES

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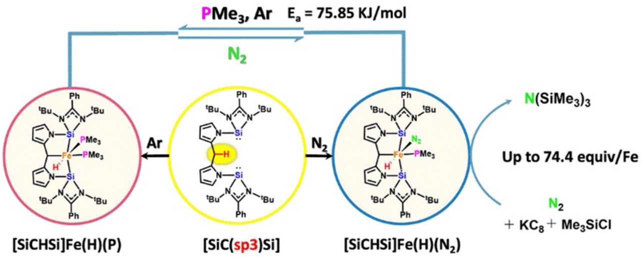
Transition metal complexes as catalysts have been widely applied in organic reactions. Phosphine and N-heterocarbene (NHC) are two kinds of usual ligands. As an analogue to the NHC, although the stable N-heterosilylene (NHSi) were simultaneously isolated, the chemistry of the NHSi develops slowly because the synthesis and derivation of the NHSi are more difficult. The recent study indicates that the NHSi is a potentially excellent ligand for transition metal complex under given conditions in comparison with phosphine and NHC ligand and will be widely used in catalytic processes.

In this presentation, a variety of silyene coordinated [PSiP] pincer cobalt hydrides were synthesized. Our study indicates that the electron properties and steric hindrance of ligands have significant effect on the stability of of silyene complexes. A new N-heterocyclic σ-silyl pincer ligand $HSiMe(NCH_2PPh_2)_2C_6H_4$ was designed. Co(III) complex $CoHCl(PMe_3)(SiMe(NCH_2PPh_2)_2C_6H_4)$ was generated by the reaction of $HSiMe(NCH_2PPh_2)_2C_6H_4$ with $CoCl(PMe_3)_3$. We have found that the introduction of silylene ligand in $CoHCl(PMe_3)(SiMe(NCH_2PPh_2)_2C_6H_4)$ can improve the catalytic activity of cobalt hydride for the Kumada coupling reaction. A novel bidentate NHSi ligand, N-(LSi:)-N-methyl-2-pyridinamine (L = PhC(N*t*Bu)$_2$), and the bis-chelate disilylene iron hydride [(Si,N)(Si,C)Fe(H)(PMe_3)] were synthesized through C_{sp2}–H activation of the NHSi ligand. Iron hydride [(Si,N)(Si,C)Fe(H)(PMe_3)] can be used as an efficient catalyst for the hydroboration reaction of carbonyl compounds at room temperature. The first bis(silylene)-based [SiC(sp^3)Si] pincer ligand with a C(sp^3)-atom anchor was synthesized. Two novel iron hydrides, [SiCHSi]Fe(H)(N_2)(PMe_3) and [SiCHSi]Fe(H)(PMe_3)$_2$ were synthesized via the C(sp^3)−H bond activation. Furthermore, [SiCHSi]Fe(H)(N_2)(PMe_3), as the first example of transition metal dinitrogen complex supported by bis-silylene ligand, could effectively catalyze silylation of N_2.



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NEW REAGENT FOR Cu-ASSISTED REDUCTIVE AMINATION OF ARYLBORONIC ACIDS

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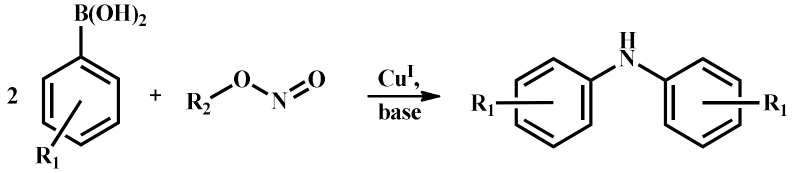
Among the C(aryl)-N bond forming reactions, copper-promoted N-arylation with aryl boronic acids is one of the widely required processes due to relatively simple and cheap synthetic protocol. Aromatic amines are applied in material science, in biology, pharmaceutical industry (arylamine moieties can be found in 37% of drug candidates and in natural products) and in many other areas making their availability a topical problem. Cu-promoted oxidative amination of aryl boronic acids with arylamines (referred to as the Chan-Lam coupling [1]) demonstrated essential advantages of the approach such as mild reaction conditions, high tolerance to functional groups and application of cheap and available reactants. Oxidative amination of aryl boronic acids was later complemented with copper-promoted reductive amination in which arylnitroso compounds were applied instead of arylamines [2]; the latter reaction was demonstrated to be preferable for synthesis of bulky amines [3].

Our recent research revealed that Cu-assisted amination of arylboronic acids has not yet exhausted its full potential. The search for new reactants which will be active in this process is of special interest for providing new synthetic strategies as well as for understanding the reaction mechanism which is still underinvestigated. A possibility for the N-O bond cleavage in Cu-catalyzed reductive amination of arylboronic acids allows suggesting that some other compounds containing the N-O bond can be also applied as aminating agents in this reaction.



We demonstrated that stable, cheap and easily available alkylnitrites can be applied as the reactants in Cu-promoted reductive amination of aryl boronic acids instead of aryl nitroso compounds (as it has been suggested in [2]) leading to diarylamines with practical 70% yield. Mild conditions, cheap reactants and ease of work-up procedure after one-pot process are the salient features of the method. The possible reaction scheme based on quantum chemical calculations clarifying the Cu-containing key intermediates will be discussed. Cu-mediated N-O bond cleavage followed by transmetalation leads to formation of the arylated nitroso complex which further reacts with the second equivalent of aryl boronic acid as it has been shown to occur in reductive amination of boronic acids with aryl nitroso compounds.

New approach broadens the scope of reactants which can be involved in Cu-assisted reductive amination of aryl boronic acids and emphasizes the synthetic value of the method.

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Re(I)-NITROXIDE SPIN-LABELED FORTEPIANO STOOL

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Stable radical derivatives of metallocenes are of an oscillating interest due to their ability to assemble into various supramolecular structures with a specific combination of magnetic, electronic, photochemical and catalytic properties [1-4]. We succeeded in synthesizing of the spin-labeled half-sandwich complex Re^{I}(CpNN)(CO)$_3$ by introduction of the 2-imidazoline nitronyl nitroxide substituent into the cyclopentadienyl ring (Fig. 1). The synthesis, electrochemical properties in solution, the results of EPR spectroscopy study and the peculiarities of magneto-structural correlations for different polymorphs of Re^{I}(CpNN)(CO)$_3$ are under discussion.

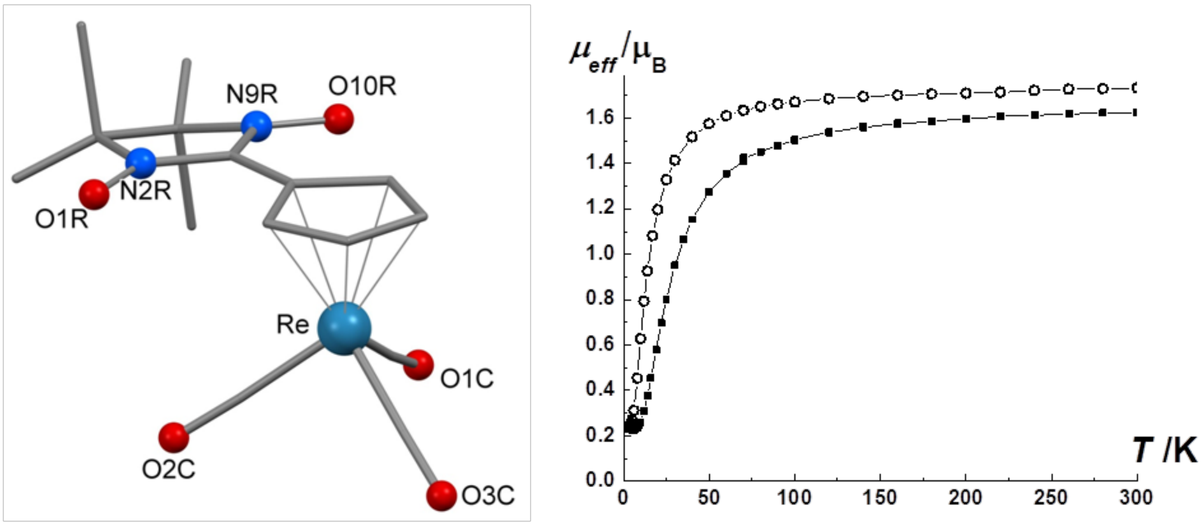

Figure 1. Molecular structure of Re^{I}(CpNN)(CO)$_3$ and temperature dependences of $\boldsymbol{\mu_{eff}}$ for for polymorphs α-Re^{I}(CpNN)(CO)$_3$ (-○-) and β- Re^{I}(CpNN)(CO)$_3$ (-■-).

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SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENT PROPERTIES OF HETEROMETALLIC COORDINATION COMPOUNDS {Zn_2Ln}

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Currently, one of the most promising areas in the design of light-emitting materials is obtaining of luminescent d-4f-heterometallic coordination compounds, whose photophysical properties can be finely tuned by selecting functional antenna ligands that make up the d-blocks, varying the ion ratio of various rare-earth elements in the complex compounds crystals, etc.

In order to clarify the ligand environment effect on the photophysical properties of compounds, we have obtained a number of complexes $[Zn_2Ln(NO_3)(phbz)_6(L)_2]$, where Ln = Eu^{3+}, Tb^{3+}; L: Py = pyridine; 2,2’-bpy = 2,2’-bipyridine; 2,3-lut = 2,3-dimethylpyridine. More significant values of quantum yields have been observed for heterometallic complexes with bpy. E.g. complex $[Zn_2Eu(NO_3)(4\text{-}phbz)_6(bpy)_2]$ has a overall quantum yield value of about 62%.

In addition to this study we obtained three systematic series of solid solutions $[Zn_2Ln^1{}_xLn^2{}_{(1-x)}(OH)(NO_3)_2(Piv)_4(phen)_2]$ (Ln = Eu, Tb, Gd) in order to identify the effect of doping of some REE ions by others on the excited state lifetimes and photoluminescence quantum yields. After carrying a detailed study of the photoluminescence properties of all the compounds, the effects of luminescence amplification of both Tb^{3+} ions by Gd^{3+} ions and Eu^{3+} ions by Tb^{3+} ions were revealed.

All the compounds obtained were characterized by X-ray diffraction, purity confirmed by powder XRD.

It is worth to note that some of above mentioned compounds is used for synthesis of NHC heterometallic complexes.

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APPLICATION OF SALT METATHESIS REACTIONS IN SYNTHESIS OF LANTHANIDE ARYLTHIOLATE AND CHALCOGENIDE COMPLEXES SUPPORTED BY Β-DIKETIMINATE LIGAND

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Molecular lanthanide complexes with Ln–Q bonds (chalcogenides and chalcogenolates, Q = S, Se, Te) are insufficiently investigated due to synthetic difficulties. Bonding with soft chalcogen-containing base is less favoured than with N- and O-donors, what makes complexes sensitive to moisture and air. Nevertheless, complexes with this extraordinary bonds exhibit unusual physical and chemical properties, for instance, magnetic or luminescent.

Bulky organic ligands are used for stabilisation of lanthanide complexes owing to their steric characteristics, which helps to stabilize molecular complexes. Due to their variety, it is possible to control number and coordination modes of another ligands and physical properties of complex. We use β-diketiminates $(^{Ar}\text{nacnac})^{-} = (\text{HC(N(Me)Ar)}_2)^{-}$ as versatile ligands, which can be modified in desired ways, and could serve as antenna ligands.

Most commonly, redox reactions are used for the synthesis of chalcogenolate complexes, which is impractical in some cases. We investigated salt metathesis reactions as another way of obtaining lanthanide thiolate and chalcogenide complexes. The convenient method of synthesis of LnI_3 was developed, and β-diketiminate complexes $[\text{Ln}(^{dipp}\text{nacnac})\text{I}_2(\text{Thf})_2]$ (dipp = 2,6-diisopropylphenyl, Thf = tetrahydrofuran) were obtained on the next stage. The remaining iodides were substituted to thiolate ligands using appropriate potassium salts to give the complexes $[\text{Ln}(^{dipp}\text{nacnac})(\text{SR})_2(\text{Thf})_n]$ (Ln = Nd, Sm, Dy, Tb, R = Ph (n = 1), Py (n = 0)). The same reactions with potassium (di)chalcogenides did not proceed even at elevated temperatures, but in case of K_2Se an unexpected complex $[\text{Sm}(^{dipp}\text{nacnac})\text{I}(\text{Thf})_2]$ formed. Luminescent properties of obtained thiolate complexes were studied.

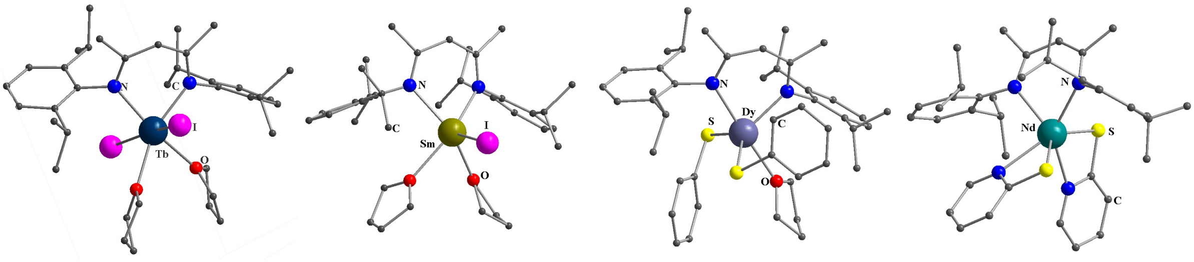

Figure 1. Examples of $[\text{Ln}(^{dipp}\text{nacnac})(\text{SR})_2(\text{Thf})_n]$ and $[\text{Sm}(^{dipp}\text{nacnac})\text{I}(\text{Thf})_2]$

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Acknowledgements.

The authors are grateful to the colleagues of the lab No. 307, NIIC SB RAS. The work is supported by the Russian Science Foundation (project No. 16-13-10294).

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TITANIUM AND ALUMINIUM COMPLEXES WITH DPP-BIAN IN ROP OF CYCLIC ESTERS

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The complexes of Al(II) and Ga(II) [1, 2] as well as Ti(III) and Ti(IV) alcoholates stabilized with 1,2-bis-(2,6-*i*Pr_2-C_6H_3)-acenaphthenequinonediimine (dpp-bian) reveal high catalytic activity in ring-opening polymerization (ROP) of cyclic esters and organic carbonates producing polymers in controllable manner. Kinetic studies along with linear dependence of polymer molecular weights on conversion confirm living character of polymerization. The dinuclear Al(II) species revealed to be an extremely active Al(II) initiator for the controlled ROP of ε-caprolactone at room temperature, outperforming all its Al(III) congeners reported thus far. According to the detailed DFT studies the metallic cooperativity between the two Al(II) metal centers rationalizes the unusually high CL ROP activity at room temperature.

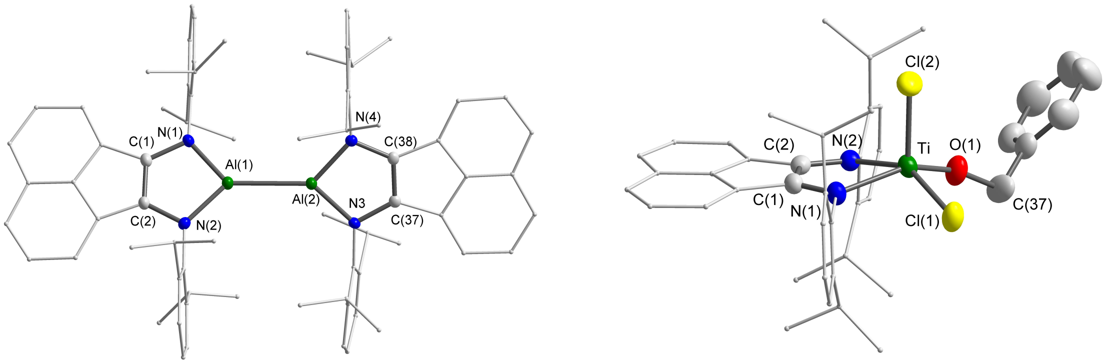

Figure 1. Structure of dpp-bian-supported metal complexes for ROP of cyclic esters

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CHEMISTRY IN MOLECULAR VESSELS

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Properties of chemical entities in confined nanospace are expected to be different from their bulk properties due to restricted rotational and vibrational motions. Such restricted motions along with other interaction/s may allow to stabilize unusual conformations of compounds in confined space of molecular cavity. Moreover, reactivity and reaction pathways in confined space may become different from traditional bulk reactions leading to the formation of unusual product/s. In this regard, chemists have been trying to design artificial molecular vessels to perform chemical reactions in their confined nanospace. Design of 3D molecular architectures having hydrophobic confined space including their use for catalytic organic transformations will be discussed. The lecture will also focus on the interior decoration of nanocages with urea moieties for new generation discrete heterogeneous catalysts for Michael addition (Figure-1).[1-7] It is also planned to focus on our recent work on the use of confined space of discrete organic cages for the nucleation of tiny palladium nanoparticles and their successful use in facile transformation of aryl halides to corresponding cyanides.

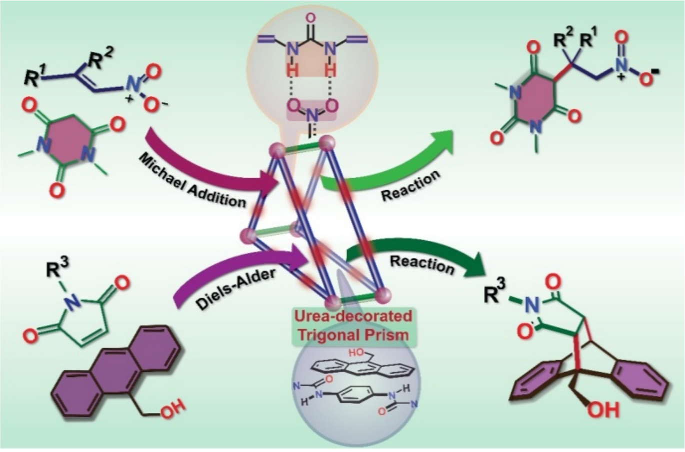

Figure 1. Urea based nano-barrel and use of its confined space for catalysis.

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ELECTRON-DEFICIENT MOLECULES OF 3-d METALS CARBOXYLATES

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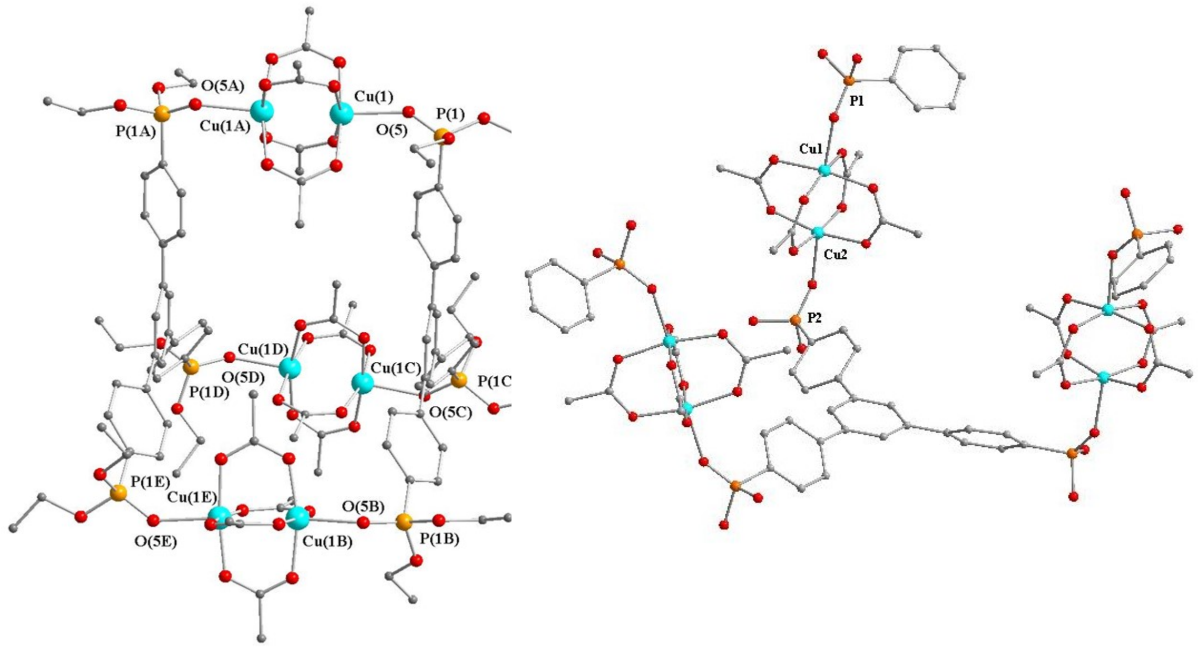
This report deals with the preparation and structure feature of electron-deficient species of mono-, bi- and trinuclear carboxylates of 3-d metals, depending on the nature of the metal (M=Zn, Cu^{II}, Ni, Co^{II}, Fe^{II}, Mn^{II}), R-substituent in the carboxylate anion (R=Bu^t, Me, Ph, $C_5H_4Mn(CO)_3$, CF_3), containing labile molecules of coordinating solvents, as well as their application:

- fixing the simplest O-, N-donor molecules;
- preparation of heterometallic complexes and polynuclear clusters;
- synthesis of coordination polymers with various geometry and dimensions.

It has been shown that the structure of coordination compounds in single crystal is determined not only by the nature of the metal and the carboxylate anion, but by the conditions of crystallization and the nature of the weak interactions arising in the crystalline cell.



Reaction in $CHCl_3$ (structure "la cage-cell"), recrystallization from benzene (structure-"3D polymer")

Part of this work was carried out in the framework of the International Associated French–Russian Laboratory of Macrocyclic Systems and Related Materials (LAMREM) of CNRS.

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TOWARDS MOLECULAR DESIGN OF SPIN-CROSSOVER COMPLEXES BASED ON 2,6-DI(PYRAZOLE-3-YL)PYRIDINES

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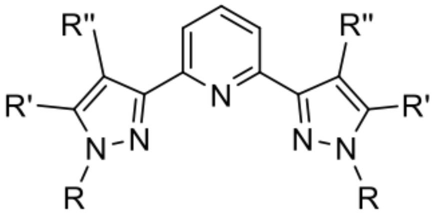
Spin-crossover (SCO) complexes with d^4-d^7 metal ions, which are able to reversibly switch between the two spin states under an applied stimulus (temperature, pressure, light irradiation, electric or magnetic field) [1], offer wide opportunities for their potential applications in high density data storage, switching, sensing and other molecular devices [2]. Most often, they have an iron(II) ion in a (pseudo)octahedral N_6 environment that results in an SCO occurring between diamagnetic low-spin (LS, S = 0) and paramagnetic high-spin (HS, S = 2) states.

2,6-di(pyrazole-1-yl)pyridine (1-bpp) is among the most studied in SCO research owing to its synthetic versatility and possibility to control the spin state of the metal ion by a judicious choice of substituents [3]. Complexes of isomeric 3-bpp are much less understood [4], as not so many of them were derived from functionalized 3-bpp, and their spin state is extremely sensitive to the environment [5], thus precluding a 'truly molecular' design [6] of SCO compounds based on 3-bpp.

In a search for new derivatives of 3-bpp that would finally make it possible, we obtained a series of iron(II) complexes $[Fe(3\text{-}bpp)_2]^{2+}$ with substituted 3-bpp ligands (Scheme 1) and probed their spin state in solids (by magnetometry and X-ray diffraction) and in solutions (by variable-temperature NMR spectroscopy). Such an extensive study allowed us to get insight into the role of different substituents in 3-bpp (with distinct steric and electronic properties and H-bonding ability) and to propose a new approach in the ligand design to produce SCO complexes of functionalized 3-bpp for many future applications.



Scheme 1. Functionalized 3-bpp ligands.

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COPPER CATALYZED REACTION OF HYDRAZONES WITH POLYHALOGENATED COMPOUNDS. AN EFFICIENT APPROACH TO ALKENES AND DIAZADIENES

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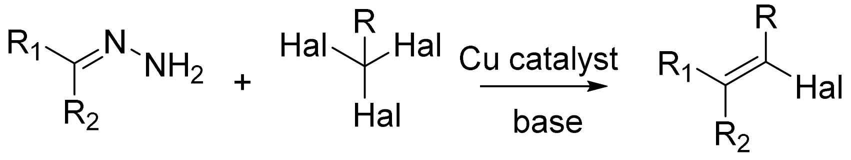
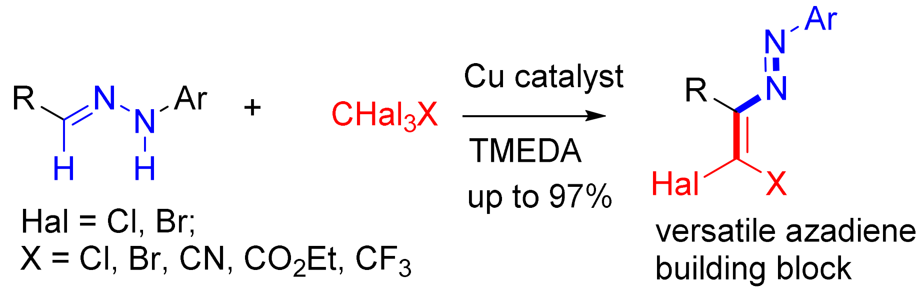
Catalytic olefination reaction represents new approach to the preparation of double C=C bond. *N*-unsubstituted hydrazones can be converted into alkenes by treatment with polyhalogenated alkanes in presence of a base and catalytic amounts of copper salts. The reaction has a wide synthetic scope allowing to prepare both alkyl and aryl substituted alkenes, including fluorinated and functionalized ones.

We demonstrated also similar transformation with N-substituted hydrazones, as a result the new carbon-carbon bond forming reaction of *N*-monosubstituted hydrazones with polyhaloalkanes to produce 1,2-diazabuta-1,3-dienes has been developed. This highly efficient copper-catalyzed transformation features a broad scope with regard to all reaction components, as well as the possibility to perform the process in a much more convenient one-pot fashion starting with easily available aldehydes and hydrazines. The synthetic usefulness of the obtained halogenated azadienes was demonstrated in their reactions with *O*-, *N*-, *S*- and *C*-nucleophiles, which opened access to a variety of valuable acyclic and heterocyclic products. Mechanistic studies revealed that this Cu-catalyzed transformation proceeds via radical pathway.

■ Catalytic olefination of N-unsubstituted hydrazones



■ Synthesis of diazabut-1,3-dienes from N-monosubstituted hydrazones



This work was partially supported by the Russian Federation President Grant for leading scientific schools № 4687.2018.3.

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SYNTHESIS OF NEW BIFUNCTIONAL o-QUINONES. SEMIQUINONE COMPLEXES WITH Fe, Co, Ni.

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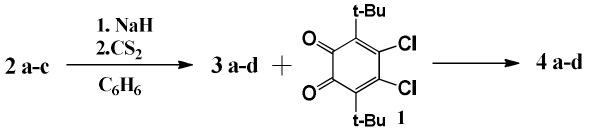
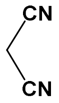
o-Quinones are both well-studied and promising redox-active chelating ligands. Introduction of functional groups into an o-quinone molecule creates additional coordination-capable sites, adds groups those bearing persistent radical fragments, as well as allows to vary the range of redox properties. Functionalized o-quinones could be incorporated as a building blocks in the construction of molecular magnets. Due to the redox-isomerism of o-quinone complexes, they are promising to creating polyspin systems.

We have found that 3,6-di(*tert*-butyl)-4,5-dichloro-1,2-benzoquinone **1** reacts with 1,1-dithiolates **3a-d** to give 4,7-di(*tert*-butyl)-5,6-dihydroxy-1,3-benzodithioles **4a-d**. All synthesized compounds were isolated and characterized by IR, NMR, EPR spectroscopy and X-ray crystallography.

In this work we present a new method of synthesis of acceptor o-quinones, annelated with a 1,3-dithiol cycle, by the reaction of compound **1** with 1,1-dithiolates. The conditions for this reaction were optimized depending on the solvent nature, reaction time and temperature.

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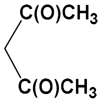
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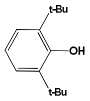
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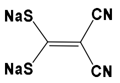
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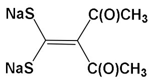
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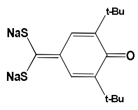
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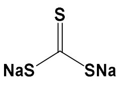
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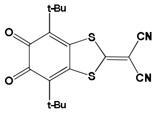
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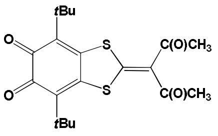
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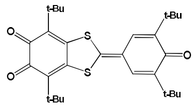
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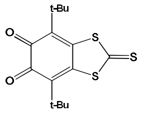
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The synthesized compounds have been tested as bifunctional ligands for the preparation of redox-active transition metal complexes.

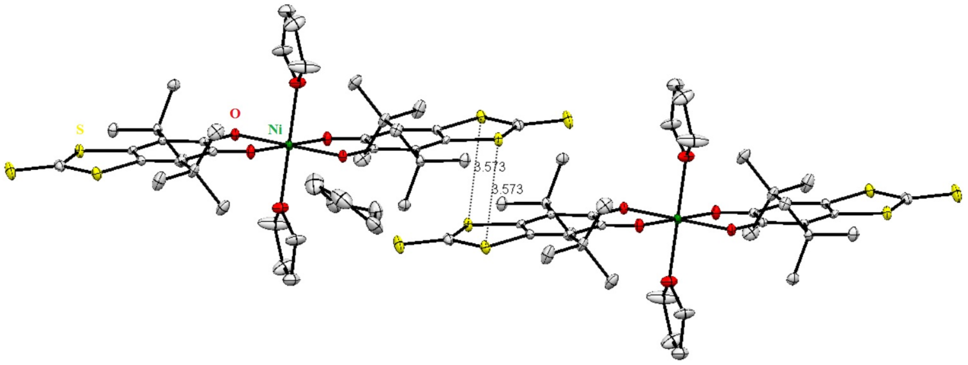

Figure 1. X-Ray structure of nickel bis-semiquinonate adduct with o-quinone **4d.**

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TRIGONAL PRISMATIC COMPLEXES FOR MOLECULAR SPINTRONICS

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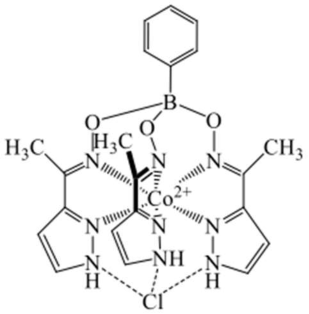
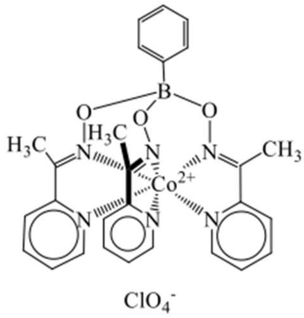
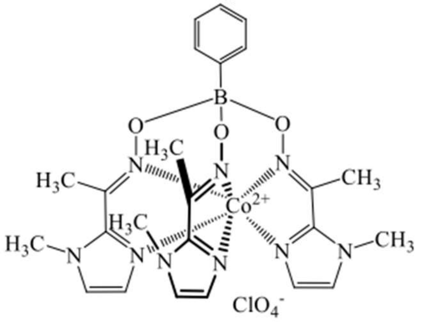
Controlling the magnetic states of individual molecules (so-called single molecule magnets, SMMs) opens wide possibilities for creating new devices for ultrahigh-density information storage. SMMs are paramagnetic *d*- or *f*-metal complexes with a large magnetic anisotropy that results in a slow magnetic relaxation between the lowest energy states with an opposite orientation of the magnetic moment. Among the SMMs based on the first row transition metal ions, cobalt(II) complexes have the largest barrier of magnetization reversal, which in the case of a two-coordinate linear cobalt(II) complex [1] approaches the theoretical limit of 450 cm^{-1}. Those linear cobalt(II) complexes (as well as their cobalt(I), iron(I) and iron(II) analogues) are, however, intrinsically unstable, making any future steps towards possible technological applications extremely challenging.

Among other coordination environments that ensure large magnetic anisotropy of the cobalt(II) ion while keeping the complex chemically stable, a trigonal prism (TP) recently emerged as an ideal geometry for new SMMs [2]. Despite several successful attempts [3] to obtain new SMMs with very large magnetization reversal barriers, these compounds are still rather unusual, as the TP geometry has been so far only provided by rather exotic rigid clathrochelate ligands.







In the talk, possible approaches toward molecular design of effective cobalt(II)-based SMMs will be discussed. Among others, coupling them with porphyrine and phthalocyanine moieties is proposed as a novel pathway to introduce them into a truly molecular spintronic device, which requires combining several magnetic centers in a single molecule with a possibility to fine tune the interaction between them.

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AZAPHOSPHOLE OR STABILIZED PHOSPHINIDENE – THERE IS A QUESTION: THE NATURE OF P ($\sigma^2\lambda^3 \leftrightarrow \sigma^2\lambda^1$) IN DIAZADIPHOSPHAPENTALENES

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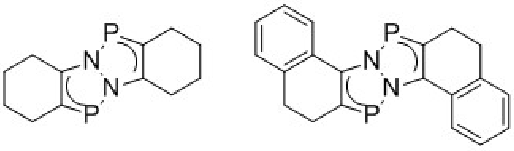
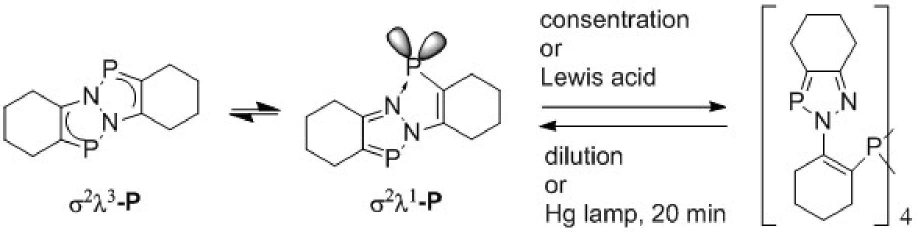
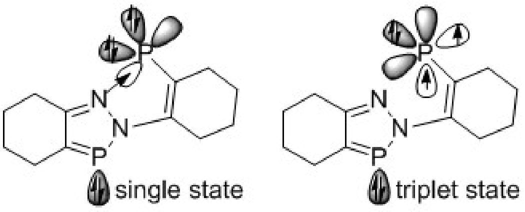
Phospholes, five-membered unsaturated heterocycles with σ^2,λ^3-posphorus demonstrating extraordinary electronic properties, are of great interest as a new type of synthones for the construction of p-conjugated materials [1,2]. 3a,6a-Diaza-1,4-diphosphapentalenes (DDPs), synthesized in our group [3], can be classified as annulated heterophospholes, more precisely, azaphospholes. DDPs revealed a novel type of 10π-electron heteroaromatic system, containing a two-coordinate and formally divalent phosphorus atom.



It was found that treatment of DDPs with Lewis acids (BPh_3, BF_3xEt_2O) induced their tetramerization. It is worth to underline tetramerization of DDPs is a concentration-depend prossess.



Our study showed that tetramers are formed through the elongation the P-N bond of DDP, followed by its breaking and oligomerization of phosphinidene-like particle. As phosphinidene molecules are known to exist in single and triple states, DFT calculations (6-31G(d) level of theory) of these states were performed increasing the P-N distance in molecules smoothly.



It was found that the elongation of the N–P bond is accompanied by an almost linear increase in the energy of the singlet form of the molecule, while the total energy of the triplet form varies only slightly. With a length of N-P bond 2.53 Å, the energies of the singlet and triplet states become equal. The distance 2.53 Å, being greater than the sum of the covalent radii of the elements (1.73 Å), is much less than the sum of their van der Waals radii (3.35 Å).

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COBALT COMPLEXES BEARING FUNCTIONALIZED O-AMINOPHENOLS: PECULIARITIES OF SYNTHETIC ROUTES, MOLECULAR AND ELECTRONIC STRUCTURES

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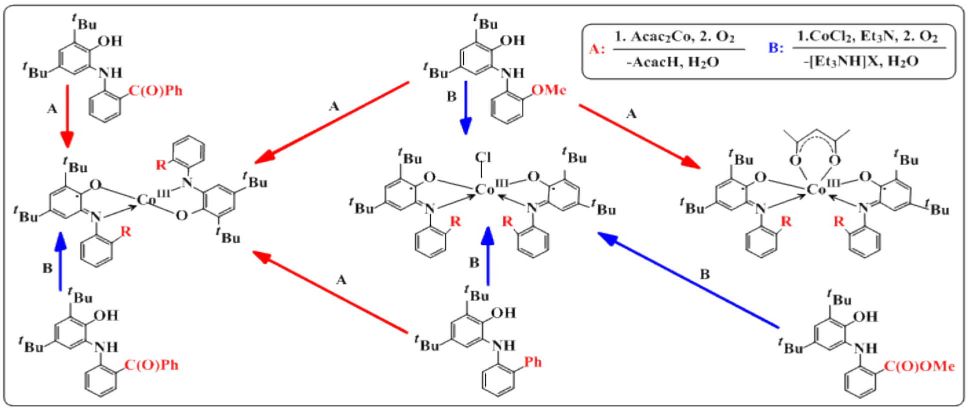
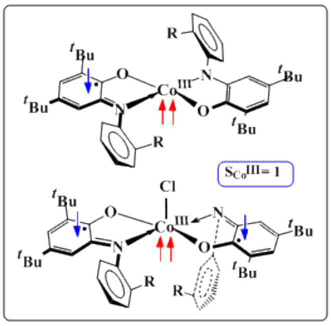
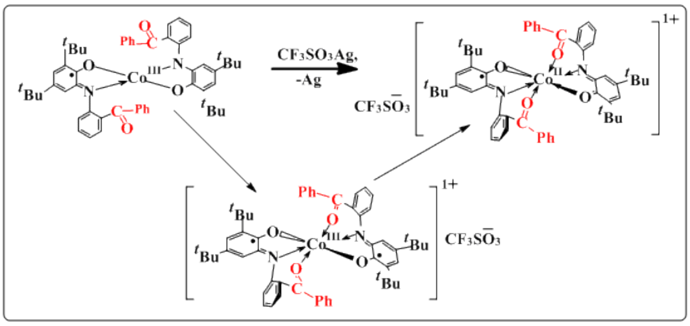
Studied objects are the Co^{III} complexes on the base of bulky *o*-aminophenols functionalized by –OMe, -C(O)OMe, -Ph and –C(O)Ph groups. Modifying the synthetic procedure through the variation of starting Co-containing compounds and ligands' substituents, targeted synthesis of the 4-, 5- or 6-coordinated Co^{III} derivatives was performed (see below).



Functionalization of ligands facilitates the stabilization of Co^{III} ion in rare intermediate spin state ($S_{Co} = 1$) (see below, left view). On the example of cobalt derivatives featuring –C(O)Ph groups, the redox-induced electron transfer (RIET) [1] (reduction of Co^{III} to Co^{II} ion despite the oxidation of initial Co^{III} complex) was first observed among the cobalt complexes with such type ligands and caused by the synergistic effect of hemilability and redox-active nature of ligand. Implementation of RIET (see below, right view) is accompanied by increase in ligands' denticity and formation of rare trigonal-prismatic coordination environment around Co^{II} ion. Details of experimental data and DFT-study will be revealing in the report.





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HOMO- AND HETEROLEPTIC CATECHOLATES OF TANTALUM

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The redox-active ligands, especially o-benzoquinone derivatives, are intensively studied due to their unique redox, magnetic, photophysical and catalytic properties. However, complexes of 4*d*- and 5*d*-transition metals still remain much less explored, than their 3*d*-congeners.

Amides of the early transition metals are handy precursors of other classes of complexes due to of basic, nucleophilic and (to a lesser extent) redox properties of the amido group. In this work we used easily available $Ta(NMe_2)_5$ for preparation of various Ta catecholates, revealing unexpectedly rich chemistry. The reaction of $Ta(NMe_2)_5$ with the 3,6-di-*tert*-butyl-catechol (H_2Cat^{36}) was expected to give the homoleptic tantalum catecholate $Ta_2(Cat^{36})_5$. Instead, anionic complex $(Me_2NH_2)[Ta(Cat^{36})_3]$ (**1**) was isolated with nearly quantitative yield.

Interaction between $Ta(NMe_2)_5$ and 3,6-di-*tert*-butyl-*o*-benzoquionone (Q^{36}) leads to oxidation of dimethylamide ligand followed by condensation producing aminoamide $Me_2NCH_2NMe^-$ and the corresponding 3,6-di-*tert*-butyl-catecholate $(Cat^{36})^{2-}$. As a result, the mixed-ligand tantalum complexes were isolated, namely, *fac*-$[Ta(Cat^{36})(NMe_2)_3(HNMe_2)]$ (**2**) and $[Ta(Me_2NCH_2NMe)_2(NMe_2)_2][Ta(Cat^{36})_2(NMe_2)_2]$ (**3**). Small amount of *cis*-$[Ta(Cat^{36})(Me_2NCH_2NMe)_2(NMe_2)_2]$ (**4**) was also obtained, and this product is considered as an intermediate in the formation of **3**. The amide oxidation is accompanied with catecholate redistribution, and the catecholate-rich complexes $[Ta_2(\mu\text{-}Cat^{36})(\mu\text{-}NMe_2)_2(Cat^{36})_2(NMe_2)_2]$ (**5**) and *cis*-$[Ta(Cat^{36})_2(NMe_2)(HNMe_2)]$ (**6**) were also isolated even at 1:1 molar ratio of $Ta(NMe_2)_5$ to Q^{36}. Complex **2** was independently from $Ta(NMe_2)_5$ and catechol H_2Cat^{36} in 1:1 molar ratio in toluene, while the same reaction in THF afforded *fac*-$[Ta(Cat^{36})(NMe_2)_3(thf)]$ (**7**). Reaction $Ta(NMe_2)_5$ and catechol H_2Cat^{36} in 1:2 ratio produces complex **6** smoothly. To the contrary, the same reaction in 2:3 ratio failed to produce the sesquicatecholate **4**, giving a mixture of **2** and **6** instead. The complexes were characterized by single-crystal X-ray diffraction and ^1H, ^{13}C and ^{15}N NMR spectroscopy.

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4-AMINO-2,1,3-BENZOTHIADIAZOLE DERIVATIVES: SYNTHESIS, STRUCTURE AND LUMINESCENT PROPERTIES

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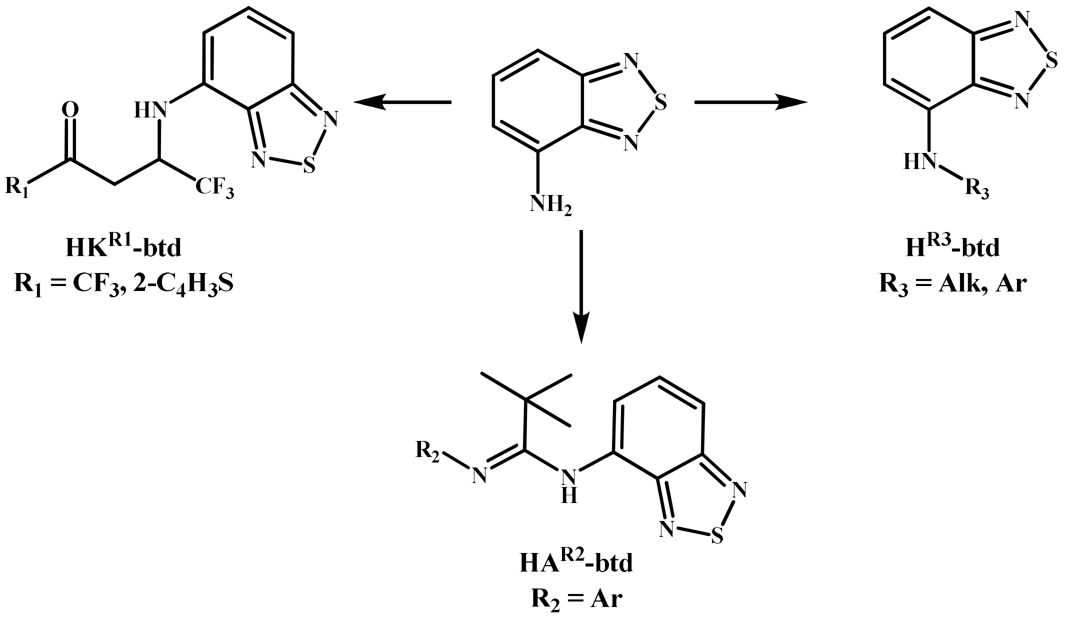
2,1,3-benzothiadiazole (btd) and its derivatives are known to have interesting photophysical and electron-withdrawing properties. [1] These properties are reported to allow using compounds on based 2,1,3-benzothiadiazole as components of dyes, organic light-emitting diodes and as fluorescent markers in biological research. [2] Coordination chemistry of btd derivatives is of particular interest, as it allows expanding the range of their functional properties. For example, the btd derivatives can act as antenna ligands sensitizing luminescence of lanthanides. [3]

One of the promising btd derivatives is 4-amino-2,1,3-benzothiadiazole (NH_2-btd). Main advantages of NH_2-btd are application as a ligand in the coordination chemistry and possibility for its further functionalization. A number of Ag(I), Zn(II), Cd(II) and Ir(III) complexes with NH_2-btd has been prepared and their photophysical properties studied. [3] In the present work, we continue studying NH_2-btd derivatives. A novel compounds have been prepared: ketoimines (HK^{R1}-btd), amidines (HA^{R2}-btd) and secondary amines (HN^{R3}-btd).



HK^{R1}-btd
$R_1 = CF_3, 2\text{-}C_4H_3S$

H^{R3}-btd
R_3 = Alk, Ar

HA^{R2}-btd
R_2 = Ar

The complexation reactions have been studied for Zn(II) and Cu(I). The luminescent properties of organic compounds and the complexes have been discussed. The structures of new compounds were established by single-crystal X-ray diffraction.

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LUMINESCENT BINUCLEAR COPPER (I) COMPLEXES BEARING THREE BRIDGED PYRIDYLPHOSPHOLANE LIGANDS

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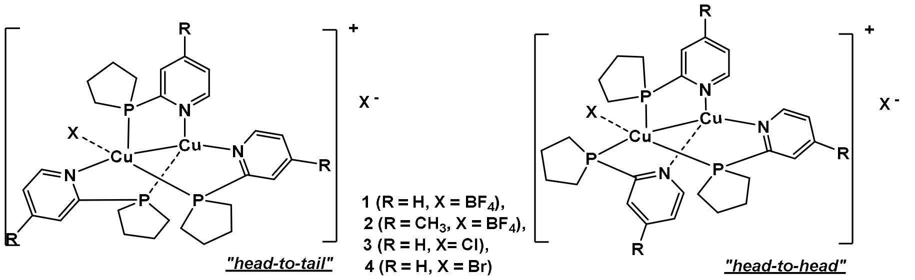
In recent years luminescent copper (I) complexes with P,N-hybrid ligands, particularly pyridylphosphines and their N-heterocyclic analogues, attracted a great interest. Their good stability, comparable low-cost and low toxicity, and high-efficient luminescence make these compounds potential applicants in the area of photofunctional materials [1. 2]. Recently we presented a series of luminescent bi- and tetranuclear copper(I) iodide complexes based on pyridylphospholanes [3]. As a continuation of this research we became interested in exploring the coordination chemistry of pyridylphosholanes with CuCl, CuBr, and $CuBF_4$. Due to less sterically hindrance of pyridylphospholanes, an extensive crowding around metal centers decrease that allow designing three-bridged bimetallic complexes in two isomeric forms *"head-to-tail"* (HT) or *"head-to-head"* (HH) (Scheme 1).



1 (R = H, X = BF_4),
2 (R = CH_3, X = BF_4),
3 (R = H, X= Cl),
4 (R = H, X = Br)

Scheme. 1.

The isomerization processes are rapidly inconvertible and were detected using variable-temperature NMR spectroscopy. At low temperatures in $^{31}P\{H^1\}$ NMR spectra three signals corresponding to two different isomers are observed. Structure of compounds **1**—**4** were also characterized using X-ray analysis. Complexes **1** and **2** were crystallized as HT-isomers, complex – **3** as HH-isomer, whereas complex **4** were crystallized both as HT and HH forms. All complexes were found to be emissive both in solutions and solid state. In solutions (dichloromethane **1**, **2**; acetonitrile **3**, **4**) complexes demonstrate week emission at the blue region of visible spectrum. In solid state at room temperature complexes **1**—**4** emit at the green region of visible spectrum (λ_{em} 520—540 nm). The photoluminescence quantum yields values are range from 10 to 0.28%. The microsecond-scale lifetimes of excited state and the large Stokes shifts (*ca.* 100-150 nm) indicate a triplet nature of emissive state.

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THEORETICAL STUDY OF C – H BOND ACTIVATION BY METAL COMPLEXES WITH MACROCYCLIC LIGANDS IN A REDUCED STATE

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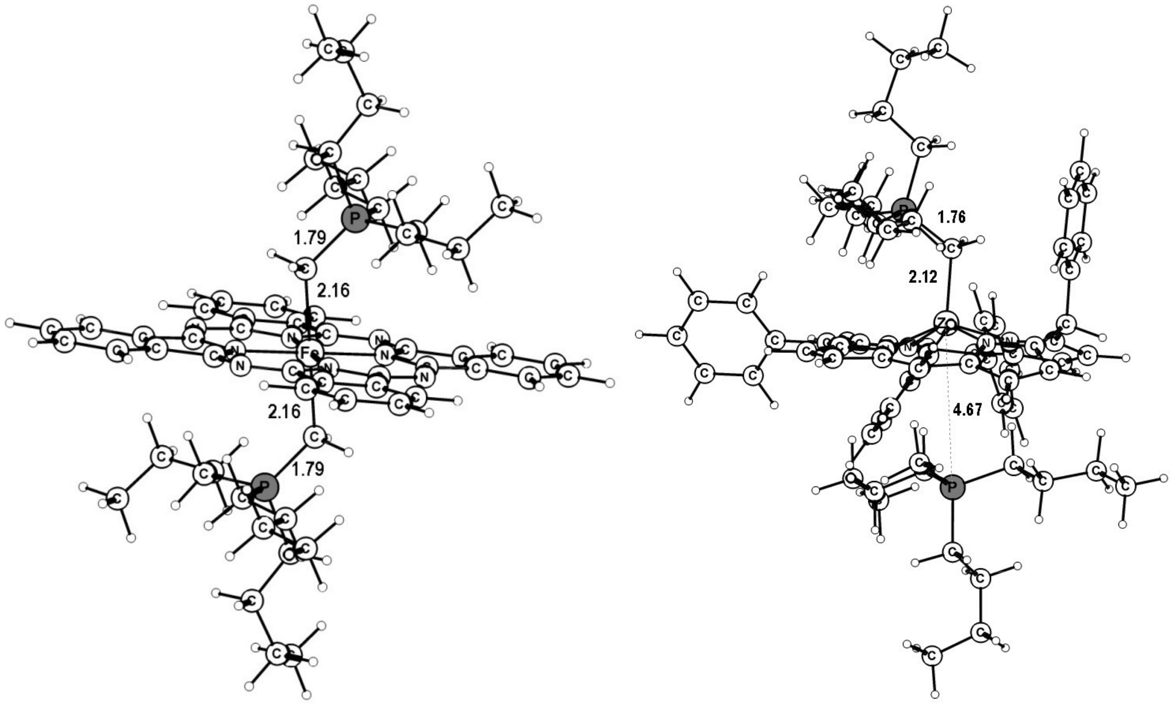
When metal complexes ML with macrocyclic ligands L are reduced to dianions, their basicity significantly increases. With the help of quantum chemical modeling using PBE functional density, the interaction of the complexes Fe and Ni, L = Porph, and Zn, L = $PcPh_4$ in the reduced state with the counterion $[PMe(Bu)_3]^+$ was investigated. The reactions of proton transfer from the methyl group of $[PMe(Bu)_3]^+$ to the macrocycle and a metal atom, accompanied by the coordination of the resulting ylide $P^+(CH_2^-)(Bu)_3$ are considered. The formation of the complex $\{Fe(PorphH)[P^+(CH_2^-)(Bu)_3]\}^-[P(CH_3)(Bu)_3]^+$ with the addition of a proton to the N atom leads to a significant increase in energy by 15.2 kcal/mol. An alternative process ultimately leads to the neutral complex $\{Fe(Porph)[P^+(CH_2^-)(Bu)_3]_2\}$ (see Fig. 1a) and the H_2 molecule with an almost zero total change in the free energy. A similar reaction in the case of M = Ni has a thermodynamic prohibition. In the case of M = Zn, the reaction of the heterolytic cleavage of the C–H bond in the methyl group with the addition of a proton to the meso-atom C (see Fig. 1b) gives a gain of 19.0 kcal/mol. An alternative process with the formation of a complex similar to 1a gives an increase in free energy by 6 kcal/mol. Under coordinating P-C bond in ylide is slightly extended by 0.05-0.08 A. The theoretical results obtained are consistent with experimental observations.



(a) (b)

Fig. 1. Calculated structure of Fe (a) and Zn (b) complexes with ylide ligands.

Acknowledgements - The calculations were performed using the computational capabilities of the Joint Supercomputer Center of RAS

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DIHYDROGEN BONDING ACROSS THE PERIODIC TABLE

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The dihydrogen bond, an interaction between a transition-metal or main-group hydride (M-H) and a protic hydrogen moiety (H-X), is arguably the most intriguing type of hydrogen bond. It was discovered in the mid-1990s and has been intensively explored since then. In this lecture, we will collate up-to-date experimental and computational studies of the structural, energetic, and spectroscopic parameters and nature of dihydrogen-bonded complexes of the form M-H···H-X, as such species are now known for a wide variety of hydrido compounds of main group elements and transition metals.[1-3]

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 transfer (Figure 1) and preparing these bonds for further transformations. The implications of dihydrogen bonding in different stoichiometric and catalytic reactions, such as hydrogen exchange, alcoholysis and aminolysis, hydrogen evolution, hydrogenation, and dehydrogenation, will be discussed.[1-5]

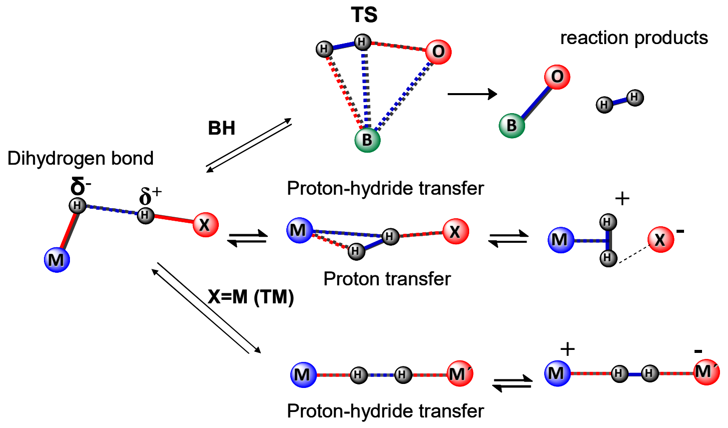

Figure 1

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SYNTHESIS AND REDUCTION PROPERTIES OF LANTHANIDE COMPLEXES (HO, DY) WITH BULKY O-IMINOBENZOQUINONE LIGAND

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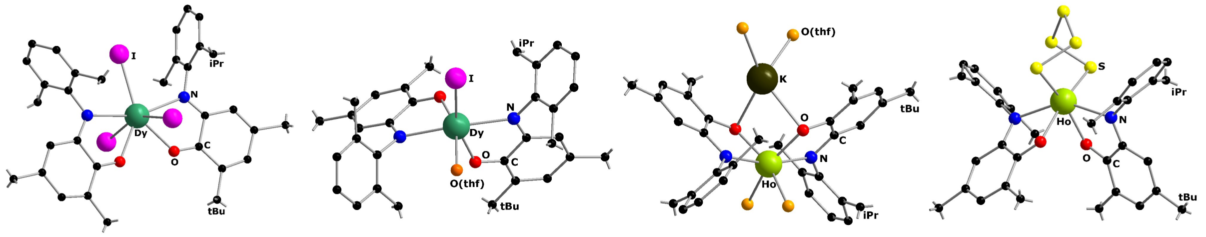
Ortho-iminobenzoquinones are much less explored redox-active ligands as compared to o-quinones (dioxolenes). In complexes iminoquinones can be in three forms: neutral iminoquinones (IQ), iminosemiquinone radical anion (ISQ^{-}) and amidophenolate dianion (AP^{2-}). Steric (and partly electronic) influence of these ligands can be tuned by changing the substituent on the nitrogen atom. Commonly, iminoquinones have lower oxidizing potentials compared to related quinones, which can lead to the compounds with unusual oxidation state of metal and ligand. By now, there are only few lanthanide complexes with this type of ligand are known, especially those with known structures.[1] These complexes can possess interesting reactivity, structural and magnetic properties especially if several paramagnetic (and redox) iminoquinone centers are present.

We describe synthesis, structures, and some properties of lanthanide complexes (Dy, Ho) with the ligand 4,6-di-*t*-butyl-N-(2,6-diisopropylphenyl)-*o*-iminobenzoquione (dippIQ). The complexes with neutral iminoquinone $[LnI_3(dippIQ)_2]$ (**1**) are unstable in solutions because of the presence of neutral dippIQ ligand. Reduction with two equivalents of KC_8 results in formation of iminosemiquinone derivatives $[LnI(dipp\text{-}ISQ)_2(thf)]$ (**2**). Reduction of complex **1** with 3 equivalents of KC_8 results in mixed-ligand complex $[Ln(dipp\text{-}ISQ)(dipp\text{-}AP)(thf)_2]$. Finally, reduction of (**1**) with 4 equivalents of KC_8 results in formation of amidophenolate complex $[\{K(thf)_2\}\{Ln(dipp\text{-}AP)_2(thf)_2\}]$ (**3**). Thus, all three types of reduced complexes, which have 2, 3, or 4 electrons "in store", can be isolated. The amidophenolate complexes can react with elemental chalcogens (E = S, Se) to form molecular pentachalcogenides $[K(18\text{-}crown\text{-}6)(thf)_2][LnS_5(dipp\text{-}ISQ)_2]$ (**4**), while the reaction with elemental tellurium proceeds only with additional activation. All obtained compounds were characterised by means of IR-spectroscopy, CHN analysis and X-ray diffraction.



(1) (2) (3) (4)

Figure 1. Crystal structures of complexes: $[DyI_3(dipp\text{-}IQ)_2]$ **(1)**, $[DyI(dipp\text{-}ISQ)_2(thf)]$ **(2)**, $[K(thf)_2][Ho(dipp\text{-}AP)_2(thf)_2]$ **(3)**, $[K(18\text{-}crown\text{-}6)(thf)_2][HoS_5(dipp\text{-}ISQ)_2(thf)_2]$ **(4)**

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OUT OF SHADOW: NEW ASPECTS OF CHEMISTRY OF CLUSTER IODIDES OF GROUP 5-7 TRANSITION METALS

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As a rule, the iodides of transition metals attract much less attention than their chloride and bromide analogues, even though a book dealing only with metal iodides has been published almost half a century ago [1]. The current interest in Mo and W lower iodides came in the wake of pioneering works of H. Gray [2], who has shown that octahedral molybdenum cluster complexes with the general formula $[\{Mo_6X^i_8\}Y^a_6]^n$, where X is an inner ligand (Cl, Br or I) and Y is an outer (apical) organic/inorganic ligand have superb photoluminescent properties. It turned out that cluster iodides of the general formula $[\{M^{II}_6(\mu_3\text{-}I)_8Y_6]^n$, where M is Mo or W, and Y is an outer (apical) organic/inorganic ligand, have superb photoluminescent properties, much superior to the bromide and chloride analogues in terms of quantum yield and phosphorescence time [3,4]. Moving to the left and to the right in the Periodic Table, we encounter pother fascinating cluster iodides. The second part of the lecture will deal with new aspects of chemistry of Ta_6I_{14}, Nb_6I_{11}, Re_3I_9 which show easy and unexpected transformation of their cluster cores into neutral $[Nb_6I_8L_6]$ or $[Re_3I_8L_2]$ derivatives. Prospects of making X-ray contrast agents with the $[Ta_6I_{12}L_6]^{2+}$ clusters will be discussed [5]. Search for new cluster iodides has been resumed by other groups and yielded a Pandora box of tungsten cluster iodides [6]. In this project it is to be extended to Ru/Rh and Os/Ir iodides.

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A COMPUTATIONAL AND EXPERIMENTAL STUDY OF METAL-DIOXOLENE COMPLEXES WITH PYRIDINOPHANE LIGANDS

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Elucidation of the electronic lability in metal complexes that undergo spin crossover (SCO) or valence tautomeric (VT) rearrangements remains a fascinating challenge for inorganic chemists. These compounds can be reversibly interconverted between forms with different chemical and physical properties upon application of a stimulus, such as heat, which makes them of interest for future applications in displays, sensors, photoresponsive devices or molecular electronics and spintronics [1].

One of the widespread types of coordination compounds manifesting VT behaviour implies the salt-like complexes comprising redox-active ligand and tetradentate macrocyclic nitrogen-containing base [2, 3]. The uniqueness of such molecules consists in strong dependence of the mechanism chosen by a molecule for the occurrence of spin transition (VT [2] or SCO [3]) on the structure and properties of the tetraazamacrocyclic ligand.

Compounds [Co(L-N_4R_2)(dbdiox)](BPh_4) (L-N_4R_2 = N,N'-di-alkyl-2,11-diaza[3.3]-(2,6)pyridinophane, R = ^{i}Pr (**1**), Et (**2**); dbdiox = 3,5-di-tert-butyldioxolene) and [M(L-N^iPr_2)(dbdiox)](BPh_4) (M = Mn (**3**), Fe (**4**)) have been synthesized and investigated. Single crystal X-ray diffraction data for all compounds at liquid nitrogen temperatures indicate trivalent metal cations and di-tert-butylcatecholate ($dbcat^{2-}$) dioxolene ligands. Above 350 K, **1** exhibits an increase in magnetic susceptibility, suggesting the onset of a VT interconversion from the low-spin Co(III)-dbcat to the high-spin Co(II)-dbsq ($dbsq^-$ = di-*tert*-butyl-semiquinonate) that is incomplete up to 400 K. In solution, variable temperature electronic absorption spectra and Evans NMR method magnetic susceptibility data for **1** indicate reversible VT interconversions in several solvents, with the transition temperature varying with solvent. Variable temperature electronic absorption spectra are temperature-invariant for **3** and **4**, while spectra for **2** in dichloromethane suggest the onset of a VT transition at the highest temperatures. Density functional theory calculations on compounds **1–4** and literature analogues [4] provide key insights into the relative energies of the different electromeric forms and the possibilities for VT versus SCO interconversions in this family of complexes.

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SYNTHESIS AND PROPERTIES OF IRON, COBALT AND NICKEL HYDRIDES

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In recent years, with the progress of experimental technology and people's expectation of green chemistry, the properties of transition metal hydrides and their applications in catalytic reactions have attracted more and more attention. Among the different transition metal hydrides with good catalytic activity, there are monohydrides, dihydrides and polyhydrides. The related catalytic processes include reductive hydrogenation or oxidative dehydrogenation, such as the reduction of triple bonds (C≡N and C≡C) and double bonds (C=O, C=N and C=C). At the same time, transition metal hydrides are closely related with the preparation of H_2 (decomposition of water) and storage (decomposition of HCOOH) in C1 chemistry. Therefore, the study on preparation, characterization and catalytic activities of transition metal hydrides is not only of great significance to synthetic chemistry, but also of great impetus to green chemistry and sustainable development.

So far, there are few known hydrides with iron, cobalt and nickel as central metal atoms, and few reports have been published on their catalytic applications. In recent years, we have synthesized a variety of hydrides of iron, cobalt and nickel by activating X-H bonds (X = C, Si, N and O) in a series of ligands with electron-rich iron, cobalt and nickel complexes supported by trimethylphosphine, and systematically studied the properties and catalytic activities of these metal hydrides. The results are of guiding significance for explaining the mechanism of catalytic reaction and designing excellent catalyst.

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LANTHANIDE TRIS- AND TETRAKIS COMPLEXES WITH SUBSTITUTED 4-ACYL-PYRAZOL-5-ONES – SYNTHESIS, STRUCTURE AND LUMINESCENT PROPERTIES

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Acylpyrazolonate ligands were extensively used for the preparation of variety of complexes with *d*-elements and selected lanthanides [1]. Two main type of complexes with lanthanides were obtained for these ligands – neutral tris complexes (**I**) and anionic tetrakis complexes (**II**), bearing cation on the outer sphere of complex. In some cases free acids with H_3O^+ or $(H_5O_2)^+$ cations were isolated. The coordination polyhedron for Ln^{3+} in tetrakis complexes is represent by perfect square antiprism, and such environment is favorable for manifestation of SMM properties.

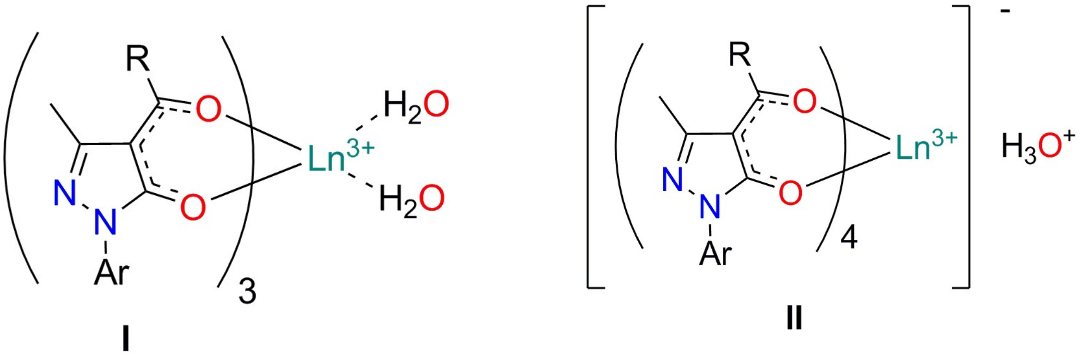

Figure 1. Chemical structures of lanthanide tris (**I**) and tetrakis (**II**) complexes with acylpyrazolone ligand.

Unfortunately, known synthetic pathways to these complexes are unreliable and often led to unpredictable result. We have investigated complicated temperature-depended equilibrium between tris and tetakis species in solutions and elaborated direct pathways to both types of complexes. Besides, some aspects of crystal structures and luminescent properties of lanthanide complexes with different composition will be discussed in the presentation.

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COORDINATION COMPOUNDS OF LANTHANIDES WITH SCHIFF BASE LIGAND

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The design and synthesis of single molecule magnets (SMMs) containing lanthanide atoms are currently of great interest in chemistry of coordination compounds. Such magnetic molecules can be potentially used for creation of magnetic storage devices with high-density information, quantum computer, spintronics and magnetocaloric materials [1]. Considerable attention is paid to the synthesis of molecules containing ions of lanthanides [2], mainly due to the presence of large magnetic moments and significant magnetic anisotropy.

We synthesized the series of new mononuclear complexes of Ln^{III} (Dy, Tb, Er, Yb, Gd, Ho) with Schiff base obtained by the condensation of 2-pyridinecarbaldehyde and 4-pyridinecarboxylic acid (HL). HL is an N,N,O-tridentate chelating ligand.

It was found that varying of ratio of initial metal salts of Ln^{III} : HL and presence/absence of triethylamine resulted in the formation of complexes with different contain and structure. The complex $[Ln(H_2O)(MeOH)(NO_3)_2(HL)]$ (Ln = Dy^{III} (**1**), Tb^{III} (**2**), Er^{III} (**3**), Yb^{III} (**4**), or Ho^{III} (**5**)) was formed in the reaction of $Ln(NO_3)_3{\cdot}5H_2O$ with HL in methanol at the 1 : 1 reagent ratio. The changes in the ratio of the initial reagents (Ln : HL = 1: 2.5) with simultaneous introduction of Et_3N in the reaction mixture led to the formation of a complex with two anions of the ligand - $[Ln(MeOH)(NO_3)(L)_2]{\cdot}MeCN$ (Ln = Dy^{III} (**6**), Tb^{III} (**7**) or Ho^{III} (**8**)). Crystallization of compounds **6** and **7** from the mixture of methanol-acetonithrile allowed to carry out new solvate form of the complex - $[Ln(MeOH)(NO_3)(L)_2]{\cdot}MeOH$ (Ln = Dy^{III} (**9**) or Tb^{III} (**10**)). The use of $Ln(OAc)_3{\cdot}4H_2O$ instead of $Ln(NO_3)_3{\cdot}5H_2O$ while maintaining the Ln^{III}: HL ratio of 1: 2.5 resulted in third type of complexes - $[Ln(L)_3]{\cdot}2H_2O$ (Ln = Dy^{III} (**11**), Tb^{III} (**12**) Er^{III} (**13**), Ho^{III} (**14**) or Yb^{III} (**15**)).

All new complexes were structurally characterized. Magnetic behaviour (AC and DC) of compounds **1-7**, **9**, **11-12** were studied. According to magnetic data, compounds (**1**), (**2**), (**7**)-(**11**) are SMMs. All these data will be discussed in the presentation.

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PALLADIUM SUPPORTED ON FUNCTIONALIZED POLYSILOXANES: SIMPLE AND REUSABLE CATALYSTS FOR C-C COUPLING

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Immobilized palladium-based catalysts designed for the C-C bond formation reactions, have been attracting more and more attention because of increasing environmental requirements. The main advantage of immobilization consists in the efficient separation of the catalyst from products formed in catalytic reaction. As a result, the minimization of the metal content in the final organic product can be achieved. This aspect is very important in pharmaceutical applications, where the organic compound is predominantly in contact with living organisms.

Different materials can be employed as supports for palladium catalysts, such as porous inorganic oxides or organic polymers. Polysiloxanes can be also considered due to their excellent chemical and thermal stability. They are non-toxic and due to their rather weak interactions with components of the catalytic systems they do not change the original reactivity. Moreover, polysiloxanes can be differently functionalized by P-, N- or S- organic groups to provide bonding centers for palladium. Sensible functionalization provides better control over the distribution of the metal on the surface of the support, which is often very important for catalytic activity and selectivity.

Considering the fact that phosphorus ligands can create some drawbacks in the environment, we concentrated our efforts on N-functionalized polysiloxanes. Palladium catalysts supported on polysiloxanes with imidazole and triazole groups were successfully applied in Suzuki-Miyaura coupling leading to non-symmetric biphenyls. In these reactions very good recyclability has been obtained although the separation step has been rather difficult due to the very small diameter of polysiloxane beads. It should be also noted that the most active catalysts containing Pd(0) nanoparticles, have been formed in situ from the immobilized Pd(II) precursor. Advantageously, imidazole and triazole groups bonded efficiently both palladium forms contributing in the catalytic process, namely Pd(II) and Pd(0).

In order to improve separation process we selected for further studies palladium supported on aminopropyl-functionalized polymethoxysiloxane in the form of microspheres. With this catalyst excellent results have been obtained in Suzuki-Miyaura coupling as well as in carbonylative coupling producing diarylketones already at 1 atm CO.

In the next generation of polysiloxane microspheres, imidazole and pyridine functions have been employed for bonding of palladium designed for Heck coupling. In reaction of 3-buten-2-one with iodobenzene the corresponding ketone was obtained with both catalysts. However recycling was better for imidazole-functionalized support. Even bigger difference between both catalysts was observed in the tandem Heck coupling of 3-buten-2-ol with iodobenzene leading to 4-phenylbutanone.

In conclusion, it was found that functional groups bonded to polysiloxane modified the catalytic activity of the immobilized palladium. In addition, the morphology of the polymer played an important role in stability and recycling of palladium catalyst.

SYNTHETIC ELECTROCHEMISTRY IN MODERN ORGANOMETALLIC AND ORGANOELEMENT CHEMISTRY

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The creation and design of new molecules and materials bearing unique electrochemical, magnetic and catalytic properties are one of key research priorities of modern synthetic chemistry. The combination of synthetic electrochemical techniques and coordination chemistry can be considered as a new powerful tool in preparation of new types of mono- and polynuclear complexes, metal-organic frameworks (MOFs) and nanosized material bearing practically useful electrochemical, magnetic and catalytic properties. The mild conditions, single-stage process, cyclic regeneration of the electrochemical catalyst, and convenient and relatively inexpensive form of the energy used are main advantages of the electrochemical methods.

Herein, we present our results obtained by using of the electrochemical techniques in application towards preparation and investigation of the properties of various types of organometallic [1,2] and organophosphorus species [3], including magnetically active dinuclear nickel [4] and cobalt [5] complexes and high reactive phosphine oxide H_3PO which is very promising intermediate for synthetic phosphorus chemistry [6]. Recent examples of the electrochemical methods are represented by preparation and *in situ* observation by magnetic resonance of superparamagnetic cobalt, nickel and iron nanoparticles [7].

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IRON (II) COMPLEXES WITH VARIOUS N, P-DONOR LIGANDS: SYNTHESIS, STRUCTURE, MAGNETIC PROPERTIES

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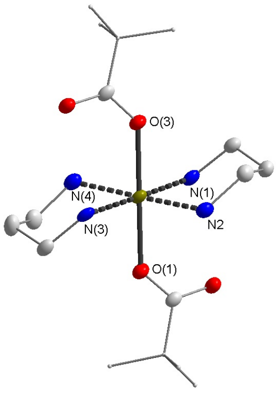
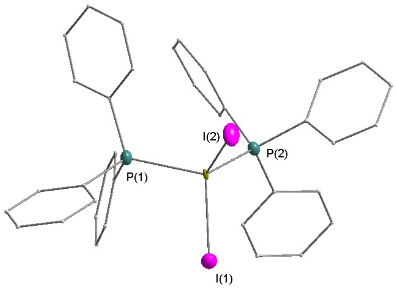
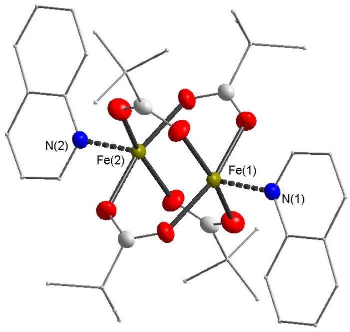
Currently, chemists face the challenge of obtaining new functional materials that can be used in the manufacture of devices for storing huge amounts of data. Such material can be prepared using substances with the properties of Single Molecular Magnet (SMM). Recently, many polynuclear compounds with the properties of SMM[1] have been synthesized. Such compounds are mainly obtained by the solvothermal method with minimal synthetic control. We believe that it is easier to manage the coordination sphere of a single nucleus, rather than an ensemble of ions. The first example of a mononuclear 3d SMM was the iron (II) $K[(tpa^{Mes})Fe]$[2] complex. Iron (II) -based monomolecular magnets may be promising materials due to the specific electronic structure of the ions of this metal.

In this work, we present the synthesis of a series of Iron (II) compounds with various N-, P-donor ligands. Some of the obtained compounds demonstrate SMM properties. Electrochemical measurements have been made for some compounds. We compared the obtained results with known SMMs of a similar structure based on cobalt (II).

Synthesis of the compounds, magnetic and electrochemical properties will be discussed in the report in details.







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SMALL-MOLECULE ACTIVATION STUDIES OF METAL–METAL-BONDED COMPOUNDS SUPPORTED BY ALPHA-DIIMINE AND RELATED LIGANDS

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Metal–metal bonded compounds with low-valent metal centers have been an active current research topic because such compounds often exhibit specific reactivity towards small molecules, affording novel adducts/complexes that may be relevant to the key intermediates of some catalytic or stoichiometric reactions. Moreover, such species with the 'stabilized' subvalent metal ions may actually 'activate' the main-group elements, endowing them reactivities that are normally only seen for transition metals.[1]

We have been interested in the construction of metal–metal bonds by using α-diimine and related *N,N*-donor ligands, which (in their reduced mono- or di-anionic form) have proven to be excellent supporting ligands for low-valent metal ions. A series of dimetallic [LM–ML] compounds with both transition and main-group metals have been synthesized and their reactions with different unsaturated organic molecules have been studied.[2] Various transformations of small molecules, including insertion, cycloaddition, different bond cleavage and bond formation, and novel coupling modes, etc., as well as rich coordination modes in the corresponding metal complexes have been observed. Notably, in some cases the redox noninnocent ligands can serve as an electron reservoir and participate in the reaction with small molecules. The synthesis and reactions of some metal–metal-bonded compounds (e.g. Mg, Al, Ga, etc.) are presented herein.

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REDUCTIVE LINEAR- AND CYCLO-TRIMERIZATION OF ISOCYANIDES BY AN AL–AL-BONDED COMPOUND

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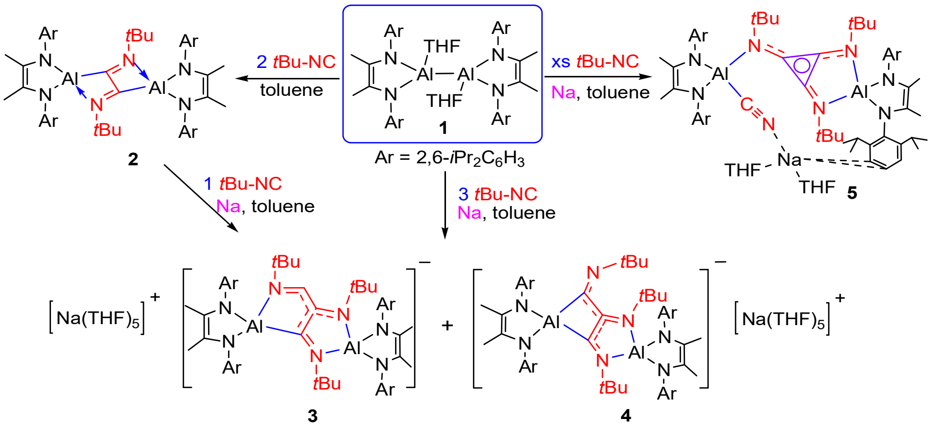
The aIsocyanides are valuable C1 building blocks for the synthesis of N-containing compounds. The oligomerizations of **more than two** isocyanide molecules are rare, although a number of 'reductive dimerizations' of isocyanides have been reported. A particularly interesting type of these couplings is the cyclo-oligomerization to form C_n rings. While the formation of deltate ($C_3O_3^{2-}$)[1] and squarate ($C_4O_4^{2-}$)[2] through U(III)-mediated cyclo-tri/tetramerization of CO has been realized, more recently, the isoelectronic isocyanides were also found to undergo reductive cyclo-tetramerization to afford the squaramidinate $[C_4N_4R_4]^{2-}$ when promoted by the quintuply bonded Cr(I) species $[^{H}L^{iPr}Cr]_2$.[3] Nonetheless, it should be noted that analogous cyclo-trimerization of isocyanides to yield the smallest member of the family, i.e. deltamidinate $[C_3N_3R_3]^{2-}$, has not yet been reported.



Scheme 1. Synthesis of complexes 2–5 from 1.

Herein we demonstrate the excellent reactivity of the low-valent Al^{II}–Al^{II}-bonded compound **1**, which can readily mediate reductive couplings of isocyanides, either dimerization or linear- and cyclo-trimerization, under mild conditions (Scheme 1). The linear trimerization products $[Na]^+[LAl\{(tBuNC)_3\}AlL]^-$ (**3** and **4**) show a tri-anionic radical core $\{(tBuNC)_3\}^{3-\bullet}$, while the cyclo-trimerization product **5** features a unique aromatic C_3 ring $[C_3N_3(tBu)_3]^{2-}$ (deltamidinate).

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METAL COMPLEX AND PHOTOREDOX CATALYZED INERT BOND FUNCTIONALIZATION

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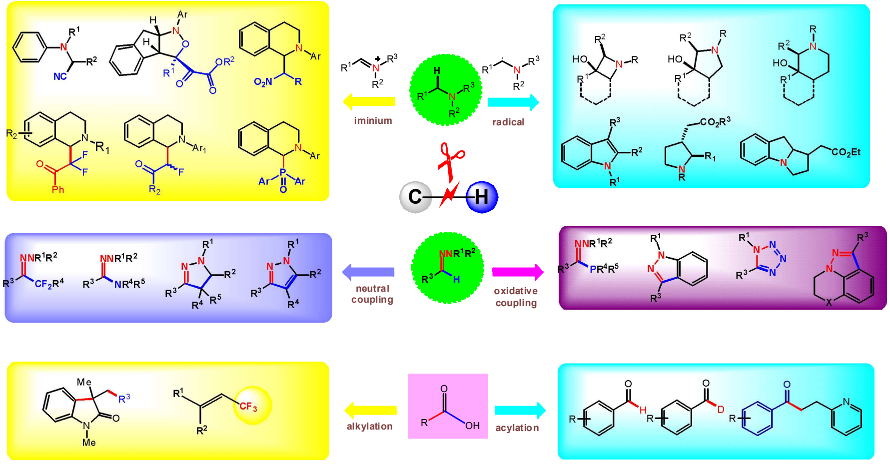
Metal complex and visible-light photoredox catalysis has witnessed rapid development and attracted considerable attention in both academia and industry. Focused on the interests of the inert bonds cleavage and functionalization, we have developed variety of effective reactions for organic synthesis.[1] With the C(sp^3)-H bond functionalization adjacent to nitrogen atom, we have discovered a tandem C-H and C-N bond sequence cleavage to rationally construct bicyclic isoxazolidine skeleton in only one step. By exploiting the aminyl radical polar crossover (ARPC) strategy, we successfully achieved C(sp^2)-H difluoroalkylation of aldehyde-derived hydrazones. This intriguling result was later applied in the amination of hadrazones and several cascade cyclization reactions for the synthesis polycyclic compounds. We have also discovered the direct deoxygenation of carboxylate acids as acyl sources with triphenylphosphine, affording diverse ketones and deuterated aldehydes.



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Organometallic Chemistry Around the World

(7th Razuvaev Lectures)

Poster Presentations

SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS VIA C–H ACTIVATION FOR PHOTOACTIVE MATERIALS

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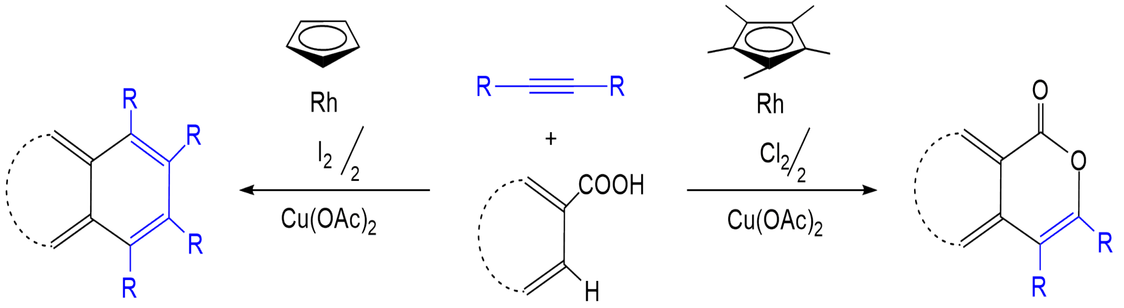
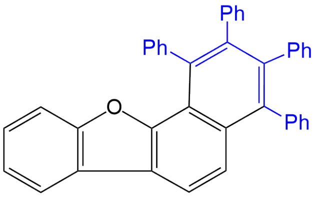
Polycyclic aromatic hydrocarbons (PAHs) have found widespread applications in optoelectronics, bioimaging, and catalysis [1]. Of our special interest is the use of PAHs in the OLED technology. Significant recent impetus in synthesis of PAHs was gained by C–H activation of aromatic compounds by the cyclopentadienyl rhodium complexes $[(C_5R_5)RhCl_2]_2$ [2]. In the present work, we demonstrated crucial influence of substituents in the cyclopentadienyl ring on chemoselectivity of oxidative coupling of aromatic carboxylic acids with internal alkynes. In particular, the use of the pentamethyl complex $[Cp^*RhCl_2]_2$ as a catalyst leads to isocoumarins as a result of incorporation of one alkyne molecule, while the parent non-methylated derivative $[CpRhI_2]_2$ facilitates decarboxylation of the acid and annulation of two alkyne molecules to give the naphthalene moiety.

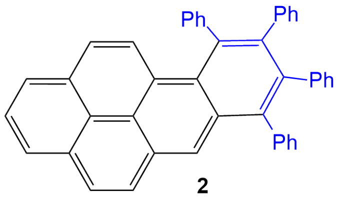


The compounds prepared have rich optical properties with strong Stokes shifts of fluorescence emission.



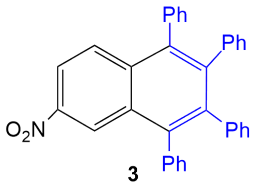
1

$\lambda_{abs}/\lambda_{em}$ = 270/380 nm
110 nm Stokes shift



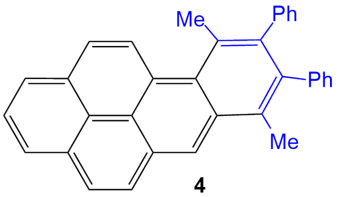
2

$\lambda_{abs}/\lambda_{em}$ = 310/430 nm
120 nm Stokes shift



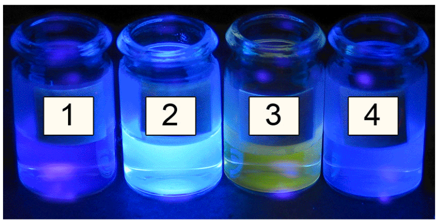
3

$\lambda_{abs}/\lambda_{em}$ = 270/570 nm
300 nm Stokes shift



4

$\lambda_{abs}/\lambda_{em}$ = 310/420 nm
110 nm Stokes shift



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SYNTHESIS OF NEW STERICALLY HINDERED CATECHOLS AND O-QUINONES VIA O-QUINONEMETHIDES

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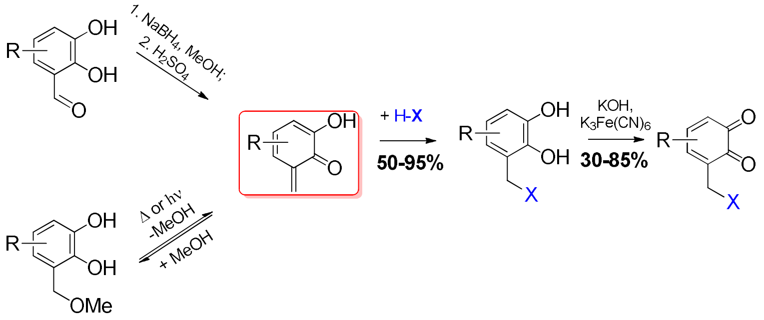
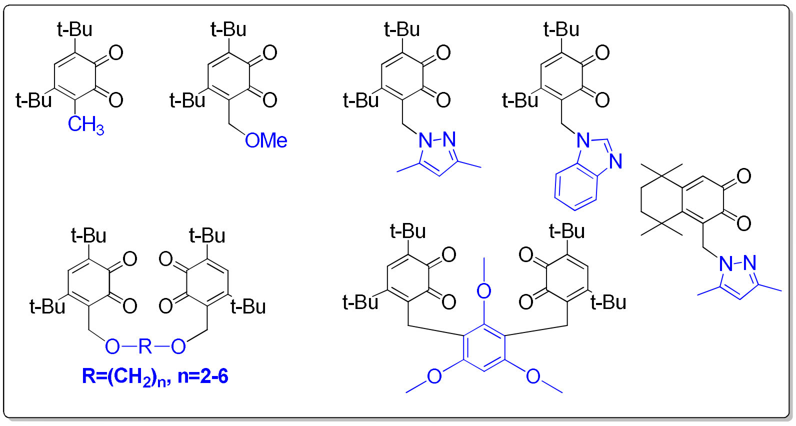
In this thesis we report to the synthesis of monomeric and oligomeric substituted 3,5-di-tert-butylcatechols [1-5] and 5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphtodiol-2,3 and their o-quinones – new redox-active ligands, new inhibitors and photoinitiators of free radical polymerization. The key stage of these syntheses is generation of spatial hindered o-quinonemethide and its reaction with monomeric and oligomeric O, N, C-nucleophiles.





This work was financially supported by Grant of President of Russian Federation (MK-2351.2019.3).

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AROMATICITY SUPPRESSION BY INTERMOLECULAR COORDINATION. OPTICAL SPECTRA AND ELECTRONIC STRUCTURE OF CARBENE ANALOGS WITH AMIDOPHENOLATE LIGAND

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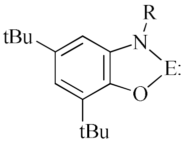
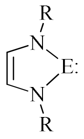


I



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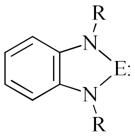

III

E = C, Si, Ge, Sn, Pb
R = Me, ^{t}Bu, CH$_2{}^{t}$Bu

To study aromaticity of 14th group N-heterocyclic carbenes tBuAPE (**I**) (AP- amidophenolate) in comparison with that of compounds **II** [1] and **III** [2], the experimental optical (UV-vis, Raman) and computational magnetic (NICS, GIMIC) criteria of aromaticity were used. Dimeric structure of compounds **I**(Sn) and **I**(Pb) [3,4] due to intermolecular coordination E-N and monomeric structure of **I**(Ge) [5] were reported previously. It was shown that dimerization leads to disappearance in the UV-vis spectrum of the long-wavelength absorption band corresponding to π-π* transition (Fig.1) and to the lack of preresonant enhancement in the Raman spectra (Fig. 2). The reason of these phenomena is suppression of 10π aromaticity in the bicycle due to partial filling of the vacant p_z orbital of E atom in dimers. The monomeric forms of compounds **I** are aromatic according to all the criteria used, their degree of aromaticity is similar to that of carbenes **III** [2].

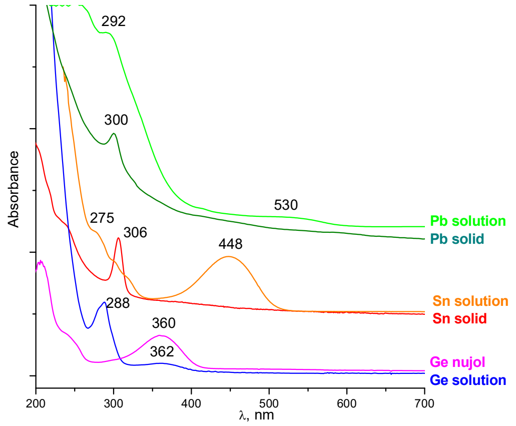

Fig.1. UV-vis spectra of compounds **I** as solids and in solution.

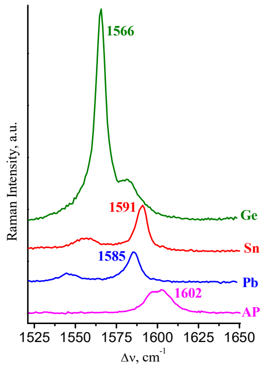

Fig.2. Raman spectra of solid compounds **I**.

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BLUE DIGERMENE (tBu$_2$MeSi)$_2$Ge=Ge(SiMetBu$_2$)$_2$: ITS ELECTRONIC STRUCTURE AND CONFORMATIONAL ISOMERISM

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The structure of digermene (tBu$_2$MeSi)$_2$Ge=Ge(SiMetBu$_2$)$_2$ (**1**) was investigated by experimental (Raman and UV-vis) as well as computational (NCA, TD DFT and QTAIM) methods. Some digeremenes were known to undergo dissociation to corresponding germylenes [1,2]. In contrast, temperature-dependent Raman and UV-vis spectra have demonstrated that **1** does not dissociate on heating either to 120 °C as a solid or to 80 °C in solution, thus preserving the integrity of its double Ge=Ge bond. This is in line with calculated thermodynamic parameters of this reaction: $\Delta H = 25.1$ and $\Delta G = 8.3$ kcal/mol. Raman and NCA results allowed estimation of the region of the νGe=Ge vibrational frequency of digermenes as 270-340 cm^{-1}. When illuminated with a red laser beam of enhanced power (>5mW), the solid **1** turns irreversibly from blue to orange-red, the colour transformation is followed by disappearance of the νGe=Ge Raman band. This process is evidently photodissociation caused by proximity of the red laser wavelength 632.8 nm to the intrinsic absorption of **1** at 616 nm. Temperature dependence of the Raman spectrum has revealed conformational isomerism in solid digermene **1** due to hindered rotation about the Ge-Si bonds, the conformers differing in mutual disposition of Me and bulky tBu groups.

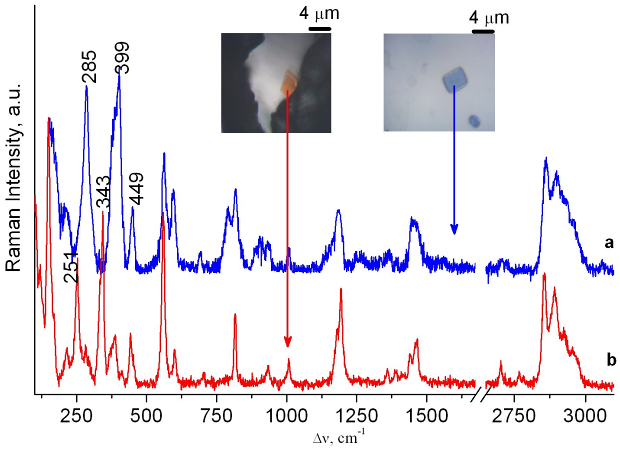

Fig.1. **a**. Initial Raman spectrum of solid **1** at room temperature; **b**. after illumination.

Acknowledgements - The authors acknowledge partial financial support from the Presidium of the Russian Academy of Sciences (program # 0085-2019-0008).

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HETEROLIGAND YTTERBIUM-ERBIUM COMPLEXES AS POTENTIAL UP-CONVERSION MATERIALS

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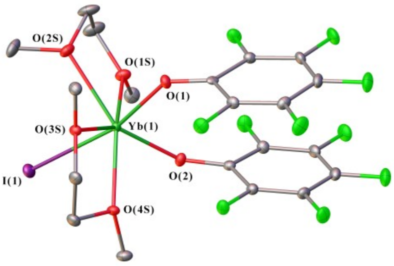
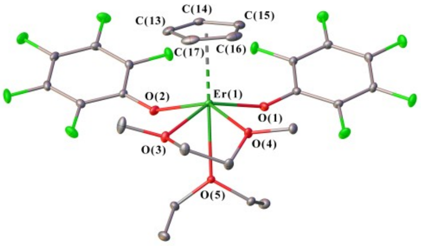
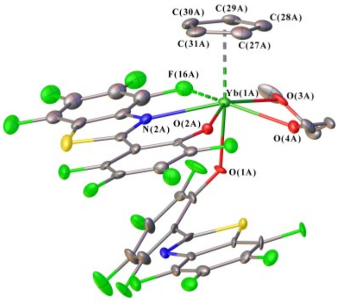
One of the urgent tasks in modern medicine and biology is the search for new luminescent substances for biovisualization and diagnostics. A possible solution of the problem is the use of up-conversion phosphors (emitters with a reverse Stokes shift). However, due to the hard requirements for such materials — the existence of a metastable excited state with a long lifetime and efficient intramolecular energy transfer — the number of such systems is extremely limited. All up-conversion materials known today are inorganic substances based on lanthanides, some of which have stable metastable states and have luminescence in a wide spectral range.

In search of new organo-metallic up-conversion materials, we have synthesized heterobimetallic heteroligand Yb-Er complexes $(C_6F_5O)_2Yb[\mu\text{-}(CF_3)_2CHO]_2Er(C_6F_5O)_2$ and $\{(SON^F)_2Er[\mu\text{-}(CF_3)_2CHO]_2Yb(SON^F)_2\}_x$ ($HSON^F$=2-(3,4,5,6-Tetrafluoro-2-hydroxyphenyl)-4,5,6,7-tetrafluorobenzothiazole). The compounds were obtained by the reaction of the iodo derivatives $LnI(OC_6F_5)_2$ (Ln = Yb, Er) or the cyclopentadienyl derivatives $LnCp(L)_2$ (Ln = Er, Yb; L = C_6F_5O, SON^F) with $[(CF_3)_2CHO]K$.in the ratio of 1: 1: 2 in THF solution. Molecular structure of the products was established with X-ray diffraction analysis.







The formation of the complexes was confirmed by MALDI spectrometry data. When excited by a laser with λ = 405 nm at 300 K, the compounds generated intense emission of Yb^{3+} ions (985 nm, transition $^2F_{5/2}$ $^2F_{7/2}$) and weak luminescence of Er^{3+} at 1540 nm (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$). Time-resolved PL excitation spectra confirmed the presence of energy transfer from ytterbium to erbium. However, the up-conversion phenomenon was not observed probably because too short lifetime of the excited state of erbium. At present, attempts are being made to modify the ligands in the complexes in order to increase the efficiency of energy transfer of Yb✹Er and increase of lifetime of metastable state of Er^{3+}, which is necessary for the implementation of the up-conversion process.

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GROUP 11 METAL PYRAZOLATES COMPLEXES WITH BIDENTATE PHOSPHORUSCONTAINING LIGANDS

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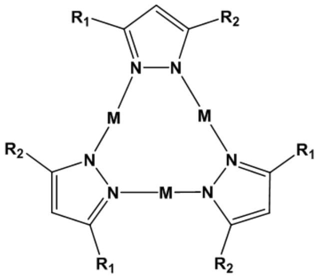
Copper(I) and silver(I) pyrazolates represent an important class of coordination compounds used in numerous fundamental areas, such as acid-base chemistry, metallophilic bonding, supramolecular assemblies.[1] It is well known that macrocyclic metal pyrazolates form stable complexes with π-bases such as arenes or sandwich compounds.[2] This class of compounds possesses high potential for producing of the light emitting materials. The ability to control photoemission properties arises due to the variation of the metal atom, substituents in the pyrazolate ligand and complexation with a wide range of bases. For example, complexes of macrocycles with organophosphorus compounds show green-blue emission in solution and solid state with high quantum yields.[3,4]



Here we report the study of complexation of copper(I) and silver(I) pyrazolates with bisphosphines ($HRC(P(Cy)_2)_2$, R=H, Ph) and pyridine-phosphines ($PyPPh_2$, $PyCH_2PPh_2$). Coordination of bases leads to the macrocycles bending along the M···M axis up to 105°. Complexes exhibit bright phosphorescence in both solution and solid state.

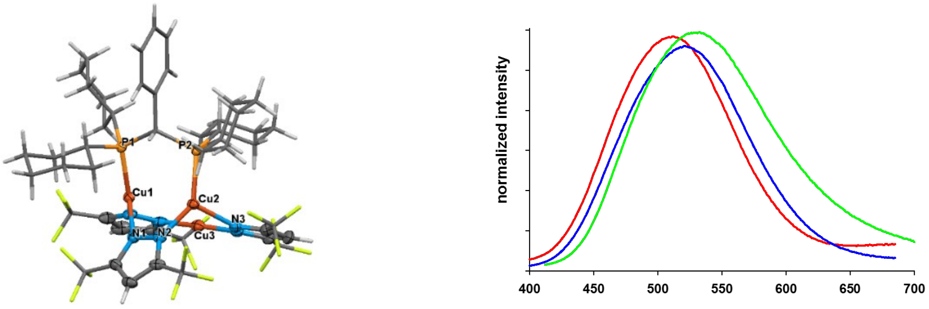


Figure 1. Structure of complex $[CuPz]_3(CPhH(P(Cy)_2)_2)$ (left) and normalized emission spectra of solid samples copper complexes at RT.

This work was financially supported by the Russian Science Foundation (project 19-73-20262)

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TRANSITION METAL COMPLEXES BASED ON FERROCENYL-CONTAINING O-IMINOPHENOLS: SYNTHESIS, STRUCTURE AND ELECTROCHEMICAL PROPERTIES.

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In coordination chemistry, the ferrocene moiety plays a significant role as a backbone or substituent in ancillary ligands due to the specific and unique geometries provided by ferrocene group; and its electronic (redox) properties, whereby the possibility of switching the redox state of the ferrocene backbone gives potential access to control of metal centre and also makes ferrocene to be promising object for the study of electron transfer processes.

The ligands derived from ferrocene and o-iminophenols were reported to be very prospective Schiff base ligands for transition metal complexes which can be quite easily modified from the viewpoint of electronic and steric properties. Systems based on the transition metal complexes with redox-active quinoid type (capable of reversible oxidation or reduction in the metal coordination sphere) and ferrocene-containing ligands are proven as promising systems in terms of charge-transfer interactions and in particular studying of intramolecular electron-transfer reaction of a donor-acceptor-linked system.

In the present paper we report on the synthesis and investigation of the structure and electrochemical properties of nickel, cobalt(II) complexes based on Schiff bases containing ferrocene-aldimine substituent (Fig. 1).

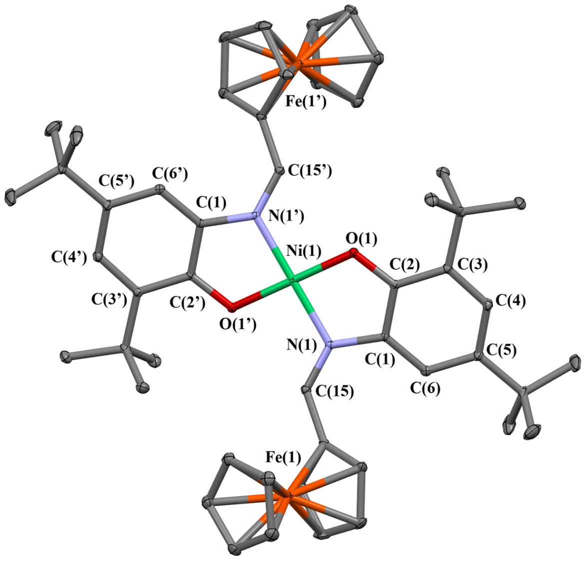

Figure 1. The molecular structure of nikel(II) bis-o-iminophenolato complexes.

Acknowledgements - This work was financially supported by RFBR № 18-33-00951 mol_a

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INVESTIGATION OF THE INFLUENCE OF THE STRUCTURE OF CROWN ETHERS ON THE REVERSIBILITY OF THE ELECTRODE REACTION IN LITHIUM ELECTROCHEMICAL SYSTEMS

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Experimental and theoretical studies of the effect of crown ethers of various structures on the reversibility of the electrode / electrolyte interface were first carried out.

Electrolyte compositions based on 1 M $LiPF_6$ in ethylene carbonate / dimethyl carbonate mixture (EC/DMC) (1:1 by weight) and 1M LiTFSI in 1,3-dioxolane / dimethoxyethane mixture (DOL/DME) (2:1 by weight) with the addition of 2 and 5 wt.% 15-crown-5 (15C5), dibenzo-18-crown-6 (DB18C6) and pentadecyl-2,4-dioxo-16-crown-5 (pentadecyl-2,4D16C5) were prepared and studied. A lithium metal anode and a $LiFePO_4$ - cathode were used as electrodes.

By the method of electrochemical impedance, it was shown that all investigated crown ethers can be adsorbed on the lithium surface. The addition of 5% by weight of pentadecyl-2,4D16C5 has the greatest effect, at which the resistance of SEI is minimal.

On the surface of the $LiFePO_4$ –cathode of three types of crown ethers, DB18C6 may be adsorbed as a monolayer, and pentadecyl-2,4D16C5 forms a bulk layer.

Using quantum chemical modeling, the adsorption energies of crown ethers and the binding energies of lithium ion with crown ether are calculated in the free and adsorbed state.

It was shown that 15C5 molecules and pentadecyl-2,4D16C5 form flat structures, this contributes to the "stacking" folding of subsequent molecules of crown ethers. For dibenzo-18-crown-6 there are steric obstacles, since one of the benzene rings is oriented perpendicularly, which will impede the transfer of the Li^+ ion from one crown ether molecule to another. It is calculated that the Li^+ ion in the complex with pentadecyl-2,4D16C5 is more mobile. In addition, this complex is adsorbed with a greater energy gain. Thus, it can be concluded that pentadecyl-2,4D16C5 better than the other two crown ethers contributes to the transfer of lithium ion from the electrolyte volume to the surface of both cathode and anode.

Based on the data obtained, Li//$LiFePO_4$ battery prototypes were assembled with electrolytes with 15C5 and pentadecyl-2,4D16C5 additives and charge-discharge cycling was performed for 100 cycles.

The results showed that both crown ethers introduce a positive contribution to the formation of SEI at the interface with the electrode, which increases the discharge capacity of batteries and stabilizes charge-discharge processes.

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ChemShip-2019/Topical Problems of Modern Chemistry
International conference “Organometallic Chemistry Around the World” (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

COMPLEXES OF GROUP 13 METALS WITH STERICALLY-HINDERED ACENAPHTHENE-1,2-DIIMINE LIGAND

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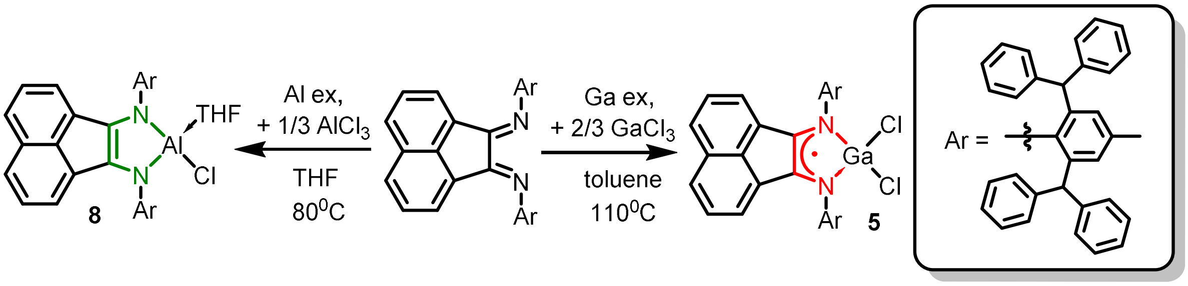
Unique stereoelectronic properties of the bis(arylimino)acenaphthenes (Ar-bian) are beginning to be appreciated and exploited for some fascinating new developments in synthetic, structural and catalytic chemistry. Sterically-hindered ligands of the Ar-bian have found widespread use in coordination chemistry due to the conformational rigidity and volume diimine helatinous fragment, as well as the possibility of varying the aryl substituents at the nitrogen atoms. The chemistry of coordination compounds of main group metals with Ar-bian ligands is intensively studied in the last years with the arm to develop new catalytic systems.

Here we present results of synthesis of new coordination compounds of group 13 metals with the redox-active acenaphthene-1,2-diimine ligand, containing at nitrogen atoms of the sterically-hindered 2,6-dibenzamide-aryl substituents, 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene (dbhmp-bian). Thus reduction of dbhmp-bian with aluminimum hydride $LiAlH_4$ leads to the complex [(dbhmp-bian)Al(H)$_2$]Li(thf)$_4$(**1**). The reaction of sodium salt dbhmp-bian (dbmp-bian)Na with mixture $LiAlH_4$ and $AlCl_3$ affords the (dbhmp-bian)AlH(thf)(**2**). The hydride (dbmp-bian)AlH$_2$(**3**) have been isolated from the reaction of (dbhmp-bian)Na with monochloroalane H_2AlCl. The gallium hydride (dbhmp-bian)Ga(Cl)H(**4**) have been prepared by the reaction of dichlorogallane $HGaCl_2$ with (dbhmp-bian)Na. The gallium dichloride (dbhmp-bian)GaCl$_2$(**5**) have been prepared by the exchange reaction of sodium salt dbhmp-bian with gallium trichloride or the reduction of dhmp-bian with gallium in a presence of gallium trichloride. The reaction of the sodium salt of dbhmp–bian with diethylchloroalane Et_2AlCl affords the dialkyl compound (dbhmp-bian)AlEt$_2$(**6**). The compound (dbhmp-bian)AlCl$_2$(**7**) was synthesized by the exchange reaction of $AlCl_3$ with (dbhmp-bian)Na or the reduction of dbhmp-bian with aluminimum in a presence of aluminimum trichloride in toluene. The reduction of dbhmp-bian with aluminimum in a presence of aluminimum trichloride in tetrahydrofuran leads to formation of complex (dbhmp-bian)AlCl(thf)(**8**).



In complexes **1-2** and **8** dbhmp-bian acts as a dianion. Complexes **3-7** contain radical-anionic dbhmp-bian. Products **1-8** have been characterized by IR, ^{1}H NMR (**1-2** and **8**), EPR (**3-7**) spectroscopy as well as by the single crystal X-ray analysis.

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SYHTHESIS, STRUCTURES AND SPECTROSCOPIC STUDIES OF NEW SCHIFF-BASE COMPLEXES OF ZINC AND COBALT(II)

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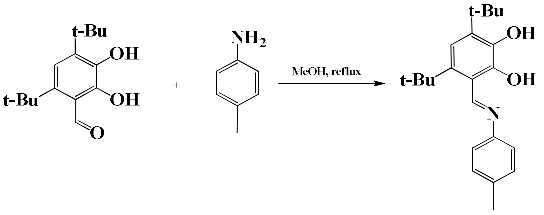
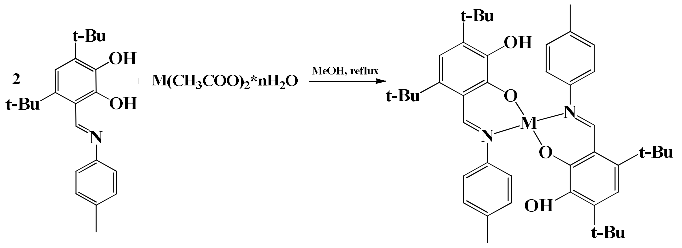
The Schiff-base (SB) ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility, and therefore they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. The research field dealing with SB metal complexes is very broad due in part to their potential interest for a number of interdisciplinary areas that include bioinorganic chemistry, catalysis, and magnetochemistry. In the area of bioinorganic chemistry the interest in the SB complexes lies in that they provide synthetic models for the metal-containing sites in metalloproteins and enzymes. Also, SB complexes have been found to be efficient catalysts for some organic reactions and have also been used as models for the activation of small molecules. Therefore, the synthesis of new compounds of this type is relevant.

We present the synthesis of a new SB, containing both fragments salicylic aldehyde and sterically hindered catechol within the structure:



Two new SB complexes of zinc and cobalt(II) were prepared by reaction:



M = Zn, n = 2; M = Co, n =4

The cobalt(II) complex is not stable in air in solution, so the synthesis was performed using Schlenk technique. The structure of the compounds was confirmed by X-ray. The resulting complexes containing a fragment of sterically hindered phenol, which provides the opportunity for post-functionalization or coordination. The presence of *tert*-butyl substituents improves the solubility of the compounds obtained. Compounds were studied by UV/Vis-spectroscopy. The zinc complex exhibits fluorescence in solution and thin film.

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LUMINESCENCE OF ORGANIC COMPLEXES OF RARE EARTH METALS UNDER X-RAY AND β-RAY EXCITATION

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One of the greatest problems of modern energy is the development of a method of direct conversion of nuclear energy into electricity. This way promises huge advantages compared with traditional nuclear power stations and radioisotope thermoelectric generators. One of the most promising direct conversion methods is based on a radiovoltaic effect similar to the photovoltaic transformation. Prototypes of such devices have already been designed on the basis of inorganic semiconductors [1]. The most effective devices include the stage of radioluminescence. A drawback of these devices is relatively low radiation stability of inorganic semiconductors.

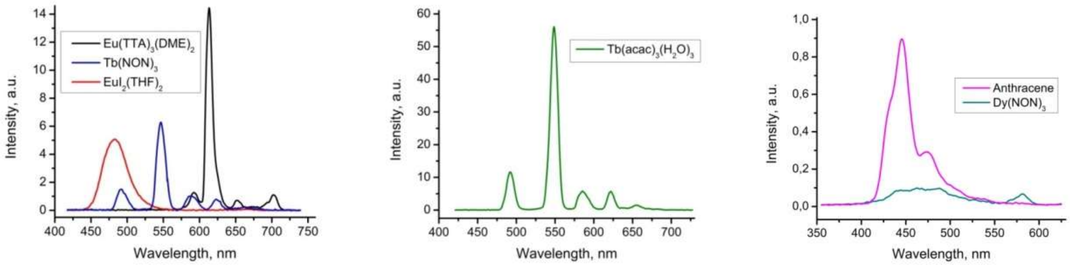

Fig. 1. X-ray excited luminescence of organo-lanthanide complexes ($\bar{E}$ 10 keV, 150 mA)

Recently we have found that organo-lanthanide complexes have possessed surprisingly high radiation stability [2]. This gave the ground for the study of their radio luminescent properties with the aim of possible further use in energy-converting devices. We investigated the luminescence of benzimidazolylphenolate (NON) trifluoro(2-thienyl)-butanedionate (TTA) and 1,3-acetylacetonate (acac) of lanthanides caused by X-ray (Fig. 1) and electron beam irradiation (Fig. 2).

The data obtained revealed that organo-lanthanides are promising materials for application in the energy transferring devices and scintillators. The mechanism of radioluminescence of organo-lanthanide complexes is discussed.

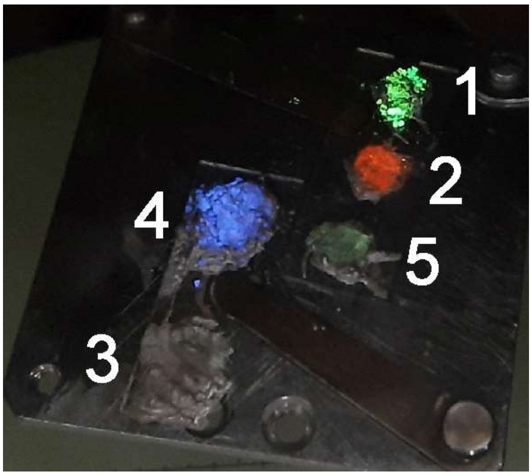

Fig. 2. The luminescence of Tb(acac)$_3$(H$_2$O)$_3$ (**1**), Eu(TTA)$_3$(DME)$_2$ (**2**), [Tb(NON)$_3$]$_2$ (**3**), Sc(NON)$_3$ (**4**) and Alq$_3$ (**5**) excited by the electron beam (U_{ac} 100 MV).

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MAGNETIC BISTABILITY OF OCTAHEDRAL IRON AND COBALT COMPLEXES BEARING SUBSTITUTED CATECHOLATE LIGANDS

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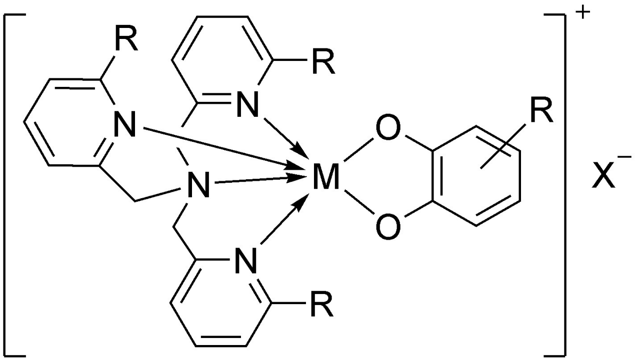
The possibility of controlling magnetic properties of coordination compounds under the action of external stimuli makes them suitable objects for the structural design of dynamic materials for the needs of molecular electronics and spintronics [1–3].

Spin-crossover and redox-isomerism (or valence tautomerism) represent the most efficient mechanisms driving the changes of spin states of transition metal complexes. The spin-crossover phenomenon caused by the electronic rearrangement within a metal ion between its low-spin and high-spin states is mainly studied in the case of iron complexes with N_6 or N_4O_2 environment, but it also occurs in cobalt systems. On the other hand, valence tautomerism – an intramolecular process consisting in reversible electron transfer between a metal ion and a redox-active ligand – has been most thoroughly studied in the case of cobalt complexes with o-quinones.

In the present work we performed a DFT theoretical modeling, synthesis and spectroscopic investigation of mono- and dinuclear systems bearing functionalized polydentane ligands.



M = Fe, Co
X = ClO_4, BPh_4, PF_6

[1] P. Gütlich, H.A. Goodwin (Eds.), Spin crossover in Transition metal Compounds. I: Topics in Current Chemistry, vol. 233. Springer, Berlin, **2004**.
[2] M.A. Halcrow (Ed.), Spin-crossover Materials: Properties and Applications, Wiley, Chichester, **2013**.
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CU(I) AND AU(I) COMPLEXES OF 1,5-DIAZA-DIPHOSPHACYCLOOCTANES CONTAINING 2-ETHYL(THIOPHEN-2'-YL) SUBSTITUENTS AT PHOSPHORUS ATOMS

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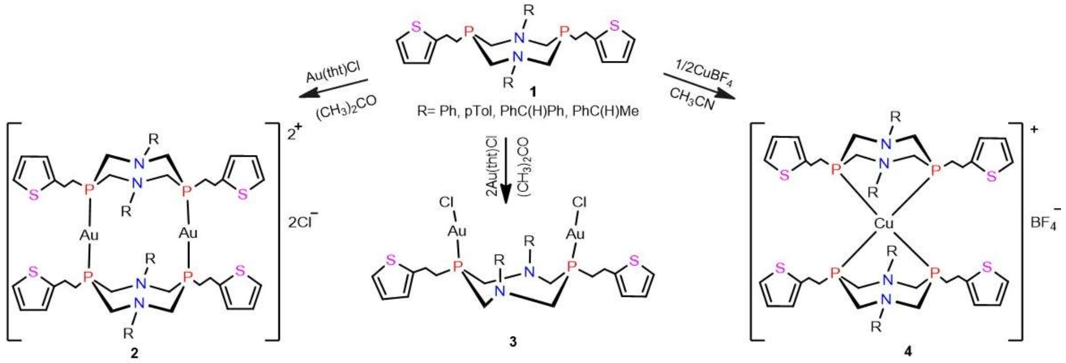
1,5-Diaza-3,7-diphosphacyclooctanes are functionalized bidentate ligands which include amino and phosphine groups in the cyclic system. The synthetic available variation of exocyclic substituents allows to tune the steric and electronic properties of these cyclic ligands. The insertion of heterocyclic groups to phosphorus atoms of 1,5-diaza-3,7-diphosphacyclooctanes gave bi- and tetradentate ligands which were employed for the synthesis of copper subgroup metals luminescent complexes [1]. Copper(I) and gold(I) complexes of 1,5-diaza-3,7-diphosphacyclooctanes containing pyridylethyl substituents demonstrate "*stimuli-responsive*" luminescence towards the VOCs (volatile organic compounds) and temperature [1,2].

The row of luminescent complexes on the basis of 1,5-diaza-3,7-diphosphacyclooctanes can be extended by insertion to phosphorus atoms any heterocyclic substituents. In this work we report the synthesis of Cu(I) and Au(I) complex of 1,5-diaza-3,7-diphosphacyclooctanes with thienylethyl substituents at the phosphorus atoms.



The interaction of 1,5-diaza-3,7-diphosphacyclooctanes **1** with Au(tht)Cl in the ratio 1:1 or 1:2 led to the formation of P,P-bridged complexes **2** and **3** respectively. Reaction with $Cu(CH_3CN)_4BF_4$ results in bis-P,P-chelate complexes **4**. Complexes **2** and **4** exhibit yellow-green luminescence in the solid state.

[1] I. Strelnik, I. Dayanova, I. Kolesnikov, R. Fayzullin, I. Litvinov, A. Samigullina, T. Gerasimova, S. Katsyuba, E. Musina, A. Karasik, *Inorganic Chemistry*, **2019**, 58, 1048-1057
[2] I. Strelnik, V. Gurzhiy, V. Sizov, E. Musina, A. Karasik, S. Tunik, E. Grachova, *CrystEngComm*, **2016**, 18, 7629-7635

Acknowledgements
This work was supported by the RSF, project № 19-43-04119

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International conference “Organometallic Chemistry Around the World” (7th Razuvaev Lectures)
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USE OF THE "REDUCTIVE APPROACH" FOR THE SYNTHESIS OF CHALCOGENIDE AND PYRAZINIDE COMPLEXES OF LANTHANIDES

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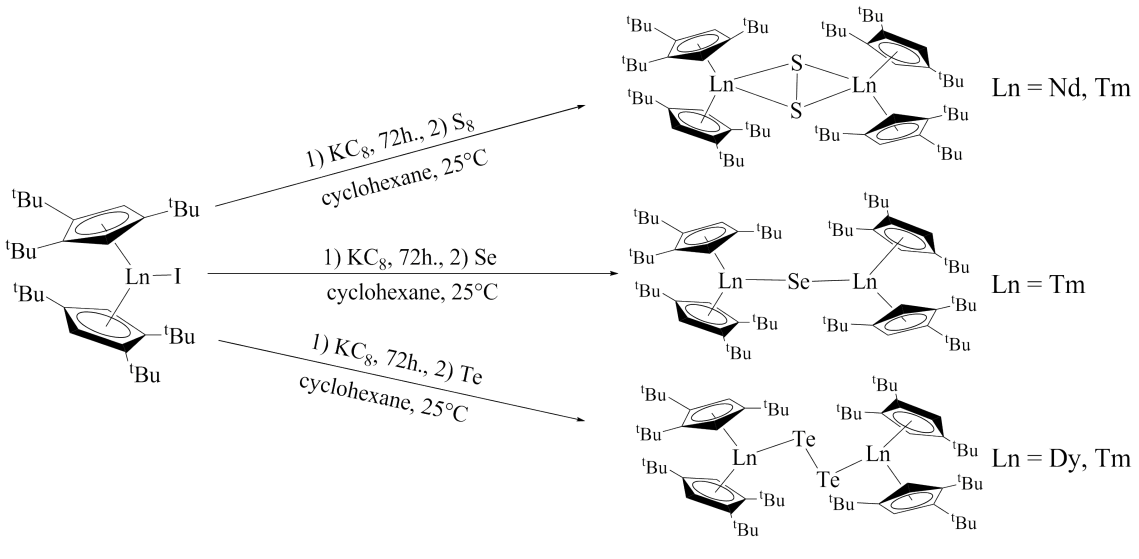
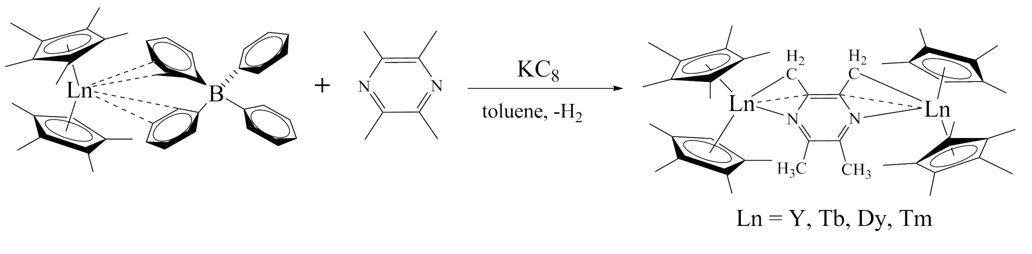
The family of the lanthanide complexes containing $\{Ln(\mu\text{-}Q_n)Ln\}$ motifs (Q = S, Se, Te) is really not representative. Such compounds are still considered as unconventional, but they attract a great attention due to expected interesting magnetic and luminescent properties.

Herewith we report the synthesis and comprehensive characterization of the new chalcogenide Ln-complexes obtained *via* interaction of the less-common Ln(II) compounds and elemental Q. For example, the reactions of $[Cp'''_2Ln]$ with Q result in a variety of the $[Cp'''_2Ln(\mu\text{-}Q_n)LnCp'''_2]$ complexes (Scheme 1). The pyrazinide $[(Cp^*_2Ln)_2(\mu\text{-}N_2C_4Me_2(CH_2)_2)]$ complexes are the possible reducing agents for Q to produce a representative library of new $\{Ln(\mu\text{-}Q_n)Ln\}$ compounds. These complexes were obtained *via* reduction of $[Cp^*_2LnBPh_4]$ in the presence of tetramethylpyrazine (Scheme 2).



Scheme 1. Synthesis of $[Cp'''_2Ln\text{–}(Q)_n\text{-}LnCp'''_2]$



Scheme 2. Synthesis of $[(Cp^*_2Ln)_2(N_2C_4Me_2(CH_2)_2)]$

Acknowledgements - Authors thank Russian Science Foundation (project No. 16-13-10294) for financial support.

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TRANSFORMATIONS INDUCED BY GA- AND AL- REDOX SPECIES

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Our research group interest was mainly concentrated on the reactivity of the gallium and aluminium derivatives of redox active ligand dpp-bian = 1,2-bis[(2,6-di-iso-propylphenyl)imino]acenaphthene. Such compounds may undergo reduction by alkaline and alkaline-earth metals and lanthanides [1], oxidative addition [2], solvate-induced intramolecular electron transfer [3], and reversible cycloadditionaddition of alkynes and isothiocyanates [4] reaction with sulfur(IV) oxide to form the dithionite complexes [5]. The report summarizes research advances in this area.

[1] a) I. L. Fedushkin, A. N. Lukoyanov, G. K. Fukin, S. Y. Ketkov, M. Hummert, H. Schumann, *Chem. Eur. J.* **2008**, *14*, 8465-8468; b) I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko, M. Hummert, *Chem. Eur. J.* **2010**, *16*, 7563-7571; c) T. Sanden, M. T. Gamer, A. A. Fagin, V. A. Chudakova, S. N. Konchenko, I. L. Fedushkin, P. W. Roesky, *Organometallics* **2012**, *31*, 4331-4339.
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[3] I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko, G. K. Fukin, *Inorg. Chem.* **2014**, *53*, 5159-5170.
[4] a) I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.* **2012**, *18*, 255-266; b) I. L. Fedushkin, A. S. Nikipelov, K. A. Lyssenko, *J. Am. Chem. Soc.* **2010**, *132*, 7874-7875; c) W. Zhang, V. A. Dodonov, W. Chen, Y. Zhao, A. A. Skatova, I. L. Fedushkin, P. W. Roesky, B. Wu, X.-J. Yang, *Chem. Eur. J.* **2018**, *24*, 14994-15002.
[5] I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, X.-J. Yang, V. A. Chudakova, A. V. Piskunov, S. Demeshko, E. V. Baranov, *Inorg. Chem.* **2016**, *55*, 9047-9056.

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THE NICKEL(II) DERIVATIVES BEARING FUNCTIONALIZED O-AMINOPHENOL

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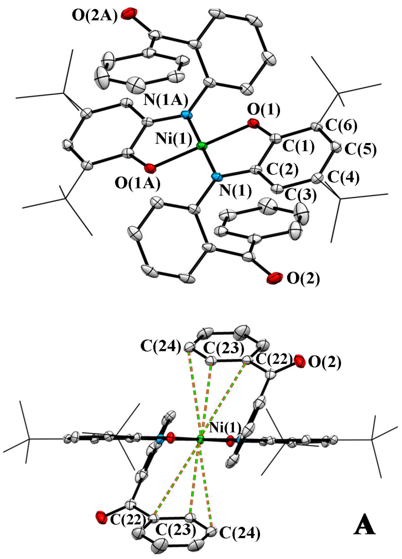
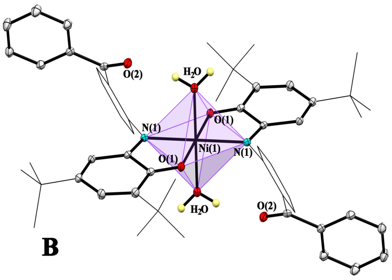


A

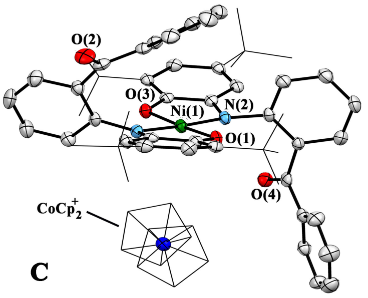
o-Aminophenol, functionalized by –C(O)Ph substituent in aniline part [1], combines redox-active and hemilabile nature [2]. Current work continues research in the field of transition metal coordination compounds on the base of above ligand: nickel was chosen as complexing agent.

Reaction between ligand and $NiCl_2 \cdot 6H_2O$ led to square-planar bis-*o*-iminobenzosemiquinonato Ni^{II} derivative, characterized by weak interaction of –Ph rings (in –C(O)Ph groups) and nickel center (view **A**). In contrast to known Ni^{II} compounds, the main peculiarity of presented complex are in cancellation of usual pattern of strong antiferromagnetic coupling between anion-radical ligands, causing the diamagnetism of compound. High-temperature (300 K) value of effective magnetic moment (μ_{eff}) is equal to 0.33 μ_B, and NMR-spectrum (298 K) is broadened.

Redox-transformations of neutral Ni^{II} complex, using one-electron oxidizing/reducing agents, produced dication hexacoordinate Ni^{II} derivative with equivalent *o*-iminobenzoquinones (view **B**) and monoanion tetracoordinate Ni^{II} compound, containing *o*-iminobenzosemiquinonato radical and *o*-amidophenolate form of initial ligand (view **C**). In dication derivative the water molecules, which are trace amounts of moisture in oxidant, occupy the vacant sites in the coordination sphere of metal, that were released due to changes in the charge of entire complex. So, generation of a positive charge by the chemical oxidation provides the turn from a square-planar to octahedral molecular geometry and corresponding alteration from low-spin (S_{Ni} = 0) to high-spin (S_{Ni} = 1) Ni^{II} state. Monoanionic Ni^{II} complex demonstrates the doublet ground state (S = 1/2) due to the presence of low-spin metal center.



B



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[1] A.V. Piskunov, K.I. Pashanova, A.S. Bogomyakov, I.V. Smolyaninov, N.T. Berberova and G.K. Fukin, *Polyhedron*, **2016**, *119*, 286-292.
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MANGANESE(III) BIS-O-IMINOBENZOSEMIQUINONATES WITH VARIOUS SUBSTITUENTS IN N-ARYL FRAGMENT OF REDOX-ACTIVE LIGAND

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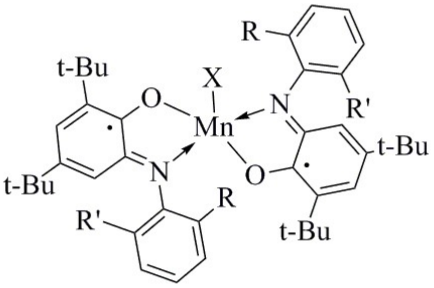
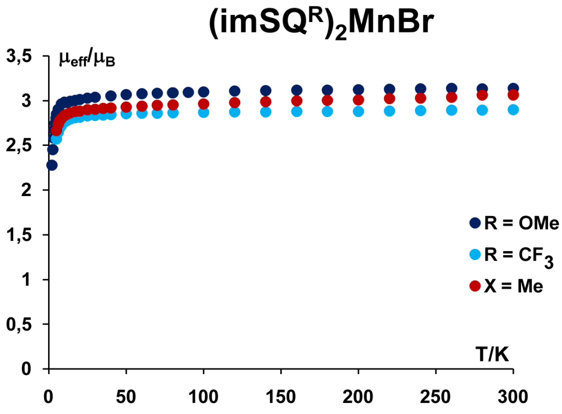
We have synthesized the series of pentacoordinated manganese(III) bis-*o*-iminobenzosemiquinonates (imSQ^R)MnX containing strong electron donor (R = Me), electron donor (R = OMe) and strong electron acceptor (R = CF_3) substituents in the *ortho*-position of *N*-aryl fragment of redox-active ligand.

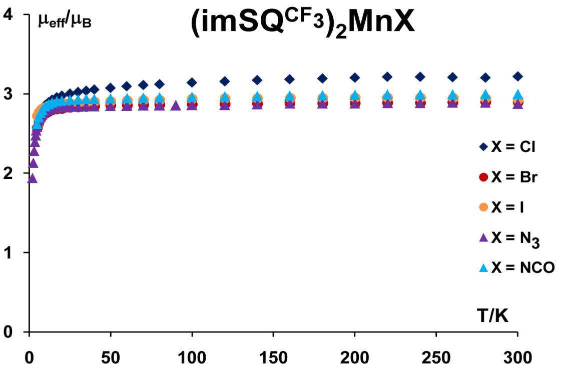


$(imSQ^R)_2Mn^{III}X$

R = OMe, R' = H, X = Cl, Br, I, N_3
R = R' = Me, X = Cl, Br, I, N_3, NCO
R = CF_3, R' = H, X = Cl, Br, I, N_3, NCO

Magnetic susceptibility of crystalline samples of all complexes (imSQ^R)MnX has been measured at 300-4 K. According to the magnetic susceptibility data the electronic structure of manganese(III) complexes $(imSQ^R)_2MnX$ does not depend neither on the nature of substituent R nor on the nature of apical substituent X. The strong antiferromagnetic metal-ligand spin interactions between high-spin manganese(III) (h.s., d^4, S_{Mn} = 2) and two radical imSQ ligands (S_R = 1/2) in all complexes yield the triplet ground state.





Acknowledgements - We are grateful to the Russian Science Foundation (grant 18-73-00268) for financial support of this work.

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NEODYMIUM–YTTERBIUM AND NEODYMIUM-EUROPIUM NITRIDE-SULFIDE CLUSTERS: SYNTHESIS AND STRUCTURE

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Earlier the heterolanthanide clusters $Nd_2LnI_5(S_3)(S_2N_2)(THF)_9$ containing two Nd^{3+} ions and one Ln^{3+} ion (Ln = Tb , Tm, Dy, Yb) were prepared by the disproportionation reaction of iodide-nitride $[(NdI)_3N_2](THF)_6$ with LnI_3 in the presence of sulfur [1,2]. In these work, the divalent YbI_2 was used instead of YbI_3 and the same trinuclear complex $[Nd_2YbI_5(S_2)(S_2N_2)(THF)_9]$ (**1**) (Fig. 1) was obtained.

$$[(NdI)_3N_2] + YbI_2 + S_8 + THF \rightarrow [Nd_2YbI_5(S_2)(S_2N_2)(THF)_9] + [Nd_3I_5(S_2)(S_2N_2)(THF)_{10}] + ...$$

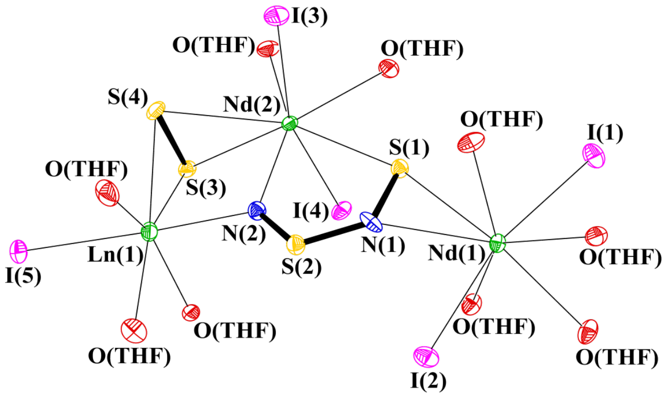

Fig. 1. Molecular structure of $[Nd_2LnI_5(S_2)(S_2N_2)(THF)_9]$ (Ln = Yb(**1**), Eu(**2**)). THF omitted except oxygen atoms.

The similar europium complex $[Nd_2EuI_5(S_2)(S_2N_2)(THF)_9]$ (**2**) (Fig. 1) was synthesized when EuI_2 was used:

$$[(NdI)_3N_2] + EuI_2 + S_8 + THF \rightarrow [Nd_2EuI_5(S_2)(S_2N_2)(THF)_9] + [Nd_3I_5(S_2)(S_2N_2)(THF)_{10}] + ...$$

It is assumed that the reactions include the sages of oxidation of LnI_2 by S_8 and formation of LnI_3 which reacts with initial $[(NdI)_3N_2]$ to give the indicated products.
In addition, it was found that the reaction of NdI_3 with $[(DyI)_3N_2]$ in THF gives new trinuclear complex $[Dy_2NdI_5(S_2)(S_2N_2)(THF)_9])$ containing two Nd^{3+} ions and one ion Dy^{3+}.

$$[(DyI)_3N_2] + NdI_3 + S_8 + THF \rightarrow [Nd_2DyI_5(S_2)(S_2N_2)(THF)_9] + ...$$

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ChemShip-2019/Topical Problems of Modern Chemistry
International conference "Organometallic Chemistry Around the World" (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

PINCER LIGANDS BASED ON SUBSTITUTED DIPHENYLMETHANES $CH_2[C_6H_3$-4-tBu-2-R$]_2$ (R = −PPh_2, −P(O)Ph_2, −P(S)Ph_2): SYNTHESIS AND REACTIVITY TOWARD ALKALI METAL ALKYLS.

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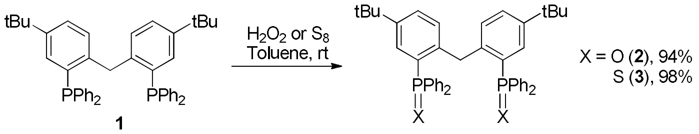
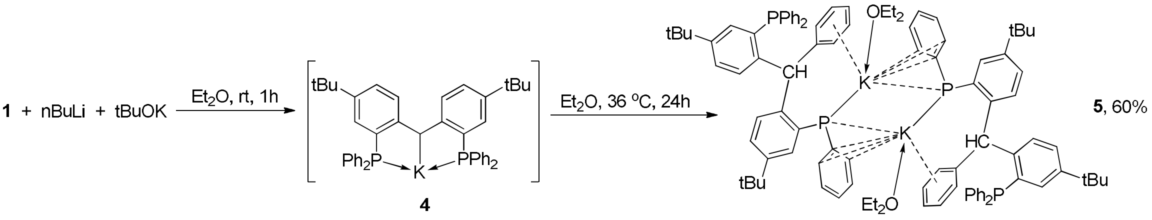
Tridentate pincer ligands are widely used in coordination and organometallic chemistry of d-transition metals due to their robust tridentate coordination to the metal centres providing high thermal and kinetic stability of their complexes along with high catalytic activity in various transformations.PCP ligands in which bonding to the metal is realized due to the formation of a covalent M−C(sp_2) bond are the most widespread among phosphorus-containing pincer ligands, while PCP pincer ligands with M-C(sp_3) covalent bond are much less investigated to date. Diphenylmethanes $CH_2[C_6H_3$-4-R'-2-$PR_2]_2$ (R' = H, tBu) containing the phosphine groups −PR_2 (R = Me, iPr, Ph) in *ortho*-positions of the phenyl rings, have been successfully used as neutral, monoanionic $[(4\text{-R'-2-}PR_2\text{-}C_6H_3)_2CH]^-$ (alkyl) and dianionic $[(4\text{-R'-2-}PR_2\text{-}C_6H_3)_2C]^{2-}$ (methylidene) ligands in chemistry of late d-transition metals. N-containing analog also was recently used for preparation of alkali metal diphenymethanides [2,2′-(4-$MeC_6H_4NMe_2)_2CH]M$(Solv) (M = Li, Na, K).[1]

In our work new pincer ligands were synthesized by oxidation of the P(III) atoms in substituted diphenylmethane $CH_2[C_6H_3$-4-tBu-2-$PPh_2]_2$ (**1**) with H_2O_2 or S_8 in toluene to afford new diphenylmethanes bearing pendant P(V) Lewis base groups $CH_2[C_6H_3$-4-tBu-2-P(X)$Ph_2]_2$ (X = O (**2**), S (**3**); Scheme 1).[2]



Scheme 1.

The trials to deprotonate CH_2 fragments of substituted diphenylmethanes **2** and **3** by n-BuLi or $LiCH_2SiMe_3$ failed, while the methylene group in **1** can be readily metallated by the Lochmann-Schlosser super-base n-BuLi/t-BuOK to form the potassium complex K[CH(C_6H_3-4-tBu-2-$PPh_2)_2$] (**4**). Complex **4** turned out to be unstable in Et_2O or THF solutions transforming into the phosphine-phosphide derivative {[PhCH(C_6H_3-4-tBu-2-PPh_2)(C_6H_3-4-tBu-2-PPh)]K(OEt_2)}$_2$ (**5**; Scheme 2) due to the migration of one phenyl group from the phosphorus atom to the central benzhydryl carbon.[2]



Scheme 2.

[1] D. O. Khristolyubov, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. S. Shavyrin, A. A. Trifonov. *Organometallics*, **2018**, 37, 1627–1634.
[2] A. Fayoumi, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. A. Trifonov. *Mendeleev Commun.*, **2019**, 29, 331–333.

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NEW Pd-ORGANIC COMPLEX WITH NITROXIDE

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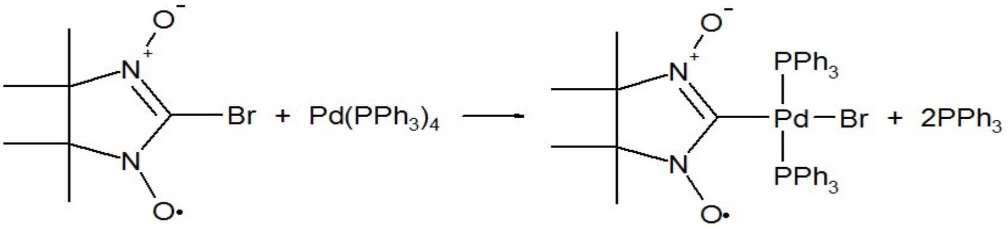
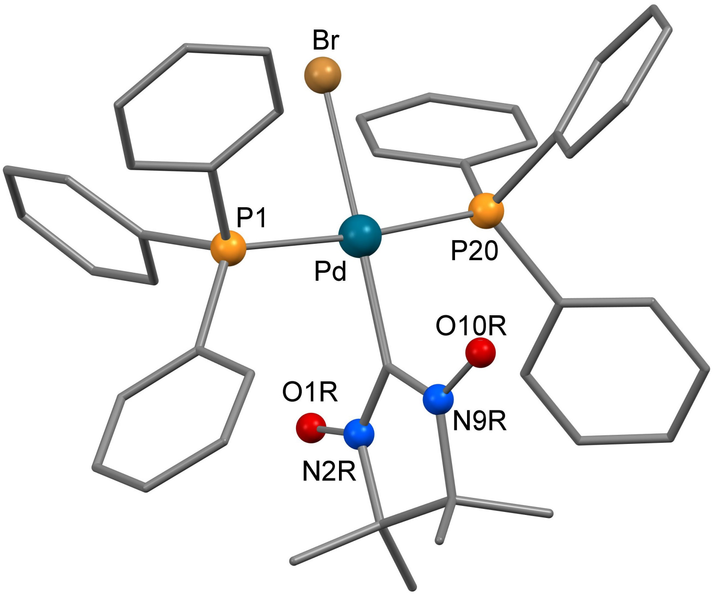
The interaction of 2-bromo-4,4,5,5-tetramethyl-2-imidazolin-3-oxide-1-oxyl (NIT-Br) with tetrakis(triphenylphosphine)palladium(0) yields a new Pd-organic compound NIT-Pd(PPh_3)$_2$Br, the structure of which was determined by X-ray diffraction. This complex is more stable and easier to obtain than NIT-Au(PPh_3), which is used to synthesize new nitroxyl radicals.





Molecular structure of NIT-Pd(PPh_3)$_2$Br

Acknowledgements – this work is financially supported by RScF grant 18-13-00380.

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ChemShip-2019/Topical Problems of Modern Chemistry
International conference "Organometallic Chemistry Around the World" (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

CONTROLLABLE SELF-ASSEMBLY OF IRON CONTAINING NANODIAMONDS - NOVEL HYBRID NANOMATERIALS

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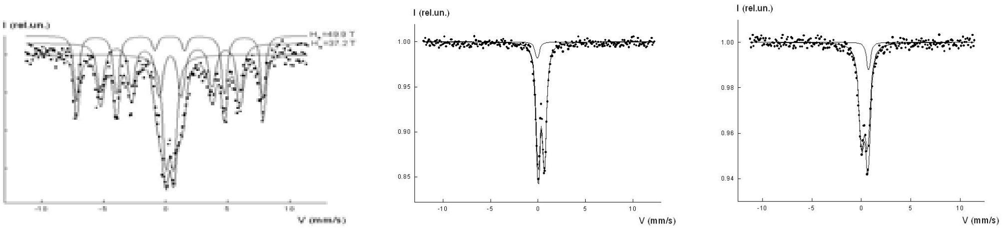
Detonation nanodiamonds (DNDs) currently attracts great scientific interest and promise technological applications due to small primary particle size (~4−5 nm) with narrow size distribution, possibility of surface functionalization, and high biocompatibility. DNDs with surface modified by metal ions or metal-containing fragments show great potential for a wide range of their potential applications in modern technologies as hybrid nanomaterials presenting various functional possibilities, for example, in magnetic and optical devices, sensor systems, drug delivery, medical imaging devices, etc. The development of efficient procedures for the preparation of such hybrid nanomaterials and the investigation of their physicochemical properties is an important issue. The series samples of the iron containing diamonds DND-COOH were synthesized using solution chemistry methods by the reaction of stable hydrosol of 4-5 nm carboxylated deagglomerated DNDs (DND-COOH) [1] and aqueous solution of $FeCl_3{\cdot}6H_2O$ in air. Composition, structure and magnetic behavior of the samples of novel hybrid nanomaterials based on iron containing diamonds DND-COOH were characterized by powder X-ray diffraction, Mössbauer spectroscopy, and Raman spectroscopy. The formation of type of hybrid nanomaterial based on iron containing diamonds DND-COOH was shown to be controllable by varying the conditions of the experiment in the «hydrosol of DND-COOH – $FeCl_3{\cdot}6H_2O$» system.



a) b) c)

Fig.1. ^{57}Fe Mossbauer spectra at 300K of the iron containing diamonds DND-COOH include "paramagnetic" doublet and: a) magnetically ordered α-Fe_2O_3 and α-FeOOH, b) γ-FeC, c) $Fe_{1-x}O$.

[1] A.E. Aleksenskiy, E.D. Eydelman, and A.Y. Vul', Nanosci. Nanotechnol. Lett., **2012**, *4*, 165-179.

Acknowledgements - This study was supported by the Russian Foundation for Basic Research (Project No. 18-29-19038).

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BINUCLEAR GADOLINIUM(III) CARBOXYLATES WITH HETEROCYCLIC N-DONORS: SYNTHESIS, MAGNETIC AND LUMINESCENT PROPERTIES, AND EPR STADIES

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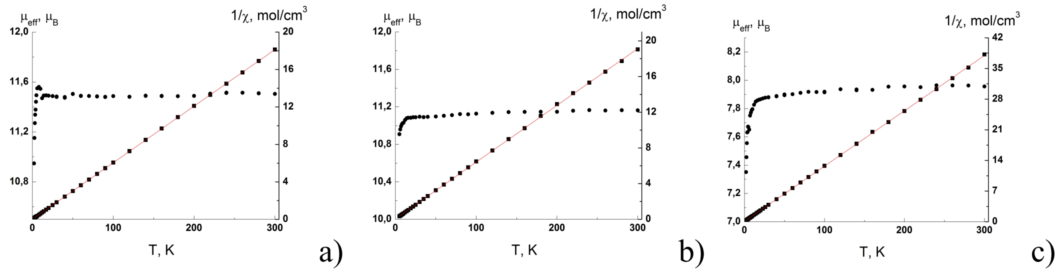
Solution chemistry methods were developed, resulting in the controllable formation of single-phase single crystals of binuclear complexes $(bath)_2Gd_2(piv)_6\cdot 2EtOH$ (**1a**·2EtOH, triclinic, *P-1*), $(bath)_2Gd_2(piv)_6\cdot 2EtOH$ (**1b**·2EtOH, Monoclinic, *C2/c*), and $(bath)_2Gd_2(piv)_6\cdot H_2O$ (**1c**·H_2O, Monoclinic, *I*2/a), where piv is $(CH_3)_3CCO_2^-$ and bath is 4,7-diphenyl-1,10-phenanthroline. The temperature-induced structural transitions of these compounds were studied. Polymorphs **1a**, **1b**, and **1c** of the composition $(bath)_2Gd_2(piv)_6$ are produced by desolvation of the appropriate solvates. **1a**·2EtOH, **1b**·1.5EtOH, **1c**·0.75H_2O, **1a**, **1b**, and **1c** were characterized by single-crystal X-ray diffraction. The magnetic properties of new complexes **1a**·2EtOH, **1b**·2EtOH, **1c**·H_2O, and previously known complexes $(L)_2Gd_2(piv)_6$, L = bpy (**2**, 2,2'-bipyridyl), phen (**3**, 1,10-phenanthroline), $(Hpiv)_6Gd_2(piv)_6$ (**4**) and coordination polimer $\{Gd(piv)_3\}_n$ (**5**) [1], were investigated by SQUID magnetometry, and the nature of the magnetic coupling between gadolinium(III) ions in **1-5** was determined. EPR studies of Gd(III) dimers are scarce, and the approaches for their spectral simulations are not straightforward. Our Q-band (34 GHz) continuous wave EPR studies of complexes **1-5** confirm the dimeric structure of compounds **1-4** and polymer-chain structure of compound **5**. All spectra indicate that Gd(III) ions interact with each other, and the half-field transition typical for both dimers and high-spin ions are observed. The energies of the singlet S_1 ($^1\pi\pi^*$) and triplet T_1 ($^3\pi\pi^*$) levels for the bath ligand in complexes **1** were estimated.



a) b) c)

Fig.1. Plots $\mu_{eff}(T)$ (●) and $1/\chi(T)$ (■) for **1a**·2EtOH (a), for **4** (b), and **5** (c), calculated data are represented by the red line.

[1] I.G. Fomina, Zh.V. Dobrokhotova, V.O. Kazak, G.G. Aleksandrov, K.A. Lysenko, L.N. Puntus, V.I. Gerasimova, A.S. Bogomyakov, V.M. Novotortsev, and I.L. Eremenko, *Eur. J. Inorg. Chem.*, **2012**, *22*, 3595–3610.

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EFFECT OF LIGANDS ON THE INTERACTION BETWEEN PINCER IRIDIUM HYDRIDES AND LEWIS BASES

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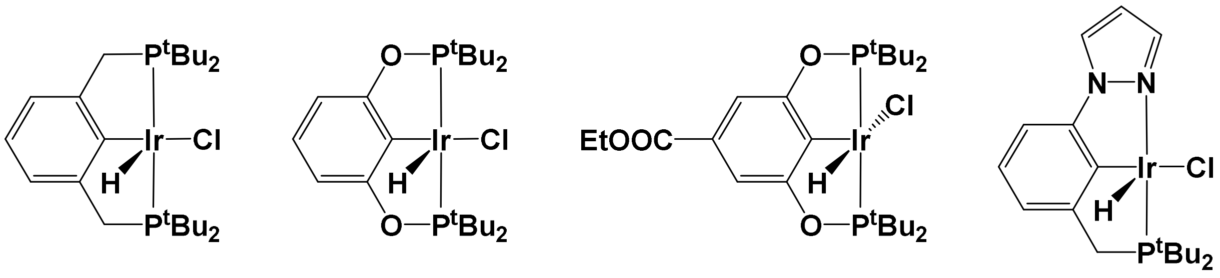
Complexes of transition metals based on pincer-type ligands are well-known effective catalysts for various processes [1,2]. Among them, iridium complexes are preferred for transfer dehydrogenation and acceptorless dehydrogenation catalysis [2].

The modification of pincer ligand could affect the electronic properties and reactivity of the complex. In order to see the pincer-ligand influence on the interaction of iridium complexes with Lewis bases we have studied the coordination of pyridine and benzonitrile to benzene based pincer hydridochlorides $[(^{tBu}PCP)IrH(Cl)]$ (**1**) [4], $[(^{tBu}POCOP)IrH(Cl)]$ (**2**), $[(^{tBu}POCOP)(CO_2Et)IrH(Cl)]$ (**3**) and $[(PCN)IrH(Cl)]$ (**4**, Figure 1). The bases could coordinate iridium atom giving a mixture of *apical* and *equatorial* hexacoordinate isomers. The combination of variable temperature NMR (^1H, ^{31}P, ^{15}N) and UV/Visible spectroscopic measurements allowed determining experimentally the structure, ratio and thermodynamic characteristics of the obtained hexacoordinate complexes.



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

Figure 1

[1] Van der Boom, M. E., Milstein, D., *Chem. Rev.*, **2003**, *103*, 1759-1792.
[2] Morales-Morales, D., et al., *Can. J. Chem.*, **2001**, *79*, 823-829.
[3] Titova, E. M.; Osipova, E. S., Gulyaeva, E. S., Torocheshnikov, V. N., Pavlov, A. A., Silantyev, G. A., Filippov, O. A., Shubina, E. S., Belkova, N. V. *J. Organomet. Chem.*, **2017**, *827*, 86-95.
[4] Osipova, E. S. et al. *Eur. J. Inorg. Chem.*, **2019**, *2019(10)*, 1389-1397.

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SCANDIUM ALKYL COMPLEXES SUPPORTED BY AZOMETHINE-DERIVED TRIDENTATE LIGANDS

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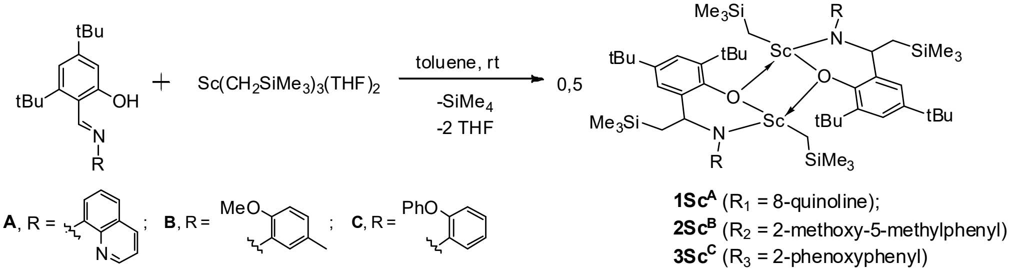
Unique and versatile catalytic properties of alkyl rare-earth compounds have made them the subject of intense study for the past few decades. Moreover, the selectivity parameters of metal-promoted catalytic transformations are strongly influenced by use of different types of ligand systems.

It was found out that reactions between the tris(alkyl) precursor $Sc(CH_2SiMe_3)_3(THF)_2$ and an azomethines **A**–**C** occurred as a Sc-C bond protonolysis followed by alkyl group migration to imino carbon atom reducing imino fragment to the amido one, giving dimeric monoalkyl scandium complexes. The structures of scandium complexes **1Sc**^{A} and **2Sc**^{B} were confirmed by X-ray diffraction analysis.



1Sc^{A} (R_1 = 8-quinoline);
2Sc^{B} (R_2 = 2-methoxy-5-methylphenyl);
3Sc^{C} (R_3 = 2-phenoxyphenyl)

Scheme 1. Synthesis of scandium compounds **1–3Sc**$^{A–C}$

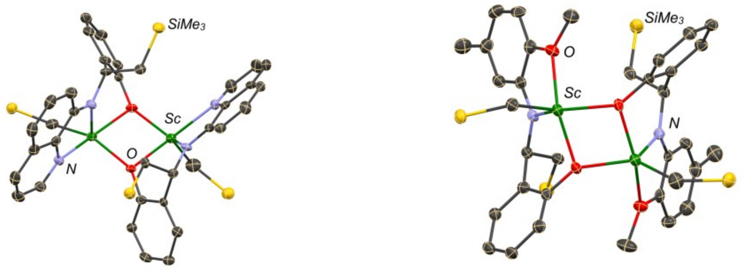


Figure 1. Molecular structures of **1Sc**^{A} and **2Sc**^{B}

Obtained compounds enabled complete conversion of 1000 equivalents of isoprene to polymer within a 4 h period or faster. The microstructures of the polyisoprenes were high in cis-1.4-content (up to 90.8%). All complexes **1–3Sc**$^{A–C}$ also turned out to be active in hydrophosphination of phenylacetylene with equimolar amount of $PhPH_2$, giving single- and double addition products mixtures in all cases. Complexes **2Sc**^{B} and **3Sc**^{C}, supported by ligands containing oxygen atom as an additional Lewis base were found to be more effective in both types of transformations.

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EFFICIENT NEAR INFRARED LUMINESCENCE OF LANTHANIDES IN PERFLUORINATED ORGANOSULPHIDE AND PHOSPHINOXIDE ENVIRONMENT

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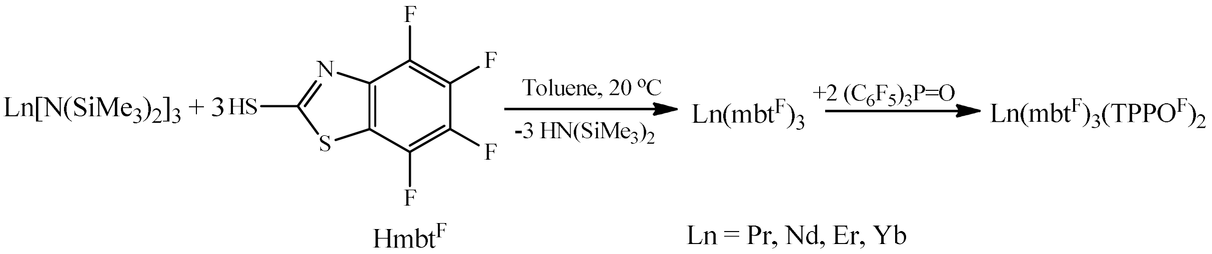
The near infrared (NIR) luminescence is in demand in many modern technologies, such as lasers and telecommunication, night vision, biomedicine and many others. The promising NIR emitters are perfluorinated organic complexes of lanthanides, since they have characteristic narrowband radiation and long lifetimes of excited states. Recently we have synthesized the lanthanide ate-complexes with perfluorinated 2-mercaptobenzothiazolate (mbt^F) ligands. [1] These complexes demonstrated a significant enhancement in intensity and lifetime of NIR luminescence despite the presence of numeric quenchers (C-H bounds) in their structure. In order to increase the NIR luminescence efficiency we have synthesized hydrogen-free complexes of lanthanides accordingly to scheme 1.



Scheme 1

The use of non-solvating toluene as a solvent and perfluorinated tris(phenyl)phosphine oxide (TPPO^F) as a neutral hard-base ligand results in formation of highly NIR-emitting complexes of Nd and Yb, whereas the derivatives of Pr and Er emit both in visible and NIR range. Time-resolved luminescent studies of the complexes revealed that the lifetime of the NIR emission is about 1 μs for Pr and exceeds several tens of microseconds for Nd, Er and Yb ions. In the case of Nd derivative the value of the emission lifetime is among the highest ever reported for organic Nd complexes. The impact of ionizing irradiation on the photoluminescence properties of the compounds has been studied. It was found that no change in the luminescence spectra is observed after irradiation.

[1] V. Ilichev, L. Silantyeva, A. Yablonskiy, B. Andreev, R. Rumyantcev, G. Fukin and M. Bochkarev, *Dalton Trans.*, **2019**, *48*, 1060-1066.

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ELECTROCHEMICAL PROPERTIES OF NEW PINCER NICKEL (II) HALIDES

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Over the past decades, the pincer ligands have attracted an increasing interest due to the unique properties of the coordination compounds they form. These monoanionic tridentate ligands are of great importance in organometallic and coordination chemistry. Their complexes with transition metals are used as homogeneous catalysts for various processes and also as functional materials with specified properties. The metal complexes formed by the pincer ligands provide an efficient alternative to the existing catalysts based on noble metals and, hence, the use of these complexes is a promising task of the modern chemical science. Therefore, nickel as the most accessible and inexpensive analog of palladium and platinum is of great practical interest [1].

Four metal halides of the (^{t}BuPCN)NiX family [X = F (**1**), Cl (**2**), Br (**3**), or I (**4**); PCN = 1-[3-[(di-tertbutylphosphino)methyl]phenyl]-1H-pyrazole] have been prepared through a direct reaction of the corresponding anhydrous NiX_2 salts and the unsymmetrical PCN pincer ligand. Combined electrochemical results [cyclic voltammetry (CV) and in situ electron paramagnetic resonance spectro-electrochemistry] reveal that the fluoride complex **1** is different from the other halides **2**−**4** in terms of electro-oxidation behavior (presence of three anodic peaks instead of one in the CV profile (Figure 1)).

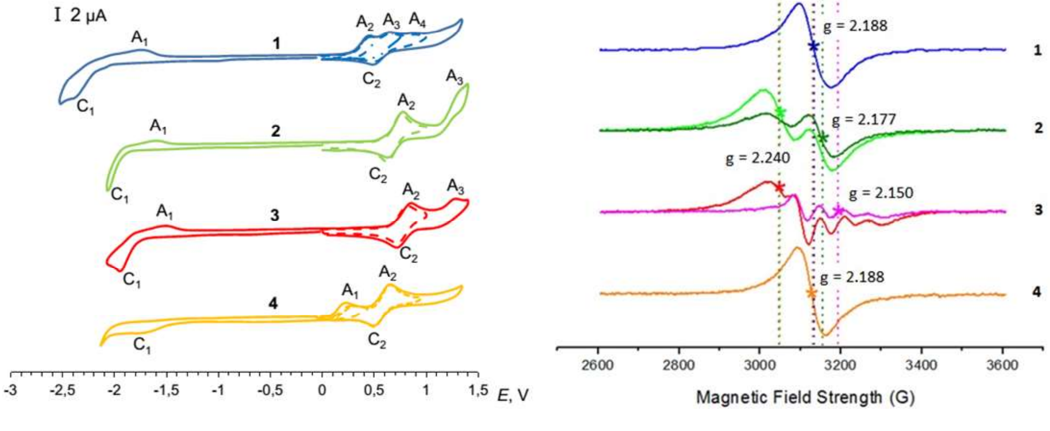

Figure 1. CV curves and EPR spectra of complexes **1**−**4**.

[1] Z .N. Gafurov, A. A. Kagilev, A.O. Kantyukov, A.A. Balabaev, O.G. Sinyashin, D. G. Yakhvarov, *Russ. Chem. Bull.*, **2018**, 67 (3), 385-394.

[2] L. Luconi, C. Garino, P. Cereia Vioglio, R. Gobetto, M. Chierotti, D. Yakhvarov, Z. Gafurov, V. Morozov, I. Sakhapov, A. Rossin, G. Giambastiani, *ACS Omega*, **2019**, *4*, 1118-1129.

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ELECTROCHEMICAL SYNTHESIS OF NEW *N*- HETEROCYCLIC CARBENE COMPLEXES OF NICKEL

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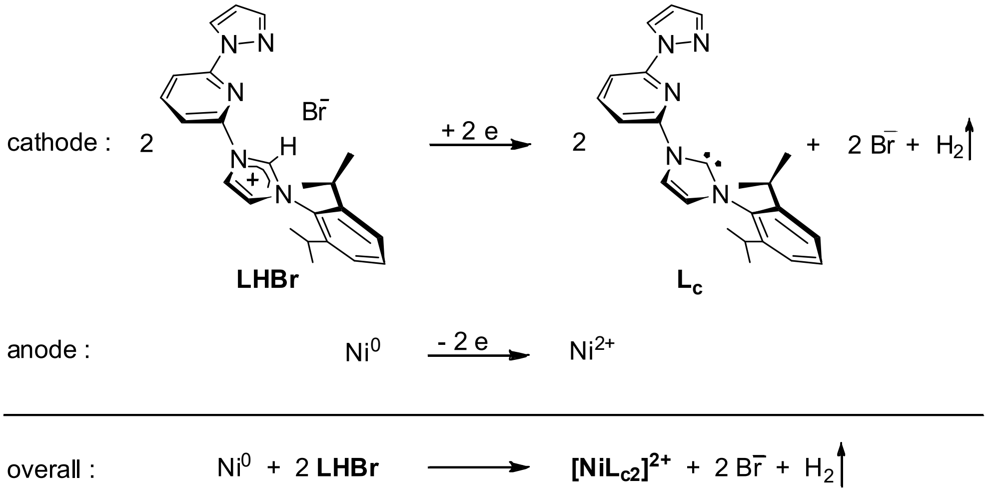
N-Heterocyclic carbenes (NHCs) are widely used as ligands in catalysis by transition metal complexes. The catalytic activity of transition metal NHC complexes is much higher than that of the transition metal complexes bearing the phosphine and nitrogen-containing ligands. They show excellent catalytic performance in different transformations of the organic compounds, especially in the carbon—carbon and carbon—element bond forming reactions. Palladium NHC complexes are very efficient catalysts for the cross-coupling reactions. On the other hand, nickel is less expensive and regarded as a promising alternative to palladium and, therefore, it attracts increasing attention from the researches [1,2].

In this work we present the electrochemical syntheses of sterically hindered pyrazolyl-pyridyl *N*-heterocyclic carbene complex of nickel, which has been monitored by mass spectrometry (ESI) method. (Scheme 1). The advantages of the electrochemical synthesis are room temperature and the use of metal plate as a metal precursor instead of the nickel complexes. Moreover, the electrochemical procedure needs a shorter reaction time (less then 1h) than the traditional chemical methods. The reactions are mainly carried out in acetonitrile; the imidazolium salt plays a role of both *N*-heterocyclic carbene source and electrolyte.



Scheme 1. Electrochemical synthesis of *N*-Heterocyclic carbenes complex of nickel.

[1] Z.N. Gafurov, A.O. Kantyukov, A.A. Kagilev, A.A. Balabaev, O.G. Sinyashin, D.G. Yakhvarov, *Russ. Chem. Bull.*, **2017**, *66*, 1529.
[2] L. Luconi, Z. N. Gafurov, A. Rossin, G. Tuci, O. G. Sinyashin, D. G. Yakhvarov, G. Giambastiani, *Inorg. Chim. Acta*, **2018**, 470, 100-105.

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LOW-VALENT DERIVATIVES OF GERMANIUM AND TIN BASED ON 9,10-PHENANTHRENEDIIMINES

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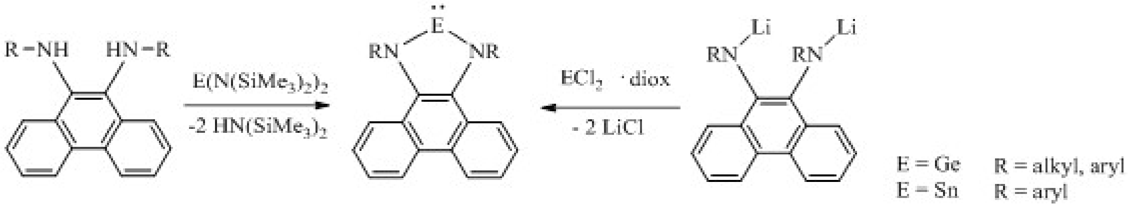
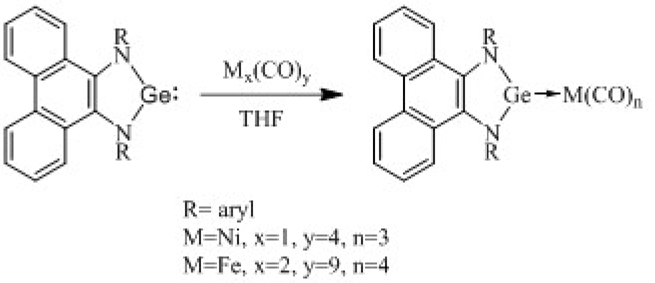
N,N'-disubstituted 9,10-phenanthrendiimines are promising ligands in coordination chemistry. Their feature is the combination of the extended aromatic system of phenanthrene and the possibility of regulating steric and electronic effects by changing substituents at nitrogen atoms.

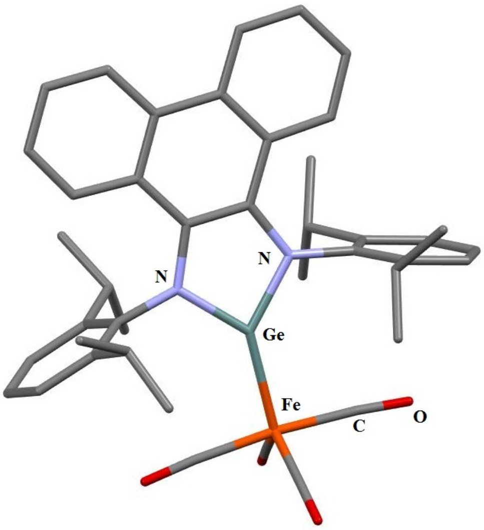
We synthesized germylenes based on diaryl, dialkyl-, and alkyl-aryl- and stannylene based on diaryl-substituted phenanthrenediimines.



Plumbylenes with any type of ligand and stannylenes with alkyl-substituted ligands are unstable and decompose during the reaction with the release of metals.

The obtained compounds are analogues of Arduengo carbene and are able to act as ligands in the construction of new metal complexes. To study this ability, we carried out reactions with transition metal carbonyls.





Acknowledgements This work was supported by the Russian Scientific Foundation (Grant 17-13-01428).

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BIS(ALKYL) RARE-EARTH COMPLEXES AS EFFICIENT CATALYSTS FOR THE HYDROARYLATION AND HYDROBENZYLATION OF OLEFINS

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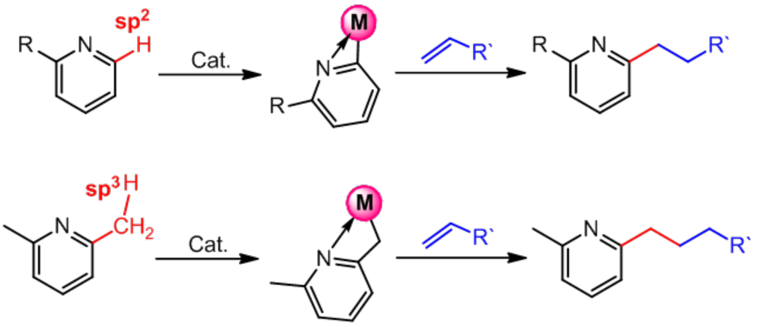
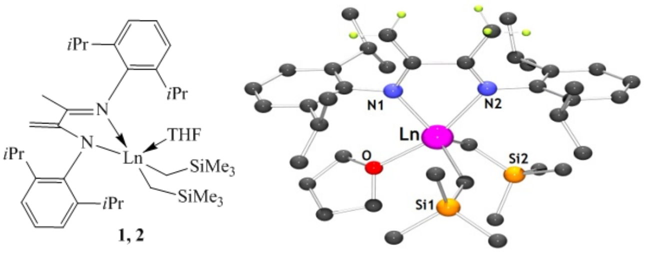
Rare-earth alkyl complexes have demonstrated unique reactivity in various organic reactions, as well as the ability to activate C-H bonds and promotion the functionalization of hydrocarbons. Of particular interest are catalytic reactions, including activation of inert C-H bonds via the formation of M-C bonds and the subsequent introduction of various substrates, due to the great prospects and opportunities of this method of obtaining valuable organic products. Pyridine-based organic molecules are widely used as various pharmaceuticals, dyestuffs, corrosion inhibitors and many others. A promising way of obtaining these compounds is catalytic arylation and benzylation of olefins (Figure 1).



Scheme 1.

A mono-anionic amido-imino ligand system was successfully employed for the synthesis of alkyl yttrium (**1**) and lutetium (**2**) complexes (Figure 1). The complexes **1** and **2** in combination with $[Ph_3C][B(C_6F_5)_4]$ proved to be excellent catalysts for *ortho*-selective of arylic and benzylic C-H addition of various pyridines to styrenes.



1, 2

Figure 1.

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LANTHANIDE (III) COMPLEXES WITH REDOX-ACTIVE LIGANDS SUPPORTED BY BULKY FORMAMIDINATES

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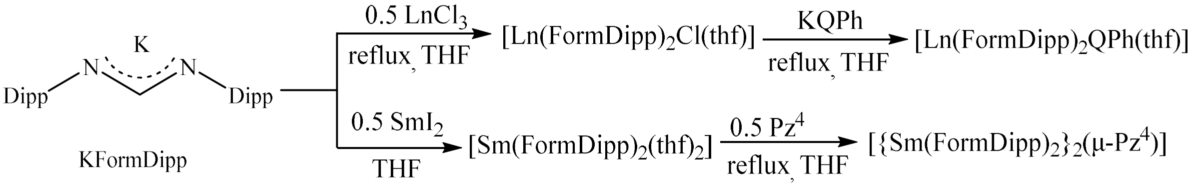
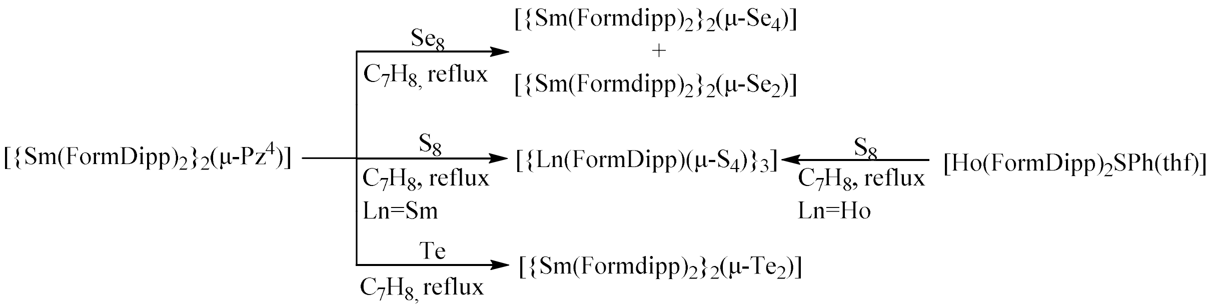
Formamidinates ($HC(NR)_2^-$) are monoanionic N-chelating ligands, whose steric and electronic properties are easily tuned by variation of the substituents R. In lanthanide chemistry the use of bulky ligands allows stabilization of Ln(II) complexes (Ln=Eu, Yb, Sm), or Ln(III) complexes with redox-active ligands. These compounds can be used as powerful reductants, for example, reactions of $[Ln^{II}(FormDipp)_2(thf)_2]$ (Ln=Sm, Yb) (FormDipp = bis(2,6-diisopropylphenyl)formamidinate) with elemental sulphur result in formation of $[\{Ln^{III}(FormDipp)(\mu\text{-}S_4)\}_3]$. [1]

In this work new Ln(III) formamidinate complexes with redox-active ligands were obtained. Reaction of $[Sm^{II}(FormDipp)_2(thf)_2]$ with tetramethylpyrazine (Pz^4) yields $[\{Sm^{III}(FormDipp)_2\}_2(\mu\text{-}Pz^4)]$, which contains reduced form of pyrazine $(Pz^4)^{2-}$. Complexes $[Ln(Formdipp)_2(QPh)(thf)]$ (Ln = Y, Tb, Dy, Ho, Er; Q = S, Se) were prepared by salt metathesis reaction of $[Ln(Formdipp)_2Cl(thf)]$ and KQPh.



The obtained compounds reduce elemental chalcogens to yield polychalcogenide derivatives. In the reaction of $[\{Sm(FormDipp)_2\}_2(\mu\text{-}Pz^4)]$ with S_8 already known $[\{Sm(FormDipp)(\mu\text{-}S_4)\}_3]$ was obtained. Reduction of Se gives two complexes: $[\{Sm(Formdipp)_2\}_2(\mu\text{-}Se_4)]$ and $[\{Sm(Formdipp)_2\}_2(\mu\text{-}Se_2)]$. In the case of Te only $[\{Sm(Formdipp)_2\}_2(\mu\text{-}Te_2)]$ was isolated. Oxidation of $[Ho(Formdipp)_2(SPh)(thf)]$ by S_8 results in formation of a trinuclear complex $[\{Ho(FormDipp)(\mu\text{-}S_4)\}_3]$.



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NEW CHALCOGENIDE HETEROMETALLIC COMPLEXES V-YB. APPROACHES TO SYNTHESIS, STRUCTURE

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At the moment one of the most promising ways to achieve a high blocking temperature in monomolecular magnets is the preparation of heterometallic complexes of lanthanides with transition metals. We chose vanadium chalcogenide complexes as precursors of such compounds.

First, we have synthesized new chalcogenide vanadium complexes with β-diimine ligand (nacnac = [HC(CMeN[2,6-diisopropylphenyl])$_2$]). The complexes [(nacnac)EV(μ,η^2-E$_2$)VE(nacnac)] containing sulfur and selenium are similar, the chalcogen atoms occupy bridging and terminal positions. The tellurium-containing complex [V$_2$(μ-Te)$_2$(nacnac)$_2$] is different, it contains only bridging Te atoms.

The obtained complexes of vanadium were reduced with $Cp^*_2Yb(thf)_2$. As a result, complexes with ytterbium [Cp*$_2$(thf)Yb(μ-E)VE(nacnac)] (E=S,Se) were isolated and structurally characterized. In the original compound, two vanadium-chalcogen bonds are broken, the resulting fragment {VE$_2$(nacnac)} is coordinated through one of the chalcogen atoms to Yb. Tellurium-containing complex does not react with ytterbocene. And as a result of the reaction with [$Cp^*_2Sm(thf)_2$], the already known compound [$(Cp^*_2Sm)_2Te$] is formed.

We also investigated the reaction of already known $V_2(^{Me}Cp)_2S_4$ complex with ytterbocene. A new heterometallic five-core anionic cluster $[Yb_4Cp^*_4S_6V(^{Me}Cp)]^-$ was obtained which crystallizes with the cation $[Cp^*_2Yb(thf)_2]^+$. A more chalcogen-saturated $V_2(^{Me}Cp)_2S_5$ complex in a similar reaction results in a neutral five-core cluster $[Yb_3Cp^*_4S_6V_2(^{Me}Cp)_2]$, the structure of which is a cuban core $\{V_2Yb_2S_4\}$ to which along one of the faces is attached a fragment $\{S_2YbCp^*_2\}$.

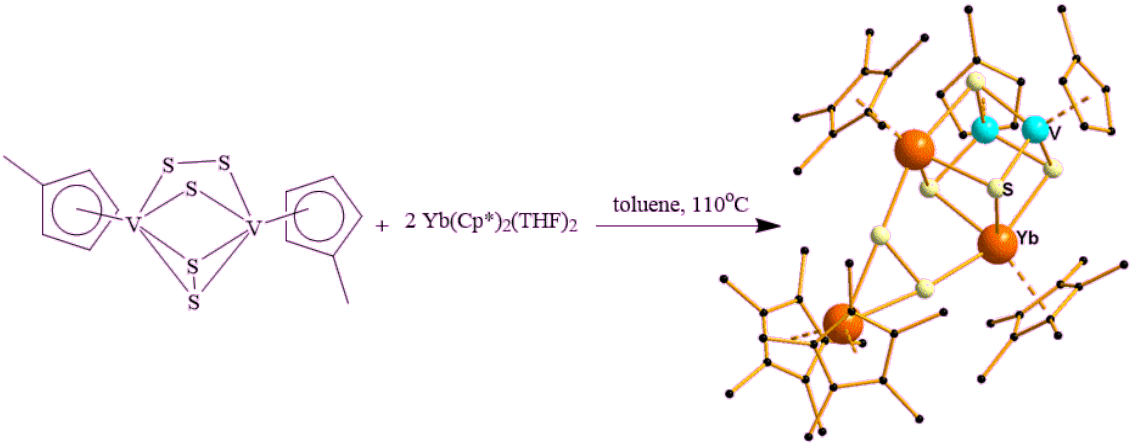

Figure 1 Scheme of synthesis $[Yb_3Cp^*_4S_6V_2(^{Me}Cp)_2]$.

Acknowledgements.

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ALUMINUM HYDRIDES WITH ACENAPHTHENE-1,2-DIIMINE LIGANDS

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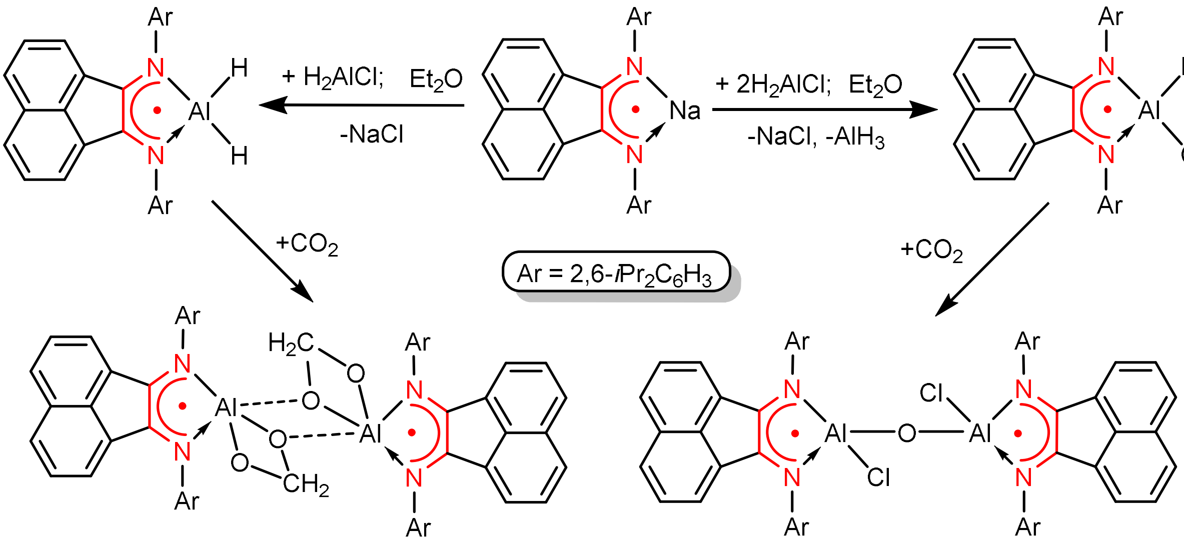
Aluminum hydrides are widely used in different industrial applications as components of Ziegler-Natta catalyst systems for αolefin polymerization and oligomerization and for the synthesis of stereoregular diene rubbers. Besides, these compounds proved to be efficient reagents for the preparation of aluminum chalcogenides and alumoxanes by controlled hydrolysis, as well as reducing agents. In some cases, the use of hydrides as selective reducing agents is limited by their high reduction potentials. One way to modify the reactivity of aluminum hydrides is to combine them with nitrogencontaining ligands. This approach was successfully applied to coordination compounds of dblock elements and to maingroup metal complexes with redox-active 1,2-acenaphthenediimine ligands.

In this work, we present the synthesis, structures, and some properties of aluminum hydrides with radical-anionic and dianionic acenaphthene-1,2-diimine ligands [1,2].



[1] V. G. Sokolov, T. S. Koptseva, M. V. Moskalev, A. V. Piskunov, M. A. Samsonov, and I. L. Fedushkin, *Russ. Chem. Bull*, **2017**, *66*, 1569–1579.
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ChemShip-2019/Topical Problems of Modern Chemistry
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September 16-21, 2019, Nizhny Novgorod, Russia

ADVANCED SIMULATION TECHNIQUE FOR THE STUDYING OF DYNAMIC EFFECTS IN CW EPR SPECTRA OF SPIN-LABELLED COMPLEXES

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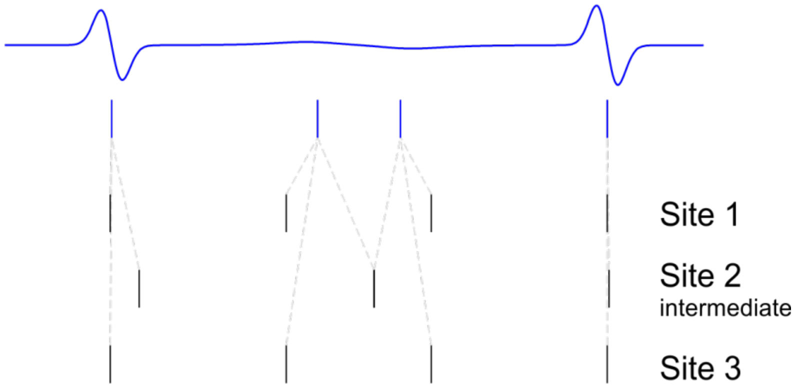
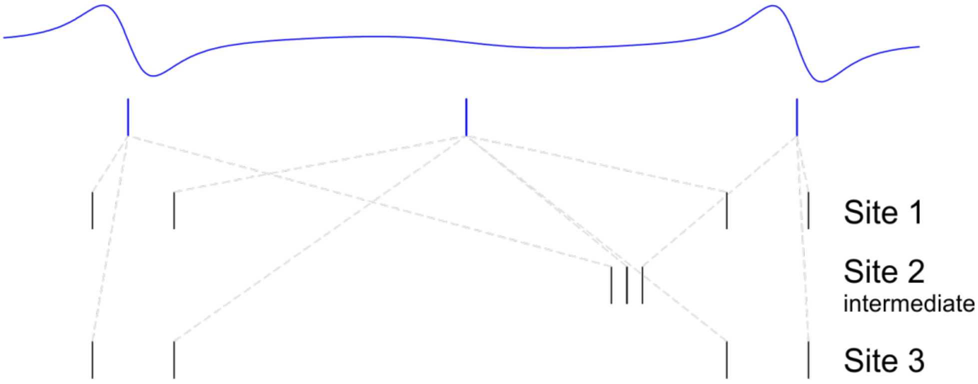
Advanced technique of simulation of dynamic processes in cw EPR spectra based on Heinzer's algorithm [1] is proposed. Novel improvements include:

- exact line position calculation via matrix diagonalization either Beit-Rabi method [2]
- compensation of additional line broadening in fast-motion regime with a minimum number of varying parameters
- automatic calculation of the sites populations from the rate constants matrix
- simple and intuitive model for parameters restriction
- multicomponent spectral simulation and natural isotope mixtures as well

These improvements allow simulation and least-square fitting of the cw EPR spectra of any possible radical particles with virtually unlimited complexity of the dynamic processes scheme. Particularly, an estimation of spectral parameters and the structure of intermediate states directly unobservable by EPR becomes possible.



Example 1



Example 2

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Acknowledgements – the work was performed in the framework of the Russian state assignment (theme 44.1 № 0094-2017-0009).

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EFFECT OF THE bpy-phen RATIO FOR THE PHOTOMECHANICAL PROPERTIES OF THE SEMIQUINONIC COBALT COMPLEXES

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It is known that complexes of the composition like $(bpy)Co(SQ)_2$ or $(phen)Co(SQ)_2$ demonstrate redox isomerism phenomena as well as their solid solutions with the general composition $(bpy)_x(phen)_{1-x}Co(SQ)_2$ [1]:

$$\mathbf{(bpy)Co(SQ)_2 \rightleftarrows (bpy)Co(SQ)(Cat)} \text{ or } \mathbf{(phen)Co(SQ)_2 \rightleftarrows (phen)Co(SQ)(Cat)}$$

SQ = 3,6-di-tert-butyl-o-benzosemiquinonate, Cat - 3,6-di-tert-butyl-catecholate,

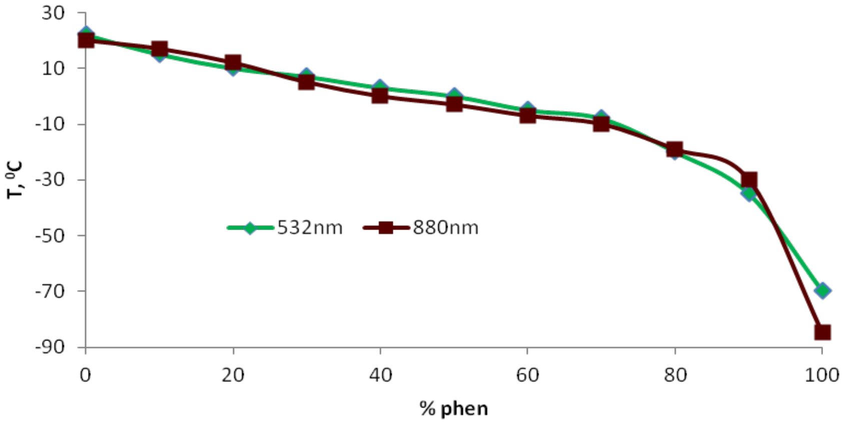
bpy = 2,2'-bipyridyl, phen = phenanthroline.

In this work it was shown that all of these complexes demonstrate photomechanical effect at different temperatures depending on the bpy/phen ratio. The effect appears under irradiation by visible (532nm) or NIR (880nm) light.


without irradiation


under irradiation

The temperature of the appearance of photomechanical effect gradually decreases with the enlarging of the phen fraction in the composition.



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Acknowledgements – the work was supported by RSF (grant 19-13-00142).

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HOMOLEPTIC DINUCLEAR LANTHANIDE COMPLEXES BASED ON FLUORINATED 1,3-DIKETONATE BEARING ACETAL FRAGMENT

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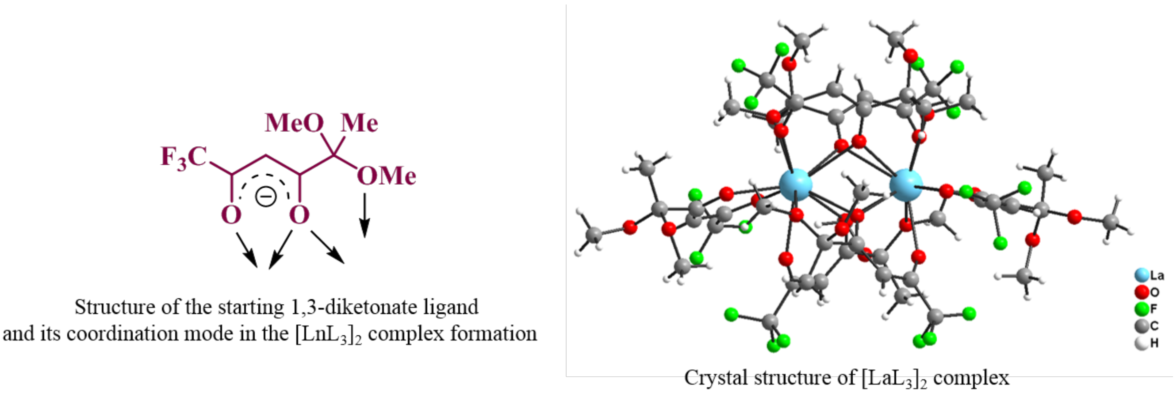
Lanthanide complexes with β-diketones have been intensively studied because of their outstanding photophysical, electric, and magnetic properties. They are therefore widely used in optical devices, diagnostics, catalysis and material chemistry.

The interaction of 1,3-dicarbonyl ligands with Ln(III) salts are usually proceeds under basic conditions and can give more than one structure type of metal complex from a single reaction [1]. In this work, a convenient route for dinuclear lanthanide diketonates preparation was described (where Ln = La, Ce).

Recently, we have elaborated a scalable approach to the novel lithium trifluoromethyl-β-diketonate that can be used in the metal complexes synthesis without extra ligands and basic additives [2, 3]. In general, the reaction of fluorinated lithium diketonate with the majority of Ln ions (from Nd to Yb) resulted in the heteroleptic dinuclear lanthanide-lithium complexes [3]. However, the interaction of LiL with La(III) and Ce(III) chlorides in the alcohol media yielded solely a dinuclear lanthanide complex, in which acetal fragments of diketonates act in a chelate-bridging manner. The structure and properties of obtained metal complexes will be discussed.



Structure of the starting 1,3-diketonate ligand and its coordination mode in the $[LnL_3]_2$ complex formation

Crystal structure of $[LaL_3]_2$ complex

Figure

[1] P. C. Andrews, F. Hennersdorf, P. C. Junk and D. T. Thielemann, *Eur. J. Inorg. Chem.*, **2014**, 2849-2854.
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X-RAY EXCITATED LUMINESCENCE OF LANTHANIDE COMPLEXES WITH ORGANIC LIGANDS

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The conversion of ionizing radiation into UV or visible or infrared light is an important task from both theoretical and applied points of view. This process is implemented in scintillators, which are widely used in medical diagnostics, in devices for detecting all types of ionizing radiation and monitoring the state of the environment, in devices for direct conversion of ionizing radiation into electric current.Currently, there are quite a lot of compounds that demonstrate high radioluminescent characteristics, but each of them has its drawbacks, so the search for new efficient and stable radioluminescent materials remains an important and challenging task.

We investigated the X-ray luminescence properties of some complexes of Nd, Sm, Eu, Tb, Dy, Tm and Er with 2-(2-benzoimidazol-2-yl)phenolate (NON), 4,4,4-trifluoro-1- (2-thienyl) -1,3-butanedione (TTA) and 1,3-acetylacetonate (acac) ligands. When excited with UV light with □ex 365 nm all the studied complexes exhibited metal-centered and/or ligand-centered emission of various intensity depending on the lanthanide.

It was found that irradiation of the complexes Eu, Tb and Dy with X-ray of 10 keV also causes luminescence but much weaker (Fig. 1). To compare the luminescence intensity, the X-ray luminescence spectrum of anthracene is given.

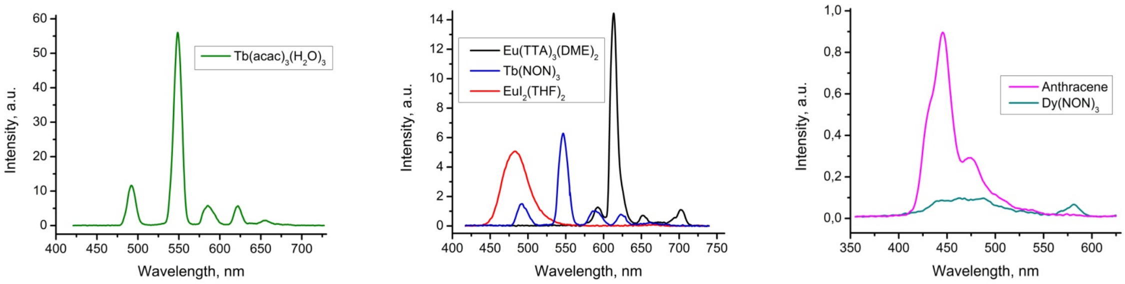

Figure 1. Radio luminescence spectra of organometallic complexes of lanthanides and anthracene

Comparison of the intensity of radioluminescence and photoluminescence showed that the latter was 300 times higher. With simultaneous excitation by X-ray and UV light, a total intensity is observed, which indicates the similarity of the mechanisms of both types of excitation.

The detected high efficiency of radioluminescence of the Eu and Tb complexes allows to consider them as promising materials for the design of radiation detectors.

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CF_3-FUNCTIONALIZATION OF INDOLES CATALYZED BY CYCLOPENTADIENYL COBALT COMPLEXES

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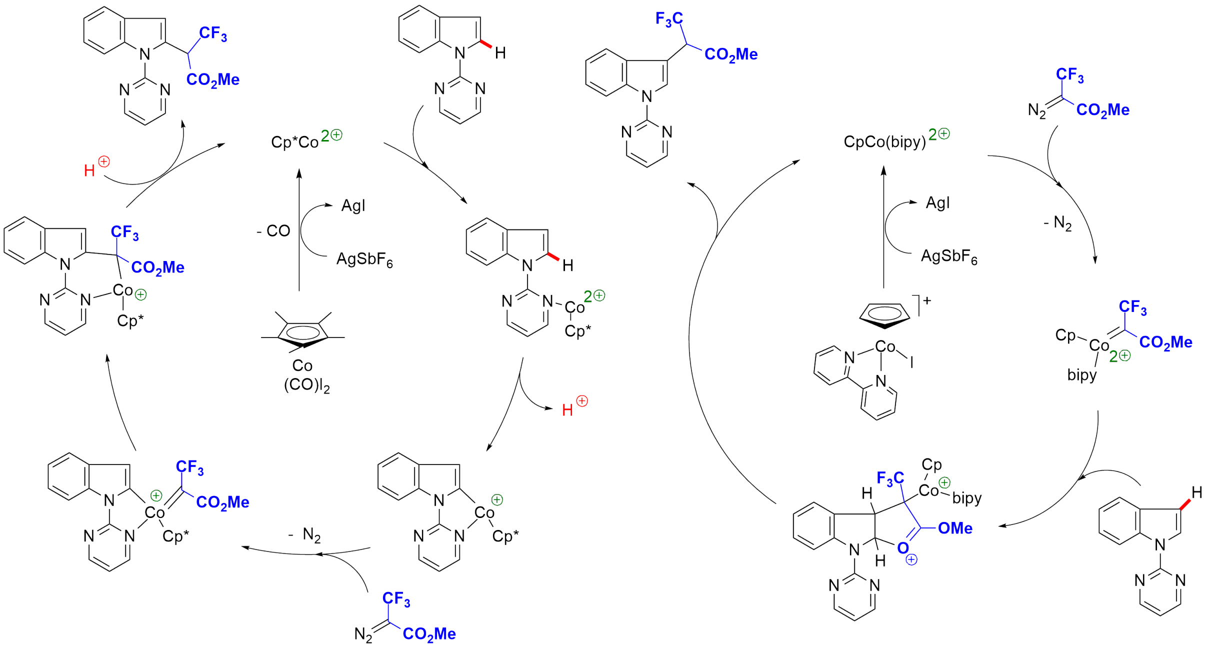
The selective incorporation of the fluorine functionalities in biologically relevant compounds has become an essential tool in drug discovery process [1]. The metal-carbene C–H insertion starting from diazo compounds (including methyl 3,3,3-trifluoro-2-diazopropionate) has proved to be the most efficient approach to solve this task [2,3]. In the present work, we developed new family of catalytic systems based on the cobalt complexes for the regioselective CF_3-functionalization of *N*-(pyrimidin-2-yl)indole at the 2- or 3-positions. In particular, we found that 2,2'-bipyridyl and 1,10-phenanthroline Co(III) complexes $[CpCo(N,N\text{-ligand})I]^+$ selectively catalyze alkylation of N-(pyrimidin-2-yl)indole with methyl 3,3,3-trifluoro-2-diazopropionate to give C3-substituted indole derivative. It should be noted that this reaction proceeds without participation of directing group (pyrimidinyl substituent) because required vacant coordination sites at cobalt atom are blocked by N,N-ligand. In contrast, similar reaction catalyzed by the (carbonyl)iodide complex $Cp^*Co(CO)I_2$ leads to C2-substituted indole as a result of chelation-assistance of pyrimidinyl group.



Structure of the catalysts as well as mechanisms of catalytic reactions will be also discussed.

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Acknowledgements - This work was supported by the Russian Foundation for Basic Research (Grant No. 16-29-10672).

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POLARIZABILITY EFFECT AS THE DISTINCTIVE FEATURE OF CHARGED MOLECULES

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The literature data on substituent influence on chemical (rate constants *k*, activation parameters) and physical (parameters of IR, NMR, EPR, NQR, UV-Vis electronic, UV photoelectron, X-ray photoelectron, and Mössbauer spectra; spectroscopic and thermodynamical characteristics of different complexes; strength, polarity, and length of the chemical bond) properties P of charged molecules, bearing an excess charge δ on the reaction (indicator) centre R_c, have been observed using the correlation analysis of narrow series.

Such series are of two types.

Classic series $X{-}C_6H_4{-}R_c^{\delta}$ (substituents X vary, the reaction (indicator) centre R_c remains constant, δ − excess charge on the R_c) obey the equation

$P = P_0 + a\sigma_I + b\sigma_R$,

where σ_I and σ_R are inductive and resonance constants of X respectively.

Non-classic series XBR_c^{δ} and XR_c^{δ} (the bridge B, say –CH=CH−, −C≡C− etc. is shorter than the $-C_6H_4-$ fragment or absent) obey the equation

$P = P_0 + a\sigma_I + b\sigma_R + \mathbf{c}\boldsymbol{\sigma}_{\alpha}$,

where $\mathbf{c}\boldsymbol{\sigma}_{\alpha}$ is the polarizability constants of X substituent.

The charge δ polarizes a substituent X of the series XBR_c^{δ} and XR_c^{δ}, thus including a dipole moment. The polarizability effect is short-range ion-dipole electrostatic interaction between the charge δ and the induced dipole.

Let's take three concrete examples.

- Reaction $X_2S + Pd(H_2O)_4^{2+} \rightarrow [X_2SPd(H_2O)_3]^{2+} + H_2O$, rate constants *k* ($M^{-1}s^{-1}$)

$\lg k = 4.28 + 15.54\Sigma\sigma_I - 16.06\Sigma\sigma_R + \mathbf{2.44}\boldsymbol{\Sigma\sigma_{\alpha}}$ S_Y=0.09 (0.86) R=0.994 (0.000)

- Complexes $XOH + Me_3Si^+ \rightarrow [Me_3Si{\cdot}XOH]^+$, enthalpy ΔH (kcal M^{-1})

$\Delta H = -30.9 + 152.3\sigma_I - 67.1\sigma_R + 26.5\boldsymbol{\sigma_{\alpha}}$ S_Y=0.2 (1.6) R=0.999 (0.947)

- X-ray PES X_4Ge 3d electron binding energy *E* (eV)

$E = 37.32 + 2.18\Sigma\sigma_I - 1.19\Sigma\sigma_R^+ + 1.37\boldsymbol{\Sigma\sigma_{\alpha}}$ S_Y=0.07 (0.34) R=0.999 (0.968)

(…) – The S_Y and R values are calculated ignoring the polarizability effect.

Thus, in all cases the polarizability effect has a large influence on properties of non-classic charged molecules.

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TRIBUTYLBORANE IN THE SYNTHESIS OF GRAFT COPOLYMERS OF COLLAGEN AND ACRYLIC MONOMERS

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A.V. Mitin, L.L.Semenycheva

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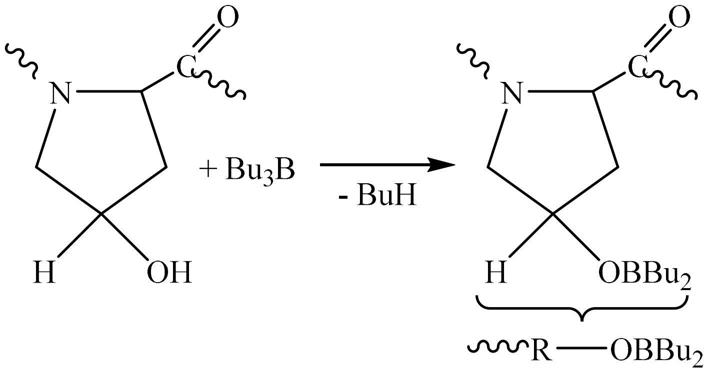
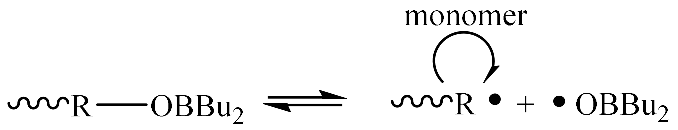
The collagen-graft copolymers with methyl methacrylate and acrylamide were synthesized. Grafting was carried out with the initiating system tributylborane - oxygen through two reaction centers: the radical and molecular. The first ones are macroradicals formed due the separation of the hydrogen from the protein’s molecule by radicals – products of tributylborane oxidation. The second ones are formed by reaction below (on the example of the amino acid oxyproline - the structural unit of collagen):



and are reversible inhibiting agents [1]:



Grafting polymerization with collagen was carried out at 60°C. The increase of the tributylborane concentration causes the growth of synthetic parts of the copolymer. Depending on the tributylborane concentration, polymethyl methacrylate achieves to 2-60 %, polyacrylamide – to 30-43 %. MWD of collagen-graft-polymethyl methacrylate has two modes, and collagen- graft-polyacrylamide MWD is single-mode.

Grafting of methyl methacrylate on collagen was carried out at temperature range 25-60°C. Independently on temperature, the percentage of polymethyl methacrylate is ~50 %. The structure of sinthesized at 25°C collagen-graft-polymethyl methacrylate, observed with scanning electron microscope, is similar to collagen. With temperature growth the destruction of collagen native structure occurs.

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Acknowledgements – The study was carried out on the equipment of the Collective Usage Center “New Materials and Resource-saving Technologies” (Lobachevsky State University of Nizhni Novgorod).”

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DIVLENT LANTANIDES AND ALKALINE–EARTH METAL COMPLEXES COORDINATED BY NHC LIGANDS – EFFICIENT CATALYSTS FOR HIGHLY REGIO- AND CHEMOSELCTIVE HYDROPHOSPHINATIONS WITH PHOSPHINE

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The formation of C−P bonds via single-step intermolecular hydrophosphination reactions of unsaturated substrates is a promising, atom-efficient route to a wide range of phosphorus-containing compounds. Despite the progress achieved in this field, a substrate scope of this reaction remains limited and mainly involves activated olefins and ubiquitous phenyl- and diphenylphosphine [1]. Addition of PH_3 to alkenes and alkynes is a progressive and convenient synthetic route to a variety of primary, secondary and tertiary phosphines.

The first example of intermolecular hydrophosphination of styrene, 2-vinylpyridine and phenylacetylene with PH_3 catalyzed by complexes $[(Me_3Si)_2N]_2M(NHC)_n$ (M = Ca, Yb, Sm; n = 1, 2) coordinated by series of NHC ligands is described. The reactions of styrene with PH3 proceed under mild conditions in quantitative yields to afford exclusively anti-Markovnikov product and allow for the chemoselective synthesis of primary, secondary and tertiary phosphines (Figure 1). Addition of phenylacetylene to PH_3 regardless the initial molar substrates ratio results in the exclusive formation of a tertiary tris-(Z-styryl)-phosphine. Crucial effect of the Lewis base coordinated to the metal center on catalytic activity in styrene hydrophosphination with PH_3 was demonstrated [2].

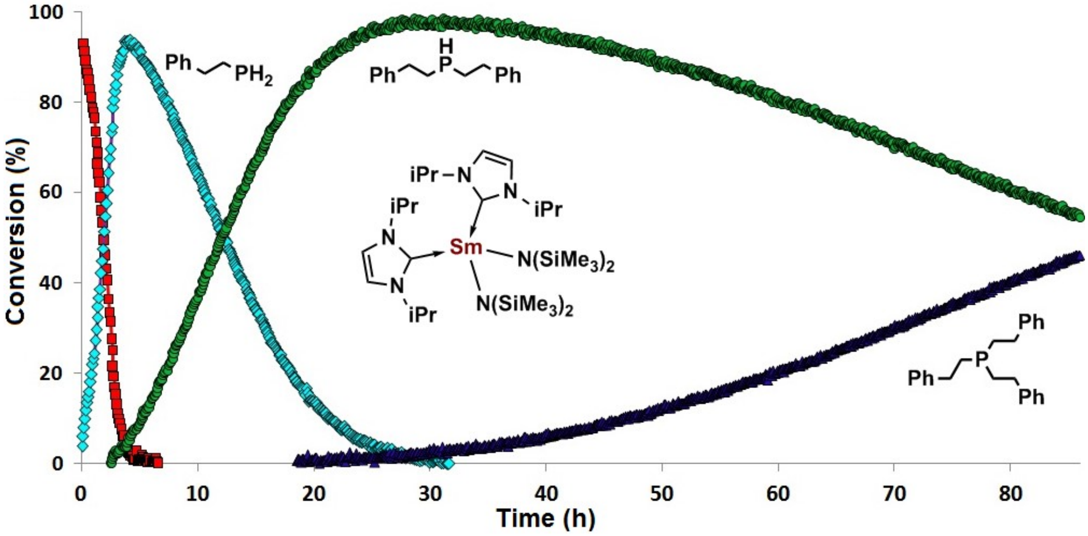

Figure 1. Plot of the reagents conversion vs reaction time for the catalytic hydrophosphination of styrene with PH_3.

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SOME THERMOCHEMICAL CHARACTERISTICS OF Mg, Zn, Sr AND Cd COMPLEXES WITH O-IMINOBENZOQUINONE LIGANDS

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Different complexes with o-iminobenzoquinone ligands organic compounds of major importance in biological systems and industrial applications as dyestuffs or pharmaceuticals. In addition, these compounds are subject of photochemical and photophysical investigations.

One of the characteristics of their practical application is the thermodynamic parameters of sublimation. However, the current set of experimental data on the thermodynamic properties of complexes with o-iminobenzoquinone ligands are incomplete, and in some cases contradictory.

In the present work was investigation of thermodynamics parameters of sublimation and vapor phase composition of complexes with o-iminobenzoquinone $Ln(L)_3$ (Ln = Mg (**1**), Zn (**2**), Sr (**3**), Cd (**4**); L = 3,5-di-tert-butyl-1,2-quinone-1-(2-oxy-3,5-di-tert-butylphenyl)imine). The compounds were purified by sublimation in vacuum for further experiments.

The temperatures of melting of the **1-4** measured by the DSC method using a differential scanning calorimeter DSC204F1 Phoenix (DSC) (Netzsch Gerätebau, Germany). The endothermic transition was detected for all compounds. This transition was associated with melting. Thermodynamic parameters of melting **1-4** are calculated.

The composition of vapor phase of **1-4** was investigation by mass-spectrometry.

The temperature dependencies of the vapor pressure compounds **1-4** were measured by Knudsen effusion method. Vaporization temperature interval was chosen according to the DSC data (40-400 °C). Thermodynamic parameters of sublimation are calculated: for sample **1** $\Delta_sH=102\pm2$ kJ/mol, for sample **2** $\Delta_sH=109\pm4$ kJ/mol, for sample **3** $\Delta_sH=114\pm5$ kJ/mol and for sample **4** $\Delta_sH=121\pm4$ kJ/mol. The complexes **1-4** are stable according to the mass-spectrometry data, there is not aggregation of molecules in the gas phase. Consequently, the calculation of vapor pressure was performed for the process of sublimation to monomeric vapor.

[1] A. A. Maleev, O.Yu. Trofimova, A. P. Pushkarev, N. V. Somov, V. V. Travkin, G. L. Pakhomov, A. V. Piskunov, M. N. Bochkarev // Nanotechnologies in Russia, 2015, 10, 7-8, 613-620

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COMPLEXES OF RARE-EARTH METALS WITH POLYDENTATE AMIDINATE LIGANDS AS A CATALYSTS OF CONTROLLED ISOPRENE POLYMERIZATION

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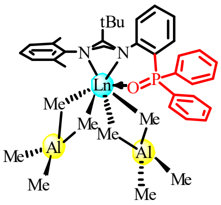
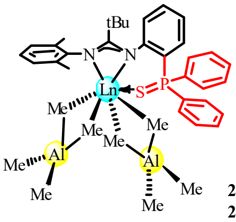
Development of efficient and selective catalysts for polymerization of readily available raw monomers in order to obtain high-quality polymeric materials has been the subject of long-standing research of international scientific groups. The production of synthetic polyisoprene is one of the promising areas for the use of lanthanide-based catalysts. Synthetic polyisoprene is an essential elastomer and it's widely used in the creation of artificial rubbers and compositions based on them. Optimization and development of new catalytic systems for the polymerization of isoprene, is of both fundamental and applied interest for creating materials with desired rheological properties.

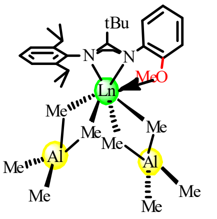
A series of new bis(tetramethylaluminate) **1–4** (La, Nd, Sm) as well as new bis (N,N-dimethyl-o-aminobenzyl) **5–6** (Y, Nd) complexes of lanthanides were obtained and structurally characterized.



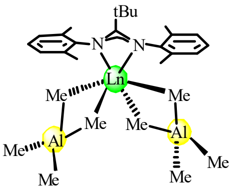
1Nd 54%
1La 58%
1Sm 56%



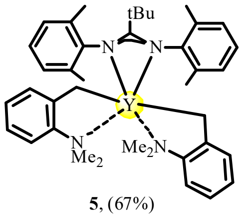
2Nd 45%
2La 78%



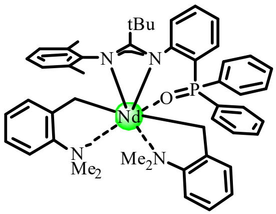
3Nd 61%
3La 59%



4Nd 72%
4La 68%



5, (67%)



6, (78%)

Using of complexes **1–6** as a test-catalysts of isoprene polymerization help us to better understand the influence of such factors on activity and stereoselectivity as: nature and bulkiness of donor groups in the amidinate ligand, ionic radius of the central metal atom, type of organoaluminum co-catalysts introduced into the catalytic systems, separately and in complex.

Acknowledgements – This work was supported by RFFI (18-43-520036).

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YTTERBIUM AND SAMARIUM COMPLEXES WITH STERICALLY HINDERED DIIMINE LIGANDS

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To date only a few examples of metal complexes containing tri- or tetraanionic redox-active ligands are known. For instance, these are the derivatives of pyridine(diimine) ligands [1, 2]. In 2003 we reported a four-step reduction of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) with sodium metal. All four sodium salts of $(\text{dpp-bian})^{n-}$ (n = 1, 2, 3, 4) have been isolated and structurally characterized [3]. Meanwhile, in the chemistry of rare earth elements, a combination of a redox-active ligand and redox-active metal allows to design the molecular systems exhibiting unusual spectral, magnetic and chemical properties [4].

Here we report the synthesis and characterization of a homo- and heterometallic lanthanide complexes, supported with tri- and tetraanionic acenaphthene-1,2-diimine ligand dpp-bian. This kind of molecule may find further application as multielectron reducing agents in organic synthesis or precursors of stoichiometric mixed metal oxides and other inorganic functional materials. Coordinatively unsaturated lanthanide complexes based on sterically hindered $^{\text{BzHd}}$Ar-bian ligand (1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene) were synthesized and structurally characterized.

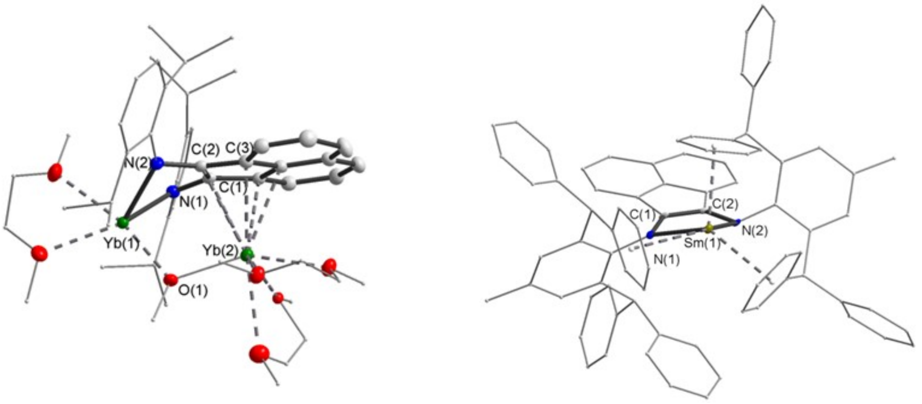

Figure 1. Molecular structures of complexes $[(\text{dpp-bian})\text{Yb}_2(\text{OMe})(\text{dme})_3]$ (left) and $[(^{\text{BzHd}}\text{Ar-bian})\text{Sm}]$ (right).

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COBALT COMPLEX BASED ON DPP-MIAN LIGAND IN THE STUDY OF HYDROARRYLATION REACTION WITH NAPHTHOL

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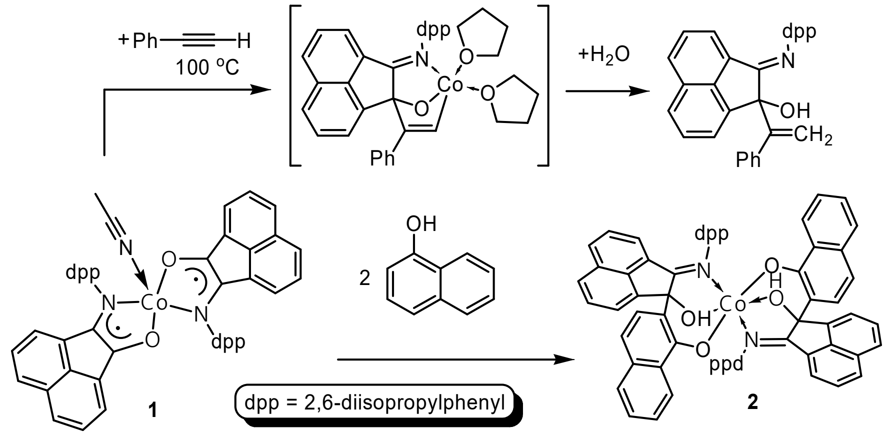
The gallium complexes based on dpp-BIAN (1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), and dpp-MIAN (2-(2,6-diisopropylphenylimino)-acenaphthylen-1-one) were shown earlier [1,2] to display catalytic activity in the reaction of hydroarylation of phenylacetylene with α-naphtol.

In this work we obtained a cobalt (II) complex (dpp-MIAN)$_2$Co(CH$_3$CN) (**1**) based on radical-anion dpp-MIAN ligands. The test reactions of complex **1** in the process of hydroarylation showed that **1** does not catalyze this reaction. However, our detailed study revealed that complex **1** reacted with both phenylacetylene and naphthol (Scheme 1).



Scheme 1

Complex **1** interacts with phenylacetylene in toluene only with strong heating to 100°C for several days. However, we failed to isolate the product in the crystalline form. To determine the composition and structure of the final compound, we carried out its hydrolysis. The ^{1}H-NMR study of the organic fraction indicates that a ligand with a phenylacetylene fragment attached is present in the final complex, similar to that formed in the reaction of the magnesium dpp-MIAN derivative with phenylacetylene. [3]

As a result of the reaction of cobalt complex **1** with naphthol, compound **2** was isolated in which naphthol is attached to the carbonyl carbon atom of a dpp-MIAN ligand (Scheme 1).

Addition occurs at the β-position of naphthol. It should be noted that in the catalytic hydroarylation of phenylacetylene by α-naphtol in presence of gallium dpp-BIAN and dpp-MIAN complexes proceeds in the β-position as well.

The data obtained form a basis to discuss the mechanism of phenylacetylene hydroarylation catalysis by metal complexes with redox-active diimine and imino-ketone ligands such as BIANs and MIANs in more detail.

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GERMANIUM COMPLEXES BASED ON DPP-MIAN LIGAND

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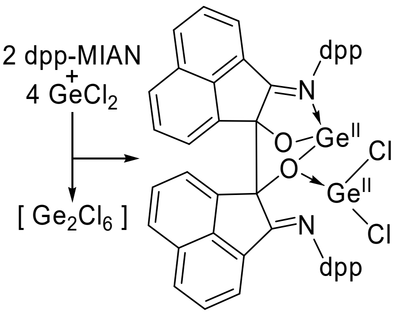
In 2019, we have shown that dpp-MIAN (2-(2,6-diisopropylphenylimino)acenaphthylen-1-one) can undergo one-electron reduction, leading to the radical-anionic complexes and reversible carbon-carbon binding of two ligands.[1] Thus, the direct reduction of dpp-MIAN with metallic tin results in a complex with doubled dpp-MIAN via the carbonyl carbon atom of the ligand. At the same time, tin(II) chloride can produce both a complex with two anion-radical dpp-MIAN and a complex with a double bis-dpp-MIAN, depending on the conditions.

In this report, we describe the complexes of germanium, which are formed also in the process of one-electron reduction of dpp-MIAN.



Scheme 1. Formation of complex **1**

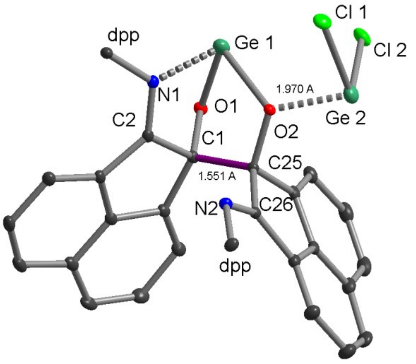
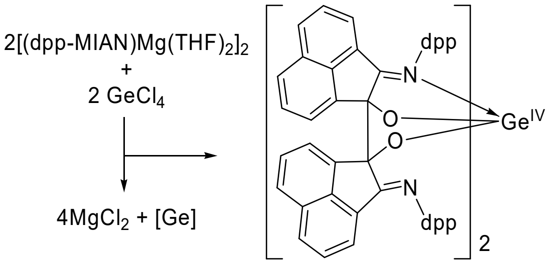


Fig. 1. Molecular structure of **1**.

As a result of the interaction with germanium(II) chloride, complex **1** is formed where dpp-MIAN accepts one electron, while only a part of germanium chloride is transformed, and the final complex **1** contains two types of divalent germanium (Scheme 1).

By the reaction of germanium (IV) chloride with magnesium complex [(dpp-MIAN)Mg(THF)$_2$]$_2$, complex **2** with two double bis-dpp-MIAN was obtained (Scheme 2).



Scheme 2. Formation of complex **2**

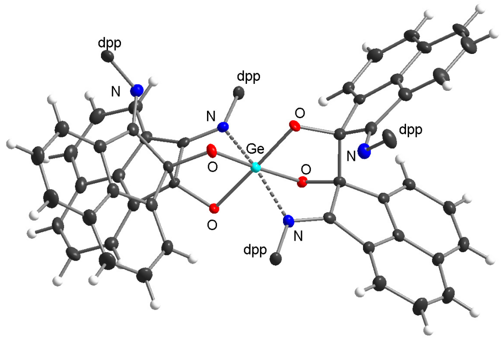


Fig. 2. Molecular structure of **2**.

[1] A. Lukoyanov, E. Ulivanova, D. Razborov, V. Khrizanforova, Y. Budnikova, S. Makarov, R. Rumyantcev, S. Ketkov, and I. Fedushkin*, Chem. Eur. J.*, **2019**, *25*, 3858–3866.

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ChemShip-2019/Topical Problems of Modern Chemistry
International conference "Organometallic Chemistry Around the World" (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

BINUCLEAR COBALT PHTHALOCYANINES AS HIGHLY EFFICIENT CATALYSTS FOR THE OXIDATION OF A MERCAPTAN

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Phthalocyanine metal complexes are very active catalysts for various oxidation reactions [1]. One example is the oxidation of mercaptans to disulfides by using cobalt(II) phthalocyanines (Co(II)Pc) as catalysts. Industrially important is the Merox (*Mer*captan *Ox*idation) process for the treatment of petroleum fractions to remove sulfur present as various thiols to less-objectionable disulfides with oxygen as oxidant without causing undesirable oxidation of hydrocarbons using Co(II)Pcs as selective working catalyst (Eq.1) [2]. As it was reported before [3], highest catalytic activities were observed for cobalt phthalocyanines adsorbed on conducting or semiconducting inorganic carriers, for polymeric phthalocyanines, and for π-extended analogues such as naphthalocyanines. Here we report significant increase of the catalytic activity from mononuclear cobalt phthalocyanine **1Co** to binuclear cobalt phthalocyanines **2Co₂**, **2ZnCo** and **2H₂Co** (Table 1) in the oxidation of 2-mercaptoethanol by molecular oxygen in THF solution containing 1.2 mM of NaOH. The preparation procedures were described elsewhere [4]. The catalytic activities (TOF) in the oxidation of 2-mercaptoethanol (Table 1) are the highest ever reported for phthalocyanines. The maximum mercaptan to **2Co₂** ratio (TON) was 700 000, the oxidation at this ratio can be repeated at least 3 times without any decrease of the activity which confirms high stability of the catalyst.

$$4RS^- + O_2 + 2H_2O \xrightarrow{Co(II)Pc} 2RS{-}SR + 4HO^- \qquad (1)$$

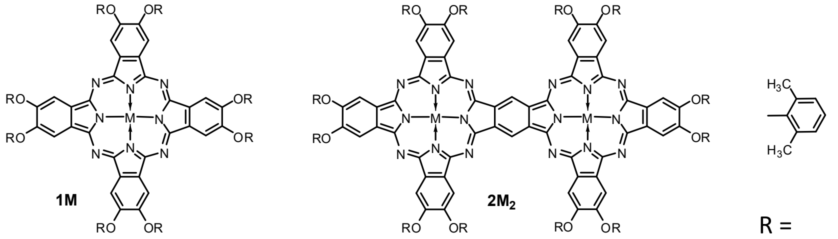

Table 1. Turnover frequencies of the oxidation of 2-mercaptoethanol by molecular oxygen.

Compound	C(Co^{II}), μM	TOF, mol(RSH) mol^{-1}(Co^{II}) min^{-1}
1Co	10	240
	1	250
2Co₂	10	3650
	2	4810
	1	4380
	0.4	3970
2ZnCo	10	3290
	1	4310
	0.4	3800
2H2Co	1	4110

Acknowledgements
This work was supported by the Russian Science Foundation (Project № 18-13-00356).

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LANTHANIDE(III)-CADMIUM(II) HETEROMETAL COMPLEXES WITH ANIONS OF AROMATIC AND ALIFATIC MONOCARBOXYLIC ACIDS: SYNTHESIS, STRUCTURE AND PROPERTIES

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[b]*A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, RUSSIA.*
[c]*P.N. Lebedev Physical Institute RAS, Moscow, RUSSIA.*
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In our research we are carrying out heterometal {Cd(II)-Ln(III)} complexes that attract a research's attention due to their photoluminescent and magnetic properties.

In the case of use of an anion of the pivalic acid (Hpiv), we obtained a series of the heterometal polymeric {Ln(III)-Cd(II)} complexes with architecture ($[Cd_2Ln(piv)_7(H_2O)_2]_n$) , Ln(III)= Ho(**1**), Yb(**2**),Tb(**3**). Trinuclear {Cd_2Ln} metal fragments of complexes **1-3** form a polymer chain due to the coordination of chelate-bridging carboxylate anions of neighboring {Cd_2Ln} residues by terminal Cd atoms.

When the anion of the trifluoracetic acid (Htfac) and 1,10-phenantroline (phen) were used it was shown that formation of heterometal{Cd(II)-Ln(III)} coordination compound was not carried out, but it lead to formation the only homometal polymeric complex $[Cd(tfac)_2(phen)]_n$ **(4)**.

The use of the fluorosubstituted derivatives of aromatic acids led us to the synthesis of a heterometal trinuclear complex with anions of the pentafluorbenzoic acid (Hpfbenz) in a presence of 2,2-bipyridine (bpy) as a ligand with architecture $[Cd_2Eu(pfbenz)_6(NO_3)(bpy)_2]$ (**5**) in which the atom of europium is connected with each terminal Cd atoms by chelate-bridging and two bridging anions of the pentafluorbenzoic acid.

In the case of use of an anion of the 2-furoic acid (Hfur) under similar to (**5)** conditions the tetranuclear complex $[Cd_2Sm_2(fur)_8(NO_3)_2(bpy)_2]$ (**6**) with two heterometal {Cd_2Ln} fragments linked by chelate-bridging carboxylate anions of the acid was obtained.

Synthesized **(5),(6)** compounds possess the photoluminescence activity. The quantum yields of this complexes are 0.8 % and 25% respectively and the lifetime of (**5**) is 2145 ms. The magnetic properties of compounds (**1**)-(**3**) were also studied and it was shown that the complex **(2)** possess properties of the single ion magnet (SIM).

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NEW ACENAPHTHENE-1,2-DIIMINES AS PRECURSORS FOR REDOX-ACTIVE MOFS

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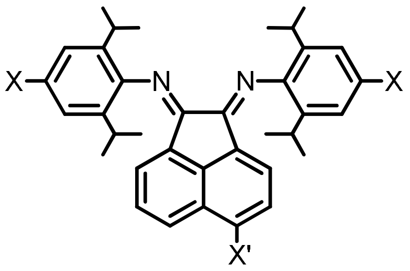
At the present time, despite of great variety of metal-organic frameworks (MOFs), the MOFs consisting of redox-active organic fragments coordinated to the metal atoms are limited to a very few examples. Among them, there are iron complexes with 2,5-dihydroxy-1,4-benzoquinone, MOFs containing ruthenium carboxylates based on TCNQ and MOFs derived from octahedral rhenium clusters [1-3]. Redox-active MOFs reveal the properties that are unknown for other MOFs, for instance, they are able to switch their spectral, magnetic and chemical properties upon external stimuli. Moreover, the typical properties of MOFs, such as absorption of small molecules from gaseous and liquid mixtures could be finely turned by changing of a charge distribution between metal and redox-active ligand.

Here we report the synthesis and characterization of a series of new functionalized acenaphthene-1,2-diimine (Ar-bian) ligands, containing of redox-active diimine fragments and redox-inactive units – precursors for redox-active MOFs. Thus, halogen substituted in naphthalene ring and N-phenyl ring (Fig. 1) as well as malonate derivative of Ar-bian have been prepared and characterized spectrally. Zinc, aluminum and gallium complexes based on these diimines have been obtained and characterized by single crystals X-ray analysis and NMR-spectroscopy.



1 (X = H, X' = Br); **2** (X = Br, X' = H);
3 (X = Br, X' = Br); **4** (X = I, X' = H)

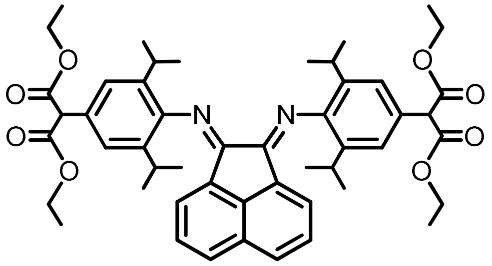


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Figure 1. Acenaphthene-1,2-diimine ligands – precursors for redox-active MOFs.

[1] Y. M. Litvinova, Y. M. Gayfulin, K. A. Kovalenko, D. G. Samsonenko, J. Leusen, I. V. Korolkov, V. P. Fedin, Y. V. Mironov, *Inorg. Chem.*, **2018**, *57*, 2072-2084;

[2] D. M. D'Alessandro, *Chem. Commun.*, **2016**, *52*, 8957-8971;

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PRODUCTION OF BIODEGRADABLE POLYMERS IN CONTROLLABLE MANNER USING GROUP 13 METAL COMPLEXES WITH DPP-BIAN LIGAND

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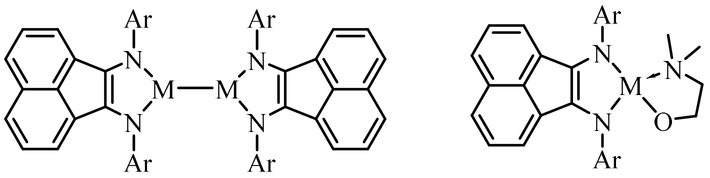
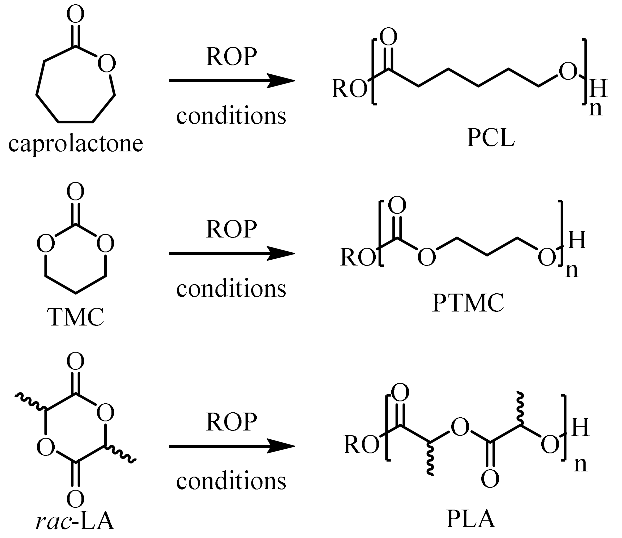
Nowadays biodegradable polymers are widely used in different fields such as medicine (temporary implants, soluble sutures), food processing industry (packing, disposable containers) etc. The most commonly used monomers for producing biodegradable materials are cyclic esters and carbonates. The physical properties of resulting materials can be tuned by chain length control and the stereoregularity of polymer. Thus the importance of an approach for the preparation biodegradable polymers in controllable manner has been arising in recent years. In the present study the ability of gallium and aluminium compounds supported by 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphtene (dpp-bian) are shown to act as polymerization catalysts of trimethylene carbonate (TMC), ε-caprolactone (ε-CL) and lactide.



M = Al, Ga   Ar = 2,6-diisopropylphenyl



Catalytic conditions were optimized and kinetic studies were carried out demonstrating the controlled nature of the ring-opening polymerization (ROP) process. A range of polymers with predictable molecular weight and narrow polydispersity were prepared and characterized. Novel complexes of dialuminum compound with coordinated monomers trimethylene carbonate and ε-caprolactone were synthesized.

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SYNTHESIS OF 3D-TRANSITION METAL COMPLEXES WITH BIFUNCTIONAL O-QUINONE, ANNELATED WITH DITHIETE CYCLE

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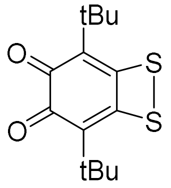
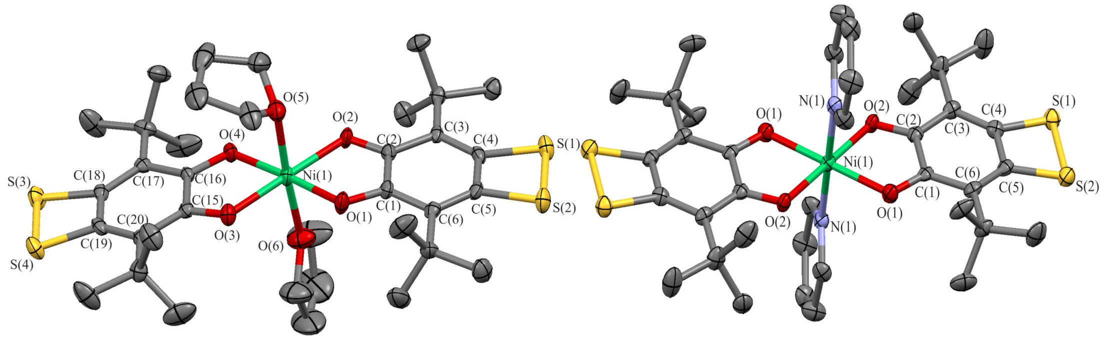
Sterically-hindered o-quinone, annelated with dithiete cycle (ditQ), combines both dioxolene and dithiolene coordination centers, ready for metal coordination. In comparison with the unsubstituted 3,6-di-tert-butyl-1,2-benzoquinone, it should be noted, that an additional dithiolene fragment, on the one hand, can significantly affect the crystal packing of mononuclear metal complexes due to intermolecular interactions. On the other hand, bifunctional ligand provides the prospects of increasing the number of magnetic centers.



ditQ

According to previously obtained data, as well as Lewis-Pearson HSAB theory, it can be assumed that 3d-transition metals will be primarily coordinated to o-quinone site with the formation of the corresponding polyspin systems. Indeed, dioxolene site is activated in treatment of $Ni(CO)_4$ with two equivalents of ditQ ligand in THF and pyridine. Hexacoordinated trans-complexes have been crystallized and characterized by X-ray crystallography. These reactions showed us the first example of trans-arrangement of tetrahydrofuran molecules relative to each other in hexacoordinated bis(o-semiquinonato)nickel complexes. Neutral pyridine ligands also have trans-configuration in coordination polyhedron.



Acknowledgements - This work was supported by Russian Science Foundation (Project № 19-73-00264)

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Co^{II} AND Ni^{II} SUBSTITUTED MALONATES WITH SINGLE-CHARGED CATIONS OF DIFFERENT NATURE

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Anions of malonic acid and its substituted analogues can serve as chelating or bridging ligands, which opens up opportunities for the synthesis of a wide range of coordination compounds: from mono- and polynuclear to polymer frame systems [1-3]. The possibility of constructing polynuclear compounds with paramagnetic atoms makes these objects promising for the production of magnetoactive compounds.

Here we present the results of the synthesis of Ni^{II} and Co^{II} compounds with the anions of cyclopropane-1,1-dicarboxylic acid (cpdc) and Rb and Cs atoms – $[Cs_2M^{II}(H_2O)_8(cpdc)_2]_n$ ($M^{II} = Ni^{II}$ (**1**) or Co^{II} (**2**)), $[(Rb_6Co_3(H_2O)_{12}(cpdc)_6)\cdot 4H_2O]_n$ (**3**), $[RbNi(H_2O)_2(cpdc)_2]_n$ (**4**). Dianions form two six-membered rings with 3d-metal atoms, thus giving rise to the bischelate fragment $\{M^{II}(cpdc)_2\}^{2-}$.

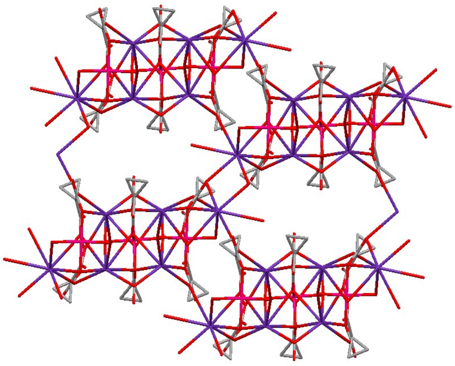

Fig. Fragment of compound **3** (hydrogen atoms are omitted)

Replacing cyclopropane-1,1-dicarboxylic acid with dimethylmalonic acid (Me_2Mal) in a system $M^{II} : R_2mal^{2-} : Kt^+$ (M^{II} = Co or Ni, R_2mal – dianions of substituted malonic acids) makes it possible to obtain 36-nuclear complexes. In particular, the compound $[Ni_{36}(NHEt_3)_{12}(H_2O)_{12.25}(OH)_{20}(HMe_2mal)_4(Me_2mal)_{26}]$ (**5**) was isolated with the triethylammonium cations. Each atom of Ni is located in the distorted octahedral environment of the oxygen atoms of acid dianions, OH-groups and coordinated water molecules [4].

Magnetic behavior of complexes were studied. It was shown that for the compound **5** exchange interactions of the ferro- and antiferromagnetic type are observed between paramagnetic centers [4]. For the compound $[(Rb_6Co_3(H_2O)_{12}(cpdc)_6)\cdot 4H_2O]_n$ it was shown that the complex is a SIM with the following characteristics: $\Delta E_{eff}/k_B$ is 48K, the relaxation time is $5.2\cdot 10^{-8}$ sec.

[1] Ungur, L., Thewissen, M., Costes, J.-P. et al., *Inorg. Chem.,* **2013**, 52, 11, 6328-6337;
[2] Gogoleva N.V., Zorina-Tikhonova E.N., Bogomyakov A.S. et al., *Eur. J. Inorg. Chem.*, **2017**, 3, 547-562;
[3] Zorina-Tikhonova E.N., Chistyakov A.S., Vologzhanina A.V. et al., *IUCrJ.*, **2018**, 5, 293-303;
[4] Vologzhanina, A.V., Zorina-Tikhonova, E.N., Matyukhina, A.K., et al., *Russ.J.Coord.Chem.*, **2017**, 43, 801-806.

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NOVEL MAIN GROUP METAL COMPLEXES OF HIGHLY STERICALLY HINDERED ACENAPHTHENE-1,2-DIIMINE LIGAND

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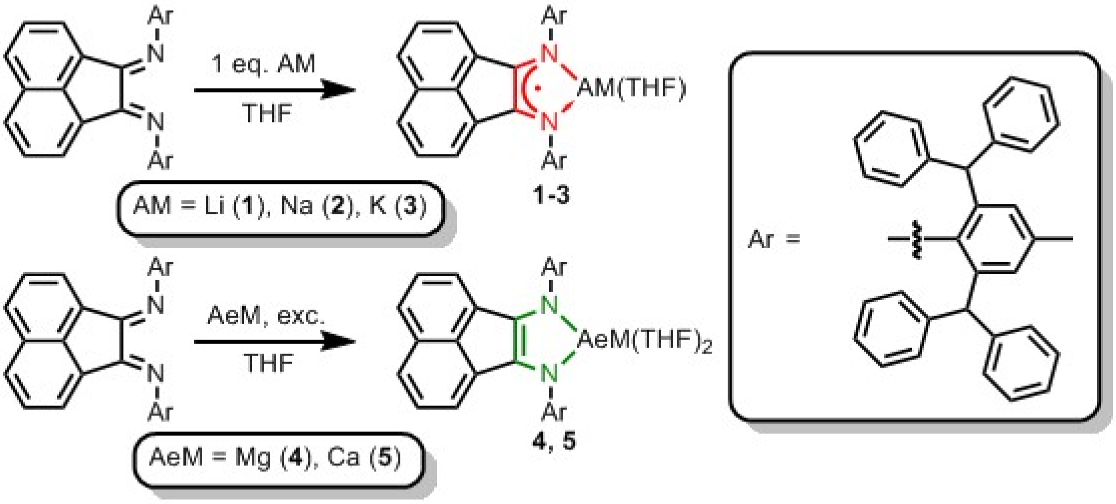
Sterically hindered acenaphthene-1,2-diimine ligands (Ar-bian) owing to their rigid backbone and diversity of bulky aryl groups at *N*-diimine atoms, have a widespread applications in coordination chemistry. For instance, complexes of Ar-bians with d-elements are powerful catalysts for alkynes hydrogenation, C–C bond formation, and especially olefin polymerisation. Complexes of main group metals based on redox-active Ar-bians ligands also have attracted rising in last decades. A major reason for the popularity of these complexes is idea of catalytic transformation of organic compounds on these systems [1-3]. Generally, these acenaphthene-1,2-diimine complexes of non-transition metals contain 2,6-*i*Pr-C_6H_3 substituents at *N*-diimine atoms (dpp-bian), whereas complexes of main group metals based on Ar-bian ligands with bulkier aryl groups compare to 2,6-*i*Pr-C_6H_3 were not synthesized yet. Here, we report on the synthesis of some new alkaline (**1-3**) and alkaline earth (**4**, **5**) metal complexes based on a highly sterically hindered 1,2-bis[(2,6-dibenzhydryl-4-methylphenyl)imino]acenaphthene (dbhmp-bian) (Scheme).



Compounds **1-5** have been isolated in crystalline form with moderate to good yields and characterised both spectral and X-ray diffraction methods. Noteworthy, the sodium complex **2** is useful precursor for preparation of aluminium and gallium hydrides or alkyls based on radical-anion of dbhmp-bian ligand.

[1] I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.*, **2012**, *18*, 255-266.
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GETEROMETALLIC ANTIMONY(V) CATECHOLATO COMPLEXES WITH DIIMINE MOIETY

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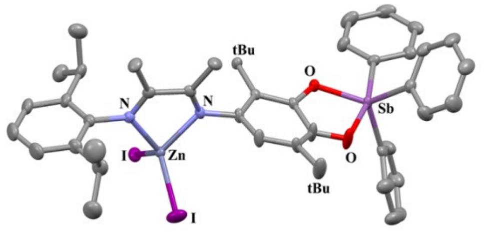
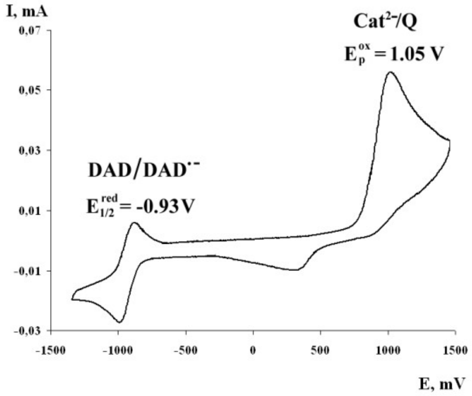
Heterometallic complexes - objects of active research used in various fields from the catalytic synthesis of fuel cells to the solar energy capture and storage. At the same time, much attention is paid to the study of interactions between different metals and metal-containing organic fragments and their effect on the electronic structure, chemical properties and reactivity. In this paper we report on the synthesis, structure, and electrochemical properties of new complex containing two metal centres (antimony and zinc) and two redox active fragments of different nature (catecholate and diazadiene).



$I_2Zn(DAD\text{-}3,6\text{-}DBCat)SbPh_3$



The complex possesses an electrochemical activity both in anode and cathode regions: diazabutadiene fragment undergoes one-electron reduction at $E^{red}_{1/2} = -0.93$ V yielding radical-anionic derivative; the oxidation of catecholato group proceeds as two-electron process at $E^{ox}{}_p = 1.05$ V to give unstable dicationic derivative with a neutral quinone form.

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SYNTHETIC ROUTES TO TITANIUM(IV) AND ZIRCONIUM(IV) CATHECHOLATE COMPLEXES

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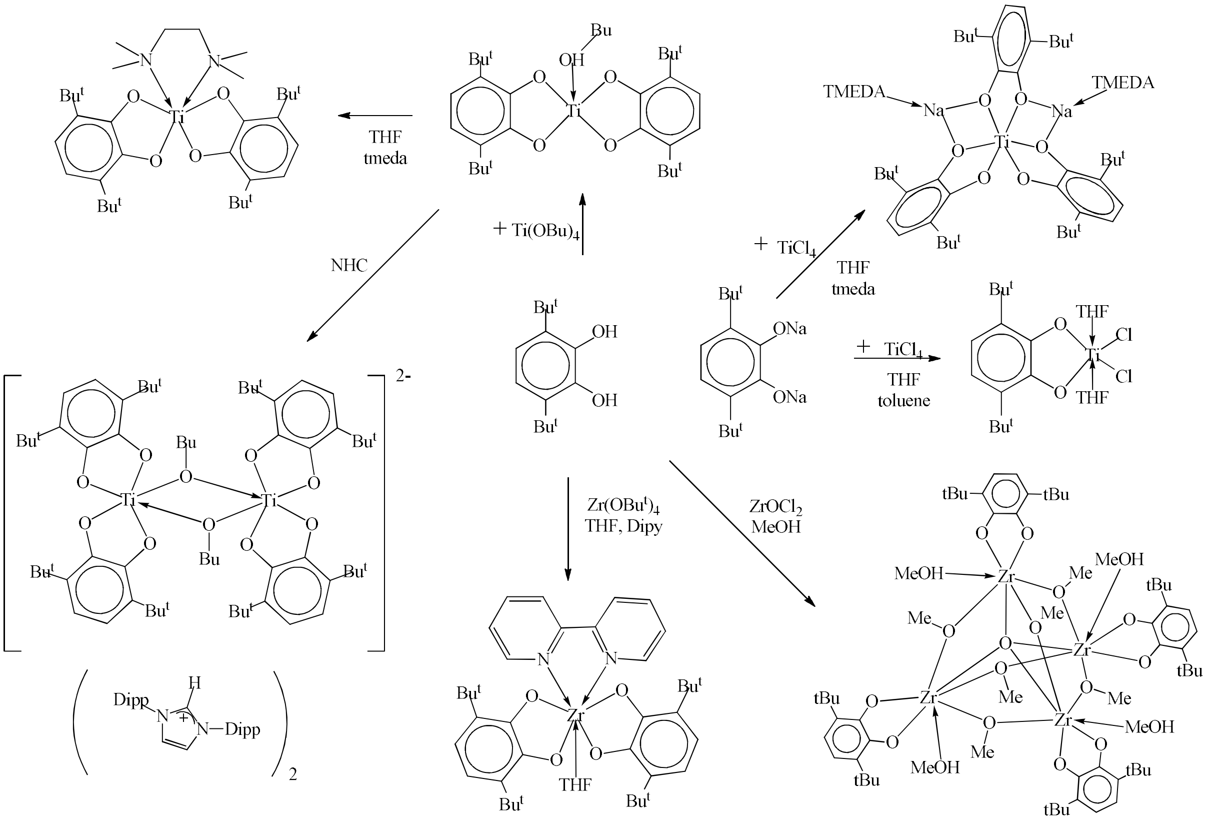
There has been a sustained and growing interest in titanium(IV) compounds containing different diolate, in particular catecholate, ligands in recent years. This type of compounds has attracted great attention due to prospects of their practical use in different fields, including medicine, the design of ceramic materials, coatings, photovoltaic cells and homogeneous or heterogeneous catalysts. The introduction of the catecholate functionality into polyoxotitanium and titanium alkoxide clusters not only facilitates the study of the cluster structures but also endows these compounds with important physicochemical properties. In particular, polyoxotitanium catecholate nanoparticles exhibit an intense absorption band in the visible region of electromagnetic radiation assigned to titanium—catechol ligand-to-metal charge transfer (LMCT), which significantly increases the efficiency of these compounds as photocatalysts.

Two synthetic approaches were used for the synthesis of 3,6-di-tert-butylcatecholate derivatives of titanium(IV). These approaches are based on the exchange reaction between sodium catecholate and titanium(IV) chloride and the reaction of 3,6-di-tert-butylpyrocatechol with titanium tetrabutoxide. The last synthetic route was found to be suitable for the preparation of zirconium(IV) compounds.



Acknowledgements: The investigation was supported by Russian Science Foundation (grant 17-13-01428).

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HETEROLIGAND PERFLUORINATED LANTHANIDE BENZOTHIAZOLATES. SYNTHESIS, STRUCTURE AND LUMINESCENT PROPERTIES.

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In recent years, much attention has been attracted to optoelectronic materials able to function under conditions of increased radiation: space, radiation therapy and diagnostics, the active zones of nuclear power plants, etc. Currently, only inorganic materials are used to function under ionizing radiation. Metal-organic substances, as an alternative to inorganic analogues, have been studied very little. Considerable attention is paid to metal complexes for use as electroluminescent materials in organic light-emitting diodes (OLED). Of particular interest are derivatives of Nd, Er, and Yb as effective materials emitting in the near infrared region. In an attempt to obtain such compounds, we synthesized a set of Sc, Nd, Sm, Eu, Ho, Gd, Er, Yb complexes with perfluorinated 2-(benzothiazol-2-yl)phenolate ligands - $Ln(SON^F)_3(DME)$ -by the reactions of silylamides $Ln[N(SiMe_3)_2]_3$ with phenol $H(SON^F)$. However, low thermal stability did not allow them to be used to obtain OLED. To solve this problem, heteroligand complexes were obtained: $Yb(SON^F)_2(NpSON)$, $Sc(SON^F)_3(bipy)$ and $Ln(SON^F)_3(phen)$ (Ln=Sm,Nd).

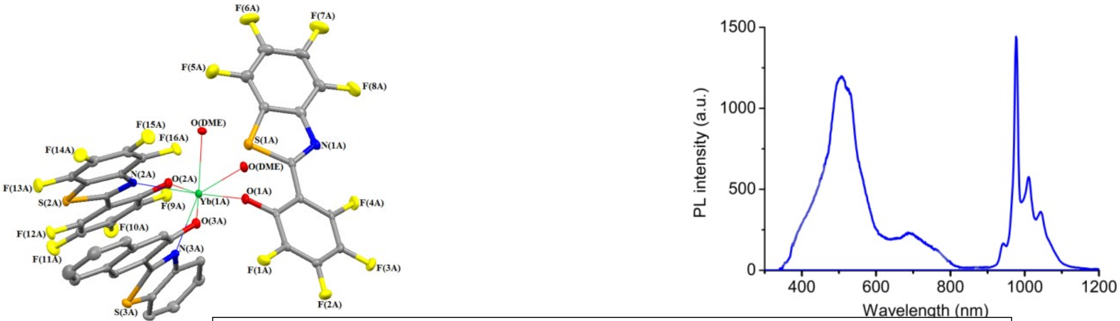

Figure 1. Molecular structures and PL spectra of $Yb(SON^F)_2(NpSON)$

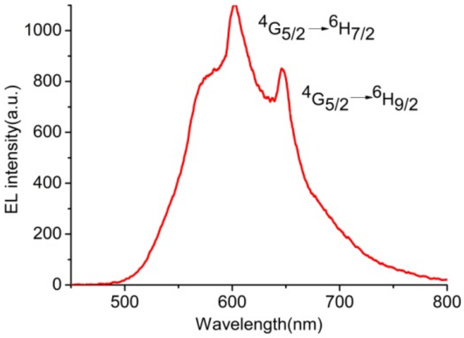

Figure 2. EL spectra of single layer device ITO/TPD/**complex** /Yb.

The PL spectra of $Yb(SON^F)_2(NpSON)$ exhibited a broad band picked at 580 nm originated from NpSON ligand (Fig.1) and the band at 978 nm attributed to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb^{3+} ion. The simple two layer devices ITO/TPD/**complex**/Yb (complex = $Yb(SON^F)_2(NpSON)$; $Sm(SON^F)_3(phen)$, $Sc(SON^F)_3(bipy)$ were fabricated. Electroluminescence was observed only on the samarium complex (Fig.2). The compounds obtained showed high radiation stability.

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TRANSITION METAL COMPLEXES BASED ON FERROCENYL-CONTAINING SCHIFF BASES

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Recently, the intensively developing region of chemistry - coordination chemistry of transition metal complexes based on redox active ligands such as o-quinones, o-iminoquinones, - attracts an attention of researchers in the fields of fundamental and applied science. Interest to these compounds is caused mainly by the fact that the redox active ligands are capable of reversibly oxidizing or reducing being in the coordination sphere of the metal.

On the other hand, metallocenes as well as redox-active ligands are able to the reversible oxidation, and can form complexes with charge transfer in systems with an electron-withdrawing moiety. The combination of such centers in one molecule is of indubitable interest in the formation of new types of o-quinone / o-iminoquinone complexes; and these compounds can be involved in a wide range of redox processes due to the ability of the transition metal, redox active ligand and ferrocene to change their oxidation state. The investigations of magnetic behavior and possible intramolecular oxidation-reduction processes of these complexes are also of great interest.

Here we report on the synthetic approach to obtaining sterically-hindered ferrocene-containing Schiff bases and heteroligand transition metals (Cr, Mn) complexes containing o-quinone and ferrocenyl redox active centers base on there (fig 1) and investigation of their molecular, electronic structures, features of redox properties and magnetic behavior.

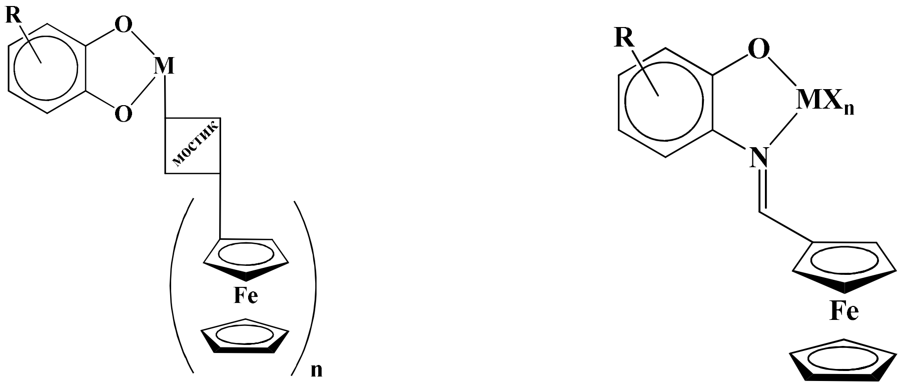

Figure 1. The novel types of heteroligand transition metals (Cr, Mn) complexes containing o-quinone and ferrocenyl redox active centers.

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IMINOPHENOLATO TIN(IV) COMPLEXES: SYNTHESIS, STRUCTURE AND REACTIONS WITH FREE RADICALS

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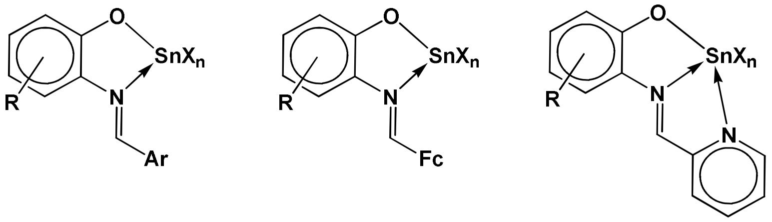
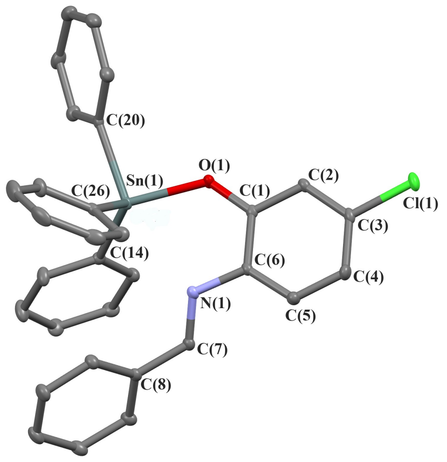
Reactions of free radicals with organic derivatives containing an imine bond are widely used for the synthesis of polyfunctional organic compounds. In the catalytic reactions this process proceeds as a nucleophilic addition to the imine radical to form functionalized amine. The known reactions of free radicals with iminophenols lead to aminophenols. On the other hand, there is practically no information in the literature about the features of the interaction of metal complexes containing o-iminophenolate ligands with free-radical particles. However, this class of reactions is very promising both from a fundamental point of view because it will allow the interconversion of different classes of ligands (o-iminophenolate and o-iminosemiquinolate) in the coordination sphere of the metal, and in terms of applied research. On the basis of this class of reactions, there are prospects for the development of synthetic methods for the functionalized redox active ligands of the o-quinone type which have different functional groups at the nitrogen atom, which are difficult to obtain by classical methods.

In the present work we have synthesized a series of tin(IV) complexes with Schiff bases, and investigated the reactions of the resulting o-iminophenolate complexes with various classes of free C-, N-, O-centered radicals.





The X-ray structure of triphenyltin(IV) 2-(5-chloro-N-phenylmethylimino)-phenolate is shown on the figure. The central tin atom Sn(1) has a distorted trigonal bipyramidal environment where the fifth coordination place is occupied by nitrogen atom N(1) of imine group (the Sn(1)-N(1) distance is 2.727(3) Å).

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RARE- AND ALKALINE-EARTH AMIDO COMPLEXES SUPPORTED BY A POTENTIALLY TRIDENTATE AMIDINATE LIGAND: SYNTHESIS, STRUCTURE, AND THEIR CATALYTIC PERFORMANCE TOWARD ROP OF RAC-LACTIDE AND E-CAPROLACTONE

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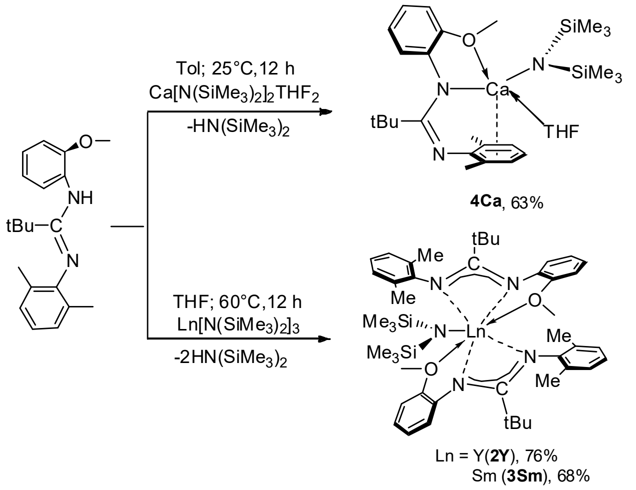
[b] A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str.28, 119991, Moscow, RUSSIA.

We synthesized the tridentate amidinate ligand bearing a pendant Lewis base group in the side arm o-$MeOC_6H_4NC$(*t*Bu)$NH(2,6\text{-}Me_2C_6H_3)$ (**1**) using previously published methods [1], and also investigated the possible types of coordination of its anionic form to rare-earth and alkaline-earth metals cations. For synthesis of amido rare-earth complexes containing the amidinate ligand **1** amine elimination protocol was used. The amidine o-$MeOC_6H_4NC$(*t*Bu)$NH(2,6\text{-}Me_2C_6H_3)$ was allowed to react with $Ln[(N(SiMe_3)_2]_3$ (Ln = Y, Sm) (2:1 molar ratio) in THF (60 °C, 12 h) (Scheme 1).



Scheme 1. The synthesis of complexes **2Y**, **3Sm** and **4Ca**.

Amido calcium complex o-$MeOC_6H_4NC$(*t*Bu)$N(2,6\text{-}Me_2C_6H_3)CaN(SiMe_3)_2$ (**4Ca**) coordinated by the ligand **1** was obtained in high yield by the amine elimination protocol. The reaction of equimolar amounts of $Ca[N(SiMe_3)_2](THF)_2$ and proligand **1** (Schemes 1) was carried out in toluene at ambient temperature within 12 h. The molecular structures of complexes **2Y**, **3Sm** and **4Ca** were established by X-ray diffraction. Amido complexes **2Y**, **3Sm** and **4Ca** were evaluated as initiators for ROP of *rac*-lactide and *ε*-caprolactone. In some experiments, ROH (R = *i*Pr, *t*Bu, Ph) was used as a co-initiator. In a typical experiment, complexes **2Y**, **3Sm** and **4Ca** allowed to convert up to 1000 equiv. of monomer to polymer within 230 min for *rac*-LA and 7 min for *ε*-CL at 20 °C in toluene.

[1] V. Rad'kov, G. Skvortsov, D. Lyubov, A. Cherkasov, G. Fukin, A. Shavyrin, D. Cui, and A. Trifonov, *Eur. J. Inorg. Chem.* **2012**, 2289–2297.

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NEW MAGNESIUM AND CALCIUM DPP-BIAN COMPLEXES IN ROP OF L-LACTIDE

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Metal complexes (dpp-bian)M(thf)$_n$ (M = Mg, n = 3; M = Ca, n = 4) supported with redox-active dpp-bian (=1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) in bisamide dianionic form give (dpp-bianH)Mg($OC_6H_2{}^tBu_3$)(dme) (**1**), (dpp-bianH)Mg($OC_6H_2{}^tBu_2Me$)(thf) (**2**) and (dpp-bianH)Ca($OC_6H_2{}^tBu_2Me$)(thf)$_2$ (**3**) by the reaction with the corresponding phenols (Fig. 1). Compounds **1**–**3** contain monoprotonated dpp-bianH which acts as a bidentate aminoamide ligand.

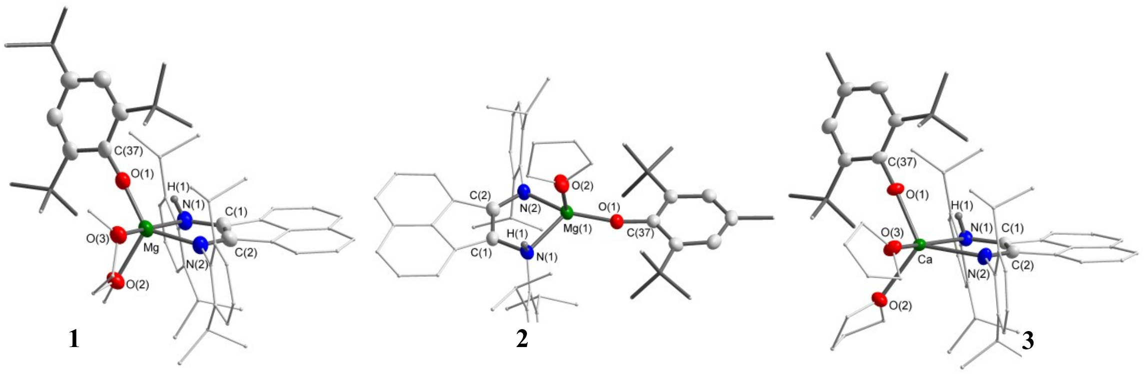

Fig. 1. The crystal structure of comlexes **1**-**3**.

For one's turn one-electron oxidation of the dianionic ligand in (dpp-bian)M(thf)$_n$ by azobenzene or dicumyl peroxide let to obtain [(dpp-bian)MgNPh(thf)]$_2$ (**4**) and (dpp-bian)CaOCHMe$_2$Ph(dme) (**5**) where the dpp-bian is in radical anion state (Fig. 2).

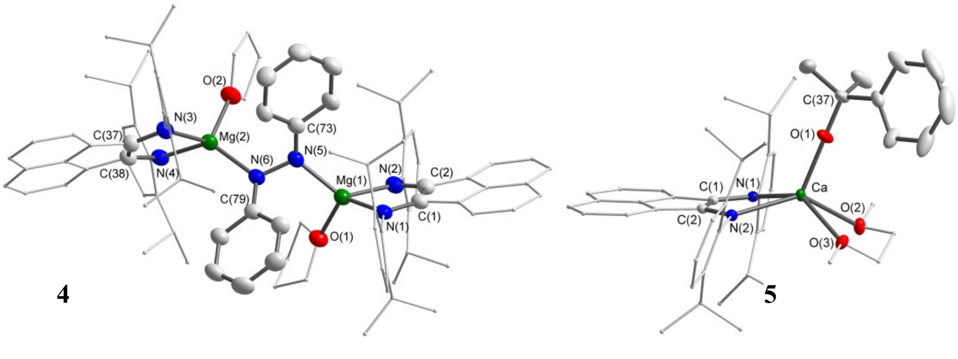

Fig. 2. The crystal structure of compound **4** and **5**.

It turned out that the metal complexes **1**–**5** exhibit moderate activity as catalysts of ring-opening polymerization (ROP) of cyclic esters in particular *L*-lactide. Broad molecular weight distribution of desired polymer reflects low controllability during polymerization in all cases. Cyclic structure of poly-*L*-lactide which has been proved by ESI mass spectrometry indicates a chain transfer reaction through a backbiting process.

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DFT STUDY OF THE UNPRECEDENTED 1-ARSANAPHTHALENE FORMATION FROM 2,1-BENZAZAARSOLE

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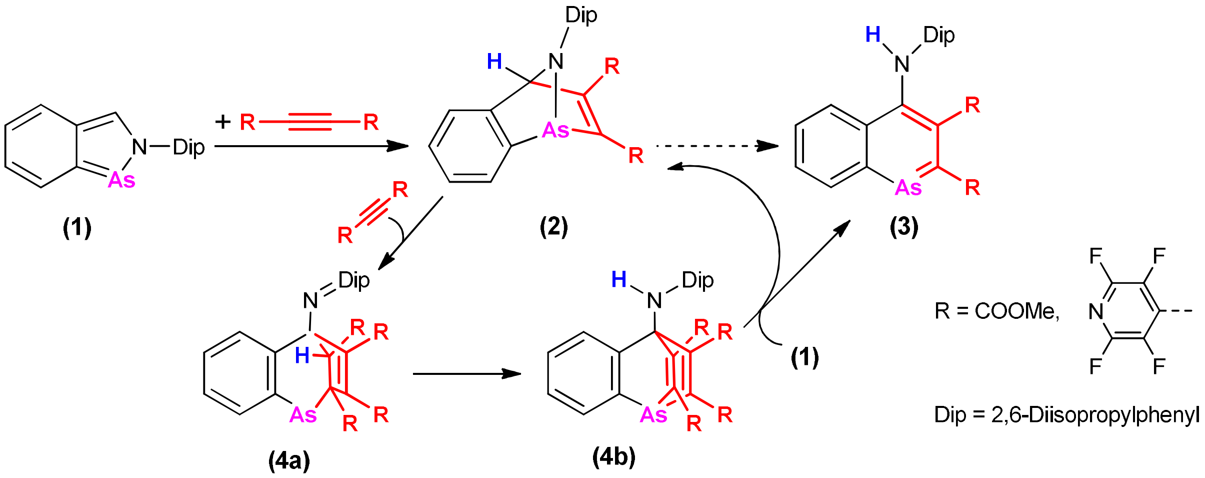
1H-2,1-benzazaarsole (**1**) demonstrates dienophile like properties in the reaction with alkynes RC≡CR (R = CO_2Me, C_5F_4N) thus forming 1-arsa-1,4-dihydro-iminonaphthalenes (**2**) [1]. These products undergo unexpected facile CH→NH proton migration leading to stable substituted 1-arsanaphthalenes (**3**). However, our DFT computations predict the direct proton migration to be unfavourable because of a very high activation barrier. The detailed reaction mechanism is suggested on the basis of quantum chemical calculations.



The energies of reactants, possible intermediates, transition states and reaction products were calculated at the M062X/DGDZVP level of DFT using the Gaussian 09 package. DFT study shows that the addition of a second RC≡CR molecule to **2** is highly exothermic and the obtained system is represented by a large number (over 20) of isomers with different positions of the unsaturated fragments and migrating H atom. Among them the **4a** species are good candidates for the intermediates providing the facile CH→NH proton shift. The **4b** molecules formed can react further with **1** giving the **2** and **3** species to continue the cycle. The participation of the **4a** and **4b** intermediates leads to a substantial decrease in the energy barriers accompanying the **2** → **3** transformation and provides the best variant of the plausible mechanism available at the moment.

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ChemShip-2019/Topical Problems of Modern Chemistry
International conference "Organometallic Chemistry Around the World" (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

INTERACTION OF BORAGUANIDINATO-STABILIZED GERMYLENE AND SILYLENE WITH ALKYNES AND ISOCYANATES: A COMPARATIVE ANALYSIS BASED ON DFT CALCULATIONS

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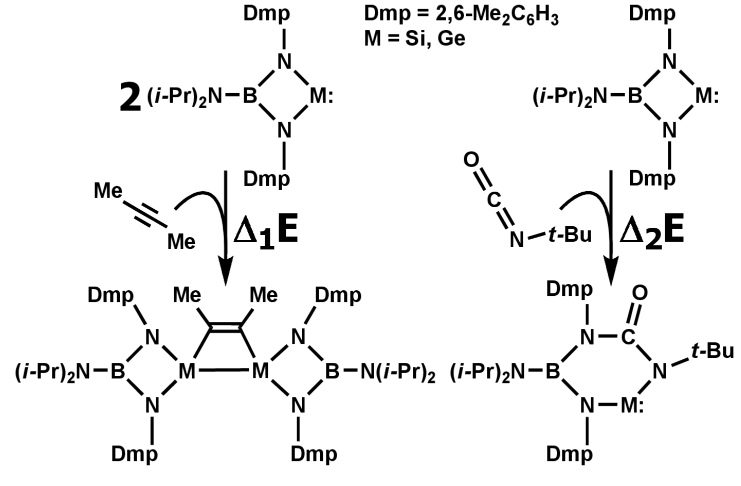
A boraguanidinato-stabilized germylene bearing the BN_2Ge ring was successfully synthesized in 2016 [1]. Further we investigated the mechanisms of the reactions with alkynes and isocyanates at the M062X/DGDZVP level of DFT [2,3]. Interaction with alkynes was established to proceed as sequential addition of the R_2C_2 molecule and another germylene species. Interaction with isocyanates occurs as insertion of the RNCO molecule into the Ge–N bond. In present work we model the processes involving an isostructural silylene to predict reactivity of a silicon analogue which has not been synthesized so far. Corresponding elementary reactions are characterized by changes of the electronic energy ΔE and thermodynamic functions. To find transition states the QST3 method is applied. In summary, reactions with alkynes appear to be more favorable for the silylene as compared to the germanium derivative (Scheme 1). At the same time there is no significant difference between the boraguanidinato-stabilized silylene and germylene reacting with isocyanates. Changes in the nature of the Si–N, Ge–N, Si–C, Ge–C, Si–Si, and Ge–Ge interactions in the key intermediates have been compared using natural bond orbitals (NBO), bonding critical point properties (QTAIM computations), the deformation electron density (DED) and electron localization function (ELF) topologies.



Scheme 1. The alkyne addition (M = Si, $\Delta_1E = -93.0$ kcal/mol; M = Ge, $\Delta_1E = -54.8$ kcal/mol) and isocyanate insertion (M = Si, $\Delta_2E = -31.1$ kcal/mol; M = Ge, $\Delta_2E = -31.0$ kcal/mol).

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NEW ORGANONICKEL SIGMA-COMPLEXES: STRUCTURE, PROPERTIES AND REACTIVITY

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Transition metal complexes are well known as active catalysts for combination processes involving organic as well as organoelement substrates, such as unsaturated hydrocarbons, phosphorus derivatives, and organic halides [1, 2].

There are a few pathways for the synthesis of organonickel sigma-complexes, however, the method of electrochemical synthesis of these complexes suggested by us has several advantages: limited number of byproducts, one pot process, precise control and monitoring of the reaction, and in particular the use of an "universal" reagent - electron. Earlier, we successfully synthesized and characterized organonickel sigma-complexes bearing sigma bonded organic fragment [3, 4].

This work describes the synthesis and characterization of new sterically hindered organonickel sigma-complexes and new methods for its activation as well as its reactivity toward organic and inorganic substrates. [5].

It was found that the electroreduction or electrooxidation of these complexes leads to the formation of a cationic form of the complex, which is capable to coordinate the molecule of substrate.

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STABLE ALKYL AND CATIONIC ALKYL COMPLEXES LN (II, III) IN CATALYSIS OF FUNCTIONALIZATION REACTIONS OF SIX-MEMBERED N-CONTAINING HETEROCYCLES

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Six-membered nitrogen-containing heterocycles are the most important structural units of most natural compounds, functional materials, and drugs. However, often, the design of such systems using standard methods of organic synthesis is complicated by the formation of by-products and harsh reaction conditions. In this regard, the development of new highly efficient and atom-economical processes of direct introduction of substituents into the heterocycle attracts close attention. Due to the presence of highly reactive Ln-C bonds, the lanthanide alkyl complexes are considered as promising catalysts for the direct alkylation of the pyridine CH bonds.

New alkyl and alkyl-cationic complexes Ln (II, III) with *tert*-butyl substituted benzhydryl ligands, which demonstrated high thermal stability, were synthesized as objects of study. Alkyl complexes of Ln (II) and alkyl-cationic complexes of Ln (III) proved to be highly effective catalysts in direct alkylation reactions of C_{sp2}-H and C_{sp3}-H bonds of pyridine and 2,6-dimethylpyridine heterocycles with various olefins and dienes, respectively. It was found that the complexes are tolerant to the presence of halogens in the olefin component in the process of catalysis and make it possible to obtain addition products with high yields. In addition, the possibility of attaching C_{sp2}-H and C_{sp3}-H pyridine bonds to internal olefins (stilbene, norbornene, norbornadiene) on Ln (II, III) complexes was demonstrated for the first time.

The process of catalytic reduction of pyridine heterocycles, accompanied by de-aromatization, is an extremely important method for creating valuable building blocks for organic synthesis. The method of restoring C = N bonds by homogeneous catalytic hydrosilylation of heterocyclic substrates has proven itself well on d-transition metal complexes, however, no example has been given of performing such reactions on lanthanide complexes. We have demonstrated the possibility of reducing pyridine, as well as quinoline, pyrazine, and phenazine with various substituted silanes on Ln (III) trisalkyl and their cationic complexes. The reduction of quinoline and pyridine with phenyl and phenylmethylsilanes proceeds with a quantitative conversion at room temperature and leads to the formation of products of 1,2-addition of silanes with 100% regioselectivity. In addition, 100% chemoselectivity of the formation of single addition products was observed, regardless of the ratio of substrates.

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THEORETICAL STUDY OF THE COORDINATION CAPABILITIES OF A WATER-SOLUBLE PENTACYSTEINE FULLERENE DERIVATIVE

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The fullerene molecule is known for its high physiological activity. Therefore, active studies are being conducted to obtain water-soluble derivatives of C_{60}, in particular, in the IPCP RAS [1]. Among these compounds, carboxylate derivatives have record-breaking solubility [2]. Carbonic anhydrases (CAs), mostly zinc-metalloenzymes, are very efficient catalysts for interconversion of the carbon dioxide and bicarbonate ion. Being involved in crucial physiological processes connected with respiration and transport of carbon dioxide/bicarbonate and they are important targets for the design of novel pharmacological agents useful in the prevention of a variety of disorders. CA inhibitors is known as the metal complexing anions which bind to the Zn(II) ion of the enzyme generating its tetrahedral geometry ion. Thus, the CA-inhibitor interaction constitutes the initial stage of the mechanism of inhibitors action. In [3] C_{60} derivative with a very complicated polydentate organic substituent was investigated as CA-inhibitor. The Zn complex with three imidazole ligands and one aqua ligands, proposed in [3], was used as a model of the active center. Water-soluble pentacysteine derivative of fullerene $C_{60}H[(NHCH(COOH)CH_2SH]_5$ has a lot of polydentate coordination centers. Its complex-forming ability was studied using the PBE density functional. It was found that this derivative in monodeprotonated form can easily replace from one to three ligands in Zn-active center. The structure of the complex with minimal number of imidazole ligands is shown in Fig. 1.

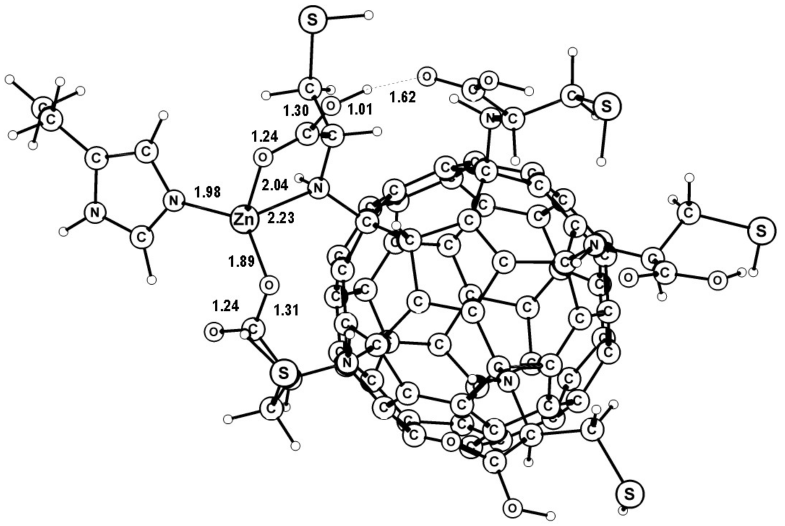

Fig. 1. Calculated structure of a three-coordination complex Zn with C_{60} derivative

[1] O.L. Kobzar, V.V. Trush, V.Y. Tanchuk, I.I. Voronov, A.S. Peregudov, P.A. Troshin and A.I. Vovk, *Mendeleev Commun.,* **2015,** *25,* 199-201.

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[3] M. Ghiasi, S. Kamalinahad, and M. Zahedi, *J. Struct. Chem.,* **2014**, *55*, 1574-1586.

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SYNTHETIC APPROACHES TO 1,4-DIAZA-3a,6a-DIPHOSPHAPENTALENES

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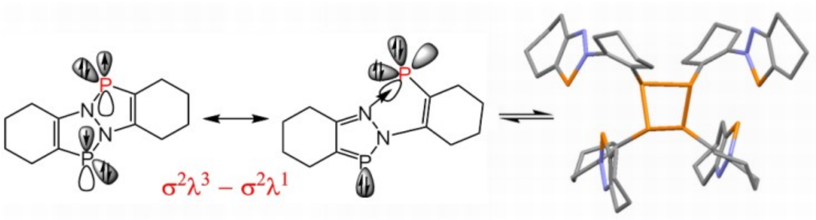
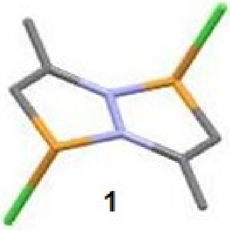
Annulated 3a,6a-diaza-1,4-diphosphapentalenes (DDP) form a unique system that can be considered as a 10π-electron aromatic one, and as a stabilized phosphinidene at the same time.

At present only two representatives of the DDP family are known based on cyclohexanone and tetralone azines as starting compounds.

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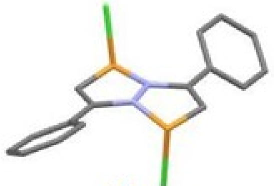
The purpose of this work is to expand the synthetic approaches to DDP class and study their chemical properties. Earlier, we have shown that the reactions between azobispyridine and organophosphorus chlorides lead to the formation of triazaphospholes [1].

We studied reactions of PCl_3 with azines of acetone, tetralone and substituted acetophenones (Scheme 1). It was shown that electron-withdrawing substituents (-F, -Cl) in aromatic ring decrease, but electron-donor groups ($-CH_3$, $-OCH_3$) accelerate the formation of corresponding dichloro-derivatives ($DDPCl_2$).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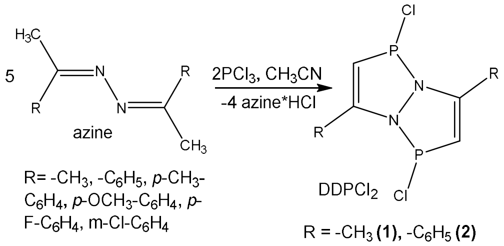
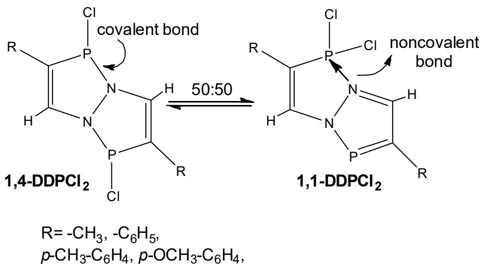


Scheme 1.

According to the X-Ray analysis, molecule **1** is centrosymmetric while the heteropentalene fragment in **2** is not planar and has a bend in the nitrogen-nitrogen bond. It was shown that the dichloro-derivatives in solution exist as equilibrium mixture of 1,1- and 1,4-isomers (Scheme 2). DFT calculations showed that 1,1- and 1,4-isomers are not significantly different in their total energy.



Scheme 2.

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STABILITY OF $Ce(OON)_3$ UNDER IMPACT OF IONIZING IRRADIATION

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Lanthanide luminescence is widely used in a lot of modern technologies such as OLED, photovoltaic cells, bioimaging and many others. However, over the past century, in the sphere of human activity, new areas have emerged and are rapidly expanding, where a new component — ionizing irradiation — is being added to ordinary conditions. Especial interest represents to study physical and chemical properties of lanthanide complexes under ionizing irradiation.

For the study we choose the cerium complex $[Ce(OON)_3]_2$ structure of which was determined earlier by X-ray diffraction method. The $[Ce(OON)_3]_2$ is quite stable in an inert atmosphere and in vacuum but is hydrolysed slowly in air. The listed properties, which are convenient for the identification of compound, stipulated our choice of $[Ce(OON)_3]_2$ as models for studying the radiation stability of metal-organic complexes.

The sample was processed by radiation generated upon the decay of ^{235}U nuclei. The full spectrum of radiation was used including α, ß, γ components and neutrons. However, since α and ß-components were filtered almost completely upon passage through the walls of the glass tubes, the material was exposed only by neutrons and γ-radiation. The study included three stages: the first two were carried out in a sustained mode (45 h), the third stage was pulse irradiation (3 ms). The dose of absorbed radiation, with the neutron flux of $6 \cdot 10^{12}$, $5 \cdot 10^{13}$ and $3.6 \cdot 10^{13}$ n/cm^2, was 12, 120 and 130 krad, respectively. It was found that crystals of the complex even after intense pulse irradiation retained their shape, which made it possible to use X-ray diffraction analysis to determine their molecular structure. Note that the study of the degradation of organic and metal-organic compounds under the action of ionizing irradiation at the molecular level has not previously been carried out. The analysis data showed that the structure of the treated complex is very slightly different from the structure of the compound which was not irradiated (Fig.1).

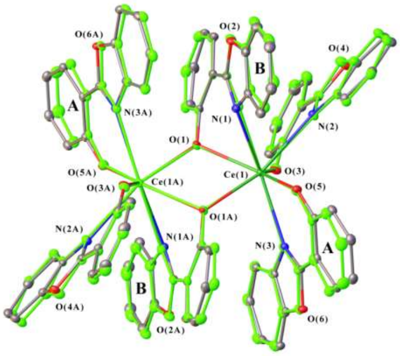

Figure 1 Molecular structure of the irradiated (grey) and non-irradiated (green) $[Ce(OON)_3]_2$ complex. Thermal ellipsoids are drawn at 30% level probability. Hydrogen atoms are omitted for clarity.

Acknowledgements
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AMIDO AND BOROHYDRIDO RARE EARTH COMPLEXES COORDINATED BY TETRADENTATE AMIDINATE LIGANDS

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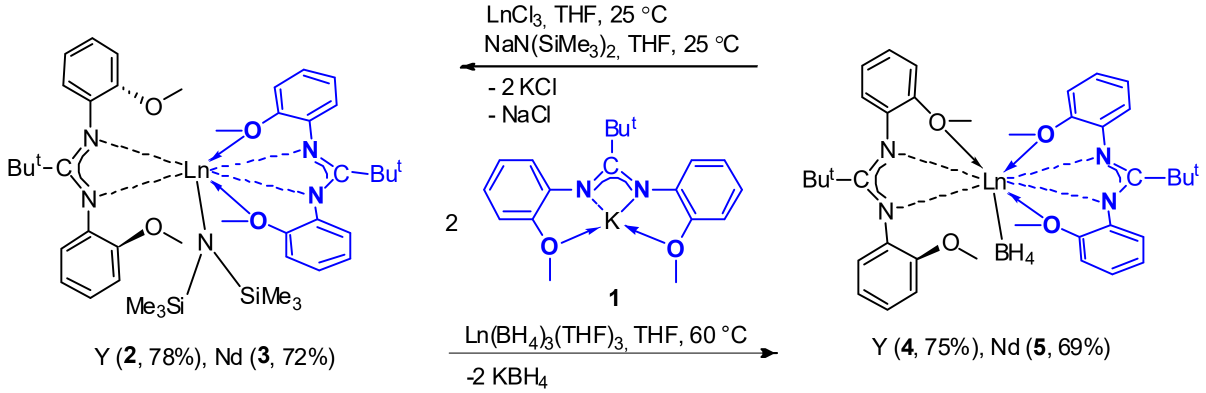
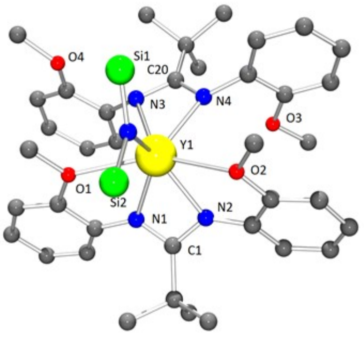
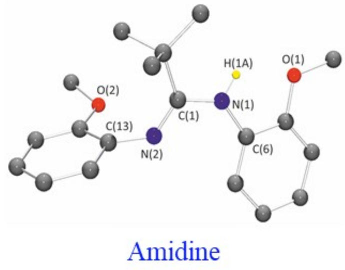
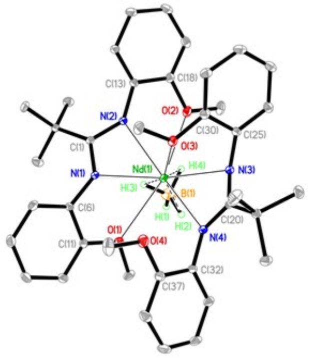
[b]A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, RUSSIA.

The successive salt metathesis reactions of $LnCl_3$ with 2 equivalents of $[Bu^tC(NC_6H_4\text{-}2\text{-}OMe)_2]K$ (**1**) and one equivalent of $NaN(SiMe_3)_2$ in THF afford bis(amidinate)amido complexes $[Bu^tC(NC_6H_4\text{-}2\text{-}OMe)_2]_2LnN(SiMe_3)_2$ (Ln = Y (**2**), Nd (**3**)). The reactions of $Ln(BH_4)_3(THF)_3$ (Ln = Y, Nd) with potassium amidinate **1** (1:2 molar ratio) in THF result in the formation of bis(amidinate)borohydrido complexes $[Bu^tC(NC_6H_4\text{-}2\text{-}OMe)_2]_2LnBH_4$ (Ln = Y (**4**), Nd (**5**)). According to the X-ray diffraction studies in complexes **2** and **3** one amidinate ligand is coordinated to the Ln^{3+} cation in a bidentate fashion (κ^2-NN), while the second one is tetradentate (κ^4-NNOO). At the same time in borohydrido neodymium complex **5** the amidinate ligands demonstrate κ^4-NNOO and κ^3-NNO coordination modes.









Amide and borohydride complexes **2**–**5** act as monoinitiators for the ring-opening polymerization of racemic lactide and ε-caprolactone, providing polymers with a good degree of control, that is, controlled molecular weights and relatively narrow polydispersities.

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CATECHOL THIOETHERS – PROMISING LIGANDS IN COORDINATION CHEMISTRY

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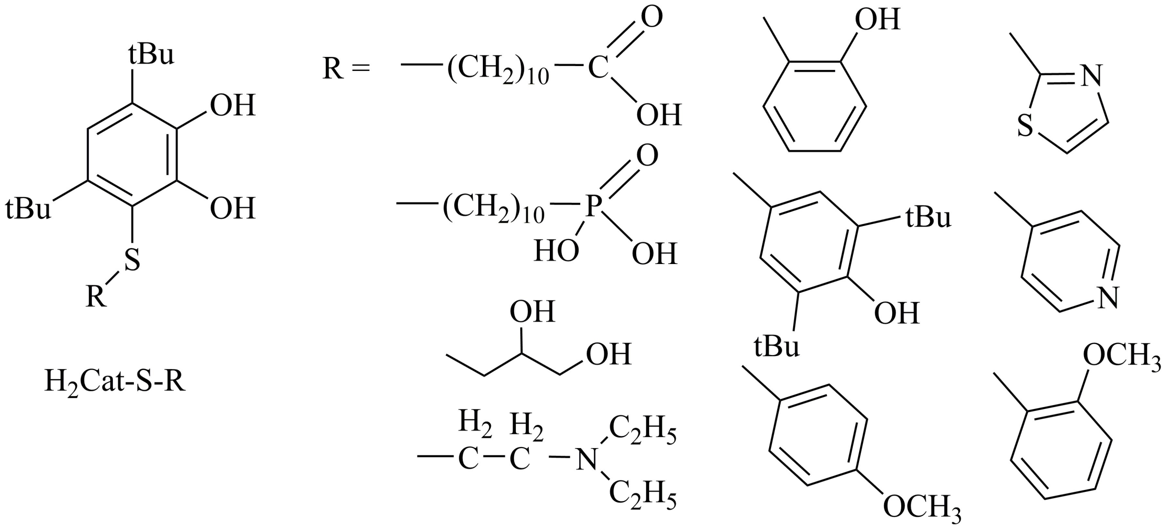
In coordination chemistry, sulfur-modified sterically hindered catechols (quinones) are widely used as chelating ligands. Catechol-based compounds have attracted interest owing to their antioxidant and radical scavenging properties [1,2] as well as their application in the synthesis of coordination polymers as multitopic ligands, in supramolecular and material chemistry [3]. The present research is focused on the development of the organic compounds containing several coordination sites based on the Michael addition reaction of sulfur containing compounds with 3,5-di-*tert*-butyl-*o*-benzoquinone.



H_2Cat-S-R

A wide choice of commercially available thio-derivatives, *o*-benzoquinones, and the simplicity of the reaction allows to modify the catechol ring by the various functional groups bonded by sulfide linker. The presence of blocking *tert*-butyl groups inhibits the reaction polymerization that is characterized for dopamine. The synthesized thioethers contain three constituent parts: redox-active sterically hindered catechol moiety, thioether linker and the additional the polar, redox-active group or heterocyclic fragments. The synthesis, structure and redox-activity of compounds are discussed.

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Acknowledgements - the work was supported by the Russian Science Foundation grant 17-13-01168.

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REACTIONS OF DIALANE WITH ISOCYANATES AND CARBON DIOXIDE

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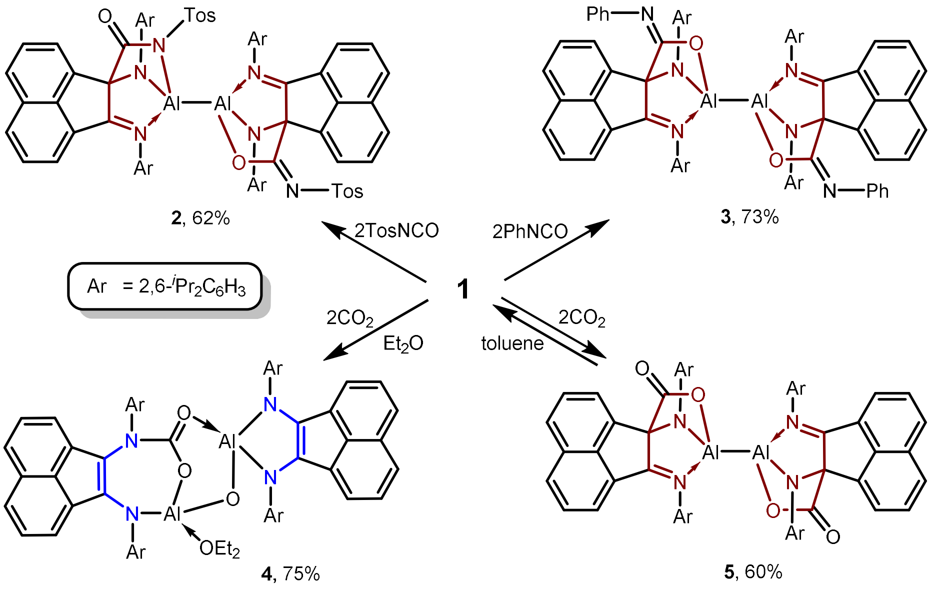
Acenaphthenediimine main group metal complexes can simulate some aspects of the reactivity of transition metal complexes. Thus, we have shown that digallane [(dpp-bian)Ga–Ga(dpp-bian)] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) is able to undergo two-electron oxidative addition of allyl chloride, allyl bromide [1], cycloaddition of isothiocyanates [2] and isocyanates [3]. In continuation of this work, we studied the reactions of digallane analogue – dialane [(dpp-bian)Al–Al(dpp-bian)] (**1**) – towards isothiocyanates, isocyanates and carbon dioxide. Dialane does react with phenyl, allyl and benzoyl isothiocyanates, although inseparable mixtures of products are formed. In case of reaction with tosylisocyanate and phenylisocyanate, derivatives **2** and **3** are formed (see scheme). It should be noted that during the formation of the product **2**, cycloaddition occurs across both C=N and C=O bonds of the isocyanate.

It turned out that the product of the interaction of dialane with carbon dioxide depends on the solvent in which the reaction takes place. In diethyl ether, the reaction with CO_2 gives the diamagnetic derivative **4**, while in toluene, the reaction is reversible and leads to the formation of a cycloadduct **5** (see scheme).



[1] I.L. Fedushkin, V.A. Dodonov, A.A. Skatova, V.G. Sokolov, A.V. Piskunov and G.K. Fukin, *Chem. Eur. J.*, **2018**, *24*, 1877-1889.
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Acknowledgements - we thank the Russian Science Foundation (project No. 19-13-00336) (the synthetic part of this work) and Russian Foundation for Basic Research (project No. №18-33-01057 mol_a) (X-ray diffraction measurements) for financial support.

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SINGLE MOLECULE MAGNETS BASED ON DY^{3+} COMPLEXES SUPPORTED BY DIAZABUTADIENE LIGANDS

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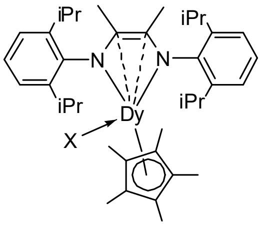
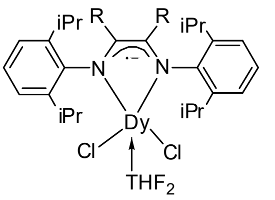
Coordination complexes exhibiting slow relaxation of their magnetization associated with magnetic bistability show tremendous potentialities for information storage or spin-based computing [1]. Single-Molecule Magnets (SMM) have been greatly enhanced by taking advantage of the fascinating properties of lanthanide ions [2]. Lanthanide ions such as Dy^{3+} exhibiting oblate electronic density are efficiently stabilized by axial crystal-field that maximizes the splitting of the m_J levels, while minimizing the Quantum Tunneling of the Magnetization (QTM) [3].

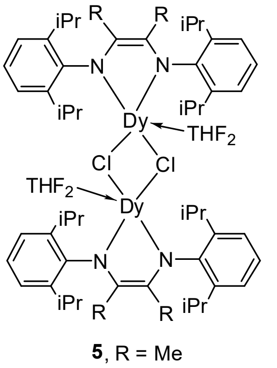
The overall approach to the design of new dysprosium SMM is to create highly symmetrical axial enviroments around the Dy^{3+} ion and stabilize thereby the 4f electronic density. In this aim, a series of heteroleptic half-sandwich [4], chloride and homoleptic Dy^{3+} complexes containing diazabutadiene ligands in [DAD^{2-}] as well as [DAD$^{\bullet-}$] forms was synthesized.



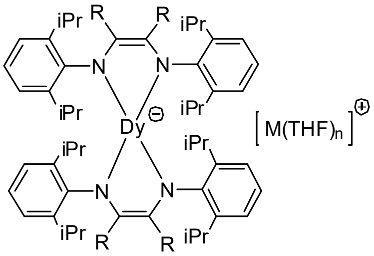
1, M = K, X = THF
2, M = Li, X = ClLi(THF)$_3$



3, R = Me
4, R = H



5, R = Me
6, R = H



7, R = Me, M = Li, n = 4
8, R = Me, M = K, n = 2
9, R = H, M = K, n = 2

All obtained homo- and heteroleptic Dy^{3+} complexes exhibit distinct slow relaxation of the magnetization dynamics and geniune Single-Molecule Magnet (SMM) behaviour.

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SYNTHESIS AND CHEMICAL PROPERTIES OF LOW VALENT GERMANIUM COMPLEXES BASED ON O,N-HELATE LIGAND.

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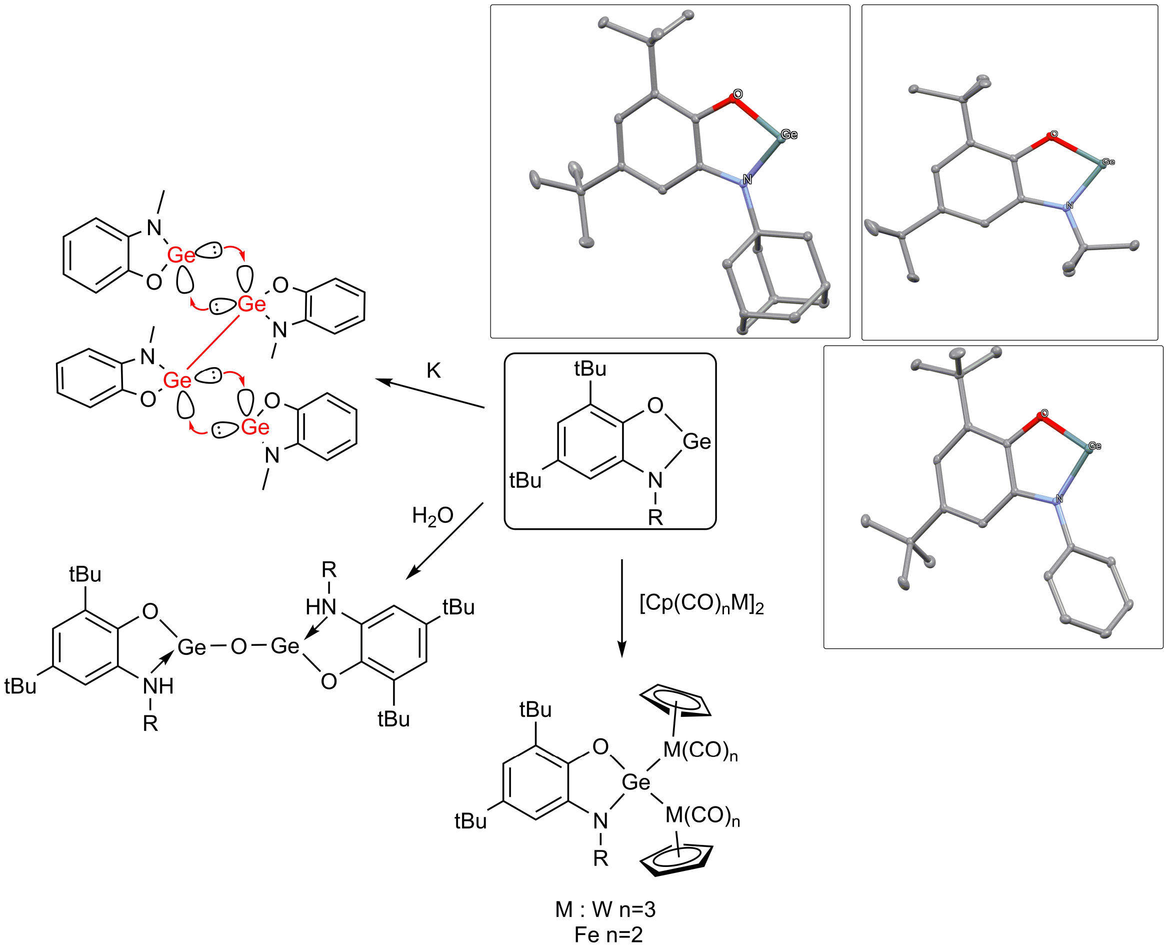
In this work we present synthesis of new O,N-heterocyclic germylenes bearing N-(R)-substituted o-aminophenols and investigation of their redox reactivity and acid-base properties. X-ray analysis of Ge(II) o-amidophenolates shows that they are monomeric in the solid state. This behavior is in contrast to the situation observed for related stannylenes and plumbylenes.

Redox active ligands such as o-aminophenoles can be used as reservoirs of electrons for bond-making and bond-breaking reactions and can support the multi-electron changes required to promote group- or atom-transfer reactions. Posessing a high degree of aromatically, heavy analogues of carbene can undergo one-electron reduction, which leads to formation butadiene-like dianion with four metallocenters in the chain.



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CYMANTRENECARBOXYLATES AND BENZOATES COORDINATION POLYMERS OF 3-d METALS

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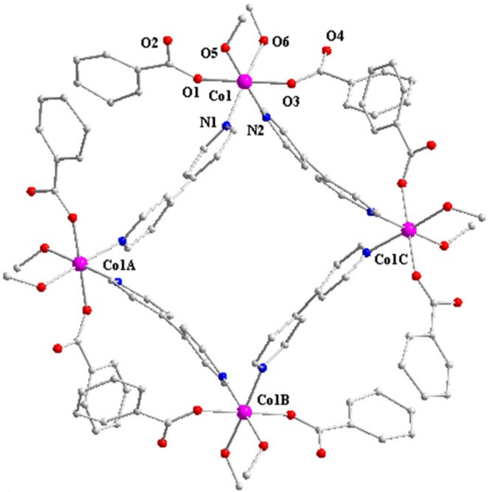
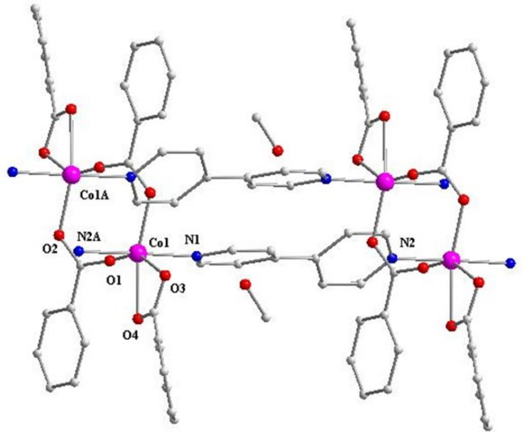
In recent years coordination polymers of metals have attracted much attention of researchers thanks to its unusual structure and physicochemical properties.

This work is dedicated to the synthesis and structure feature of metals 3-d polymers prepared by the reactions of bidentate γ, γ'-dipyridyl and M [(OOCR]$_2$[O(H)Me] $_4$) adducts (M = Zn, Cu^{II}, Ni, Co^{II}, Fe^{II} , Mn^{II}, R = Ph, $C_5H_4Mn(CO)_3$):

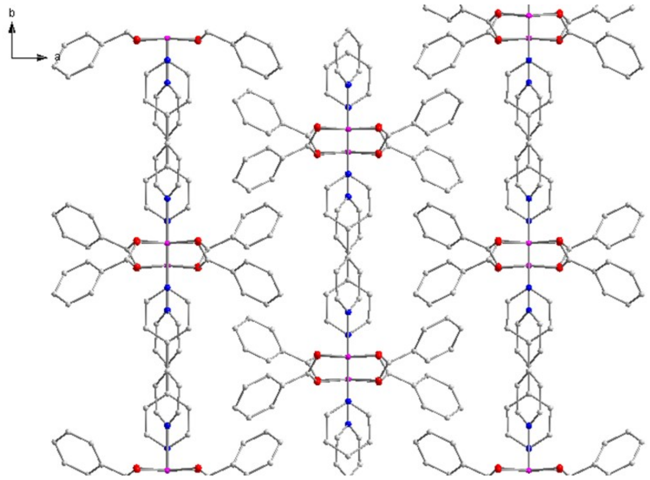
R=Ph:



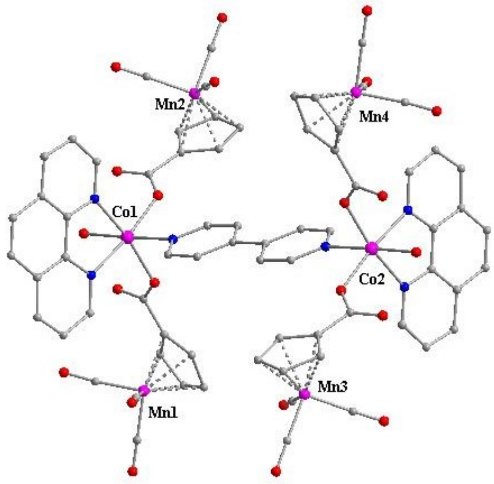
M=Co, Ni



M=Co



M=Mn



R=$C_5H_4Mn(CO)_3$, M=Co

Acknowledgements – We thank the Russian Foundation for Basic Research for the financial support of the research (grant № 18-33-01161)

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POLYMERIZATION OF STYRENE IN THE PRESENCE OF 2-CYANOPROPYL IODIDE AND CATHECHOLATES OF TIN(IV)

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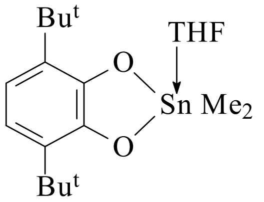
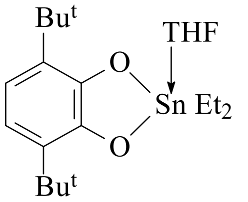
Iodine-containing compounds can be used to produce methacrylic polymers with desired molecular weight characteristics, either individually or in combination with various compounds [1].

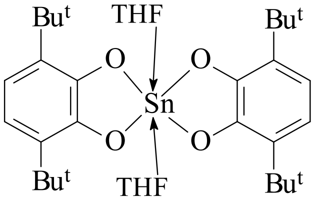
The aim of our work was to investigate the influence of combinations iodine-containing compounds and catecholate complexes of tin(IV) on polymerization of styrene (**St**) at 90-110°C. Complexes ***1-3*** and 2-cyanopropyl iodide (**CP-I**) were studied in these processes.



1



2



3

The introduction of 0.1 mol.% **CP-I** leads to decrease of the St autopolymerization rate at 90-110°C. The number average molecular weight (**M_n**) of the polyST does not change during the process and is ~ 25-30 kDa at 110°C. Each of the complexes ***1-3*** at 0.1 mol.% concentration also decreased of the St autopolymerization rate in this conditions. M_n of the samples are ~ 160 kDa in case **1** and ~ 90 kDa in the presence of **2** and **3**.

The effect of the combination of **1-3** and **CP-I** on the kinetic features of polymerization and the characteristics of polyST depends on **1-3**. Binary systems **1 / CP-I** and **2 / CP-I** initiated the process of polymerization. Conversion of St reaches 90%. The dependence of M_n polySt on monomer conversion is linear, but the polydispersity indexes (**Đ**) is 2.5-3.0. In case of **3** conversions of St does not exceed 60%. M_n of polySt samples increases proportionally with conversion and Đ is 1.8-2.2. As a rule, an increase in the concentration of the complexes leads to a decrease in the rate of polymerization and the maximum conversion of St. Linear growth of number average masses is preserved, and Đ decreases to 1.6-1.7 regardless of the composition of the complex.

Thus, under certain conditions, the combination of complexes **1-3** and **CP-I** makes it possible to obtain polySt with high yields and Đ of less than 2.0.

[1]. P Lacroix-Desmazes and J Tonnar, *Polym. Sci.: A Compr. Ref.*, **2012**, https://www.sciencedirect.com/science/referenceworks/97800808786213, 159-180.

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LUMINESCENCE EFFICIENCY OF NEW EU(III) THIOPHENE-BASED 1,3-DIKETONATES CONTAINING PERFLUORINATED CHAINS OF VARIOUS LENGTH

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The lanthanide ions emit narrow bands from visible to near infrared spectral ranges and have many uses in optoelectronic devices. Organic ligands are used for the population of excited states of the ions and their structure and chemical composition have a profound effect on the efficiency of lanthanide luminescence.

The range of new Eu(III) 1,3-diketonate complexes containing fixed thiophene fragment and perfluorinated chains of various lengths were synthesized [1] and the study of the luminescent features were performed. It was shown that triplet level energy of the investigated ligands independents of the fluorinated chain. As a consequence, the efficiency of energy transfer from ligand to metal is almost unchanged. However, the increase in chain length affects the site symmetry of the europium ion (III) and changes the probability of the electronic transitions. It was also shown that the luminescence quantum yields reach the saturation with the increasing chain length. The findings are significantly different from obtained results for analogous pyrazole-containing compounds [2].

This study was supported by the Russian Scientific Foundation (project №19-13-00272).

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2. *Varaksina E.A., Taydakov I.V., Ambrozevich S.A., Selyukov A.S., Lyssenko K.A., Jesuse L.T., Freire R.O.* Influence of fluorinated chain length on luminescent properties of Eu^{3+} β-diketonate complexes. Journal of Luminescence 196, 161–168, 2018

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EFFECT OF SIO_2 NANOPARTICLES ON THE COORDINATION ENVIRONMENT OF LI^+ ION IN A POLYMER-CONTAINING ELECTROLYTE

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The work was carried out as part of the development of new nanocomposite polymer electrolytes (NPE) for electrochemical devices. NPEs were obtained by the reaction of radical polymerization of polyethylene glycol diacrylate (PEG-DA) in a liquid aprotic 1 M $LiBF_4$ electrolyte in gamma-butyrolactone (GBL) in the presence of SiO_2 nanoparticles.

By the method of electrochemical impedance, it was shown that the dependence of conductivity on the content of SiO_2 has 2 maxima at 2 and 6 wt.% SiO_2 nanoparticles. Usually in such systems there is one maximum, which is caused by the formation of conductive paths of ions along the surface of the nanoparticles.

The purpose of this investigation was to study the coordination environment of lithium ions in this nanocomposite system using IR spectroscopy and quantum-chemical modeling using the non-empirical PBE exchange-correlation functional and the extended H [6*s*2*p*/2*s*1*p*], C, O [10*s*7*p*3*d*/3*s*2*p*1*d*], Li [10*s*7*p*3*d*/4*s*3*p*1*d*]. All calculations were performed using the NATURE software package and the computational capabilities of the Interdepartmental Supercomputer Center of the Russian Academy of Sciences (Moscow).

Using the Fourier transform infrared spectroscopy method, we investigated all the compositions of NPE, the initial PEG-DA, liquid electrolyte and solvent. The study of the IR spectra of samples of different compositions showed that nanocomposite polymer electrolytes have similar spectra in the absence of SiO_2 and in the presence of SiO_2, except for the composition containing 2 wt.% SiO_2.

As an indicator of spectral shifts reflecting changes in the molecular composition of the electrolyte, we chose a band in the region of 1650–1850 cm^{-1}, associated with stretch vibrations of the carbonyl group. The intensities of all the experimental bands in this area were calculated and compared with the theoretical IR spectra of the 5 different complexes obtained by quantum-chemical modeling. There are a solvate-separated pair, contact pair and free ions Li^+ and BF_4^- surrounded by molecules of GBL.

By comparing the theory and experiment, it was shown that an increase in the intensities of the lines of the experimental spectra of 1763, 1782, 1792, 1796, 1806 cm^{-1} is associated with an increase in the number of free ions. Thus, it has been proven that SiO_2 nanoparticles are involved in increasing conductivity not only in creating conductive paths for ions, but also in causing salt dissociation with an increase in the number of mobile ions.

Acknowledgements – This work was performed in accordance with the state task, state registration No. 0089-2019-0010.

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SYNTHESIS AND MOLECULAR STRUCTURE OF THE FIRST POLYNUCLEAR METALLAMACROCYCLIC Sr(II)-Cu(II) COMPLEX BASED ON GLYCINEHYDROXIMATE LIGANDS

G. Zabrodina, G. Zhigulin and M. Katkova

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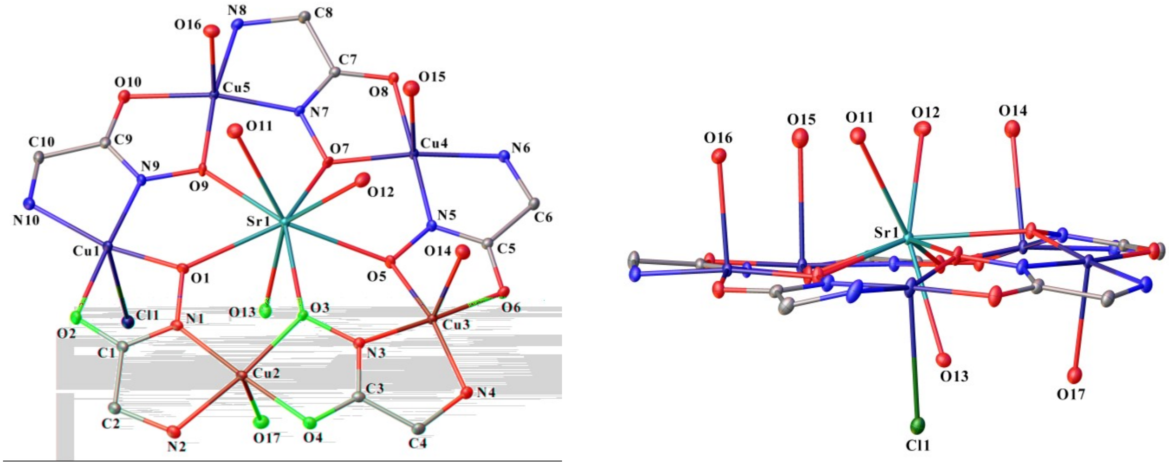
Recently, the aminohydroximate ligands have found wide applications in fascinated class of polynuclear metallamacrocyclic compounds named as 15-MC-5 metallacrowns. The popularity of water-soluble polynuclear metallamacrocyclic complexes is largely due to their rich coordination chemistry, ease of synthesis and diverse properties combined with a range of applications, such as sensors, catalysts, higher capacity sorbents, and contrast reagents for magnetic resonance imaging. We examined the glycinehydroxamic acid as a simple ligand for preparation of the first water-soluble polynuclear metallamacrocyclic Sr(II)-Cu(II) complex. Starting from the neutral glycinehydroxamic acid, the complex $Sr(H_2O)_3[15\text{-}MC_{CuGlyha}\text{-}5](Cl)_2$ was synthesized and characterized structurally and spectroscopically. The single-crystal structure reveals the classic metallamacrocyclic 15-MC-5 configuration. The Sr(II) ion is located at the center of the $15\text{-}MC_{Cu(II)Glyha}\text{-}5$ ring and coordinated by five oxygen atoms of the cycle in the equatorial plane and additional three oxygen atoms of the water molecules in apical positions. As a result the Sr ion has an eight-coordination environment (CN = 8) with the geometry of a triangle dodecahedron. The $15\text{-}MC_{Cu(II)Glyha}\text{-}5$ moiety is not planar.



Top and side views of the molecular structure $Sr(H_2O)_3[15\text{-}MC_{CuGlyha}\text{-}5](Cl)_2$.

Acknowledgements
This work was supported by the Russian Science Foundation (Project № 18-13-00356).

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SYNTHESIS OF NEW DERIVATIVES 5,5,8,8-TETRAMETHYL-5,6,7,8-TETRAHYDRONAPHTHALENE-2,3-DIOL

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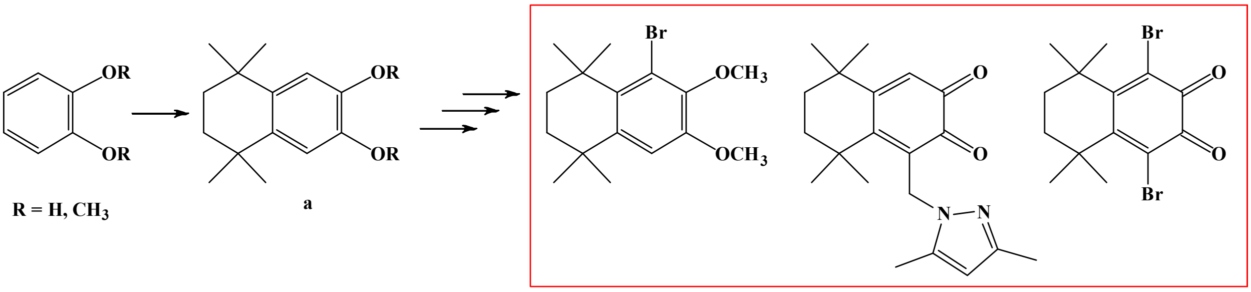
[2]National Research Lobachevsky State University of Nizhny Novgorod

o-Benzoquinones are widely distributed both in the chemistry of high-molecular compounds (components of photoinitiating systems, inhibitors of free-radical polymerization), and in the coordination chemistry of transition and non-transition metals as ligands of variable valence. It is known that the introduction of two tert-alkyl substituents contributes to a significant increase in the kinetic stability of o-quinones. The most studied representatives of o-benzoquinones are 3,5- and 3,6-di-tert-butyl-o-benzoquinones and their derivatives. In this paper, the synthesis of new representatives of pyrocatechins / o-benzoquinones based on 5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2,3-diol (a) - compounds containing tertiary alkyl substituents in position 4 and 5 of the pyrocatechol / quinone fragment.



New tri- and tetra-substituted pyrocatechin / quinone derivatives were synthesized and characterized with different substituents in positions 3 and 6. The work is being carried out with the financial support of the grant of the President of the Russian Federation (project No. MK-2351.2019.3)

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OPTICAL PROPERTIES OF 15-METALLACROWNS-5: INVESTIGATION BY DFT MODELING

G. Zhigulin, M. Katkova, and S. Ketkov

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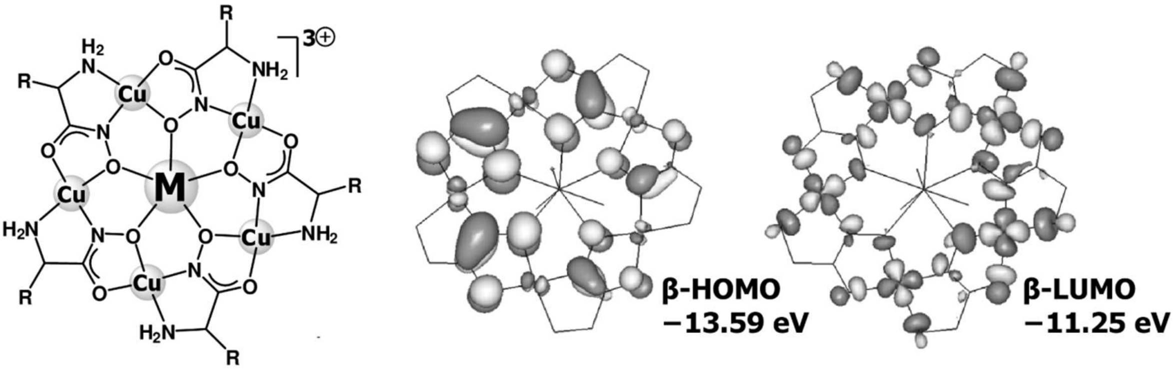
Optical properties of the α-aminohydroximate 15-metallacrowns-5 bearing copper and rare earth cations have been interpreted in terms of Kohn-Sham orbital analysis at the B3LYP/DGDZVP and τ-HCTHhyb/x2c-TZVPall levels with employing PCM. Calculated values of the energy gaps between β-LUMO and β-HOMO obtained for cationic forms of the 15-metallacrowns-5 agree well with absorption band position in the region of 575 nm (2.16 eV) of the UV-visible spectra. Transformations of the highest occupied orbitals arising from R substituent variation are described. Modeling of the protonated glycinehydroximate Cu(II)-Y(III) complex (R = H) explains its halochromic behavior as a result of imine nitrogen atom protonation.



Fugure 1. Overall structure of the 15-metallacrowns-5 and frontier molecular orbitals obtained at the B3LYP/DGDZVP level (M = Y, R = H).

Acknowledgements. This work was supported by the Russian Science Foundation (Project № 18-13-00356).

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COBALT(II, III) COMPLEXES BASED ON FERROCENYL-CONTAINING O-IMINOPHENOLS

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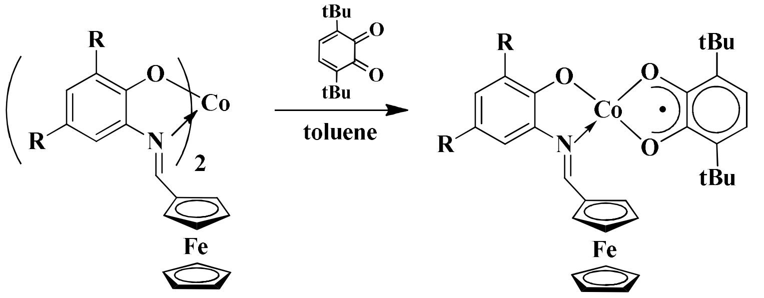
The appearance of ferrocene in the middle of the 20th century has revolutionized chemistry, and now many attention is paid to the investigation of ferrocenyl compounds largely due to its applications in catalysis including asymmetric and enantioselective catalysis, optical and redox devices, battery and other, sensing, and medicine.

Design of heteroleptic transition metal compounds containing o-quinone (capable of reversible oxidation or reduction being in the coordination sphere of the metal) and ferrocenyl redox-active centers and investigation of their molecular and electronic structure, redox-properties and magnetic behavior are of great interest. Such type compounds are perspective precursors for the synthesis of redox rich complexes bearing redox-active centers of different nature and as the promising agents for study of the electron-transfer reactions.

New cobalt(II) bis-o-iminophenolato complexes of the type (Fc-CH=N-ArO)$_2$M^{II} where M = Co, Ar = C_6H_4; M = Co, Ar = 4,6-tBu-C_6H_2; M = Ni, Ar = 4,6-tBu-C_6H_2 have been synthesized by the reaction of ferrocenyl-containing Schiff bases with cobalt(II) chloride and cobalt(II) acetate in methanol solution in the presence of base. Complexes have been characterized in details by IR-spectroscopy, mass-spectrometry, cyclic voltammetry and the Evans method. Their interaction with 3,6-di-tert-butyl-o-benzoquinone leads to new cobalt(III) o-benzosemiquinone complexes of the type (Fc-CH=N-ArO)$_2$M^{III}(3,6-DBSQ) possessing a doublet spin state with resolved EPR spectra (Fig. 1).



R = H, (Fc-(L)O)$_2$Co^{II}
R = tBu, (Fc-(4,6-L)O)$_2$Co^{II}

R = H, (Fc-(L)O)$_2$Co^{III}(3,6-DBSQ)
R = tBu, (Fc-(4,6-L)O)$_2$Co^{III}(3,6-DBSQ)

Figure 1

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International conference "Organometallic Chemistry Around the World" (7th Razuvaev Lectures)
September 16-21, 2019, Nizhny Novgorod, Russia

SOLID-STATE REDOX-ISOMERIC TRANSFORMATION IN THE SERIES OF NOVEL BIS(DIOXOLENE) COBALT COMPLEXES WITH DI(2-PYRIDYL)IMINE ANCILLARY LIGAND

A. Zolotukhin[a], M. Bubnov[a], A. Bogomyakov[b], V. Cherkasov[a]

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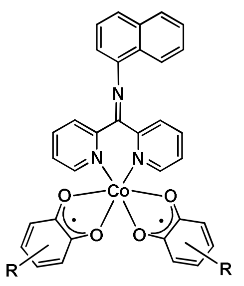
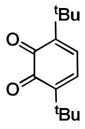
Six-coordinated bis-o-semiquinonato cobalt derivatives attract the great interest which is caused by their magnetic properties and, on the other hand, the solid-state redox-isomerism phenomenon that observed for these compounds [1].

A series of novel bis(dioxolene) cobalt complexes based on naphtyl-substituted di(2-pyridyl)imine ligand was synthesized. The obtained compounds were characterized by IR-spectroscopy and variable temperature magnetic susceptibility measurements.





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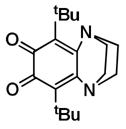

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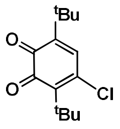

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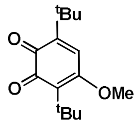

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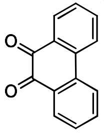

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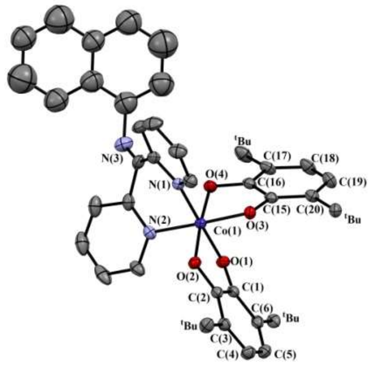
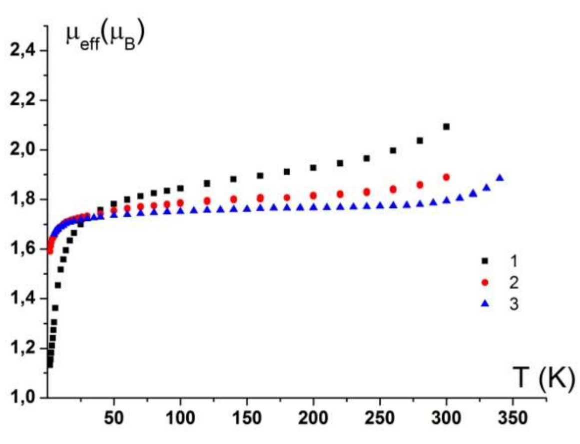
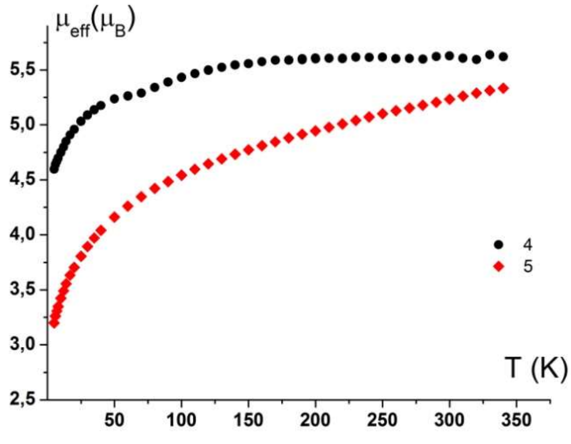


It was shown that complexes with derivatives of 3,6-di-tert-butyl-o-quinone undergo redox-isomeric transition in the solid state at around room temperature. Decrease in the electron-acceptor ability of the redox-active ligand leads to the formation of bis-o-semiquinone derivatives of divalent cobalt, which do not demonstrate the redox isomeric transition (complexes 4 and 5).





References
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Acknowledgements - The authors are thankful to Russian Science Foundation (grant №18-73-00276) for financial support.

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Russian-Chinese Workshop on Coordination and Supramolecular Chemistry

THIACALIX[4]ARENES DERIVATIVES: A SCAFFOLD FOR SUPRAMOLECULAR SYSTEMS DESIGN

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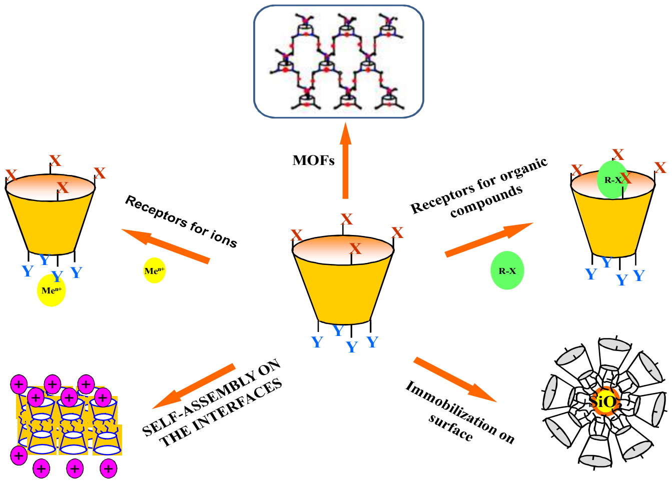
Lower rim thiacalix[4]arenes derivatives in *cone* and *1,3-alternate* conformations have many advantages to create a wide range of precursors for the design of very sophisticated supramolecular architectures.



These compounds can be considered as technological platform for nanomaterials design by self-assembly method. Particular attention will be paid to the application of calixarene derivatives for the construction of various supramolecular and nanosystems, devices and "smart" materials: nanoparticles, metal-coordinated networks, Langmuir-Blodgett nanolayers, molecular magnets etc.

Acknowledgments. The authors gratefully acknowledge of the RSF (19-73-20035) and RFBR grants (17-03-00389 and 19-03-00519) for the financial support.

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SUPRAMOLECULAR SELF-ASSEMBLY OF AMPHIPHILIC (THIA)CALIXARENES WITH SUBSEQUENT POLYMERISATION AS A TOOL FOR NHC SUPPORTS WITH CONTROLLED MORPHOLOGY FOR CATALYSIS.

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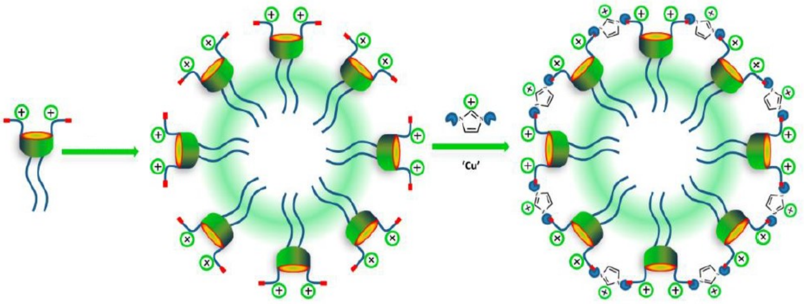
Metal complex catalysis, allowing a molecules modification with atomic precision, leads to a significant saving of resources and decrease of by-products and, therefore, completely corresponds to several principles of “green chemistry”. Taking into account the high cost of noble metals, effective catalytic systems are usually anchored on a support, which makes it possible to use them in the reactions many times. Typically, a catalytic act in supported catalysts occurs on the surface of the catalyst without engaging the support itself. However, nature itself offers a different model of an effective catalyst. If we look at the functioning of metalloenzymes, catalytic transformations occur in an active “pocket”, the functions of which, in addition to directly chemical transformation, include the binding of substrates and their corresponding orientation. Thus, the presence of “pockets” can give a significant increase in activity and a change in the selectivity of the catalyst. The use of macrocycles having a hydrophobic cavity for the design of metal complex catalysts provides a large surface area and the presence of reaction “pockets”. Macrocyclic amphiphiles allows you to form the “core” of the particle using self-assembly in aqueous solutions, and the presence of appropriate functional groups in the macrocycle allows subsequent covalent crosslinking to fix the resulting “core”.

Herein we propose the synthesis of highly organized nanostructures with controlled morphology and properties using supramolecular self-assembly of multidentate (thia)calixarene ligands as a support for metal complex catalysis.



Acknowledgements We thank the Russian Science Foundation for the financial support of this work (grant No. 19-13-00095).

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(THIA)CALIXARENE NHC COMPLEXES OF Pd(II) AND Cu(I) FOR GREEN CATALYSIS IN ORGANIC AND WATER MEDIA

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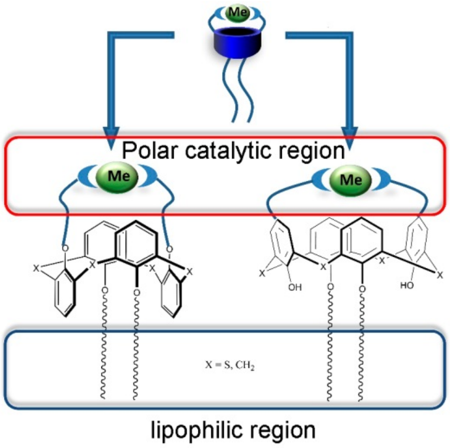
[b] *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov 8, Kazan,420088, Russia*

The idea of creating micellar catalysts, that can solubilize water-insoluble substrates and conduct traditional organic transformations in aqueous solutions, attracts much attention of researchers. Despite the fact that micellar catalysis has been successfully developing for more than half a century, there are only few studies related to metal-complex catalysis in the micellar medium. Even fewer works related to very promising and stable amphiphilic N-heterocyclic carbene (NHC) complexes of transition metals. The use of macrocycles with NHC chelate ligands opens great prospects for the production of new amphiphilic metal complex compounds.



The possibility of stepwise selective functionalization of the (thia)calixarenes lower and upper rims with lipophilic fragments on one side, and NHC ligands with additional polar groups to regulate the lipophilic-hydrophilic balance, on the other side of the macrocyclic cavity will give wide series of amphiphilic structures in the “1,3-alternate" stereoisomeric form.

Herein we show the synthesis of new amphiphilic N-heterocyclic carbene (NHC) complexes of palladium and copper on the thiacalixarene and classical calixarene platform and their calytic activity in different coupling reactions in organic and water media.

Acknowledgements We thank the Russian Science Foundation for the financial support of this work (grant No. 18-73-10033).

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INVESTIGATION OF INTRAMOLECULAR COMPLEXES OF HYDROXYALKYLAMINES FOR CHELATION OF ^{68}GA WITH PSMA-HBED-CC.

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Nowadays, PET (positron emission tomography) is a powerful diagnostic and imaging technique which requires short-lived positron emitting isotopes. ^{68}Ga ($T_{1/2}$=67.71 min) deserves special attention because of its availability from long-lived ^{68}Ge/^{68}Ga generator systems. This isotope forms stable complexes with various biomolecules such as peptides. Buffer solutions play a great role in labeling reactions of biologically active molecules with radiometals. Typically, buffer solutions of sodium acetate or HEPES are commonly using for ^{68}Ga-radiolabelling. Besides tris(2-hydroxymethyl)aminomethane hydrochloride (TRIS-HCl) can be utilize for production ^{68}Ga-DOTA-NOC. Here we investigate the possibility of application tris(2-hydroxyethyl)amine (TEA) **[A]** and TRIS **[B]** salts with biologically active acids such as benzoic (1), salycilic (2), hygrosuccinic(3), succinic (4), as well as drugs Trekrezan® (**5A**) as buffers in the labelling of PSMA-HBED-CC (PSMA-11) with ^{68}Ga.

The ^{68}Ga was obtained from a ^{68}Ge/^{68}Ga generator system (Cyclotron Co., Ltd, Obninsk, Russia). ^{68}Ga was eluted from the generator and trapped on the STRATA-SCX resin (100 mg) using 5 ml of 0.1 M HCl. Solution of 98% acetone, 0.05 M HCl (0.5 ml) was slowly passed over the resin to elute $^{68}Ga^{3+}$. Ready to radiolabelling eluate was used as stock solution. In a typical reaction, a 5 µg of PSMA-11 peptide (solution 250 µg/ml; 20 µL) was dissolved in 100 µL of 1 M of alkanolamine buffer solution. Afterward, 50 µL aliquot of $^{68}GaCl_3$ (15-40 MBq) was added to the reaction. Labeling was performed in sealed glass vial (100 °C, 10 min). After cooling radiochemical conversion (RCC) was determined by radioTLC. According to Ph. Eur. the radiochemical purity of product must be at least 91%, with a maximum 3% of gallium in colloidal form and 2% of $^{68}Ga^{3+}$. Our data (Tab. 1) show that salts **1-4A, 3-4B,** and **5A** are good enough to produce ^{68}Ga-PSMA-11 with high RCCs. Other compounds **1-2B** are showing medium RCC's, so it's necessary to thoughtful purification of reaction media with solid-phase extraction prior the injection. Reagent **5A** looks the most promising for the synthesis of ^{68}Ga-based radiotracers because of its approved as a pharmaceutical (Trekrezan®, adaptogen and immunomodulator). We suppose that these TEA and TRIS derivatives play not only buffer role, but also as a chelator for ^{68}Ga. Implementation of presented results into clinical production of radiopharmaceuticals is in progress.

№	**X^-**	**$NH^+(CH_2CH_2OH)_3$ [A] (N=3)**			**$NH_3^+C(CH_2OH)_3$ [B] (N=3)**		
		$^{68}Ga^{3+}$,%	**$^{68}Ga_{col}$,%**	**RCC,%**	**$^{68}Ga^{3+}$,%**	**$^{68}Ga_{col}$, %**	**RCC,%**
1	$PhCO_2^-$	3±2	3±1	94±3	16±6	21±2	63±8
2	$Ph-CH=CH-CO_2^-$	8±6	8±2	84±5	0	67±2	33±2
8	$HO_2C-CH_2-CH_2-CO_2^-$	1±1	1±1	98±2	0	1±1	99±1
9	$^-O_2C-CH_2-CH_2-CO_2^-$	2±2	2±1	96±3	0	1±1	99±1
14	o-$Me-C_6H_4-O-CH_2CO_2^-$	0±0	0.5±0.5	99.5±0.5	-	-	**-**

Acknowledgements The reported study was funded by RFBR according to the research project № 18-33-00216.
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DESIGN OF CHIRAL METAL-ORGANIC FRAMEWORKS FOR HETEROGENEOUS ASYMMETRIC CATALYSIS

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Among the recognized porous materials, metal-organic frameworks (MOFs) are a fascinating class of crystalline porous materials with significant prospects for addressing current energy and environmental challenges, including gas storage, separations, catalysis, smart sensors, and energy storage. In recent years, chiral MOFs has shown excellent performance in chiral separation, asymmetric heterogeneous catalysis and chiral recognition. However, it remains a challenge to design and synthesize chiral MOFs for task-specific applications

In this talk, we will report the synthesis of chiral MOFs with high catalytic efficiency and enantioselectivity from organic linkers derived from chiral ligands/catalysts including metallosalen, biphenol and spinol.

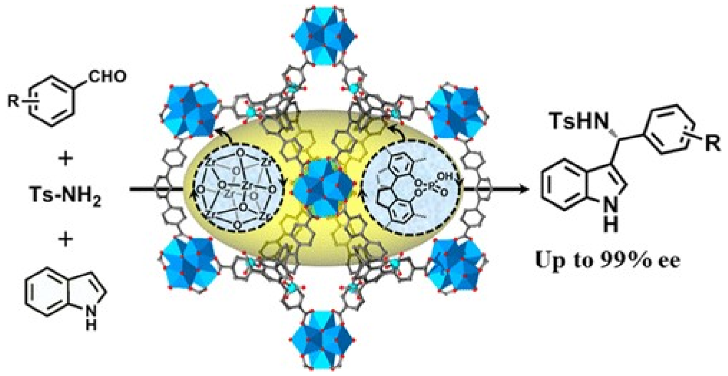

Figure 1. Chiral Spinol-based MOFs for heterogeneous asymmetric catalysis

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DEPROTONATION OF METHANOL COORDINATED BY NICKEL AND COBALT ATOMS IN THE PRESENCE OF TRIETHYLAMINE

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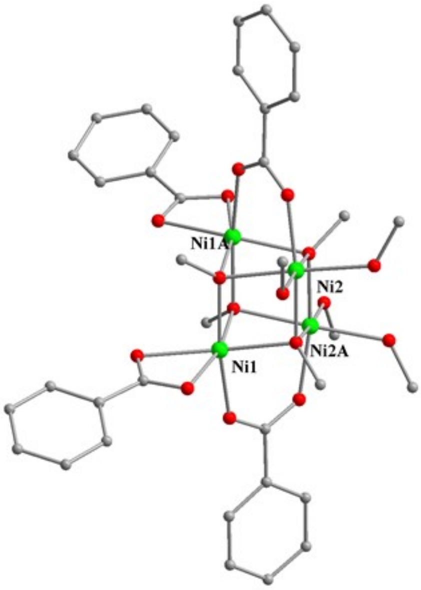
It was found that slow diffusion of triethylamine into the methanol solution of adducts $M(OOCPh)_2[O(H)Me]_4$ (M=Ni, Co) leads to the formation of monocrystals of tetranuclear isostructural clusters $(\eta^2\text{-}OOCPh)_2M_2(\mu^3\text{-}OMe)_3(\mu\text{-}OOCPh)_2M_2[O(H)Me]_4$(M=Ni(**1**), Co(**2**)):



According to the X-ray diffraction data four metal atoms being at non-bonding distances M...M 2.8813(8)Å, 3.0964(8)Å, 3.1692(9)Å and 2.9280(4)Å, 3.1464(4)Å, 3.2186(4)Å (in clusters **1** and **2** correspondently) are connected by four tridentate-bridging alcoholate anions OMe (Ni-O 2.021(3)Å- 2.061(3)Å; Co-O 2.0595(15)Å- 2.0989(14)Å). The opposite faces of the tetrahedron are additionally bonded by the μ-benzoate bridge (Ni – O 2.108 (3) Å –2.161 (3) Å; Co – O 2.1389 (15) Å –2.2020 (15) Å). Two neighboring metal atoms have η^2-OOCPh anions (Ni-O 2.017 (3) Å-2.037 (3) Å; Co-O 2.0595 (15) Å - 2.0630 (15) Å), and two opposite to them atoms have two coordinated alcohol molecules (Ni-O 2.079 (3) Å-2.097 (3) Å; Co-O 2.0955 (17) Å-2.0989 (14) Å).

Acknowledgements – We thank the Russian Foundation for Basic Research for the financial support of the research (grant № 18-33-01161)

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ACTIVATION HETEROCUMULENES BY REDOX-ACTIVE COMPLEXES OF XIII GROUP METALS

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In the current work we report on the chemical properties of gallium and aluminium complexes, [(dpp-bian)Ga–Ga(dpp-bian)] (**1**), [(dpp-bian)Ga–Na] (**2**), [(dpp-bian)Al–Al(dpp-bian)] (**3**), which contain redox-active ligand dpp-bian = 1,2-bis[(2,6-di-iso-propylphenyl)imino]acenaphthene. These complexes exhibit a number of remarkable properties: SO_2 [1] and CO_2 small molecule activation, redox dualism [2], two-electron oxidative addition [3], reversible addition of isothiocyanates [4] and other attractive features in the reactions against a wide range of organic substrates containing functional groups N=C=O, N=C=S, N=C=N, $N=N^+=N^-$, C=C=O etc. [5]

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CONFINED ELECTRON TRANSFER FOR SUPRAMOLECULAR CATALYSIS WITHIN METAL-ORGANIC ARCHITECTURES

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Through incorporation of electron transfer pairs in both the ground and excited states into redox active Werner type hosts with electronic acceptor/donor guests, the Duan group has developed a promising method to mimic natural enzyme systems in terms of redox transformations within a confined microenvironment. The host-guest systems fix and isolate the donor-acceptor pair with a short through-space separation, and without a through-bond electron transfer pathway. The confined electron transfer behavior differed from both the classical inter- or intramolecular photoinduced electron transfer (PET) processes that obey the Rehm-Weller or the Marcus theory. It has been proposed that this new electron transfer behavior assists in the stabilization of the charge-separated pair, which promotes redox transformations in both the ground and excited states. The unique communication between the dye guest and the host is direct confined PET from the excited state of the dye to the host, which could provide meaningful insight into the secrets of substance and energy metabolism in biological systems. Through modulation of the active site of nicotinamide adenine dinucleotide (NADH) models, the redox-active molecular host facilitated the confined electron transfer from the active sites of the NADH models to the substrate for biomimetic hydrogenation in the inner space of the host. The host-guest chemistry within the dye-containing metal-organic hosts permitted additional thermodynamic activation and modification of the electron transfer route for chemical reactions. The regiospecific and stereospecific PET processes within the host are at an early stage of development, however they have already proved important in the forging of organic reactions with tandem steps or intrinsic selectivity. By incorporating the oxidation catalyst and the aforementioned chiral group into one framework, an amphipathic framework-based host prompted the asymmetric dihydroxylation of aryl olefins.

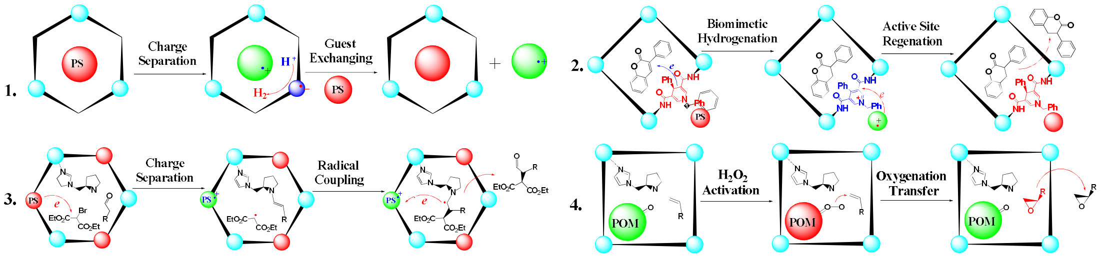

Figure 1. Confined electron transfer and redox catalysis within metal-organic architectures.

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POROUS COORDINATION POLYMERS: DELIBERATE SYNTHESIS, STRUCTURE AND FUNCTIONAL PROPERTIES

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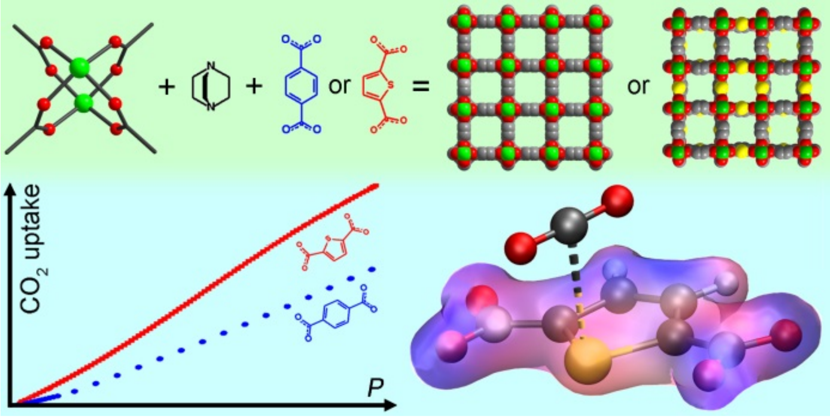
Selective adsorption and separation properties, and detection of small organic molecules are among the most valuable properties of metal-organic framework (MOF) based materials. Here we describe our recent results on deliberate synthesis, structural characterization, host-guest chemistry and investigation of functional properties for novel types of microporous metal-organic frameworks.

Isoreticular porous MOFs based on Zn_2–paddle wheels, connected through thiophenedicarboxylates and N-donor linkers $[Zn_2(tdc)_2L]$ are very similar to the prototypic terephthalate $[Zn_2(bdc)_2dabco]$. However, the substitution of benzene to thiophene linker substantially increases the carbon dioxide adsorption as well as CO_2/N_2 adsorption selectivity. The CO_2 uptake on $[Zn_2(tdc)_2dabco]$ approaches the best values reported in the literature although this compound possesses no basic amine functions nor open metal sites, which is manifested by a low isosteric heat of adsorption. The quantum chemical calculations confirm the definitive role of heterocycles and, particularly, sulfur atoms in CO_2 binding *via* induced dipole interactions.



Substitution of both pyridine and pivalate ligands in the heterometallic molecular complex $[Li_2Zn_2(piv)_6(py)_2]$ with bpy and terephthalate bridges (R-bdc^{2-}, R = H, Br, NH_2, NO_2) results in isoreticular porous frameworks $[Li_2Zn_2(R\text{-}bdc)_3(bpy)]$. The introduction of different substituents R onto the terephthalate linkers affects the free volume of the porous compounds and gas adsorption behavior. The CH_4 and CO_2 adsorption and relative selectivities have been investigated in detail, and interestingly, a fascinating interplay of luminescence properties with wavelength of excitation and nature of the host aromatic guest molecules has been observed.

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NOVEL PHOTOSENSITIZERS WITH TUNABLE PROPERTIES BASED ON TETRAPYRROLIC COMPOUNDS

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The report provides an overview of current data on the design, synthesis, photophysical properties of tetrapyrrole compounds and hybrid materials on their basis as photosensitizers for antimicrobial photodynamic therapy, anti-cancer drugs, new types of materials for energy conversion. Particular attention will be paid to the methods of post-synthetic modification of macrocycles and tuning their properties using external factors.

The report will use both the data obtained in the scientific group of the author of the report[1-5] and the overview of leading scientific groups devoted to the discussed subject.

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BIOMIMETIC MOLECULAR RECOGNITION IN WATER

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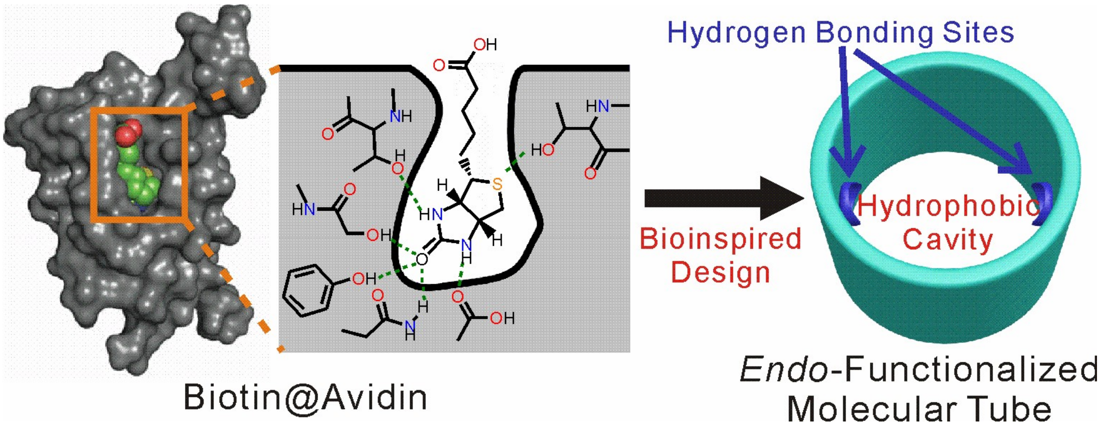
Selective recognition of hydrophilic molecules through hydrogen bonding in water is a generally-accepted challenge for supramolecular chemistry but commonplace in Nature. These hydrophilic molecules can be environmental contaminants, biomarkers for diseases, and drug molecules. By mimicking the binding pocket of natural receptors, *endo*-functionalized molecular tubes were proposed to meet this challenge. In this presentation, I will show that molecular tubes with inwardly-directed hydrogen bonding donors are able to selectively recognize a wide variety of hydrophilic molecules in water. The binding was revealed to be driven by combining hydrophobic effects with hydrogen bonding. In addition, I will also demonstrate the unique applications of these molecular tubes in fluorescent sensing of environmental contaminants, optical chirality sensing of the products of asymmetric catalysis, and shear-induced dissipative assembly of a transient yet stretchable hydrogel.



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ORGANOMETALLIC MACROCYCLES, CAGES AND THEIR APPLICATION

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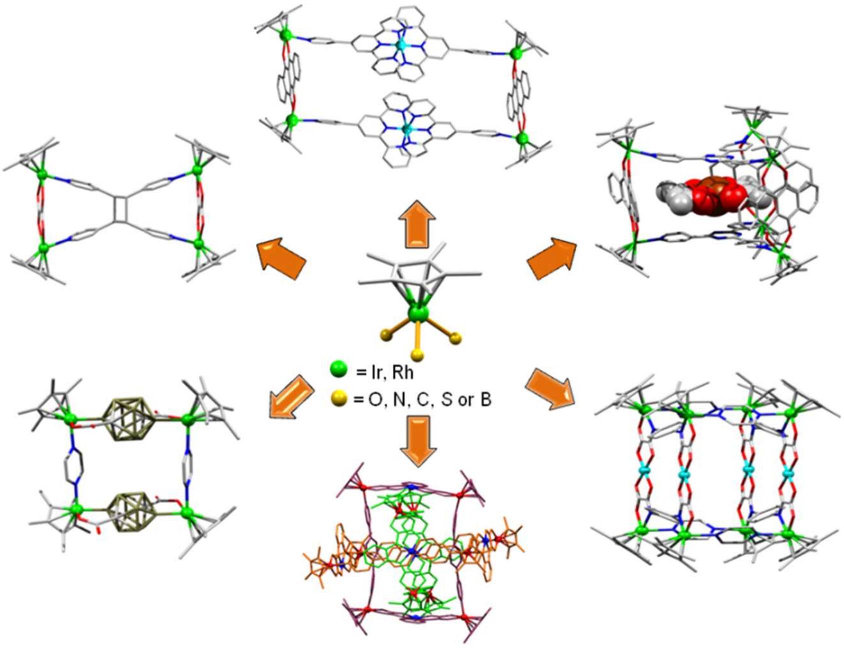
The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1] One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands. Half-sandwich transition metal complexes (Cp*M, Cp* = ^{5}-C_5Me_5) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous Cp* rings. In the protected space below the Cp* ligands, various bidentate or tridentate ligands can be accommodated.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.[2] We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed muticomponent self-assembly under mild condition. [3]

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SYNTHESIS, STRUCTURE AND PROPERTIES OF Cu(II), Co(II), Ni(II) AND Zn(II) COORDINATION COMPOUNDS WITH HYDROXYALKYLAMINES

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Hydroxyalkylamines, which include tris(2-hydroxyethyl)amine (TEA), tris(hydroxymethyl)aminomethane (TRIS) and tris(2-hydroxypropyl)amine (TPA), are low-toxic substances and are used in biochemistry and molecular biology as buffers, in cosmetology as a pH-balancer in various cosmetic products, and in pharmaceutics (drugs Trometamine, Cerumenex (USA), etc.).

With the purpose of obtaining new biologically active compounds for medicine and agriculture, in this study previously unknown coordination compounds based on hydroxyalkylamines (TEA, TRIS, TPA), transition metals (Cu(II), Co(II), Ni(II), Zn(II)) and carboxylic acids (cinnamic (Cin), salicylic (Sal), benzoic (Benz), succinic (Suc)) were obtained. The composition and structure of the synthesized complexes were confirmed by the data of single-crystal X-ray diffraction, IR spectroscopy, mass spectrometry and elemental analysis. A number of cationic mononuclear complexes $[Co(TEA)_2](Sal)_2$ (**1**), $[Co(TEA)_2](Cin)_2$ (**2**), $[Co(TEA)_2](NO_3)_2$ (**3**), $[Co(TEA)_2](Suc)$ (**4**) and $[Cu(TEA)_2](Suc)$ (**5**), consisting of $[M(TEA)_2]^{2+}$ cations and anions of carboxylic acids were synthesized by TEA interaction with cobalt (II) and copper (II) salts [1]. The binuclear complexes $[Zn_2(TEA)(Benz)_3]$ (**6**), $[Co_2(TEA)_2(Suc)(NO_3)_2]$ (**7**), $[Co_2(TEA)_2Cl_2]Cl_2$ (**8**), $[Cu_2(TEA)_2(Sal)_2](H_2O)$ (**9**) and $[Cu_2(TEA)_2(Cin)_2](H_2O)]$ (**10**) were also synthesized and characterized [2]. Contrary to TEA, the interaction of TRIS and TPA with metal salts is extremely poorly studied, in spite of the great prospects of obtaining bioactive compounds based on them. In this regard, complexes of TRIS and TPA with zinc (complexes **11** and **12**), copper (II) (**13**, **14**), cobalt (II) (**15**, **16**) and nickel (II) (**17, 18**) cinnamates, as well as copper (II) (**19** and **20**), zinc (**21, 22**), cobalt (II) (**23**, **24**) and nickel (II) (**25, 26**) benzoates were obtained and characterized. Structures of the two complexes **13** and **18** were determined by single-crystal X-ray diffraction. Both complexes, $[Cu(TRIS)_2](Cin)_2$ (**13**) and $[Ni(TRIS)_2](Cin)_2$ (**18**), are cationic, mononuclear. In the complex **13**, the copper atom is tetracoordinated by two TRIS ligands through a nitrogen atom and one oxygen atom. The structure of the complex **18** is similar to the cationic complexes of TEA **1-5** with octahedral coordination of the central metal atom. TPA, as TEA, acts as a tridentate ligand through a nitrogen atom and two oxygen atoms of two hydroxypropyl groups. The thermal stability of the synthesized compounds in the temperature range of 40-650 °C and their antimicrobial activity (*Escherichia coli, Staphylococcus aureus, Candida albicans, Aspergillus niger, etc.*) were studied.

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DYNAMIC COVALENT CHEMISTRY IN WATER

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Imine[1] condensation has already been employed as one of the most powerful dynamic covalent reaction motifs in the syntheses of macrocycle, cage, as well as some mechanically interlocked molecular entities such as rotaxanes, catenanes and Borromean rings. However, this dynamic reaction is not amenable in aqueous media for self-assembly because imine linkages are apt to undergo hydrolysis into their parent aldehyde and amino precursors. We thus developed novel dynamic covalent bonds based on hydrazone[2,3] and oxime[4] in order to realize high-yielding synthesis in water.

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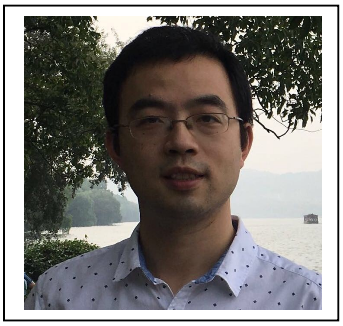
Biography



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ENHANCED INTERSYSTEM CROSSING FOR EFFICIENT ULTRALONG ORGANIC PHOSPHORESCENCE THROUGH BORON CLUSTERS

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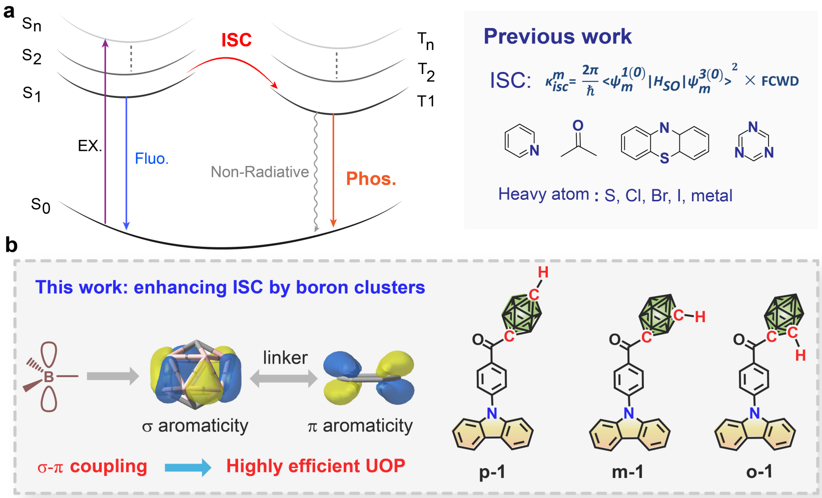
Heavy-atom free ultralong organic phosphorescence (UOP) is attractive due to its wide applications in optoelectronic devices and bioimaging[1]. However, limited by weak intersystem crossing (ISC) in heavy-atom-free luminophores, few strategies can address this issue and realize efficient UOP under ambient conditions[2]. Herein, the boron clusters (carboranes) were firstly used for UOP. Experimental and theoretical studies reveal that carboranes can improve ISC by both a larger spin-orbit coupling constant and restriction of fluorescence channel, which devotes a highly emissive UOP with quantum efficiency of 7.1%.

As shown in the figure below, we have proposed and demonstrated an effective strategy to realize highly emissive UOP by boron clusters. Owing to the intramolecular electronic communication between the σ-aromatic cage and π-unit, these heavy-atom-free organic compounds are able to display enhanced ISC, and redshift in absorption spectra, leading to visible-light excited UOP with a long lifetime up to 0.666 s. The multiple intermolecular interactions, particularly from carboranyl groups such as Bcage–H…π□ interactions devoted to suppressing non-radiative decay to obtain the high-efficiency UOP under ambient conditions, which represents excellent orange-red UOP among the heavy atom-free materials. Moreover, such carborane cage embedded compounds possess motional molecular conformations, making variable emission behaviors possible in crystalline state including thermochromism and mechanochromism.



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ALKYL COMPLEXES OF LN(II) AND CA – UNIVERSAL CATALYSTS FOR INTERMOLECULAR C−E (E = C, N, SI, P, S) BOND FORMATION

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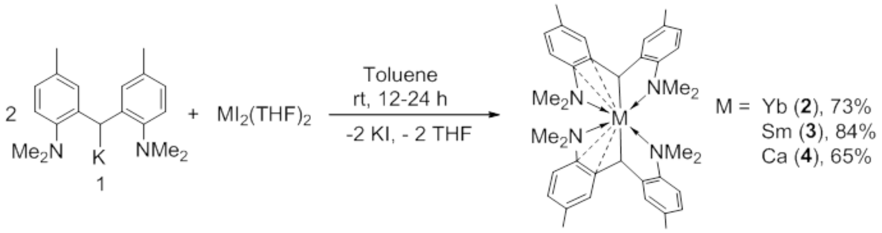
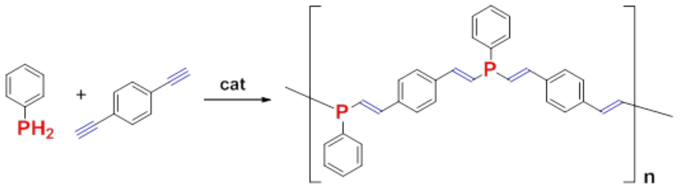
Rare earth metal σ-bonded alkyl complexes are widely investigated through last decades due to their unique reactivity in various stoicometric and catalytic reactions. Despite the large amount of known alkyl species of Ln^{III} their divalent analogues (Yb, Sm and Eu) remain scars. Alkyl complexes of heavy alkaline-earth metals (Ca and Sr), which in most cases are isostructural and demonstrate chemistry similar to Yb^{II} and Sm^{II} respectively, are also poorly investigated.

For preparation of Ln^{II} and Ca alkyl complexes the tridentate bis(2-(dimethylamino)-5-methylphenyl)methanido ligand $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]^-$ was used and bis(alkyl)s $[2,2'\text{-}(4\text{-}MeC_6H_4NMe_2)_2CH]_2M$ (M = Yb^{II}, Sm^{II}, Ca) were synthesized. Presence in *o*-position of the phenyl rings additional NMe_2-groups capable for coordination to the M^{2+} ions allows to achieve high stability of such diphenylmethanido species.



It has been shown that complexes **1–4** are affective catalysts for intermolecular C−E bonds formation. They demonstrated high activity and selectivity in a wide range of intermolecular hydroamination, hydrophosphination, hydrotiolation and hydrosilylation reactions of alkenes and acetylenes and also in intermolecular styrene hydrobenzylation by Me-substituted pyridines.

High activity and selectivity of complexes **1–4** made it possible to carry out the catalytic synthesis of organophosphorus polymers by double addition of primary phosphines RPH_2 to bis(ethinyl) substituted aromatic substrates. Thin films of the obtained organophosphorus polymers showed photoluminescent and semiconductor properties.



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SYNTHESIS, STRUCTURE AND PROPERTIES OF {Cd(II)-Ln(III)} COMPLEXES WITH ANIONS OF MONOCARBOXYLIC ACIDS

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Carboxylate heterometallic complexes of d10 metals with lanthanide atoms draw the notice of investigators due to the possible demonstration of unusual photoluminescence properties. The synthetic method based on the variation of N-donor ligand and the anion of monocarboxylic acid allows us to reveal the patterns of the obtainment of compounds with the predetermined structure and to follow the change of their properties simultaneously.

Using the 3,5-di-*tert*-butilbenzoic acid anion (Hdtbbenz), a new trinuclear heterometallic complex $[Cd_2Ln(dtbbenz)_7(EtOH)_x(H_2O)_{4-x}]$ (**1**) (Ln(III) = Eu (**1**), Tb, Dy, Sm, La) was obtained. Involving of the monodentate (L = pyridine, 2,4- lutidine, phenanthridine, 2,3-cyclododecenopyridine), chelating (L = 2,2'-bipyridine, 1,10-phenanthroline) or bridging (L = pyrazine, 4,4'-bipyridine, 5-methylpyridin-2-amine, 1,2-di(pyridin-4-yl)ethene) ligand into the system allowed us to either fully or partly substitute coordinated solvent molecules in the structure of the complex (**1**) by molecules of N-donor ligand. Also on examples of obtained complexes with monodentate ligands (2,4-lutidine) the contrast of the Cd (II) chemistry from earlier received {Zn(II)-Ln(III)} analogues was shown.

The use of the 2-furoic (Hfur), benzoic (Hbnz), and 4-(Trifluoromethyl)benzoic (HCfbenz) acids salts in the reaction lead to the reorganization of the metal core and use of 2,2'-bipyridine (bpy) allowed this isolation of the tetranuclear complexes $[Cd_2Ln_2(fur)_8(NO_3)_2(bpy)_2]$ (Ln(III)=Eu, Tb, Sm, Gd), $[Cd_2Ln_2(Cfbenz)_{10}(bpy)_2]$ (Ln(III)=Eu, Tb) and $[Cd_2Eu_2(bnz)_{10}(EtOH)_2(bpy)_2]$.

When we used salts of pentafluorobenzoic acid (Hpfbenz) in the presence of chelating ligand (L': 1,10-phenanthroline, bathophenanthroline), we managed to isolate 1D-polymeric complexes $\{Cd_2Tb_2(pfbenz)_8(NO_3)_2(L')_2\}_n$. The polymeric structure is not typical for the compounds of such type, because all the previously described Cd-Ln complexes with the chelating ligands possess molecular construction. Apparently the stabilization of the polymeric structure is connected with the intramolecular interactions of the pentafluorobenzoate substituents with unfluorinated aromatic fragments. in an attempt to synthesize Zn-Ln compound with pentafluorobenzoic acid and 1,10-phenanthroline, the complex with similar compound is formed, but it is non-polymeric

Synthesized {Cd(II)-Ln(III)} (Ln = Eu, Tb, Sm) compounds possess photoluminescence activity. The overall quantum yields are ranging from 0.2 to 66%.

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THIADIAZOLE CALIX[4]ARENE DERIVATIVES AS DNA COMPACTING AGENTS

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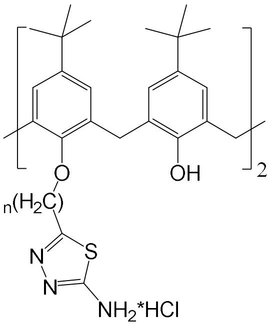
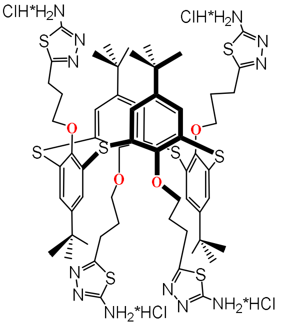
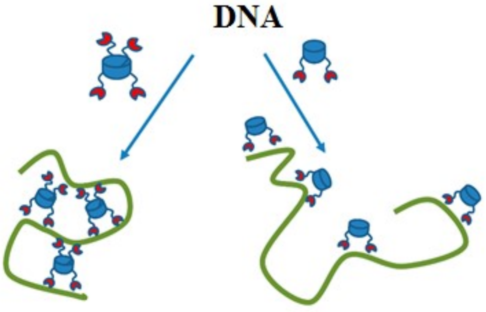
Important challenge in gene therapy is to search efficient and safe gene carries capable of compacting, protecting and delivering nucleic acids into the cell. Calixarenes are versatile macrocycles with opportunity to introduce several appropriate functional fragments to perform multivalent binding with target biomolecules. Their easy synthesis, variety of stereoisomeric forms and low toxicity levels make them really promising molecules for gene delivery applications.

We carried out synthesis of calix[4]arene and thiacalix[4]arene derivatives with two or four aminothiadiazole fragments on the lower rim in *cone* (in the case of two fragments) or *1,3-alternate* stereoisomeric form (in the case of four fragments). Obtained macrocycles were found to be watersoluble and study of their binding with Calf Thymus DNA (DNA CT) was done using ethidium bromide as fluorescent probe. Size and zeta-potential were measured using dynamic and electrophoretic light scattering.







The obtained thiadiazolyl derivatives of calix- and thiacalix[4]arene are capable of effective interaction with DNA CT. An increase in the number of thiadiazolyl fragments from two to four leads to an increase in the stability constant of the calixarene-DNA complex from 2.1 to 3.6 logarithmic units. It was found that a macrocycle containing four thiadiazolyl fragments in a 1,3-alternate stereoisomeric form is capable of 6-fold compaction of DNA CT, while macrocycle with two thiadiazolyl fragments is capable only of 2-fold compaction.

The obtained thiadiazolyl derivatives of calix- and thiacalix[4]arene are capable of effective interaction with DNA CT. A macrocycle containing four thiadiazolyl fragments is capable of 6-fold compaction of DNA CT, which is interesting from the point of view of creating non-viral transfection systems for gene delivery.

Acknowledgements This work was funded by RFBR (N. 17-03-00389).

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NEW POROUS DISCRETE STRUCTURE AND 1D COORDINATION POLYMER BASED ON THIACALIX[4]ARENE

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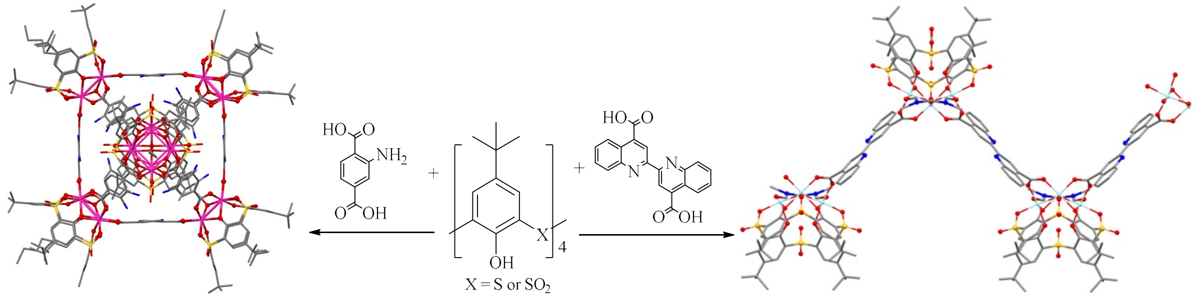
Thiacalix[4]arenes in *cone* conformation are attractive multidentant organic ligands able to form with metal ions different polynuclear coordination compounds promising interesting physical properties, such as exhibit catalytic activity and specific adsorption properties[1-3].

In this paper we report synthesis and structure of new coordination compounds (coordination cage and 1D coordination polymer) obtained by interaction between *tert*-butylsulfonylcalix[4]arene (Scheme 1, X=SO_2) as molecular building block with different dicarboxylic acids as co-ligands (2-Aminoterephthalic acid, 2,2-biquinoline-4,4-dicarboxylic acid) and transition metal cations (cobalt (II) and zinc (II)). Thus, we have shown that varying the structure of the co-ligand leads to form different types of coordination compounds, which have a cavity in the case of compound **1** and a porous structure in the case of a 1D coordination polymer **2** and therefore potentially possess adsorption properties (Figure 1).



1 **2**

Scheme 1. Synthesis and crystal structure of new coordination compounds.

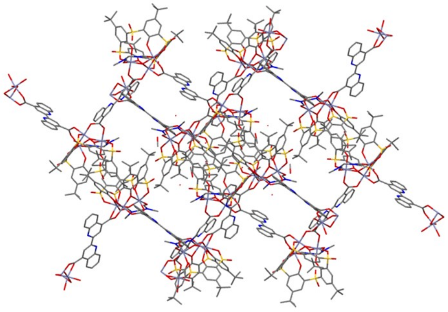


Figure 1. Packing of new 1D coordination polymer.

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DESIGN OF NEW MANGANESE CLUSTERS BASED ON (THIA)CALIX[4]ARENES

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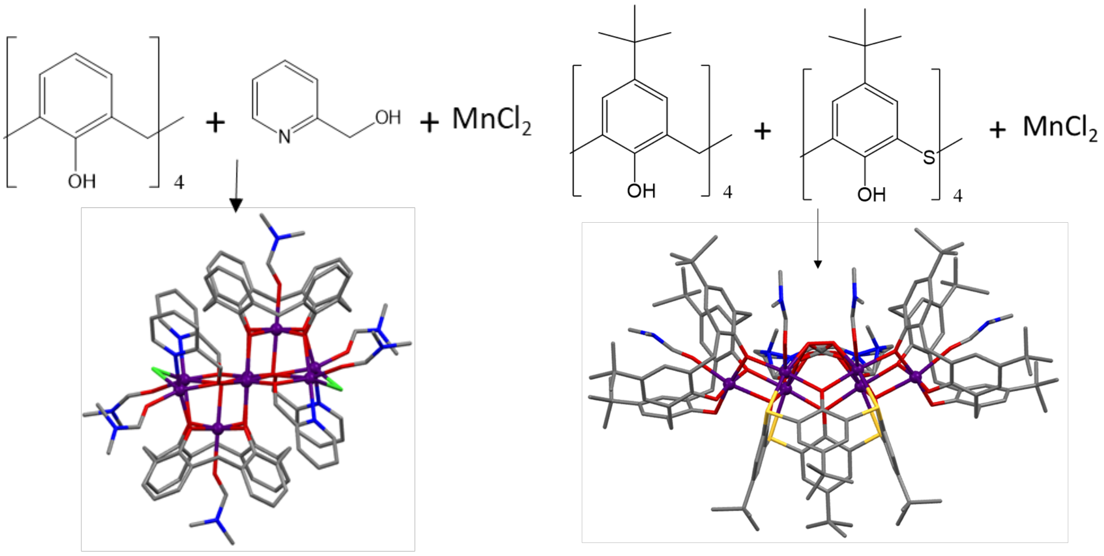
In recent years polymetallic clusters with paramagnetic metal cations have been actively studied due to the ability to exhibit single molecular magnet properties. (Thia)calix[4]arenes due to their pre-organized cavity and presence of close hydroxyl groups are suitable ligand for formation of complex compound in crystalline phase with *3d* metal cations, especially, manganese cations displaying the single molecular magnet behavior[1-4].

The introduction of additional coligands capable of coordinating with metal cations can change the geometry and magnetic properties of the resulting complex compound. Therefore, in this work we synthesized new manganese clusters based on calix[4]arene using pyridylmethanol and thiacalix[4]arene as co-ligands(Scheme 1). It is important that obtaining a "mixed" cluster based on thia- and calix[4]arene indicates possibility for obtaining new "mixed" clusters, including various types of calixarenes.



$[Mn_8\text{-}(C[4]A)_2(colig)_4DMF_6(OH)_2]$ $[Mn_6\text{-}(TCA)(C[4]A)_2(DMF)_6(MeOH)_3]$

Scheme 1. Synthesis and crystal structure of new manganese clusters based on calix[4]arene involving pyridinemethanol and thiacalix[4]arene.

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ChemShip-2019/Topical Problems of Modern Chemistry
Russian-Chinese Workshop on Coordination and Supramolecular Chemistry
September 16-21, 2019, Nizhny Novgorod, Russia

DESIGN (THIA)CALIX[4]ARENE BASED NEW COORDINATION COMPOUNDS

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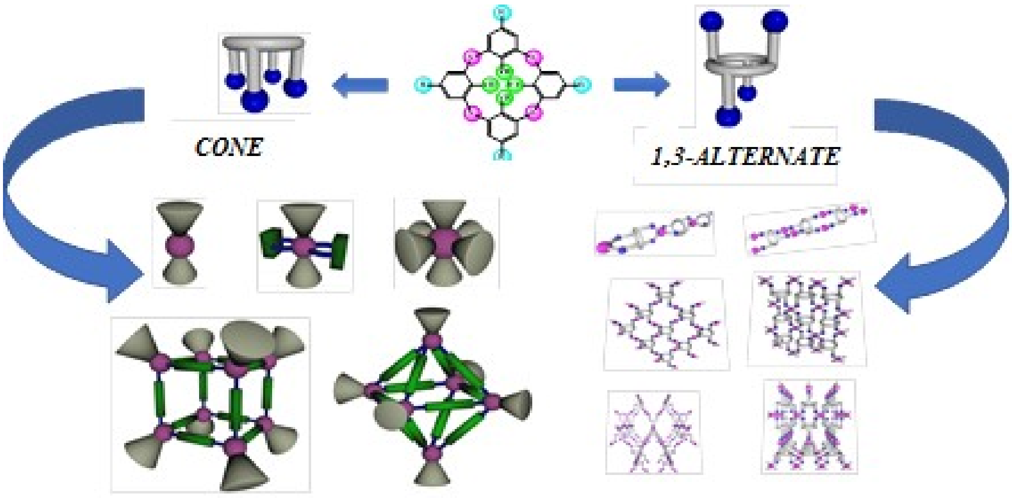
.

(Thia)calix[4]arenes present versatile molecular platform extremely adopted for generation of various crystal state supramolecular assemblies. Being fixed in two symmetrical conformations (*cone* or *1,3-alternate*), they can be involved in formation of either discrete cluster-like coordination compounds (cages) or extended coordination polymers while coordinating with metal cations [1-3] (Scheme 1). Controlling on the self-assembly of these compounds by the rational design of (thia)calix[4]arene platform in the crystalline phase in combination of used organic co-ligands may lead to creation of new functional materials which can exhibit attractive physical properties (molecular magnets, photocatalytic activity, etc.) [4].

Here we report the new metal clusters, cages and coordination polymers obtained as a result of the interaction of (thia)calix[4]arenes in *cone* and *1,3-alternate* stereoisomeric forms with *d* and *f* metal cations.



Scheme 1.

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COORDINATION ASSEMBLY OF METAL-ORGANIC MATERIALS (MOMS) FOR CATALYSIS

Cheng-Yong Su

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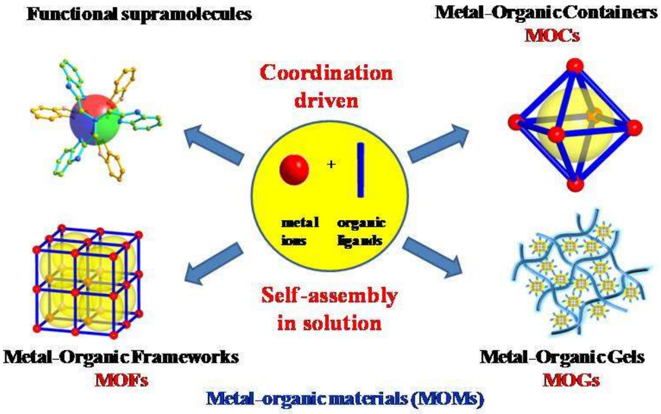
Coordination supramolecular engineering is targeted for the design, assembly, modification and application of metal-organic materials (MOMs) with well-defined structures by using kinetically or thermodynamically versatile metal-ligand interactions as driving forces, among which metal-organic frameworks (MOFs) and metal-organic cages (MOCs) have drawn much attention. One interesting feature of MOFs and MOCs is that they both can provide confined chemical space competent for catalysis, reminiscent of natural enzyme. In this lecture, I will report our recent work on coordination assembly of MOCs as supramolecular reactors, coordination interspace engineering of MOFs as crystalline reactors, and construction of nanoscale hierarchical porous MOFs (HPMOFs) as nanoreactors.



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LANTHANIDE-ORGANIC ASSEMBLIES: NEW ARENA FOR SUPRAMOLECULAR CHEMISTRY

Qing-Fu Sun

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Coordination-assembled supramolecular containers have shown potential applications in sensing, biomimetic catalysis, stabilization of fleeting species, drug-delivery et al. By employing the metal-driven assembly strategy, numerous of metallocycles/cages constructed with transition-metals have been reported. While rare-earth ions have a lot of optical, electromagnetic and catalytic properties to offer to the aesthetically appealing 3D supramolecular edifices, directed-assembly with rare-earth metals is difficult due to their unpredictable and labile coordination numbers/geometries. We are interested in the rare-earth supramolecular chemistry, particularly in the designed assembly and fine-tuned photophysical properties of multinuclear lanthanide-organic polyhedral (LOPs) complexes. Recently, precise syntheses of LOPs with different molecular composition and geometry have been accomplished in our group [1-2]. Photophysical including chiroptical properties of the LOPs have been investigated, with proof-of-concept applications such as highly selective and efficient sensing toward biological relevant molecules/ions [3-4], ion separation [5], single-molecular ratiometric luminescent thermometers [6], photosensitizers et al. We envisage that these LOPs will find many applications in the biomedical and material fields.

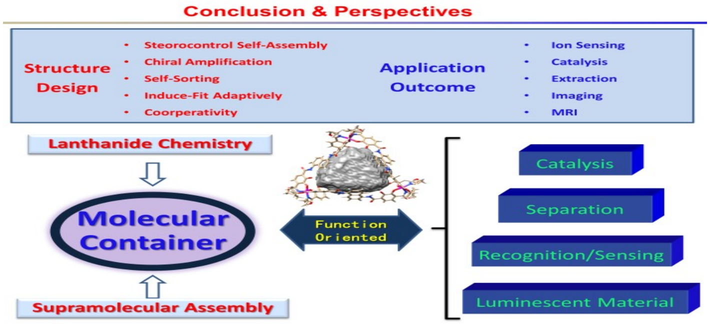

Figure 1. Rare-earth supramolecular chemistry: Structure and function.

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RARE- AND ALKALINE EARTH METAL COMPLEXES FOR CATALYTIC C-C AND C-E BOND FORMATION

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Rare- and alkaline earth alkyl complexes deserve particular interest as highly active species that exhibit unique reactivity and ability to promote activation and derivatization of unsaturated and saturated hydrocarbons.

New families of readily accessible and thermally stable homoleptic Ln(II) and Ln(III) alkyl complexes containing bulky and polyidentate ligands were synthesized and characterized. The synthesis, structures and reactivity of new and heteroleptic Ln(II) and Ln(III) alkyl species supported by various ancillary ligands will be considered as well.

New alkyl complexes proved to be highly efficient, selective and universal catalysts for formation of C-C, C-P, C-N, C-S and C-Si bonds.

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METAL-ORGANIC FRAMEWORKS BASED ON 2,5-DI-HYDROXY-3,6-DI-TERT-BUTYL-PARA-QUINONE

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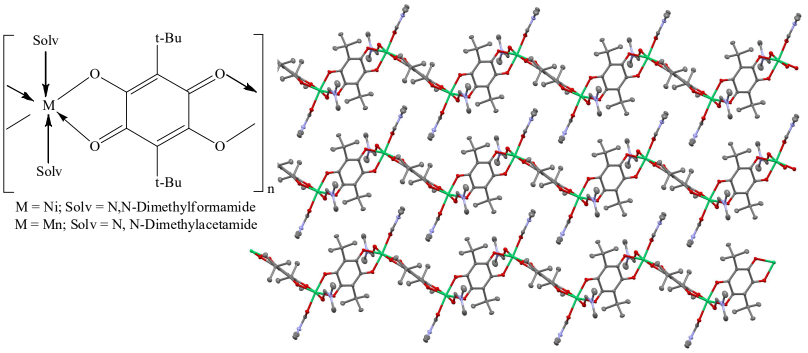
G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, RUSSIA.

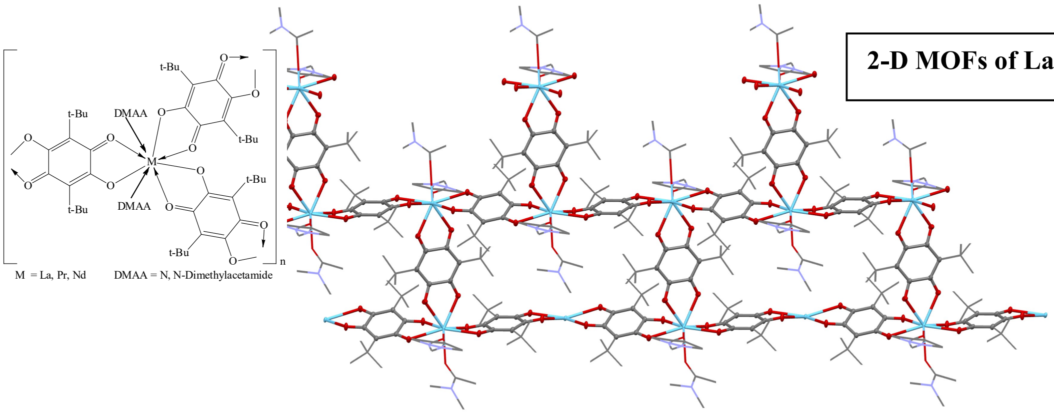
Metal-organic frameworks are one-, two-, or three-dimensional crystalline compounds based on ions or clusters of metals and bridged organic ligands.

We report the synthesis of one- (Ni, Mn), two- (La, Pr, Nd), or three-dimensional (La) MOFs.



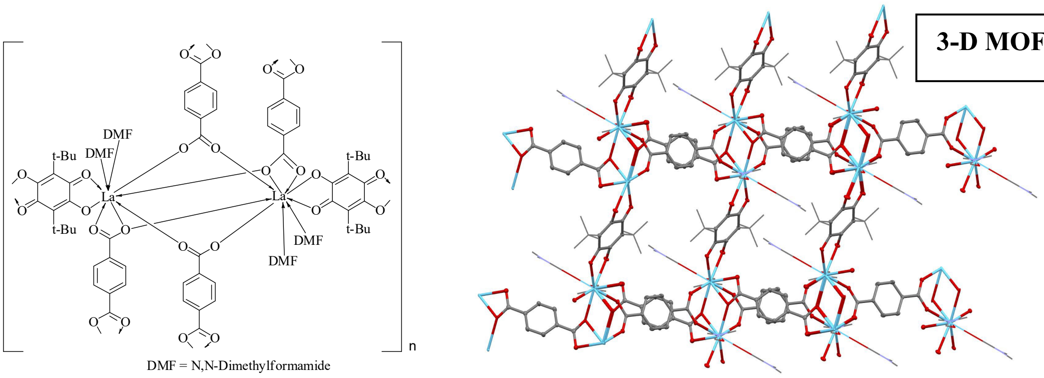
M = Ni; Solv = N,N-Dimethylformamide
M = Mn; Solv = N, N-Dimethylacetamide

1-D MOFs of Ni and Mn



M = La, Pr, Nd DMAA = N, N-Dimethylacetamide

2-D MOFs of La, Pr and Nd



DMF = N,N-Dimethylformamide

3-D MOFs of La

All complexes were characterized by IR-spectroscopy, TGA and DTA, X-ray phase, X-ray diffraction and elemental analyses.

Acknowledgements - We are grateful to the Russian Foundation for Basic Research (grant 18-29-04041 мк) for financial support of this work.

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HIGHLY EMISSIVE ORGANIC SINGLE-MOLECULE WHITE EMITTERS: *O*-CARBORANE-BASED LUMINOPHORES

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The development of organic single-molecule white emitters holds a great promise for advanced lighting and display applications. Since white light covers the whole visible region, white-light devices are usually fabricated by the incorporation of multicomponent emitters that exhibit three primary or two complementary colors of light. This approach, however, encounters many thorny problems, such as spectral instability, bad color reproducibility and fabrication complexity. The best strategy to solve these problems is to develop single-molecule white emitters. To date, however, few strategies enable single-molecule luminophores to emit white light efficiently in the solid state because the white-light emission requires precise manipulation of excited state properties and overcomes the low luminous efficiency in the solid state. Therefore, the design of a highly emissive solid-state white emitter still remains a big challenge.

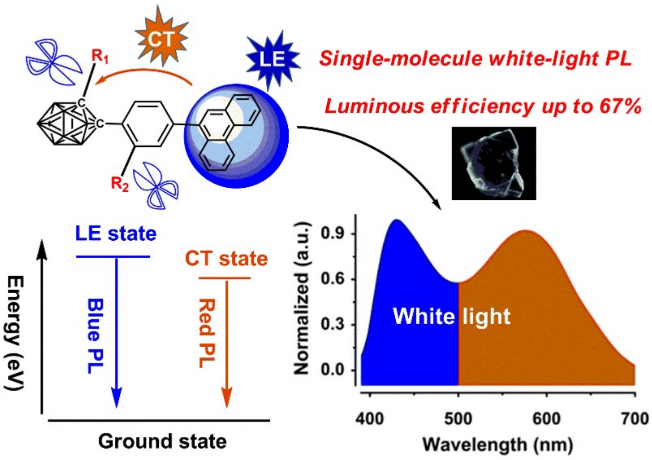

Figure 1. The design strategy for single-molecule white emitters

o-Carborane is known as an icosahedral boron cluster, which bears multiple properties including three-dimensional cage structure and dual electronic effects, and has proven to be a promising building block for photofunctional materials. According to previous work, *o*-carborane can modulate the excited state properties of iridium complexes effectively displaying the tunable emission wavelength and high luminous efficiency. Inspired by these results, we design a new class of *o*-carborane-based single-molecule white emitters. Through the optimization of the π-conjugated donors, *o*-carborane-based phenanthrene is capable of inducing a complementary-color white light with a CIE coordinate of (0.33, 0.36). Through further fine tailoring the molecular structure of phenanthrene by suitable substituents, both the crystal packing structures and intermolecular hydrogen bonds can be tuned to lead to significantly improved white-light luminous efficiency of 67%, which displays the efficient luminous efficiency among the single-molecule white-light emitters in the solid state.[1]

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BISPIDINES: HOW SPATIAL PRE-ORGANIZATON HELPS IN BIOMEDICAL, ANALYTICAL AND CATALITIC APPLICATIONS

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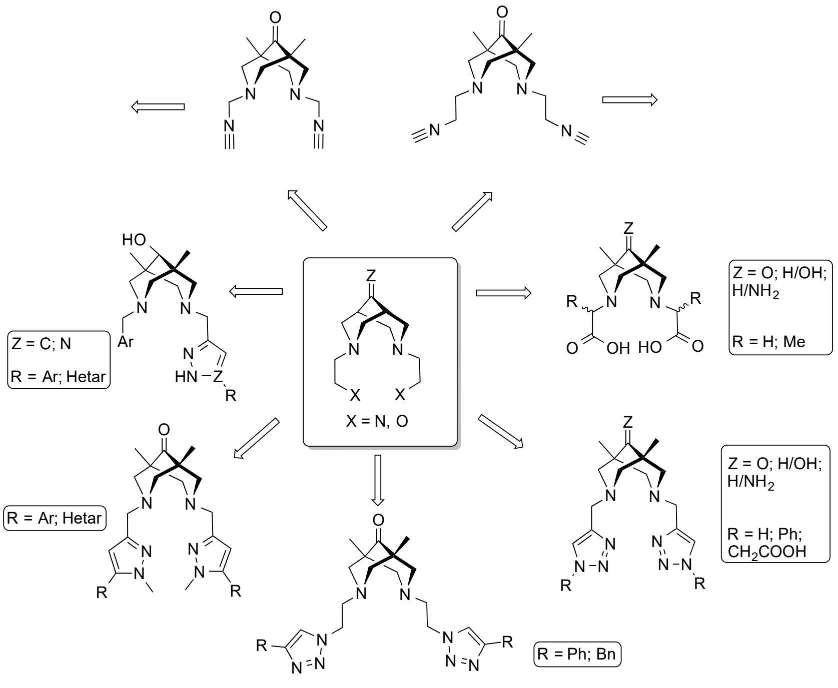
***N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB of RAS, Novosibirsk, Russia*

Spatial pre-organization of the receptor component is a key factor governing the proper 3D arrangement of the participants of the supramolecular assemblies. Widely known are several quite effective classes of supramolecular host systems like crown-ethers, calixarenes, cucurbiturils and others. Among others, we would like to mention 3,7-diazabicyclo[3.3.1]nonanes, aka «bispidines». Indeed, in this system one could easily functionalize almost all positions of the bicyclic core, particularly, both nitrogens and carbon at position 9, aiming to decorate the molecule to fulfill the desired task.



During the lecture the audience will have an opportunity to listen to our recent results on the study of the properties of various bispidine-based systems (conformations, biological activity, radiocopper, gels, chiral ligands, etc.),[1,2] including their use to support the concept of «stereoelectronic chameleons».[3]

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ANION-COORDINATION-DRIVEN ASSEMBLY

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Bearing opposite charges, cations and anions are contrary in most cases. Yet they are quite similar in some other aspects. It has been found that anions display very similar coordination behavior to the well-known classical coordination chemistry of transition metals. In particular, like the preferable coordination number (CN) and geometry adopted by a certain d^n configuration of metal ions, an anion (e.g. tetrahedral) also tends to form complexes with a typical coordination number and geometry (e.g. CN = 12 for tetrahedral anions). Although the coordination properties of anions are far less well-defined than transition metals, the similarities between them provide effective design strategies for anion ligands and enable the Anion-Coordination-Driven Assembly (ACDA) of a broad scope of supramolecular architectures.

In recent years we have designed a class of oligourea ligands, which show excellent coordination affinity toward tetrahedral oxoanions. Based on the resemblance of coordination between phosphate/oligourea and metal-ion/oligopyridine, a variety of supramolecular structures, including triple- and double-stranded helicates, cages, and macrocycles, with anions as the coordination centers have been constructed. These anion-based supramolecular systems exhibit promising host-guest chemistry, such as stabilization of reactive species (P_4 and As_4), selective recognition of biomolecules (choline and derivatives etc.), supramolecular chirality transfer, and supramolecular catalysis. Moreover, some unusual properties, such as adaption of both host and guest during inclusion, peripheral template effect, etc., have been observed for the anionic assemblies. These results clearly demonstrate that ACDA is a powerful new approach to complex supramolecular assemblies.

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QUANTUM SIZE EFFECT IN THE METALLIC AND BIMETALLIC NANOPARTICLES OBTAINED VIA THE THERMOLYSIS OF Fe(II), Co(II), Ni(II), Cu(II), Zn(II) SALTS OF CARBOXYLIC ACIDS

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Quantum size effect is detected in Co, Ni, Cu nanosized particles (NSPs,) and in their solid solutions obtained via the thermal decomposition of maleates $[M(H_2O)_n(C_4H_2O_4)](H_2O)_m$ (n = 1, 2; m = 0, 1), $[M(H_2O)_4(C_4H_3O_4)_2]$ (M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II)) and ortho-phthalates $[M(H_2O)_n(C_8H_4O_4)](H_2O)_m$ (n = 1, 2; m = 0 - 2), $[M(H_2O)_6(C_8H_5O_4)_2]$, $[Cu(H_2O)_2(C_8H_5O_4)_2]$ (M = Fe(II), Co(II), Ni(II)) upon heating up in a helium flow to 500 °C.

It is established that the size of metal nanoparticles, incorporated into polymer matrix (and additionally contained in a polymer or graphene shell), increases from 3.5 nm to 5 nm (Co) [1] and from 4.5 nm to 7 nm (Ni) [2] upon the transition from maleate composites to phthalate composites. Polymeric conglomerates containing shell-less Cu NSP_s, the average size of which ranges from 7.5 to 50 nm, are incorporated into a composite polymer matrix obtained via the thermolysis of Cu(II) maleate and phthalate. Diameter of Fe NSP_s (in the absence of shell) embedded into the polymer matrix increases from 150 nm to 175 nm upon the decomposition of maleate and phthalate, respectively. The thermolysis of Zn(II) maleates results in ZnO nanoparticles (with an oval shape) with average sizes of 13.5x40 nm. They are embedded in a polymeric matrix. The oxide phase is reduced to yield Zn upon heating to 675 °C.

The binary systems Co(II) – Ni(II) or Zn(II) acid maleates contain continuous series of solid solutions. The destruction of Co/Ni solid solutions on the Curie curve upon the second-order phase transition in the bimetallic NSP_s is the example of quantum size effect. The bimetallic NSP_s (smaller than 25 nm) are formed under $[(Co_xNi_{1-x})(H_2O)_4(C_4H_3O_4)_2]$ $(0<x<1)$ thermolysis with the formation of range of heterogeneity of two phases. The decomposition of $[(Co_{0.1}Zn_{0.9})(H_2O)_4(C_4H_3O_4)_2]$ leads to the segregation of metallic Co (d = 2.5 Å) [3] atoms embedded in the channels of the ZnO structure, that act as a catalyst for the spontaneous growth of uniform carbon nanotubes on the surface of the composite at $T \leq 500$ °C. This process may be considered as a manifestation of the quantum size effect. The usage of such catalyst may lead to the significant reduction of energy intensity of process.

Discrete decay of solid solution on the binodal curve limiting field of heterogeneity of Cu/Ni solid solutions via the thermolysis of ortho-phthalate $[Cu_{0.56}Ni_{0.44}(H_2O)_2(C_8H_4O_4)](H_2O)$ is the evidence for the quantum size effect. The formation of the three bimetallic phases, at least, with NSP_s of various diameters (40-85 nm, 15-25 nm, and 10-15 nm) in the composite via the thermolysis of this compound confirms such effect.

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THE SYNTHESIS AND REGULATION OF FLEXIBLE METAL-ORGANIC FRAMEWORKS CONSISTED BY MULTIPLE SECONDARY BUILDING UNITS

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Flexible metal-organic Frameworks (Flexible MOFs), which can also be called soft porous crystals (SPCs), have reversible phase transition phenomenon under external stimulation. Flexible MOFs have been widely studied for its rare structural flexibility among the crystalline structures. The flexibility of MOFs is generally derived from the dissociation of coordination bonds in the flexible secondary building units (SBUs). The paddle-wheel unit, which is the most common soft SBUs, has been reported in Zn(BDC)(dabco), MIL-88 and other flexible structures. However, due to the relatively weak coordination bond in the paddle-wheel SBUs, it will easily dissociate and fracture, which leads to the irreversible phase transition of MOFs and limits the application of such flexible materials.

To solve this problem, we introduce the triazolate di-nuclear SBU, which has strong coordination bonds, into the MOFs structure to construct flexible MOFs with multiple SBUs[1]. This kind of material not only has the structural flexibility, but also maintains the structural stability under external stimulation. In addition, we synthesized a series of flexible MOFs materials through post-modification strategies such as ligand substitution[2], guest molecule exchange[3], and metal doping[4].

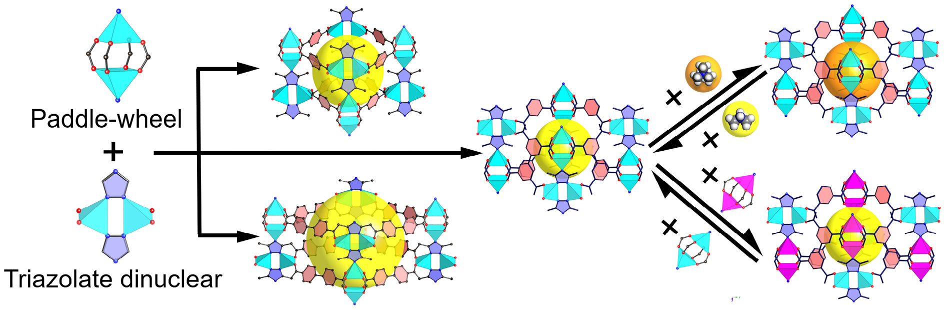

Fig. 1 *A series of flexible Metal-Organic Frameworks consisted by multiple Secondary Building Units*

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SYNTHESIZE SUPERHYDROPHOBIC MOF CATALYST FOR CATALYSING SONOGASHIRA REACTION IN WATER EFFICIENTLY

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As a new class of porous crystalline materials, metal-organic frameworks (MOFs), usually constructed from organic linkers and inorganic metals/metal clusters, have high BET surface area, tunable structures and tailorable functionalities. [1] Hence they have drawn great of attention in many fields, such as gas sorption and separation, heterogeneous catalysis, chemical sensing, luminescence, drug delivery, and so on. [2] But among the more than 20,000 known MOFs, only a few dozen exhibits both the thermal and chemical stability desired for harsh environments, especially in water, acid/base solutions. So it is necessary to constructing novel hydrophobic MOFs to improve stability for various applications especially for ctalysis. Here we develop a superhydrophobic catalyst based on the strategy, namely UiO-67-Oct-L^2-X%-$Pd^{(II)}$ (X presents the ratio of L^2), through constructing mixed ligands MOF with C_8-chain ligand and Pd-containing ligand. In contrast, their counterpart, UiO-67-L^2-36.4% -$Pd^{(II)}$, is synthesized based on the same method except using normal ligand instead of hydrophobic ligand with C_8 chain. Remarkably, hydrophobic UiO-67-Oct-L^2-35.7%-$Pd^{(II)}$ exhibits significantly higher catalytic activity in Sonogashira reaction in water at room temperature and enhanced recyclability compared to the hydrophilic UiO-67-L^2-36.4% -$Pd^{(II)}$ and other reported supramolecular catalysts.

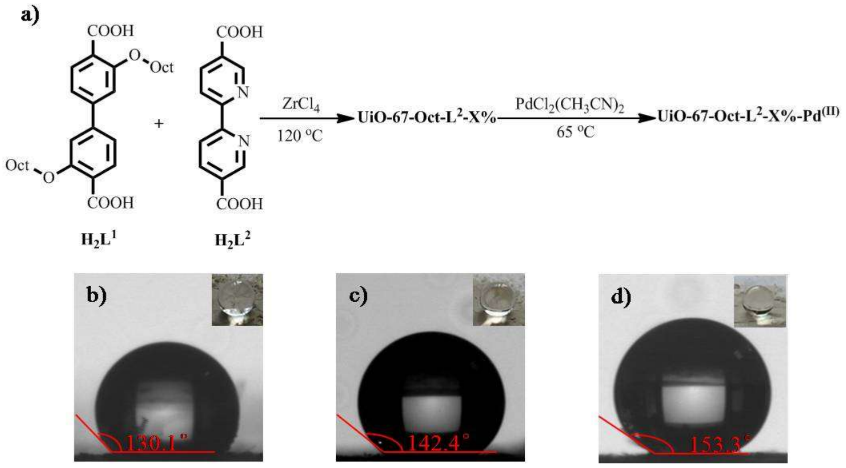

Figure 1 a) The synthetic route for UiO-67-Oct-L^2-X%-$Pd^{(II)}$; Static water contact angle and digital photogragh of b) UiO-67-Oct-L^2-61.3%-$Pd^{(II)}$; c) UiO-67-Oct-L^2-47.8%-$Pd^{(II)}$; d) UiO-67-Oct-L^2-35.7%-$Pd^{(II)}$.

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