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ORAL PRESENTATIONS

**ZACA REACTION (Zr-CATALYZED ASYMMETRIC
CARBOALUMINATION OF ALKENES) AS AN EMERGING TOOL FOR
ASYMMETRIC SYNTHESIS OF FEEBLY CHIRAL COMPOUNDS OF
HIGH (99%) ENANTIOMERIC PURITY**

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THE MAIN TRENDS IN MODERN TRANSITION METAL CATALYSIS

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The following topics will be discussed:

1. Palladium nanoparticles (PdNPs) formed *in situ* from Pd(II) salts or complexes in cross-coupling reactions (Suzuki, Heck, cyanation, carbonylation)
2. Replacing the Pd-catalysis with the catalysis by Ni and Cu complexes in the substitution and addition reactions.

PALLADIUM-CATALYZED OXIDATIVE CARBOCYCLIZATIONS

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Carbocyclizations, annulation processes involving carbon–carbon bond formation via carbometalation, constitute an extremely important and useful class of reaction for the syntheses of carbocyclic and heterocyclic compounds. We have recently developed a number of selective palladium-catalyzed oxidative carbocyclizations, often involving the use of molecular oxygen as the oxidant in a biomimetic approach.¹ Mild oxidative C–C bond formation under aerobic conditions can be achieved via this approach.

In recent applications we have developed oxidative borylative carbocyclization of enallenes,^{1c} oxidative carbocyclization/arylation of enallenes,^{1d} oxidative arylative carbocyclization of allenynes,^{1e} and diarylative carbocyclization of enynes.^{1f}

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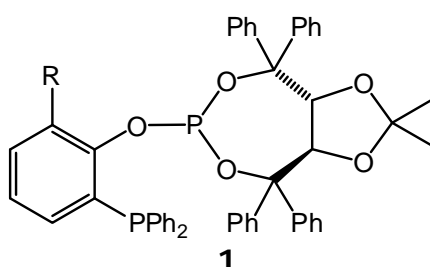
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PHENOL-DERIVED MODULAR PHOSPHINE-PHOSPHITE LIGANDS IN ENANTIOSELECTIVE TRANSITION METAL CATALYSIS

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In search for new powerful and tunable ligands for enantioselective transition metal catalysis, we have developed an efficient (4-steps) modular synthesis of novel chiral phosphine-phosphite ligands starting from readily available phenolic precursors.^[1] These ligands, e.g. Taddol-derived compounds of type **1**, have then been applied with outstanding success in a variety of C–C bond forming transformations such as Cu-catalyzed 1,4-additions and allylic substitutions using Grignard reagents,^[2] Rh-catalyzed hydroboration,^[3] hydroformylation^[4] and [4+2]-cycloaddition^[5] reactions, or Co-catalyzed 1,4-hydrovinylations.^[6]



The presentation will give an overview on the synthesis and applications of this new class of ligands in organic synthesis.

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NANOELECTRONICS: MOLECULAR METAL WIRES AND RELATED MOLECULAR MATERIALS

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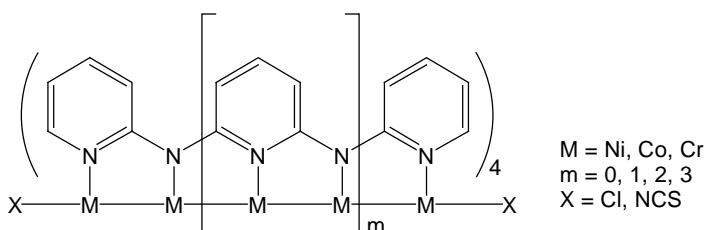
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We have designed a series of new ligands such as oligo- α -pyridylamines, and used them to construct an unique class of quadruple helix of metal strings. This achievement leads to a new direction to the application of molecular wires in the nanoelectronics.

The outline is as follows:

I. Linear Metal String Complexes⁽¹⁻³⁾

- Synthesis, Structure, Bonding



II. Potential Application as Molecular Metal Wires & Molecular Switches⁽⁴⁾

- STM Study on the Conductivity of Metal Strings
- C-AFM Measurements of Single Metal String Molecules
- Comparative Study on the I–V Characteristics (Theory V.S. Experiment)

III. Tuning of the Metal Strings⁽⁵⁻⁸⁾

- Naphthyridyl Amino Ligands: Low Oxidation Mixed Metal Strings
- Asymmetrical Ligands: Toward Molecular Rectifier
- Heteronuclear Metal String Complexes

IV. Conclusion

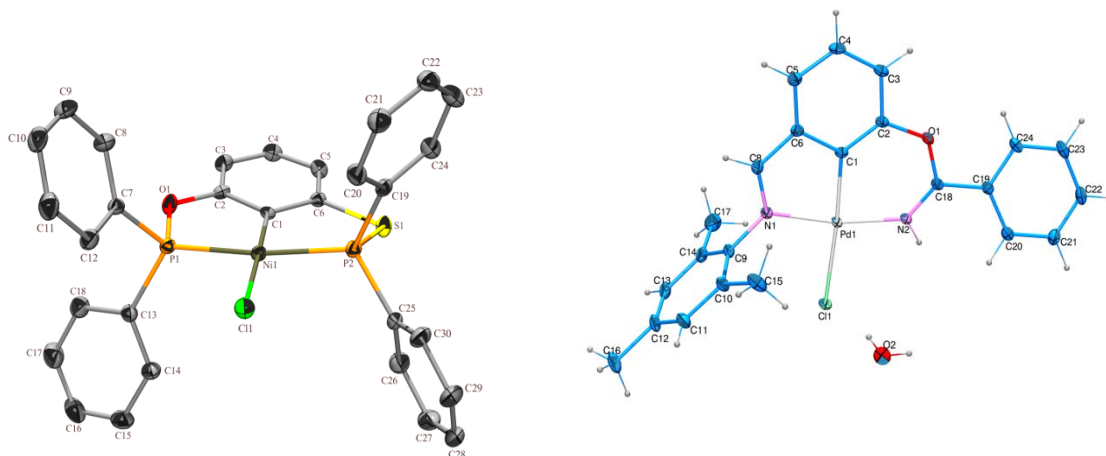
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NON-SYMMETRIC Pincer Compounds. Recent Advances and Potential Applications

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Pincer compounds have become mayor protagonists in organometallic chemistry and catalysis due to their physical properties and exceedingly good reactivities and selectivities. In the last decade these properties have been further tuned and basically tailored for a specific transformation. Thus, in essence chemists related to this area have become tailors in the design and synthesis of new ligands and their transition metal derivatives to suit a specific process or transformation. The nature of the ligand often defines the kind of reactivity that these complexes will present and people has conceived the possibility of combining different properties by including different functionalities or donor atoms in a single ligand and in this way be able to attain radically different reactivities than thus observed by using ligands having a sole functionality or donor atom. In this line, the following talk will be presenting recent advances on the design of new pincer ligands and their complexes as well as some of the potential applications these species may have relevant to metal mediated organic synthesis.



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TUNING THE REACTIVITY IN A CLASSIC ORGANOMETALLIC RADIOPHARMACEUTICAL SYNTHON

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The basic synthetic procedures followed in applied radio-pharmacy necessitate pre-requisites such as ease of preparation, one-step synthesis, aqueous medium, stability and pH accessibility. Thus, the introduction of organometallic compounds into radiopharmacy was thus rather unattractive until recently. Significant interest has however been shown over the past decade or more in rhenium and technetium complexes bearing the organometallic *fac*-[M(CO)₃]⁺ entity (M = Tc(I), Re(I)), as potential diagnostic and therapeutic radiopharmaceuticals, respectively. The potential application thereof for the diagnosis and treatment of cancer was spearheaded by and has to be credited to a large extent to Alberto *et al.* [1]

Characteristics which render complexes of the type *fac*-[M(CO)₃(H₂O)₃]⁺ so attractive for application in nuclear medicine are the inert organometallic *fac*-[M(CO)₃]⁺ core, from classic crystal field considerations, and the relative labile water molecules bound to it. Several promising compounds have been synthesized in the last few years by employing these tri-carbonyl synthons by linking it to biomolecules as target director systems. Moreover, the potential that complexes of the general form *fac*-[Re(CO)₃(*L,L'*-Bid)(H₂O)]ⁿ (*L,L'*-Bid = neutral or mono-anionic bidentate ligands, n = 0, +1) could be activated therefore exists and might be efficient for potential use in radiopharmacy, especially considering the [2+1] mixed ligand approach proposed by Alberto *et al.* [1] An extensive kinetic study of the effect of bonded ligands on the reactivity of normally inert Re(I)-tricarbonyl complexes, as classic low-spin d⁶ complexes, was thus considered essential for the possible use of this organometallic synthon in radiopharmacy, either as a diagnostic or as a therapeutic tool.

A range of complexes with systematically varied bidentate ligands and donor atoms and evaluated the lability and mechanism of substitution of the 'labile site', occupied by a coordinated aqua/methanol ligand by simple monodentate nucleophiles, was therefore selected for the current investigation. Thus, the first comprehensive kinetic study of coordinated methanol substitution reactions in (i) *fac*-[Re(CO)₃(*L,L'*-Bid)(MeOH)]ⁿ [*L,L'*-Bid: *N,N'*-Bid (1,10-phenantroline, 2,2'-bipyridine); *N,O*-Bid (2-picolinate, 2-quinolate, 2,4-pyridinedicarboxylate, 2,4-Quinolinedicarboxylate and Schiff base backbones); *O,O'*-Bid (tropolonate, tribromotropolonate and 3-hydroxyflavonate)] with (ii) a representative number of monodentate entering nucleophiles, ranging from halides to pyridines and S and P donor groups, with supporting X-ray diffraction data to fully characterize starting complexes and products, will be discussed. [2] A four order-of-magnitude of activation for the methanol substitution is induced as manifested by the second order rate constants with (*N,N'*-Bid) < (*N,O*-Bid) < (*O,O'*-Bid). A dissociative interchange mechanism is proposed.

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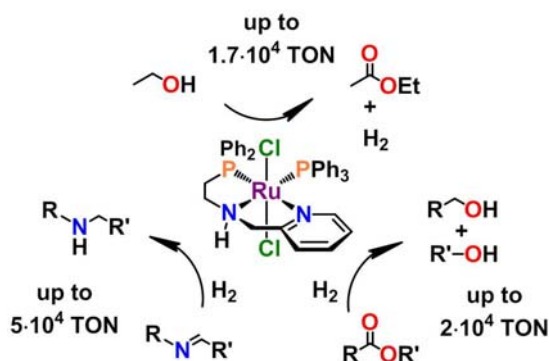
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FROM ESTERS TO ALCOHOLS AND BACK

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Reduction of esters is a common reaction in organic chemistry, however, the classical methods using main-group hydrides are hazardous and they are accompanied by excessive formation of chemical waste. New pincer-type ruthenium and osmium catalysts from our laboratory: $\text{MHCl}(\text{CO})(\text{NNHP})$, $[\text{MH}(\text{CO})(\text{NNP})]_2$, and $\text{RuCl}_2(\text{PR}_3)(\text{NNHP})$ facilitate a green ester reduction process affording alcohols under hydrogen gas, under basic or neutral conditions, with practically no by-product waste. The same catalysts are efficient for hydrogenation of compounds with polar double bonds (e.g. imines) and for acceptorless dehydrogenative coupling (ADC) of primary alcohols, $\text{C}_n\text{H}_{2n+1}\text{OH}$ ($n > 1$), affording symmetrical esters. $\text{RuCl}_2(\text{PPh}_3)(\text{NNHP})$ is a particularly outstanding air-stable ruthenium catalyst that has unprecedented efficiency for ethanol dehydrogenation to ethyl acetate under reflux (TON up to 17,000) and for hydrogenation of esters and imines at 40 °C while using as low as 50 ppm [Ru].



GREEN CATALYTIC REACTIONS FOR SUSTAINABLE DEVELOPMENT

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Two methods for activation of $\text{sp}^3\text{C-H}$ bond will be presented.

1) The C-H activation induced by α -heteroatom effect provides fundamental and highly useful general method for carbon-carbon bond formation (1). Coordination of heteroatom of substrates to low valent transition metal hydride phosphine complexes $\text{MH}_n(\text{PR}_3)_n$ ($\text{M}=\text{Ru}, \text{Ir}, \text{Rh}, \text{Re}$) would give α -transiton-metalated intermediates, which undergo reaction with various substrates. This concept was discovered in 1978 on the C-H activation of tertiary amines. Since then such α -C-H activation has been performed on many substrates such as nitriles, ketones, isocyanates, trifluoromethylated compounds and led to unique and selective carbon-carbon bond formation (2, 3).

2) The second method is the oxidation of C-H bond with molecular oxygen via metal oxo species or flavinhydroperoxy species which are derived from either metal catalysts or organocatalysts (4). Typically, aerobic oxidation of tertiary amines in the presence of hydrogen cyanide gives α -cyanoamines (5), which are important precursors of amino acids. Aerobic lumiflavin catalyzed oxidations of amines and sulfides proceed selectively with high efficiency under very mild conditions (7, 8). Furthermore, aerobic lumiflavin catalyzed Baeyer-Villiger oxidation of ketones proceeds chemoselectivley.

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SPIN CROSSOVER COORDINATION POLYMERS WITH INTERESTING MAGNETIC PROPERTY

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A potential bridging triazole-based ligand, **atz** (trans-4,4'-azo-1,2,4-triazole), is chosen to serve as building sticks and incorporated with a spin crossover metal center to form a framework. Coordination polymers of iron(II) with the formula $[\text{Fe}(\mu\text{-atz})_3]\text{X}_2\cdot 2\text{H}_2\text{O}$ (where $\text{X} = \text{ClO}_4^-$ (**1** $\cdot 2\text{H}_2\text{O}$) and BF_4^- (**2** $\cdot 2\text{H}_2\text{O}$)) in a 3D framework and $[\text{Fe}(\mu\text{-atz})(\mu\text{-pyz})(\text{NCS})_2]\cdot 4\text{H}_2\text{O}$ (**3** $\cdot 4\text{H}_2\text{O}$) in a 2D layer structure were synthesized and structurally characterized. The magnetic measurements of **1** $\cdot 2\text{H}_2\text{O}$ and **2** $\cdot 2\text{H}_2\text{O}$ reveal spin transitions near room temperature; that of **3** exhibits an abrupt spin transition at ~ 200 K with wide thermal hysteresis; the spin transition behavior of these polymers are apparently correlated with the water contents of the sample. Crystal structures have been determined both at high spin and at low spin states for **1** $\cdot 2\text{H}_2\text{O}$, **2** $\cdot 2\text{H}_2\text{O}$ and **3** $\cdot 4\text{H}_2\text{O}$. Each iron(II) center in all three polymers is octahedrally coordinated with $\mu\text{-atz}$ or $\mu\text{-pyz}$ ligands, which in turn links the other Fe center forming a strong 3D or 2D network; counter anion and water molecules are located in the voids of the lattice. A zigzag chain of water molecules with strong H-bonds is found between the 2D layers, a distinct correlation between the thermal hysteresis with the amount of water molecules is found in this polymer.

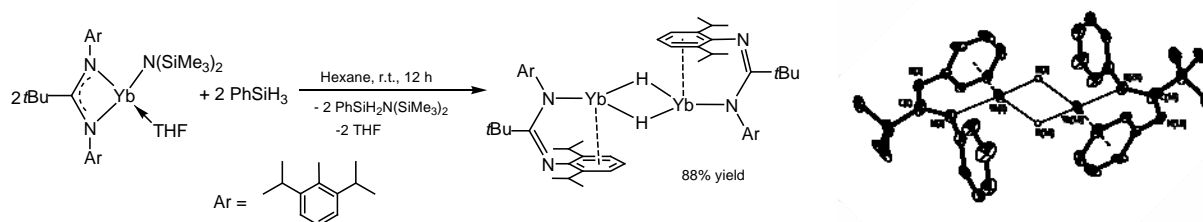
RARE EARTH HYDRIDO COMPLEXES SUPPORTED BY N,N-LIGANDS

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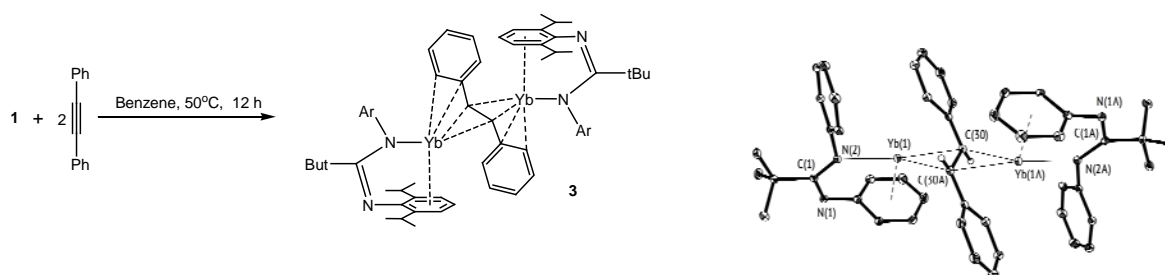
The synthesis, structures and reactivity of novel classes of rare earth hydrido complexes supported by N,N-ligand systems will be considered.

Yb(II) hydrido complex $[\{t\text{BuC}(\text{NC}_6\text{H}_3-2,6-i\text{Pr}_2)_2\}\text{Yb}(\mu\text{-H})_2]$ (**1**) supported by bulky amidinate ligand was synthesized by the σ -bond metathesis reaction of amido complex $\{t\text{BuC}(\text{NC}_6\text{H}_3-2,6-i\text{Pr}_2)_2\}\text{YbN}(\text{SiMe}_3)_2(\text{THF})$ with equimolar amount of PhSiH_3 .

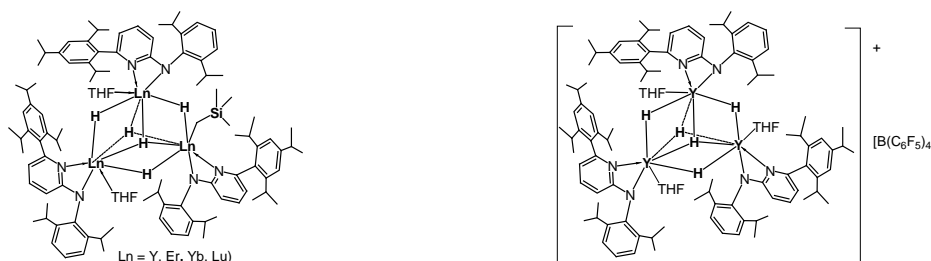


The amidinate ligands in **1** chelate the Yb(II) ions *via* κ^1 -amide and η^6 -arene interactions performing a coordination mode different from the κ^2 -N,N'-chelating one detected in the parent amido complex.

The Ln(II) hydrido complexes containing several reaction centers are of great interest for investigation of the reactivity pattern. The presence of low valent Yb(II) ion and hydrido ligand provides a basis for a rich redox chemistry of these complexes. The Yb–H bond can undergo insertions of multiple bonds and σ -bond metathesis reactions with the reagents containing acidic X–H bonds. Moreover the Yb ion can coordinate Lewis bases, while the basic M–H bond can form complexes with Lewis acids. The reaction of **1** with mild oxidant N,N'-dimethylthiuramdisulfide occurs without H_2 evolution but regardless the reagents ratio affords the bis(dithiocarbamato) amidinato Yb(III) complex $\{t\text{BuC}(\text{NC}_6\text{H}_3-2,6-i\text{Pr}_2)_2\}\text{Yb}(\text{S}_2\text{CNMe}_2)_2$ (**2**). The reaction of **1** with 2 moles of $\text{PhC}\equiv\text{CPh}$ regardless the reagents ratio affords a product of addition of two Yb–H bonds to $\text{PhC}\equiv\text{CPh}$ molecule – $[\{t\text{BuC}(\text{NC}_6\text{H}_3-2,6-i\text{Pr}_2)_2\}\text{Yb}]_2(\mu\text{-}\eta^4\text{-PhCHCHPh})$ (**3**)



A series of trinuclear alkyl-hydrido and cationic hydrido clusters of Y, Er, Yb and Lu will be described.



SYNTHESIS AND C–S BOND CLEAVAGE REACTION OF BRIDGED AND NON-BRIDGED HETERODINUCLEAR ORGANOPLATINUM-MANGANESE COMPLEXES

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Cooperative effects of different transition metals attract considerable interests in relation to multi-metallic catalyses. We previously reported series of heterodinuclear organoplatinum and – palladium complexes $L_2RM-M'L'_m$, which show characteristic reactivities including organic group transfer along transition metals, enhanced CO insertion, E-selective allyl transfer process, selective desulfurization, in addition to catalytic reactions such as hydrometallation, carbonylation of thietane and etc. [1]. In this presentation, synthesis and reactivity difference of the isomeric bridged and non-bridged heterodinuclear organoplatinum-manganese complexes toward thiranes and thietanes. Treatment of $Pt(CH_2CMe_3)X(dppe)$ with $Na[Mn(CO)_5]$ in THF smoothly gave corresponding bridged heterodinuclear complexes $(dppe)Pt(COCH_2CMe_3 \kappa^2C,O)Mn(CO)_4$ (**1**). Introduction of CO gas into a benzene solution of **1** gave a non-bridged complex $(dppe)(COCH_2CMe_3)Pt-Mn(CO)_5$ (**2**). Non-bridged complexes **2** reacted with cis- and trans-2-butene sulfide to cause facile heterolytic Pt-Mn bond cleavage to give corresponding platinum complexes coordinated by thiamanganacyclic ketone with inversion stereochemistry by S_N2 type mechanism. Further heating liberated trans- and cis-2-butenes with retention stereochemistry. In contrast, the bridged complex **1** caused direct desulfurization of cis- and trans-2-butene sulfide were evolved with retention of configuration, giving cis- and -trans-2-butenes, respectively. The bridging acyl ligand in the dinuclear complexes seems to control the stereochemistry of C–S bond ring opening reaction. Mechanistic aspects of this selectivity difference in the reaction will be discussed

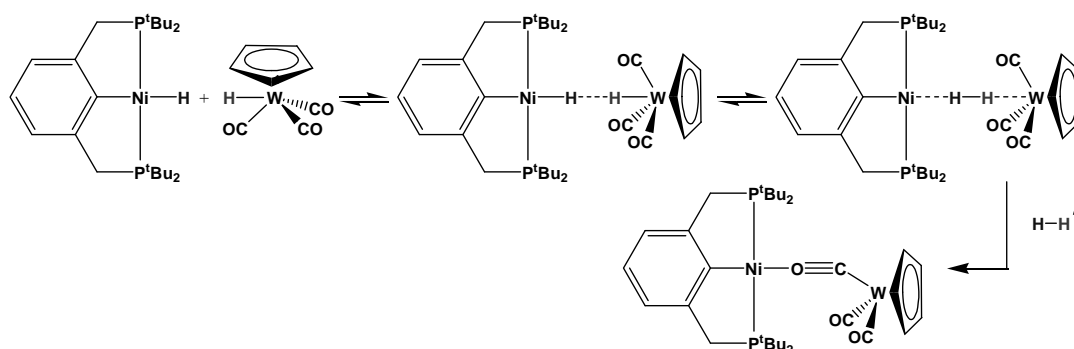
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DIHYDROGEN BONDING AND PROTON TRANSFER BETWEEN TWO TRANSITION METAL HYDRIDES

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Unconventional hydrogen bonding involving transition metal complexes is attracting considerable attention and several efforts have been made to unravel and rationalize many conceivable interactions.¹ However, dihydrogen bonded adducts where transition metal hydride complexes serve both as proton acceptor and proton donor in a hydrogen bond have not been described yet, although dihydrogen evolution was observed when “hydridic” and “acidic” hydride complexes were allowed to react. In this contribution we report on the reaction of the acidic complexes $\text{CpM}(\text{H})(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$)² with the pincer hydrides $(^t\text{BuPCP})\text{M}'(\text{H})$ ($^t\text{BuPCP} = 2,6\text{-C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu}_2)_2$, $\text{M}' = \text{Ni}, \text{Pd}$). On the basis of combined crystallographic, spectroscopic (solid state and solution VT NMR and VT IR), and DFT analysis we have collected a large body of evidence for the first example of a dihydrogen bonded adduct between the two transition-metal hydrides with opposite polarities.³



The peculiarities of this adduct structure have been revealed computationally. The dihydrogen bonded adduct precedes proton transfer and H_2 evolution. Kinetic studies of H_2 evolution have shown that proton transfer is the rate determining step, the reaction product being the bimetallic ion pair $[\text{CpM}(\text{CO})_2(\mu\text{-}\kappa, \text{C}: \kappa, \text{O-CO}) \cdots \text{M}'(^t\text{BuPCP})]$. Another remarkable finding is the structure of the reaction intermediate, which is the $\mu, \eta^{1:1}\text{-H}_2$ species featuring an end-on coordination mode between the two transition metals. Such complexes could be considered as models for the heterolytic H_2 splitting by transition metal based frustrated Lewis pairs.

This work is supported by the Russian Foundation for Basic Research (RFBR, project 11-03-01210) and the CNR-RAS bilateral agreement.

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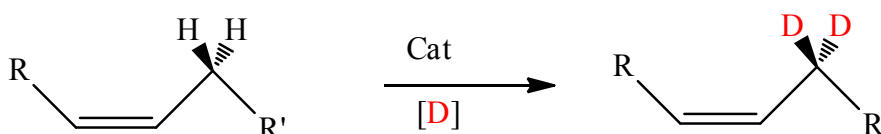
DEVELOPMENT OF ORGANOMETALLIC CATALYSTS FOR SITE SPECIFIC H/D EXCHANGE

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Site-specific H/D exchange involving C–H bonds of organic and biologically active substrates has become increasingly important. For example, recent reports illustrated that site-specific deuteration of poly-unsaturated fatty acids (PUFAs) enhanced their oxidation stress resistance, which could be a quite promising tool to fight age-related diseases such as Friedreich's ataxia and Parkinson's.¹ However, the syntheses of these deuterated materials (PUFAs are deuterated at the bis-allylic positions) require quite long and laborious procedures damaging their commercial viability. In fact, literature search revealed that catalytic site specific deuteration is predominantly confined to substrates containing phenyl group(s) and/or are sterically restricted.² Even though a ruthenium based catalyst was developed for deuteration of non-restricted allylic positions, it also deuterated other positions by “zipping” the double across the entire molecule.³ Thus, we want to share our recent results regarding H/D exchange at exclusively allylic positions using transition metal catalysis (Scheme 1).

Scheme 1



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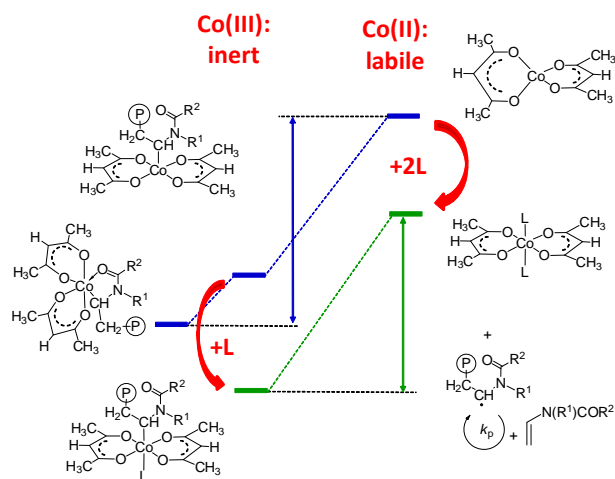
ORGANOMETALLIC MEDIATED RADICAL POLYMERIZATION (OMRP) OF VINYL AMIDES: NEW POLYMERS AND NEW MECHANISTIC UNDERSTANDING

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Controlling the radical polymerization of monomers that generate unstabilized radical is a current challenge. Vinyl amides are such type of monomers. OMRP, using $\text{Co}(\text{acac})_2$ as controlling agent through both a reversible termination and a degenerative transfer protocols, has been successfully applied to control the polymerization of the closely related vinyl acetate and to make controlled architectures based on this monomer, including block copolymers.¹ Coordination of neutral ligands (donor solvents) to $\text{Co}(\text{II})$ in the trapping complex and to $\text{Co}(\text{III})$ in the dormant species has paramount importance in the polymerization control and in the system switching ability from one monomer to the next in block copolymer synthesis.² This presentation will highlight the coordination chemistry of $\text{Co}^{\text{II}}(\text{acac})_2$ and $\text{R-Co}^{\text{III}}(\text{acac})_2$ with a variety of ligands and the rationalization, through DFT calculation, of recent results in the controlled polymerization of cyclic and open *N*-vinyl amides (formamide, acetamide, pyrrolidone, caprolactame, ...).² The effect of hydrogen bonding, in addition to monomer coordination, needs to be invoked to fully rationalize the observed trend of reactivity. We thank the ANR program “OMRP” and the IUF for funding; CINES and CICT (project CALMIP) for free computational time.



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NEW TRENDS IN STEROID MODIFICATION: CROSS-COUPLING AND CuAAC REACTIONS FOR NEW BILE ACID AMPHIPHILES AND AROMATASE INHIBITORS

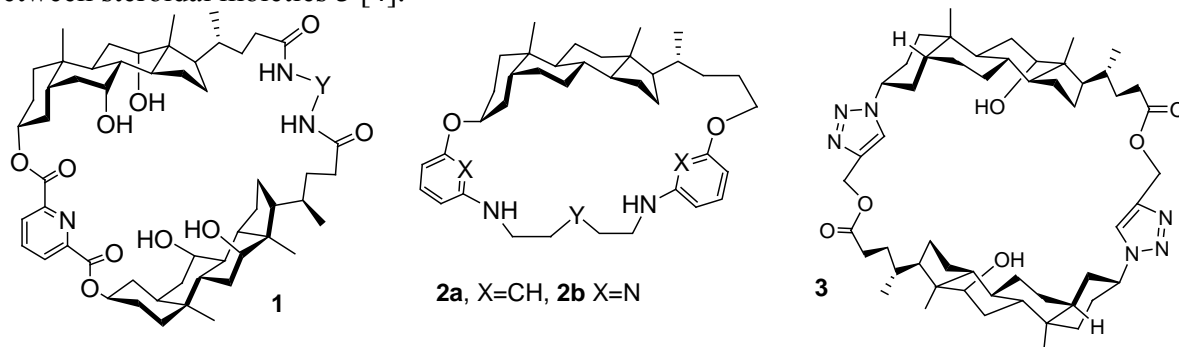
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We have used several modern synthetic approaches for the modification of steroids, among which are Pd-catalyzed arylation, ethynylation and amination, CuAAC reaction, etc.

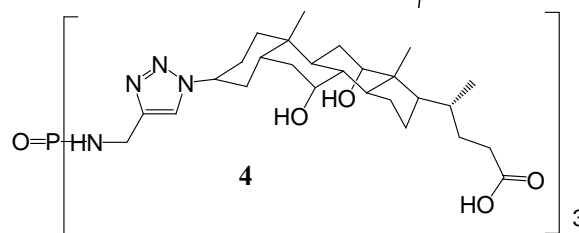
Recently we have shown that 4- and 6-bromo- and chlorosteroids, 3- or 17-iodosteroids can be successfully used in Pd-catalyzed cross-coupling reactions for introduction of aryl or ethynyl substituents [1]. Some of substances thus prepared demonstrated high activity in the inhibition of the breast cancer cell (MCF-7 line) growth.

Macrocycles containing bile acid moieties attract a keen attention of chemists due to their unique properties as selective artificial receptors, as architectural components in supramolecular chemistry. Several approaches to the synthesis of previously unknown polyoxaazamacrocycles derived from bile acids have been compared: i) via acylation of α,ω -diamines by cholates with formation of macrocycles similar to **1** [2]; ii) via Pd-catalyzed amination of bis(aryl-) or bis(hetaryl-) ethers to afford macrocycles **2** [3]; iii) via CuAAC reaction, which form 1,2,3-triazole cycle as a link between steroidal moieties **3** [4].



Also CuAAC reaction was applied for synthesis of new tripodal ligands and organogelators similar to **4**, and for synthesis of bile acids – peptide conjugates [5].

The other important area of our research deals with the development of ways to involve hydrophobic steroids into chemical and microbiological transformations in aqueous media. For example this approach allowed for essential improvement of technology used for the synthesis of phytohormone 24-epibrassinolide [6].



We are grateful to RFBR (grant 11-03-00265a) for financial support.

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OXIDATIONS OF ALKANES AND ALCOHOLS UNDER MILD AND GREEN CONDITIONS

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Alkanes are very rich carbon compounds but their use as raw materials for organic synthesis has been hampered by their high inertness. Their conversion into organic products with an added value is a challenge in chemistry, and alkanes usually are used as fuels, with complete loss of C to atmosphere and resulting noxious environmental effects. Development of mild and green processes for their functionalization, as well as for further reactions of derived products, namely alcohols, would promote the potential of their application towards alternative raw materials for organic synthesis.

Results obtained in this field by the author's research Group will be described herein, namely concerning the following main types of reactions:

- i- Peroxidative oxidations of alkanes to alcohols and ketones, catalyzed by aquasoluble transition metal complexes (e.g. with water soluble scorpionates, or multinuclear copper catalysts) in particular bioinspired species, and promoted by water and/or acid;
- ii- Oxidations of alcohols, e.g., solvent-free microwave-assisted peroxidative oxidation and aerobic oxidation, with green features.
- iii- Metal-free and metal-promoted hydrocarboxylations of alkanes to carboxylic acids, in partially aqueous medium, upon reaction with CO and water as solvent and hydroxylating agent;
- iv- Metal-catalyzed alkanes carboxylations to carboxylic acids in non-aqueous media (comparative purposes).

Some of the systems feature the highest reported catalytic activities for alkane functionalizations under mild conditions and possible mechanisms will be discussed.

Acknowledgements: Co-authors of cited refs. are acknowledged. Work supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its PTDC program.

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PINCER LIGANDS AS POWERFUL TOOLS FOR CATALYSIS IN ORGANIC SYNTHESIS

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Homogeneous catalysts demonstrate the selectivity and activity desired for industrial fine chemical synthesis, and present trends in this field are moving towards the development of multi-step, one-pot processes where low solvent and salt waste is generated, and energy efficiency is provided to produce a cost-effective end-product.[1] However, these one pot cascade, tandem, or domino catalyzed reaction sequences rely on catalyst, substrate and solvent compatibility, on catalyst stability and on the possibility to protect these catalysts from mutual deactivation (*e.g.*, by binding these to suitable (in)soluble supports or by using compatible, stable catalysts that can catalyze different reactions[2]).

Pincer ligands are powerful tools to achieve many of these objectives as we have shown. The synthesis and properties of a variety of pincer organometallics will be discussed that have surprising stability but still are versatile catalysts as well. Moreover, the use of the pincer ligand backbone to immobilize the pincer-metal catalyst onto a variety of supports will be illustrated by various examples.

Initially we explored the use of carbosilane dendrimers as chemically inert supports that had 12 or 36 pincer-metal catalysts attached to their periphery.[3] In recent studies we made use of supports that have very rigid core-shell structures.[4] The synthesis of these soluble supports with up to 12 catalytic sites at their periphery requires only a few steps. They have sizes amounting to 3.5 nm. Experiments showed that these catalysts can be used in a continuous manner applying membrane reactor technology without detectable metal or ligand leaching.[4]

Our most recent studies have been concentrated on the immobilization of pincer metal catalysts onto soluble supports (2–3 nm sizes) via non-covalent binding.[5] In this way a number of catalytic species become linked to the support in an one-step procedure. These supports can provide new properties to the catalyst, *e.g.* makes it water-soluble or puts the catalytic site in a chiral environment.[5]

Another fascinating, recent development is the directed inhibition of a lipase, *i.e.*, cutinase, immobilized on beads with a single pincer-metal catalytic site. The resulting bio-organometallic hybrid catalyst (see X-ray)[6] in combination with uninhibited lipase can operate as a material for the kinetic resolution of racemic alcohols to the enantiopure compound.

Proof-of-principle of these approaches will be discussed and will be put in the perspective of closing the gap between homogeneous and heterogeneous catalysis.

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POLYMERIC LADDERPHANES: MIMICKING DNA CHEMISTRY AND BEYOND

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A polymeric ladderphane is defined as multiple layers of cyclophanes where the tethers are part of the polymeric backbones.^{1,2} By ring opening metathesis polymerization of bisnorbornene derivatives using Grubbs-I catalyst, double stranded polymeric ladderphanes with a range of linkers (ferrocenes, porphyrins, oligoaryls, crown ethers as well as chiral linkers) are conveniently obtained.¹⁻⁴ Triple stranded ladderphanes are also obtained by a similar strategy.⁴ Replication of a single stranded polymer for the synthesis of complimentary polynorbornenes as well as a range conjugated oligomers/polymers with well-defined molecular weight and narrow polydispersity will be discussed.^{5,6} The photophysical and magnetic properties, electrochemical behavior, self assembly and microscopic images as well as chemical modifications of these polymeric double stranded ladderphanes will be presented.

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MOLECULAR RECOGNITION AND SWITCHING OF Re-BASED METALLACYCLES

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The preparation of a new class of neutral, luminescent Re-based metallacycles is described. The compounds can be assembled in near quantitative yield using a novel *orthogonal-bonding* strategy, which permits a variety of structures, such as molecular rectangles, boxes, cages, tubes, and molecular rotors, to be prepared. The metallacycles are remarkable in terms of their structure, light-emitting properties, multiple functional sites, and selective recognition capabilities. The molecular information, molecular recognition, and molecular switching of the metallacycles will be discussed.

NEW Co(I)-CATALYSTS FOR [2+2+2] CYCLOADDITION REACTIONS

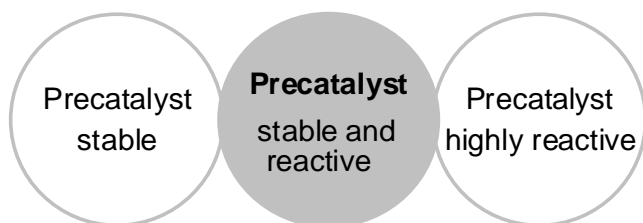
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A large number of transition metals are able to catalyze [2+2+2] and related cycloaddition reactions. The cyclotrimerization reaction is a highly useful and strategic reaction for the assembly of complex organic structures. Access to a significant increase of molecular complexity is granted by the concurrent or successive formation of several bonds leading to the cyclic products. Recently also the catalysis by chiral transition metal complexes for the synthesis of biaryl enantiomers developed significantly.¹

Cobalt complexes belong to the first generation of catalyst systems for cyclotrimerisation reactions, which have been evaluated in complex synthetic endeavours. For many complexes, rather high temperatures and/or photochemical energy need to be applied. Photochemical energy input allows the use of mild reaction conditions and sensitive chiral substrates as well as the direct conversion of gaseous coupling partners like acetylene.² We have recently reported the synthesis and structural characterization of highly reactive CpCo-olefin complexes for the first time by establishing ligand exchange reactions from a new bismonoolefin complex.³ The chemistry of these complexes and their heavier element congeners rhodium and iridium was found to be very interesting to compare in cycloaddition reactions as well as other addition reactions.⁴

The development of new chiral and achiral Co(I)-complexes still draws attention. The combination of stable precatalysts on one side, combined with sufficient catalytic activity under rather ambient conditions on the other side remains an attractive target. We will present results on the development of new catalysts combining both features.



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A CHIRAL POROUS METAL-ORGANIC FRAMEWORK, (S)-KUMOF-1, AS THE HETEROGENEOUS CATALYST FOR ENANTIOSELECTIVE REACTIONS

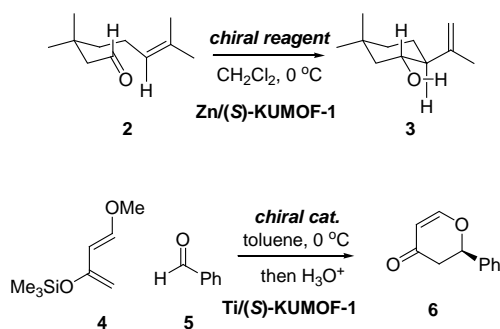
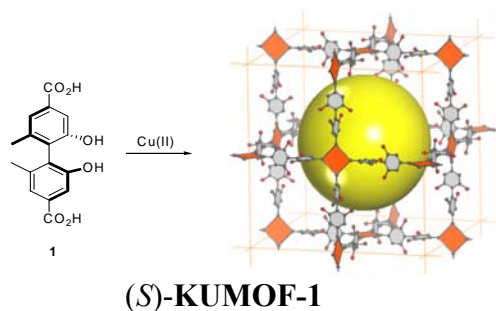
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Chiral metal-organic frameworks (MOFs) constitute a unique class of multifunctional hybrid materials and are envisioned as a heterogeneous catalyst for enantioselective reactions. Despite some pioneering works on catalytic enantioselective reaction promoted by chiral MOFs, there is still a need for practical catalysts and many fundamental issues must be answered; 1) the preparation of practically useful chiral MOFs¹ and 2) the evidence of utilization of all active sites in the MOFs.²

We have designed and synthesized a chiral metal-organic framework, (S)-KUMOF-1 ($\text{Cu}_2(\text{S})\text{-1})_2(\text{H}_2\text{O})_2$, **1** = 2,2'-dihydroxy-6,6'-dimethyl(1,1'-biphenyl)-4,4'-dicarboxylate) of which non-interpenetrating NbO type framework provides a spacious pore ($2 \times 2 \times 2 \text{ nm}^3$) and is equipped with potential catalytic sites exposed into the pore. Two reactions, the carbonyl-ene reaction with modified MOF after replacement of the protons on biphenol on the organic links with Zn(II) and the hetero-Diels-Alder reaction with Ti(IV), respectively, were studied.

In this maneuver, we observed that the reaction occurs entirely inside the pores for a given substrate and the reaction rate of the heterogeneous reaction by this specific MOF is comparable to that of its homogeneous counterpart. In addition, it is also observed that the enantioselectivities are significantly improved by extra steric bias provided from the frames of the MOF. These observations reinforce the legitimacy of the strategy of using a chiral MOF as a highly enantioselective heterogeneous catalyst.



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RECENT ADVANCES IN NICKEL *N*-HETEROCYCLIC CARBENE CHEMISTRY

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This presentation describes recent advances in the chemistry and the catalytic reactions of half-sandwich nickel complexes that bear *N*-heterocyclic carbenes (NHCs) as ligands. The syntheses and structures of neutral and cationic complexes of general formula [CpNi(NHC)X] (X = Cp, Cp*, X = Cl, I and [CpNi(NHC)S]⁺ (S = CH₃CN, acetone), respectively, will be discussed. The talk will then concentrate on three facets of this research:

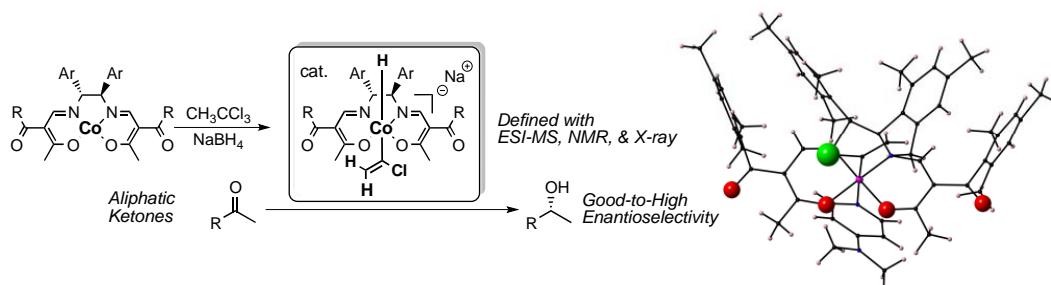
- 1) The use of these complexes as catalysts for the Miyaura-Suzuki coupling of aryl halides.
- 2) The base assisted C–H activation reactions of α-C–H bonds of ketones and of nitriles that are carried out by these complexes. The intramolecular C–H activation of the α-C–H bonds of nitriles, that are attached to the NHC ligand as a side-arm, leads to new nickelacycles; acetone undergoes a remarkable double C–H activation reaction.
- 3) The recent use of Ni-NHC half-sandwich complexes as catalysts for the hydrosilylation of aldehydes and ketones, via probable CpNi(NHC) hydride intermediates.

DESIGN AND STRUCTURE DETERMINATION OF COBALT COMPLEX CATALYSTS FOR ENANTIOSELECTIVE BOROHYDRIDE REDUCTION OF ALIPHATIC KETONES

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The enantioselective reduction of carbonyl or imine derivatives is one of the most reliable methods to provide various optically active compounds. From our research group, optically active cobalt(II) complexes with a conventional reductant, sodium borohydride, ^{[1], [2]} were proposed for the catalytic enantioselective reduction of ketones as well as imines to afford the corresponding alcohols and amines in high-to-excellent yields with high enantioselectivities. Based on the theoretical and analytical studies on the cobalt-catalyzed borohydride reduction, ^[3] newly designed cobalt(III) complex catalysts were recently released to employ the enantioselective reduction of aliphatic ketones. By using the optically active ketoiminatocobalt(II) complex in the presence of 1,1,1-trichloroethane, several aliphatic ketones were successfully applied to the present catalytic enantioselective reduction to be converted into the corresponding secondary alcohols in good-to-high yields with high enantioselectivities. ^[4] Based on the ESI-MS, NMR, and X-ray analyses, ^[5] it was confirmed that on the cobalt(III) complex 1-chlorovinyl group, derived from the precursor 1,1,1-trichloroethane, was attached as an axial ligand. The 1-chlorovinylcobalt(III) complex was enough stable to be purified by a conventional chromatography. The recovered complex could be employed as the catalyst for the enantioselective borohydride reduction. Also several times of recycle use of the 1-chlorovinylcobalt(III) complex was examined.



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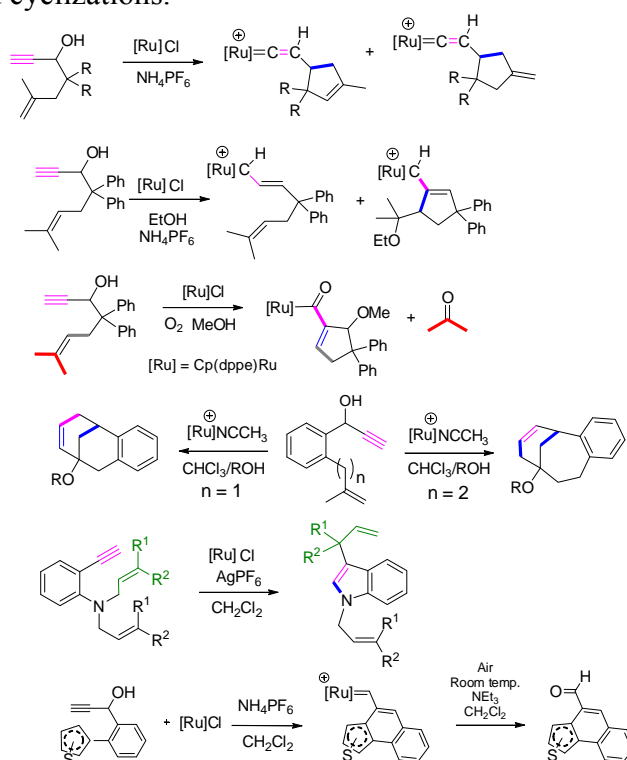
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CYCLIZATION REACTIONS OF ENYNES THROUGH ORGANOMETALLIC Ru COMPLEXES

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Organometallic Ru Complexes play key role in inducing novel C–C bond formation reactions of acetylenes and various enyne compounds. When the triple bond is accompanied with other unsaturated groups or functional groups with heteroatom, novel reactions take place. Cyclization of enyne compounds could be readily induced by cationic ruthenium complexes. Methyl substituents on the olefinic portion of the organic enyne plays important role in controlling the reaction pathway involving carbocationic intermediates. Interestingly, facile oxygenation reactions are also observed in the ruthenium induced cyclizations.



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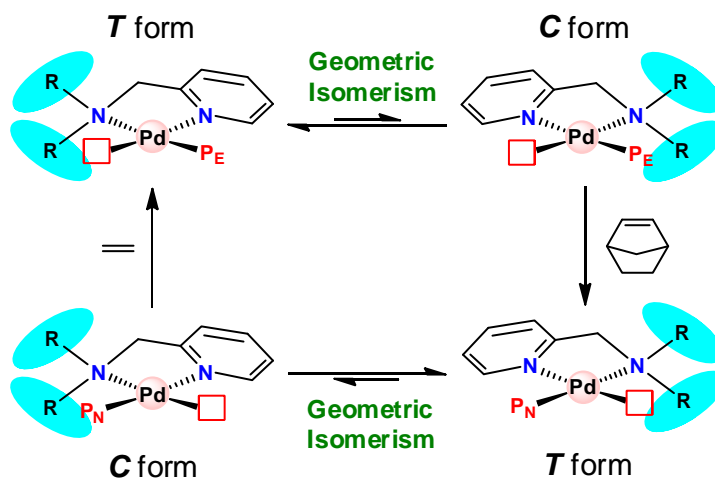
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GEOMETRIC ISOMERISM IN SQUARE PLANAR ORGANOPALLADIUM COMPLEXES WITH UNSYMMETRIC BIDENTATE AMINOPYRIDINE LEADS TO REACTIVITY DIFFERENTIATION IN NORBORNENE INSERTION AND ALTERNATING ETHYLENE-NORBORNENE COPOLYMERIZATION — A KINETIC AND MECHANISTIC APPROACH

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Cationic methylpalladium complexes bearing hetero-functional bidentate ligands of α -aminopyridines have been found to be effective precursors for catalytic alternating copolymerization of ethylene (E) and norbornene (N) under mild conditions.¹ Both of the square planar methyl and norbornyl palladium(II) complexes exhibit facile reversible geometrical isomerization. The geometric isomers show distinct reactivity toward olefin-insertion reactions. Detailed kinetic studies by means of variable-temperature NMR technique on ethylene-insertion, norbornene-insertion, as well as the geometric isomerization have been examined. Corresponding DFT calculations for such fundamental paths have also been investigated. Both approaches reveal consistent results, indicating that the *cis*-isomers undergo olefin insertion more facile than the *trans* analogues. An unprecedented mechanism in which the reversible geometric isomerization and the geometric isomer-distinguished kinetics lead to the alternating E-N copolymerization will be presented.



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TRANSITION METAL COMPLEXES BASED ON L,8-NAPHTHYRIDINE LIGANDS-PREPARATION AND CATALYSIS

S.T. Liu

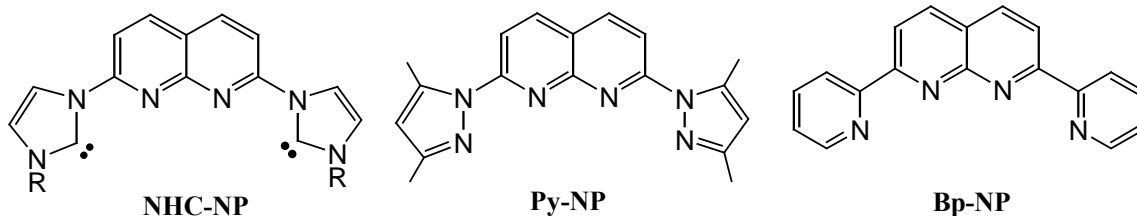
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Ligands, that can coordinate two metal centers in close proximity, have received much attention recently. Such dinuclear complexes may show unusual properties and synergism between the two metals during the catalysis.¹ In our recent works, we have studied the coordination chemistry of various metal ions toward a series of l,8-naphthyridine based ligands and their catalysis.

Palladium complex [$\{\text{Pd}_2(\text{NHC-NP})_2\text{Cl}_2\}(\text{PF}_6)$] (**1**) containing NHC ligands was prepared via the carbene transfer reaction. Structural analysis shows that **1** consists of two Pd ions coordinating by two NHC ligands from two **NHC-NP** ligands in *trans* fashion. Due to the geometrical constrain and strong donating ability of NHCs, complex **1** provides an excellent reactivity on the cross coupling product on the Kumada–Corriu reaction of ArBr with cyclohexylmagnesium bromide.^{2a}

Reaction of nickel(II) chloride with **Py-NP** in a 2:1 molar ratio gave an excellent yield of chloride-bridged dinickel complexes [$\{(\text{Py-NP})(\mu\text{-Cl})_2\text{Ni}_2\text{Cl}_2(\text{CH}_3\text{OH})_2\}$] (**2**). Crystal structure of **2** shows that the distance between nickel atoms is ca. 3.2 Å. This dinickel complex **2** has been tested in the catalytic homo-coupling of terminal alkynes leading to 1,3-diynes with the use O₂ as the oxidant, showing excellent activities. The catalytic activity of this complex is better than those of the mono-nuclear species.^{2b}

Treatment of a mixture of Pd₂(dba)₃ and (PhCN)₂PdCl₂ with **Bp-NP** in CH₂Cl₂ at ambient temperature yielded a water-soluble and air stable tripalladium species. Crystal structure shows that this complex is with the composition of [Pd₃(**Bp-NP**)₂Cl₄] and three palladium metal ions is arranged in a “L” shape geometry.^{2c} This tri-palladium complex can act as a Lewis acid for the promotion of the condensation reaction of carbonyl compounds with indoles. Other metal complexes will also be discussed.



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Ru(II) AND Os(II) BASED SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

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Dye-sensitized solar cells (DSSCs) have practically considered as a feasible alternative to conventional amorphous silicon solar cells. As a result, numerous organometallic sensitizers have been designed and synthesized, among which the most common sensitizers are ascribed to N3, N719 and black dye, respectively. Recently, we reported a new family of ruthenium(II) and osmium(II) complexes containing functionalized azolate chelate, together with *bis*(4,4'-dicarboxy-2,2'-bipyridine) or even 4,4',4''-tricarboxy-2,2':6',2''-terpyridine, respectively. These azolate coupled group 8 metal sensitizers were synthesized and subsequently characterized using photophysical methods and spectroscopic means. Upon optimization, some of our Ru(II)-based sensitizers, even without the utilization of thiocyanate ancillary, could produce a conversion efficiency of $\geq 10\%$, the results of which are superior to that of N719 and black dye reference solar cells prepared in our studies.

POSTER PRESENTATIONS

P1: CATALYTIC OXIDATION OF U^{4+} TO U^{6+} BY OXYGEN IN THE PRESENCE OF CATALYST "MUHAMEDZHAN-1"

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Recently, much attention has been devoted to new methods of intensifying situ leaching of uranium using a variety of oxidants. Currently, there are new types of oxidants. Therefore, urgent is the development and introduction of new methods for the catalytic oxidation of U^{4+} to U^{6+} .

Objective – development of new technology of catalytic oxidation of U^{4+} to U^{6+} catalyst "Muhamedzhan-1", which will reduce the consumption of sulfuric acid, hydrogen peroxide acidification.

The essence of the catalyst "Muhamedzhan-1" is the oxidation of U^{4+} to U^{6+} in weakly acidic solutions, then the regeneration of spent catalyst oxygen. Salts of uranium(IV) interaction with the catalyst solution are oxidized to U^{6+} on the total chemical reaction:



The reaction of the regeneration of spent catalyst KT_{Red} oxygen is described by the following reaction:



Oxidation of uranium takes place through a complex multistage mechanism.

In the period from 3 to 9 December 2010, in the physical-chemical laboratory uranium mine "Appak" we have carried out laboratory tests of catalyst "OEM" for the oxidation of U^{4+} to U^{6+} 3 - samples of samples (PR, sampler GTR 199bl - № 62, 201bl - № 125). BP on 07.12.10.

Results before and after treatment with sand and clay cores are shown in Table 5.3.

As is evident from the results in the processing of sand cores (4-4-4 B) 25 g / l sulfuric acid content of uranium in solution is 147.8 g / l, and after treatment with 10 ml of catalyst "Muhamedzhan-1" - 184.1 g / l.

Similar results were obtained when processing the clay core (1-2-3 H) 25 g / L sulfuric acid content of uranium in solution is 62.8 g / l, and after treatment with 10 ml of catalyst "Muhamedzhan-1" - 84,9 g / l.

In the period from 2 to 3 April 2011 conducted pilot tests of the catalyst "Muhamedzhan-1" to improve the yield of uranium in solution, increased RedOx Potential and a decrease in pH Geotechnological landfill in the uranium mine in South Inkai.

Advantages of the method:

1. Complete replacement (100%) hydrogen peroxide in the air when acidification;
2. Reduce the consumption of sulfuric acid at 20%;
3. Decrease in pH in the leaching solution 0.5–0.6;
4. Increased RedOx Potential in the 100–150 mV due to the air.

Table 1. Results of catalytic oxidation of U(IV) to U(VI) solution of the catalyst "Muhamedzhan-1" in the uranium mine "Appak" for sand (4-4-4 V) and clay (1-2-3 H) core

Time, h	Component	1-2-3 H						4-4-4 B					
		25 g/l	Catalyst 5ml	Catalyst 10ml	12g/l	Catalyst 1ml	Catalyst 2ml	25 g/l	Catalyst 5ml	Catalyst 10ml	12g/l	Catalyst 1ml	Catalyst 2ml
1	U, mg/l	48,3	53,1	50,5	48,1	63,1	65,5	118,6	124,6	129,3	118,6	125,6	139,3
	pH	0,91	0,92	0,90	0,91	0,92	0,90	0,93	0,96	0,91	0,93	0,95	0,92
	OBII, V	0,479	0,512	0,600	0,470	0,513	0,592	0,500	0,414	0,400	0,500	0,534	0,610
4	U, mg/l	55,7	65,2	62,8	55,2	74,7	77,2	126,5	147,3	149,4	139	149,4	154,6
	pH	0,81	0,84	0,86	1,14	1,17	1,18	1,95	0,92	0,88	1,16	1,17	1,17
	OBII, V	0,455	0,502	0,691	0,454	0,446	0,445	0,446	0,504	0,695	0,450	0,546	0,635
16	U, mg/l	62,8	69,4	84,9	63,3	78,1	83,3	147,8	164,0	184,1	156,7	169,4	178,3
	pH	0,94	0,88	0,87	1,1	1,15	1,18	0,93	0,89	0,86	1,14	1,17	1,15
	OBII, V	0,438	0,593	0,689	0,442	0,524	0,626	0,437	0,596	0,649	0,493	0,546	0,642

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P2: SYNTHESIS OF FERROCENE GROUP CONTAINED CONDUCTING POLYMER AND ITS ELECTROCHROMIC PROPERTIES

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The application of electrical stimuli can result in drastic changes in the chemical, electrical, optical and mechanical properties of conducting polymers. Thanks to these properties, these materials are used for making smart devices. Because of changing optical properties via electrochemical means, CPs can be used in smart windows and polymeric data storage devices. For synthesis desired polymers that used in these technological applications, design of monomer is so crucial [1,2].

In this work, new electroactive dithiaphosphorus compounds will be synthesized by reaction between Ferrocenyldithiadiphosphotane and thiophene derivatives (Fig.1). Electrochromic and electrochemical applications of hybrid polymers formed by electrochemical polymerization of the monomers containing both organic and inorganic groups will be investigated.

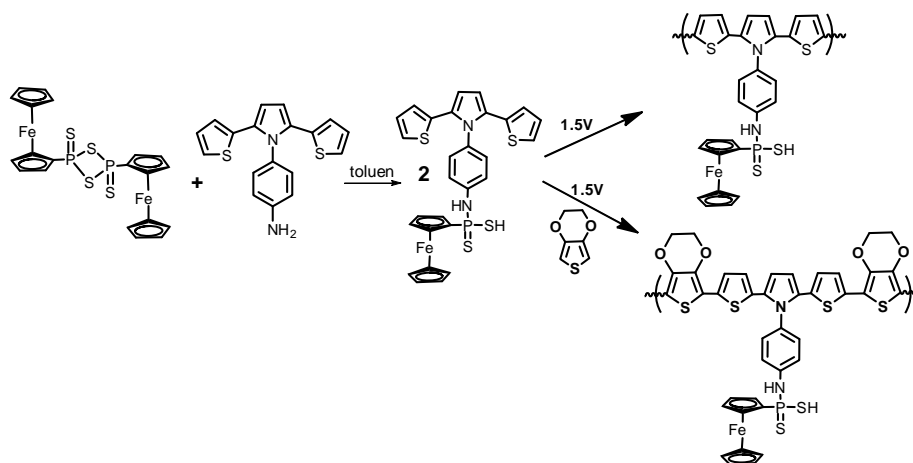


Figure 1. Synthesis route of the polymer and copolymer

References:

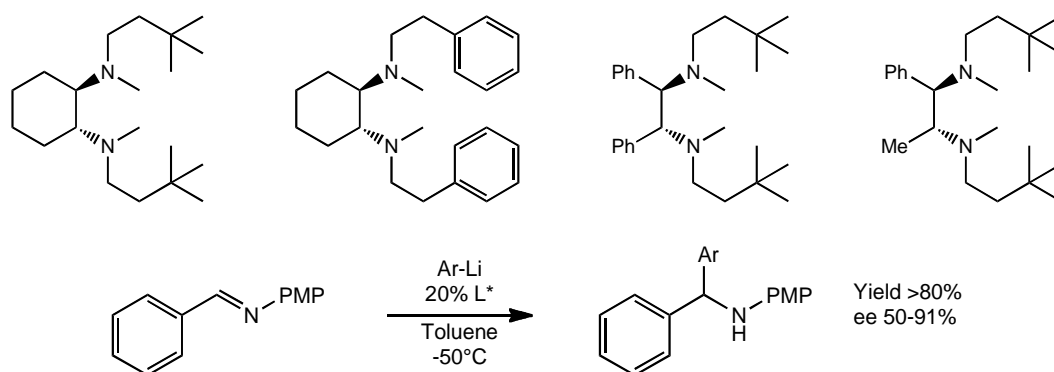
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P3: NEW APPLICATIONS OF CHIRAL DIAMINES IN ASYMMETRIC SYNTHESIS

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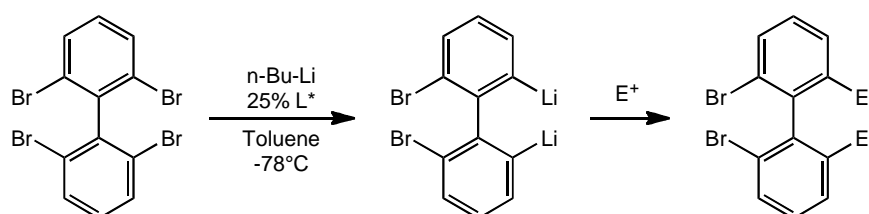
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Chiral diamines have long been used as ligands in organolithium chemistry. Among them, (–)-sparteine is the most commonly used despite the quasi-absence of availability of its enantiomer. Therefore, many chemists have described alternative chiral diamines or sparteine surrogates. We shall focus on the synthesis of new chiral diamines, and their evaluation in now and unknown reactions.



These diamines perform very well in sub-stoichiometric amounts, in the addition of aryl-Li reagents to imines.

More interestingly, the unprecedented Li–Br exchange will be discussed with the following main substrate:



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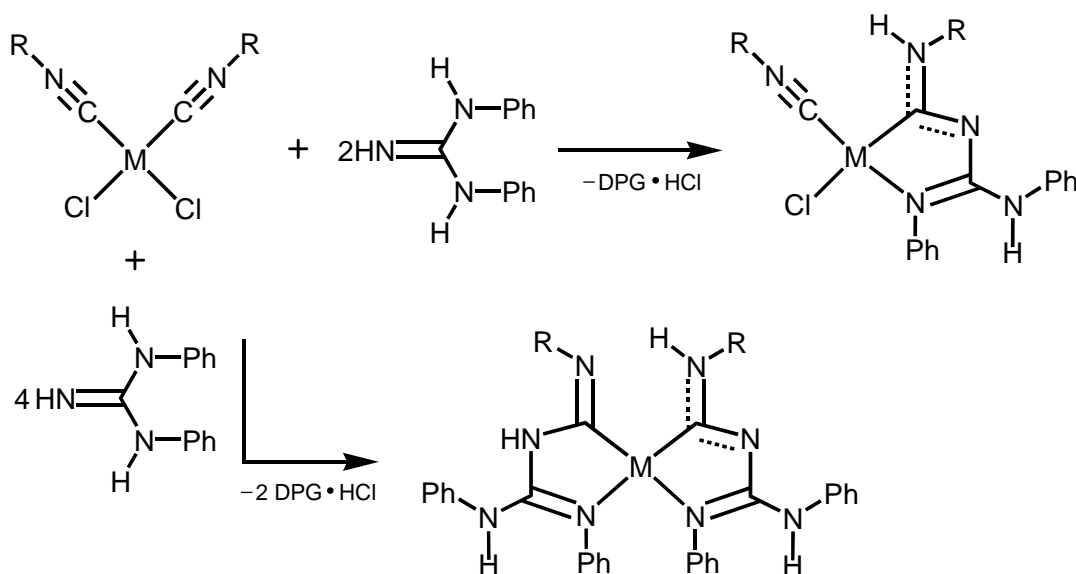
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P4: METAL-MEDIATED NUCLEOPHILIC ADDITION OF 1,3-DIPHENYLGUANIDINE TO ISONITRILES

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The nucleophilic addition of 1,3-diphenylguanidine $\text{HN}=\text{C}(\text{NPh})_2$ (DPG) to isonitriles, activated by coordination to platinum(II) or palladium(II) metal centers, proceeds at room temperature and at a molar ratio 1:2 generating the monoaddition product and, after reflux in CHCl_3 at a molar ratio 1:4, the bisaddition species (Scheme 1).



Scheme 1

The obtained compounds were characterized by elemental analyses, high resolution ESI mass-spectrometry, IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies, and their structures in the solid state were studied by X-ray crystallography.

This work was supported by Russian Fund for Basic Research (grant 11-03-00483-a) and the Scientific Council of the President of Russian Federation (Grant MK-120.2011.3).

P5: METAL-MEDIATED COUPLING OF NITRILES AND DIBENZYLHYDROXYLAMINE

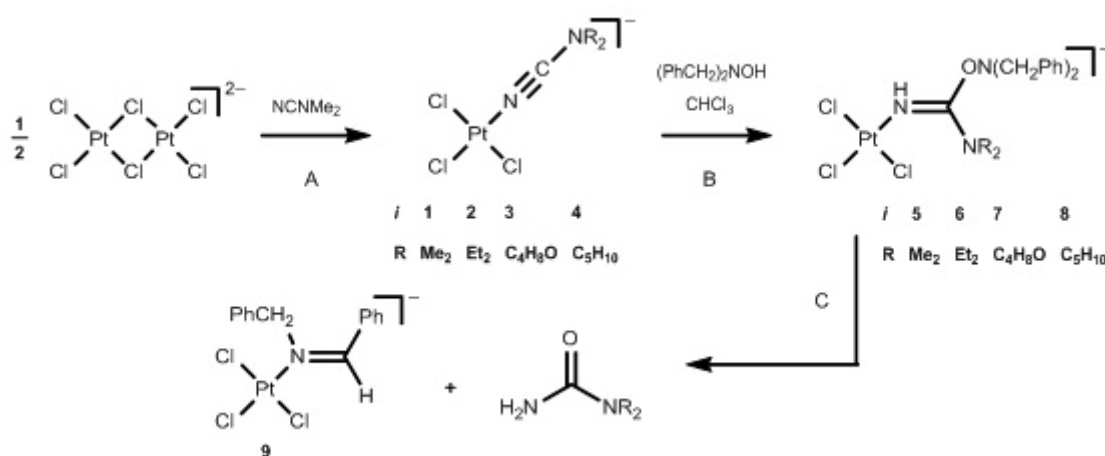
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The reaction between the binuclear complex $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{Pt}_2\text{Cl}_6]$ and various dialkylcyanamides, NCNR_2 , at 110–125 °C resulted in the formation of the platinum(II) complexes $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{NCNR}_2)]$ (Scheme 1, A; $\text{R}_2 = \text{Me}_2$ **1**, Et_2 **2**, $\text{C}_4\text{H}_8\text{O}$ **3**, C_5H_{10} **4**). The treatment of **1–4** with $\text{HON}(\text{CH}_2\text{Ph})_2$ brings about the generation of the imino complexes $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3\{\text{NH}=\text{C}(\text{NR}_2)(\text{ON}(\text{CH}_2\text{Ph})_2)\}]$ ($\text{R}_2 = \text{Me}_2$ **5**, Et_2 **6**, $\text{C}_4\text{H}_8\text{O}$ **7**, C_5H_{10} **8**) (Scheme 1, B).



Scheme 1

Compounds **5–8** are converted to the imino complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3\{(\text{PhCH}_2)\text{N}=\text{CHPh}\}]$ (**9**, Scheme 1, C) and the corresponding dialkylureas H_2NCONR_2 for 1–4 h at room temperature. All complexes were fully characterized by elemental analyses (C, H, N), ESI-MS, IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic techniques, and by X-ray crystallography (for complex **1**).

In order to evaluate the reactivity of the NCNR_2 in comparison with the conventional nitriles, we conducted a competitive reactivity study of the nucleophilic addition of dibenzylhydroxylamine to the NCR ($\text{R} = \text{Ph}$, NMe_2 , CH_2Ph) metal-bound species and found that the coordinated nitriles react with dibenzylhydroxylamine and the reactivity increases in the following order of the substituents $\text{CH}_2\text{Ph} < \text{NMe}_2 < \text{Ph}$.

This project has been supported by the Russian Foundation for Basic Research (grants 11-03-00262 and 12-03-00076), Saint-Petersburg State University (grant 2011–2013) and Fundação para a Ciência e a Tecnologia (FCT), Portugal (Project PTDC/QUI-QUI/098760/2008).

P6: POLYMER-PROTECTED PALLADIUM CATALYSTS FOR 3,7,11-TRIMETHYLDODECYNE-1-OL-3 HYDROGENATION

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Catalysts based on noble metals nanoparticles stabilized with polymers are often used in selective hydrogenation of different types of unsaturated compounds. In this paper we studied supported on MgO palladium nanoparticle stabilized with poly-2-methyl-5-vinylpyridine (PMVP). Pd content was varied from 1.0 to 5.0%. For comparison we have synthesized 5% Pd/MgO catalysts without polymer. The prepared catalysts were tested in the reaction of 3,7,11- trimethyldodecyne-1-ol-3 hydrogenation.

The increase of the palladium content in the catalyst leads to an increase in the rate of reaction, but selectivity to alkenol is reduced from 86% on to 1% Pd-PMVP/MgO to 82% on 5% Pd catalyst (Table 1). Catalyst prepared without the polymer shows properties similar to PMVP-palladium catalysts with high metal content.

Table 1. Effect of palladium content in Pd-PMVP/MgO catalysts on hydrogenation of 3,7,11-trimethyldodecyne-1-ol-3.

Reaction conditions: T=50 °C, P_{H2}=1atm, m_{kat}=0.05g, C₁₅=0.9×10⁻³mol, solvent C₂H₅OH

Catalyst, % Pd	5.0 Without polymer	With polymer			
		5.0	3.0	1.5	1.0
W·10 ⁻³ , mol/sec	31.5	25.6	33.9	15.5	6.2
S _{C=C} , %	80.0	82.0	81.0	85.0	86.0

Thus, introduction of the polymer to the 1.0–1.5%Pd/MgO catalysts promotes formation of olefinic alcohol. The optimal system is 1.5% Pd-PMVP/MgO. This catalysts was modified with iron-group metal (Co, Fe, Ni) (Table 2) to reduce the content of palladium.

Adding 0.5% of the second metal (Co, Fe, Ni) to 1% Pd (total percentage of the active phase is 1.5%) leads to the increase the catalyst activity. The best results was obtained on the catalysts modified with Ni. This catalysts shows also high selectivity.

Table 2. The effect of the second metal (Co, Fe, Ni) additive to 1%Pd-PMVPP/MgO catalysts on hydrogenation of 3,7,11-trimethyldodecyne-1-ol-3.

Reaction conditions: T=50°C, P_{H2}=1atm, m_{kat} = 0.05g, C₁₅=0.9×10⁻³mol, solvent C₂H₅OH

Catalyst	1.0% Pd			
	Without additive	+ 0.5% Fe	+ 0.5% Co	+0.5% Ni
W·10 ⁻³ , mol/sec	6.2	12.2	13.6	22.3
S _{C=C} , %	86.0	72.0	82.0	86.0

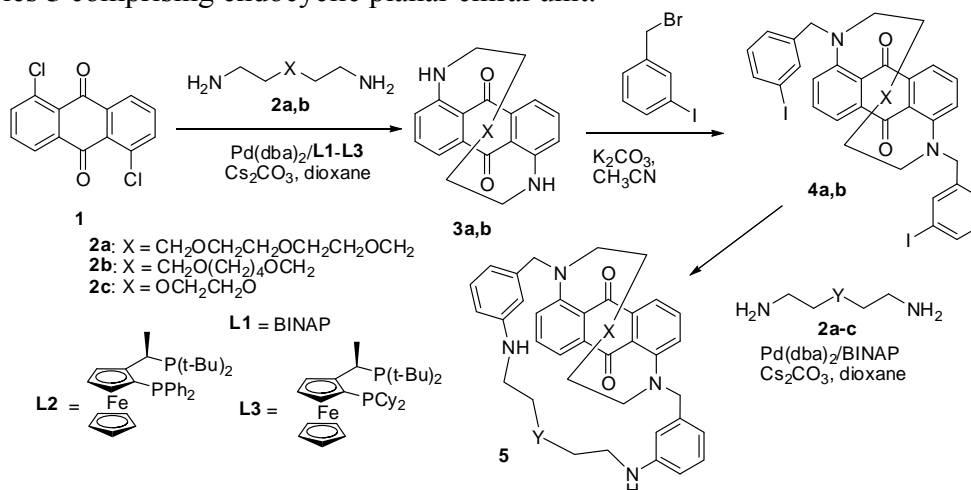
Thus, modification of polymer-palladium catalyst with nickel leads to an improving its properties in the reaction of 3,7,11-trimethyldodecyne-1-ol-3 hydrogenation. The most active and selective catalyst system is 1.5% (Pd-Ni) -PMVP/MgO at a ratio of Pd:Ni = 2:1.

P7: TRANSITION-METAL CATALYSIS AND ORGANOCATALYSIS IN THE SYNTHESIS OF MACROCYCLES WITH ENDO- AND EXOCYCLIC CHIRAL MOIETIES

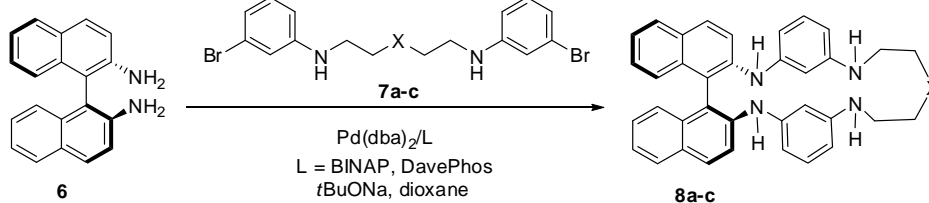
A.D. Averin, O.K. Grigorova, I.P. Beletskaya

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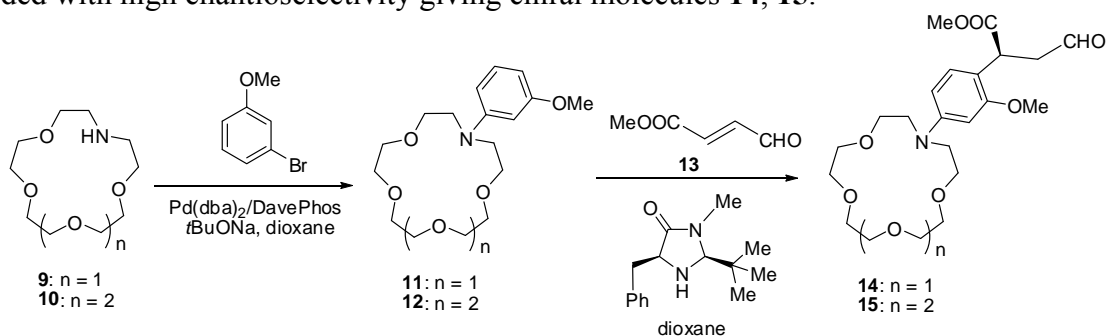
Macrocycles **3**, synthesized from 1,5-dichloroanthraquinone (**1**), were further modified with two *m*-iodobenzyl substituents, and the second macrocyclization reaction with oxadiazines **2a–c** afforded macrobicycles **5** comprising endocyclic planar chiral unit.



Another approach to chiral macrocycles with endocyclic chiral moiety is the application of a chiral aromatic diamine **6** in the Pd-catalyzed reactions with *N,N'*-bis(3-bromophenyl) substituted diamines **7** which resulted in the chiral macrocycles **8**.



The introduction of the exocyclic chiral unit can be achieved by the combination of transition-metal catalysis and organocatalysis: at the first step *N*-(3-methoxyphenyl) substituted azacrown ethers **11**, **12** were obtained, and at the second step they participated in the Michael addition to enal **13** which proceeded with high enantioselectivity giving chiral molecules **14**, **15**.



P8: SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL MEASUREMENTS OF NOVEL BALL-TYPE 4,4-(1,1-((4-METHOXYPHENYL)METHYLENE)BIS(NAPHTHALENE-2,1-DIYL))BIS(OXY) BRIDGED Co(II), Zn(II), Cu(II) PHTHALOCYANINES

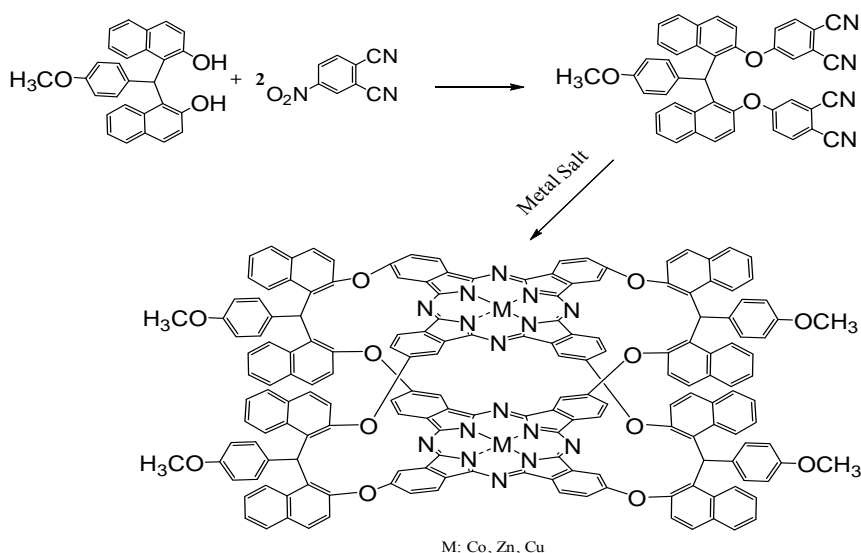
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Phthalocyanine compounds (Pcs) have lately received renewed attention in new application areas, such as non-linear optics, data storage devices, laser dyes [1], photodynamic cancer therapy [2], photosensitizers and semi-conductive materials [3]. Especially Zinc Pc complexes display interesting properties as potential photosensitisers in photodynamic cancer therapy. For this reason, the synthesis and the electrical and gas-sensing properties of various types of phthalocyanine compounds have been investigated [4].

The structures and electrochemical, electrical, spectroscopic properties of Pcs can be changed through using different substituents and central metal ions [5]. Beside their excellent properties, low solubility in organic solvents limits Pcs applications in many fields. Nevertheless, the solubility of Pc compounds can be enhanced by adding various adequate functional groups at the periphery of the Pc ring. Peripheral substitution with different kinds of substituents such as alkyl, alkoxy and electron-withdrawing or electron-donating groups leads to Pc derivatives soluble in most of the organic solvents.

In this study, we have reported the synthesis, characterization and electrochemical properties of novel mono-nuclear Co^{II}Pc, Cu^{II}Pc Zn^{II}Pc and ball-type homo-binuclear Co^{II}-Co^{II}, Cu^{II}-Cu^{II}, Zn^{II}-Zn^{II} Pcs phthalocyanines peripherally bridged with 4,4'-(1,1'-((4-methoxyphenyl)methylene)bis(naphthalene-2,1-diyl))bis(oxy) group.



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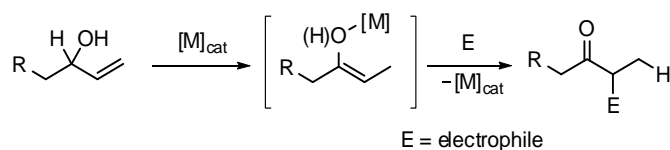
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P9: IRIIDIUM-CATALYZED FORMATION OF CARBON–CHLORINE BONDS. SELECTIVE SYNTHESIS OF ALPHA-CHLOROKETONES

A. Bermejo, N. Ahlsten, B. Martín-Matute

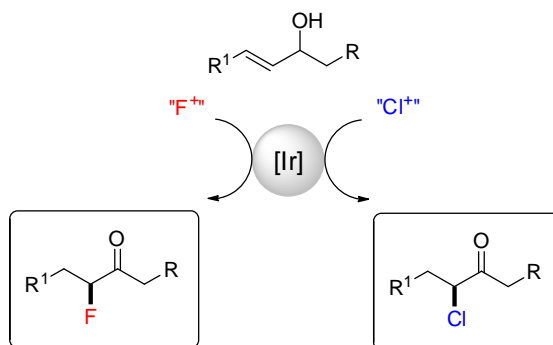
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Allylic alcohols can be isomerized into carbonyl compounds in the presence of a transition metal catalyst. If electrophiles are present in the reaction media, α -functionalized carbonyl compounds can be formed as single constitutional isomers (**Scheme 1**). [1]



Scheme 1.

Recently, we found that α -fluorinated ketones can be prepared as single isomers by combining an iridium-catalyzed isomerization of allylic alcohols with electrophilic fluorinations. [2] We describe here our latest results on the formation of C–Cl bonds under transfer hydrogenation conditions catalyzed by iridium complexes. [3] The present catalytic process affords α -chloroketones from allylic alcohols as single constitutional isomers in good to excellent yields (**Scheme 2**). Synthetic applications and mechanistic aspects will be described.



Scheme 2.

[1] For tandem isomerisation / C–C bond formation from allylic alcohols, see: a) Cuperly, D.; Petriguet, J.; Crévisy, C.; Grée, D. *Chem. Eur. J.* **2006**, *12*, 3261. b) Cadierno, V.; Crochet, P.; Gimeno, J. *Synlett*, **2008**, 1105. c) Bartoszewicz, A.; Livendahl, M.; Martín-Matute, B. *Chem. Eur. J.* **2008**, *14*, 10547. d) Ahlsten, N.; Martín-Matute, B. *Adv. Synth. Catal.* **2009**, *351*, 2657. e) Bartoszewicz, A.; Jezowska, M.; Laymand, K.; Möbus, J.; Martín-Matute, B. *Eur. J. Inorg. Chem.* **2012**, *in press*.

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P10: INTERACTION OF THE NEGISHI REAGENT WITH CONJUGATED DIACETYLENES

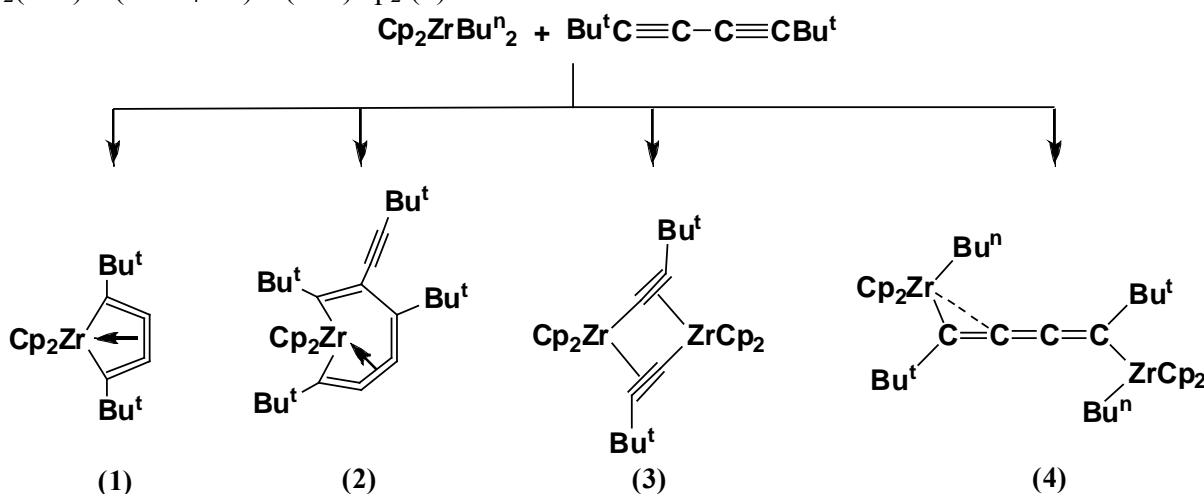
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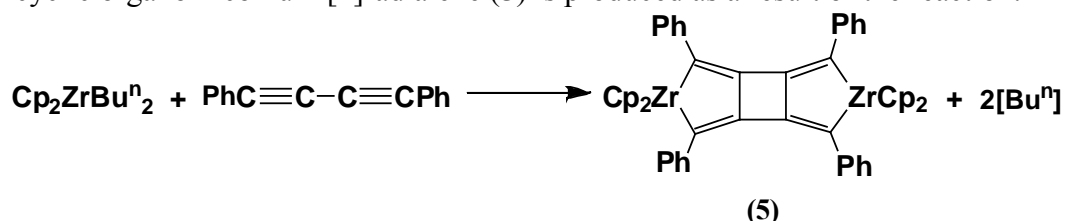
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Recently, we have reported [1] on the synthesis of di-*n*-butylhafnocene $\text{Cp}_2\text{HfBu}^n_2$, which is a hafnium analog of the Negishi reagent $\text{Cp}_2\text{ZrBu}^n_2$. It turned out that the synthesized $\text{Cp}_2\text{HfBu}^n_2$ is much more stable than $\text{Cp}_2\text{ZrBu}^n_2$ and decomposes, generating " Cp_2Hf ", only at 100 °C. It was also shown that under these conditions $\text{Cp}_2\text{HfBu}^n_2$ readily reacts with 1,4-disubstituted butadiynes $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$ ($\text{R} = \text{Bu}^t, \text{SiMe}_3, \text{Ph}$) to form various hafnacycles.

In the present work, the reactivity of 1,4-disubstituted butadiynes towards the Negishi reagent was investigated. It has been established that the interaction of $\text{Cp}_2\text{ZrBu}^n_2$ with 1,4-bis(*tert*-butyl)butadiyne $\text{Bu}^t\text{C}\equiv\text{C}-\text{C}\equiv\text{CBu}^t$ results in the formation of four products, viz., a five-membered zirconacyclocumulene complex $\text{Cp}_2\text{Zr}(\eta^4-\text{Bu}^t\text{C}_4\text{Bu}^t)$ (1), a seven-membered zirconacyclocumulene $\text{Cp}_2\text{Zr}[\eta^4-\text{Bu}^t\text{C}_4(\text{Bu}^t)-\text{C}(\text{C}_2\text{Bu}^t)=\text{CBu}^t]$ (2) as well as small amounts of dimeric acetylide $[\text{Cp}_2\text{ZrC}\equiv\text{CBu}^t]_2$ (3) and binuclear butatrienyl complex of zirconocene $\text{Cp}_2(\text{Bu}^n)\text{Zr}(\text{Bu}^t\text{C}_4\text{Bu}^t)\text{Zr}(\text{Bu}^n)\text{Cp}_2$ (4).



The interaction of the Negishi reagent with 1,4-diphenylbutadiyne proceeds quite differently. In this case, a tricyclic organozirconium [4]radialene (5) is produced as a result of the reaction.



The protolysis of complex 5 with HCl in THF gives rise to quantitative formation of Cp_2ZrCl_2 and the corresponding organic [4]radialene.

This work was supported by the Russian Foundation for Basic Research (№ 12-03-00036-a).

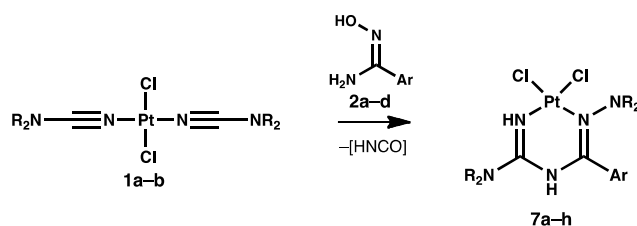
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P11: PLATINUM(II)-MEDIATED AMIDOXIME–DIALKYL CYANAMIDE CASCADE REACTIONS PRODUCE AMIDRAZONE LIGANDS

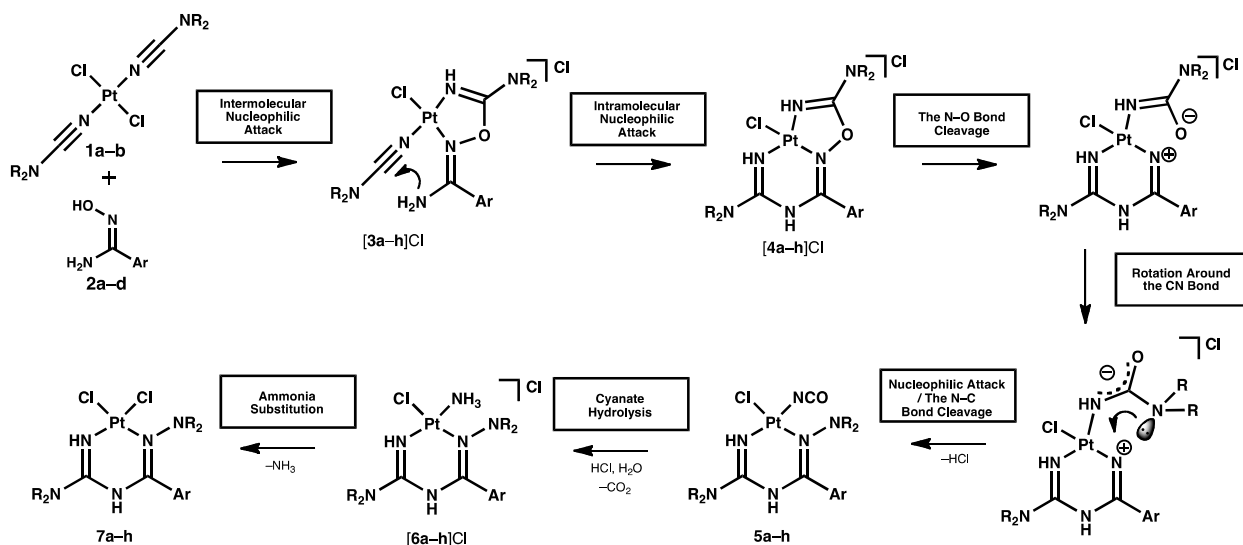
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The novel cascade reaction between the complexes *trans*-[PtCl₂(NCNR₂)₂] (R₂ = Me₂ **1a**, C₅H₁₀ **1b**) and the aromatic amidoximes *p*-R'C₆H₄C(NH₂)=NOH (R' = Me **2a**, H **2b**, CN **2c**, NO₂ **2d**) at 40 °C in 1:1 molar ratio in presence of 1 equiv of (PhCH₂)₃N followed by addition of 1 equiv of *p*-toluenesulfonic acid results in formation of amidrazone complexes **7a–h** in 49–60% isolated yields.



The mechanism was studied by ESI-MS technique and ¹H NMR and the intermediates, viz., cyanate complexes **5a–h** were isolated from the reaction mixtures. Based upon experimental data the following plausible mechanism of the reaction was proposed:



The mechanism includes (i) nucleophilic addition of the amidoxime to the coordinated dialkylcyanamide by the HO-group, (ii) intramolecular nucleophilic attack of the amide moiety to the coordinated dialkylcyanamide, (iii) intramolecular nucleophilic substitution, (iv) hydrolysis of the ligated cyanate, and (v) substitution of the ligated ammonia by chloride.

All 16 isolated complexes were characterized by elemental analysis, ESI-MS, IR, and ¹H NMR techniques and 8 species were also characterized by single-crystal X-ray diffraction.

ACKNOWLEDGMENTS

The authors express their gratitude to the Russian Fund of Basic Research (grants 12-03-00076 and 11-03-90417), Saint-Petersburg State University (research grant 2011–2013).

P12: AN ORTHO-SUBSTITUENT: TO ACCELERATE OR TO DECELERATE THE ARYL HALIDES CROSS-COUPPLING REACTIONS?

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Traditionally, the *ortho*-substituted aryl halides enter into cross-coupling reaction with difficulty. The reason is the steric factor which prevents a general stage for these reactions: an activation of the aryl halide with a transition metal complex named an oxidative addition (OxAdd). This is the stage responsible for what will whether the catalyst activate one or another organic substrate. Therefore, an understanding of OxAdd pathways is very important for the development of new catalytic processes.

We have studied the relative reactivity of *ortho*-bromo substituted toluene, anisole and anilines (as with *N*-alkyl groups and without them) in several C-C bond formation reactions: Pd-ADC catalysed Suzuki cross-coupling and carbonylation catalysed with Co- and Pd-complexes. The steric factor manifests itself differently in these processes depending on the nature of the metal. Substituents in the *ortho*-position to the reaction centre slowed the reaction catalysed by Pd-complexes. In the case of cobalt catalyst the sign of the steric effect changes, and the carbonylation of the *ortho*-substituted bromobenzenes is accelerated in compare with unsubstituted bromobenzene.

This dependence of the *ortho*-effect sign from the metal nature can be explained within the concept of several possible ways to activate an organic halide. OxAdd can occur by different mechanisms. Two of which are realisable when aryl halides are used as substrates: a concerted pathway (OxIn) and an anion-radical activation (SET). Palladium complexes are likely to activate the aryl halide by OxIn, whereas the catalysis of cobalt complexes proceeds through a stage of electron transfer.

Acknowledgements: The authors thank Saint-Petersburg State University for a research grant, the Federal Targeted Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013" (contract P676 from 20/05/2010), and Russian Fund for Basic Research (grant 11-03-00048-a).

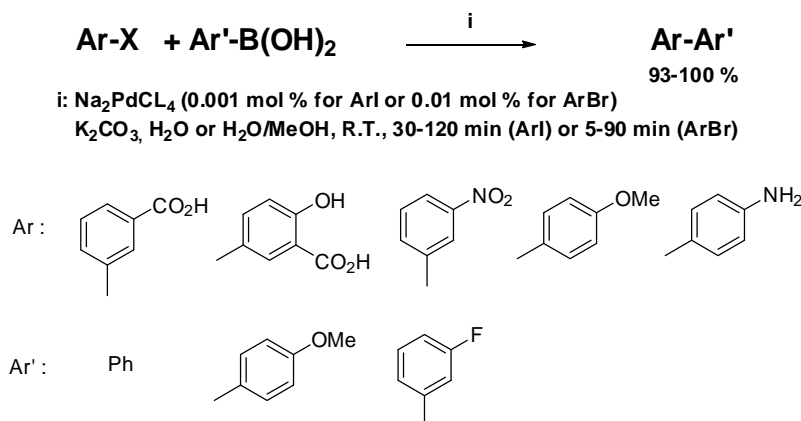
P13: VERY FAST SUZUKI-MIYaura REACTIONS WITH LOW LIGANDLESS PALLADIUM LOADING IN AQUEOUS MEDIA

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The palladium-catalyzed cross-coupling of aryl halides with arylboronic acids, the Suzuki–Miyaura reaction [1], represents a highly effective method for carbon–carbon bond formation in the synthesis of biaryl compounds. Although many efficient palladium catalysts with novel P- and N-ligands have been discovered for the reaction, also of great importance are the protocols that utilize \square ligandless \square Pd-catalysts in water or aqueous media. Water has clear advantages as a solvent for use in this type of reactions because it is cheap, readily available, and nontoxic. There are, however, problems associated with low stability of ligandless catalytic systems at high catalyst loading or long reaction time at \square homeopathic \square palladium concentration in organic solvents [2]. Here, we report that Na_2PdCl_4 (**1**) at low loading, in combination with water or water/MeOH as the solvents, is an efficient catalyst for the coupling of aryl halides with aryl boronic acids at room temperature by exposure to air.

For initial studies, we performed the Suzuki–Miyaura coupling of 3-iodobenzoic acid and phenylboronic acid. In the presence of 0.001 mol % of complex **1**, the reaction proceeded in water at room temperature (2.5 equiv of K_2CO_3) in less than 10 min, clearly indicating the high activity of the catalyst. The product was isolated in 96% yield. The reaction of electron-rich water-insoluble 4-bromoanisole also proceeded at room temperature in aqueous methanol at 0.01 mol % catalyst loading, giving cross-coupling products with ~100% yield in 5 min. Examples of the coupling reactions of aryl iodides and bromides with aryl boronic acids at room temperature are presented below.



We thank the Russian Foundation for Basic Research (11-08-00353-a) for financial support of this work.

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P14: A HIGHLY ACTIVE HETEROGENEOUS PALLADIUM CATALYSTS SUPPORTED ON SILICA-CARBON NANOTUBES HYBRIDS

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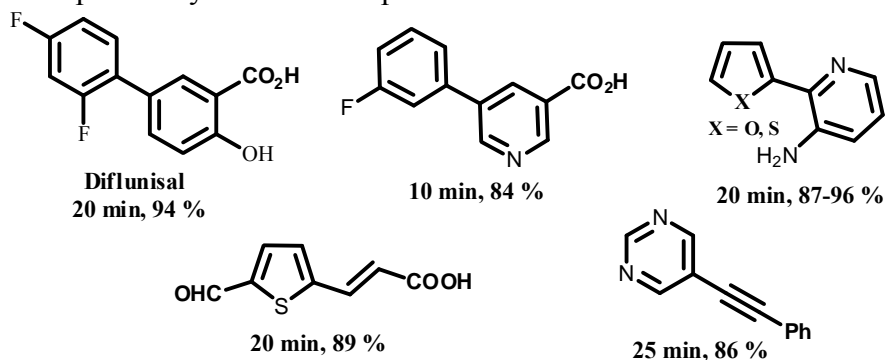
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Heterogeneous catalysts have recently drawn much attention in organic synthesis based on sustainable and industrial standpoints, as they have many advantages over homogeneous catalysts, owing to their stability, recoverability, reusability, etc. We report here an efficient heterogeneous catalytic system for cross-coupling reactions based on the precipitation of Pd nanoparticles (PdNPs) from the solution of Pd(0) complex on silica-carbon nanotubes hybrids. MWCNT/SiO₂ supports have been obtained by sol-gel process under acid catalysis using suspension of multiwall carbon nanotubes in aqueous ethanol and TEOS, methyl- or phenyltriethoxysilanes as silica sources. Characterization of catalysts was performed using FTIR, XRD, XPS, and TEM. The method developed have shown to be efficient for the preparation of the catalytic materials and uniform deposition of palladium nanoparticles.

The resulting Pd materials, PdNPs/MWCNT/SiO₂, show homogeneous distribution of palladium clusters (TEM images) with sizes 2–3 nm. The PdNPs/MWCNT/SiO₂ is found as highly effective recyclable catalysts in Suzuki, Heck and Sonogashira reactions in water as a green solvent. The cross-coupling reactions were performed at low Pd content using various aryl(heteroaryl) bromides, 1.2 equiv of an arylboronic acid, olefins (acrylic acid or styrene) and phenylacetylene in the presence of ~0.1 mol% of Pd and 2.5 equiv of K₃CO₃ in water under reflux. All of the cross-coupling reactions exhibited high yields within 10–30 min even though they were carried out in air atmosphere. Therefore, the PdNPs/MWCNT/SiO₂ catalytic hybrids effectively promoted the coupling reactions at low Pd content in the absence of any ligands, and the system was stable toward air and water. The new heterogeneous catalysts could be recovered by simple filtration and reused 8–10 times without any loss of the catalytic activity. Furthermore, no leached Pd was found in the filtrate and products after the removal of the catalyst by the inductively coupled plasma (ICP) assay. We suggest that only the interaction of the metallic centers with the delocalized π -electron density on the MWCNT surface could be the responsible for the stabilization of the PdNPs. Furthermore, this interaction must be strong since these hybrids exhibit very high catalytic activity, and even more important, excellent recyclability.

Examples of the compounds synthesized are presented below.



We thank the Russian Foundation for Basic Research (11-08-90421-Ukr_f_a) and State Foundation for Basic Research of Ukraine (F40. 3/047) for financial support of this work.

P15: CYCLOPALLADATED OCTACARBAMOYL- AND OCTATHIOCARBAMOYL-RESORCINARENE COMPLEXES

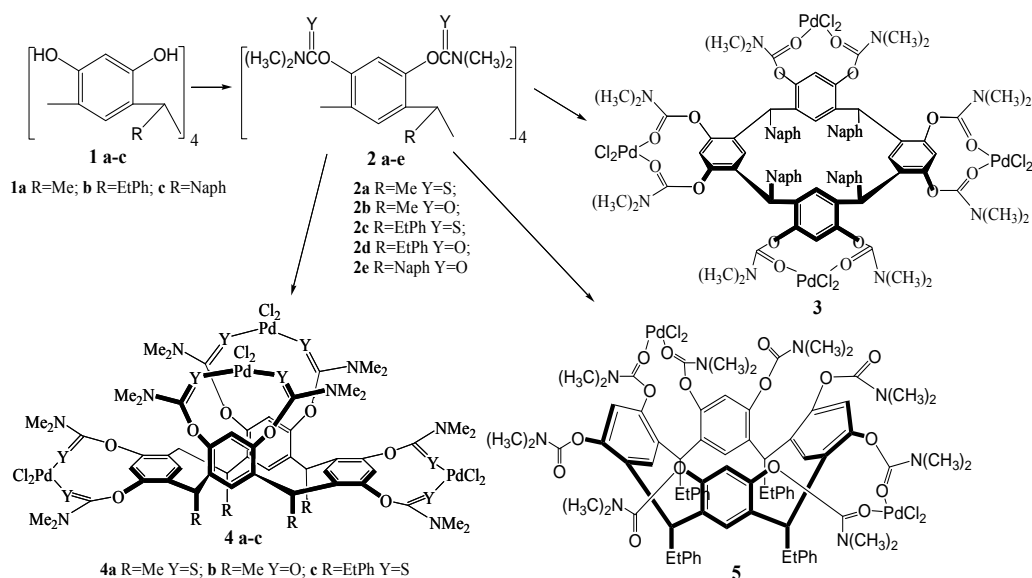
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This communication deals with the synthesis of cyclopalladated resorcinarene complexes the promising catalysts in stereospecific reactions.

With the intent to study effect of resorcinarene matrix pre-organization on the orientation of the metal rings, resorcinarenes **1 a–c** existing in different conformations were chosen.

Perfunctionalized ligands **2** were synthesized by the reaction of resorcinarenes **1** with N,N-dimethylcarbamoyl and N,N-dimethylthiocarbamoyl chlorides in the presence of Cs₂CO₃.



The reactions of ligands **2** with PdCl₂ and Pd[C₆H₅CN]₂Cl₂ were carried out in dichloromethane at 35–40°C. The spatial separation of functional groups of neighboring benzene rings in the ligands **2 a–c, e** promoted the formation of complexes containing four 10-membered metal rings in which Pd is coordinated by chelating pairs located in the same benzene ring. The resulting products exist in the *chair* (**3**) and *staggered boat* (**4a–c**) conformations.

The complexation pathway changed for the coordination of Pd by octacarbamoyl-resorcinarene **2d**. As a result of interconversion in polar solvents, the *crown* conformation became the predominant one. The carbamoyl groups attached to neighbouring benzene rings approached each other; this resulted in the formation of metallocavitand **5** containing two diagonally arranged 12-membered metal rings. The carbamate groups that remained free moved away from each other and were no longer capable of chelation.

This work was supported by the RFBR (grant No. 12-03-00213a).

P16: SYNTHESIS AND CHARACTERIZATION OF CHIRAL MONOCYCLOPENTADIENYL TITANIUM COMPLEXES

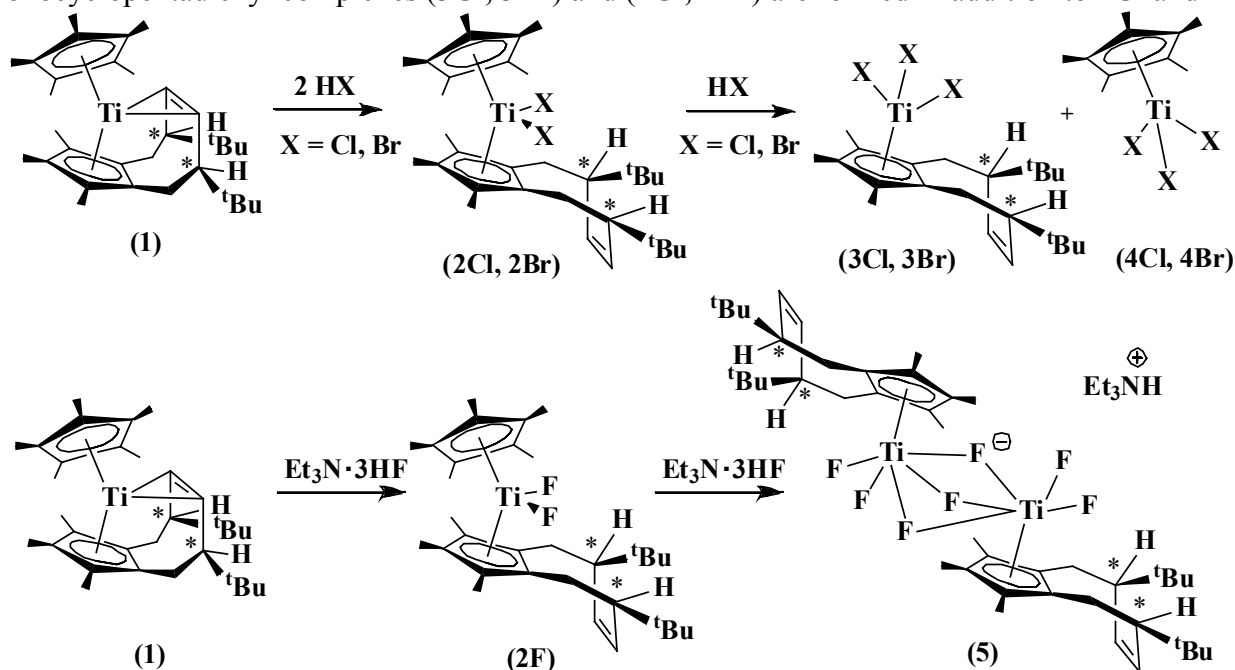
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Previously, we have found that the reduction of permethyltitanocene dichloride $\text{Cp}^*_2\text{TiCl}_2$ with magnesium in THF at room temperature in the presence of $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$ affords a tricyclic alkyne complex (**1**) [1] whose reaction with HCl or Br_2 immediately leads to the corresponding dihalogenide derivatives (**2Cl**) and (**2Br**) [2].

Here, we report that the interaction of **1** with $\text{Et}_3\text{N}\cdot 3\text{HF}$ results in the formation of an analogous difluoride complex (**2F**) as well as an unusual dimeric anionic heptafluoride complex (**5**). It has been also found that if the reaction of **1** with HCl or HBr is carried out for several days at 60°C , monocyclopentadienyl complexes (**3Cl**, **3Br**) and (**4Cl**, **4Br**) are formed in addition to **2Cl** and **2Br**.



The synthesized new complexes **2F**, **3Cl**, **3Br** and **5**, like **1**, **2Cl** and **2Br**, are chiral. They were isolated in an analytically pure state and were characterized by NMR spectra. The structure of complexes **2F**, **3Cl** and **3Br** has been confirmed by an X-ray analysis.

This work was supported by the Russian Foundation for Basic Research (№ 12-03-00036-a).

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P17: INTERACTION OF TERT-BUTOXY SUBSTITUTED SILYLMETHYL MAGNESIUM CHLORIDES WITH MONOCHLOROANHYDRIDES OF PHOSPHORUS(III)-CONTAINING ACIDS

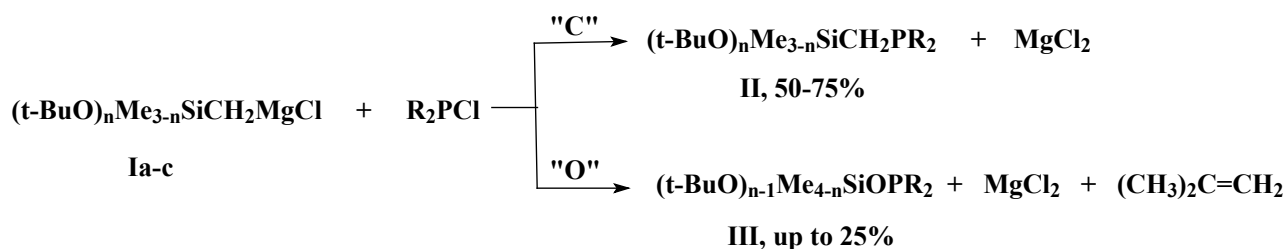
I.A. Bykova, E.A. Monin, V.M. Nosova, A.V. Kisin, P.A. Storozhenko

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Alkoxy substituted silylmethyl magnesium chlorides of $(\text{AlkO})_n\text{Si}(\text{Me})_{3-n}\text{CH}_2\text{MgCl}$ ($n=1-3$) general formula (**I**) are of interest because of their implementation for synthesis of phosphorus ligands for supported metal complexes [1] but *tert*-butoxy derivatives of this type were practically unknown and **were not used** for this purpose. Meanwhile these Grignard reagents with bulky *tert*-butoxy groups in the molecule should be more stable than analogous substances with ethoxy or isopropoxy groups at silicon and may be **readily** used in synthesis of phosphorus ligands with different structure.

It was found that *tert*-butoxy substituted silylmethyl magnesium chlorides of $(t\text{-BuO})_n\text{Si}(\text{Me})_{3-n}\text{CH}_2\text{MgCl}$ (**Ia-c**, $n=1-3$) general formula synthesized recently reacted with different monochloroanhydrides of phosphorus(III)containing acids in THF both on "C"-center and "O"-center.

The first route of this reaction was preferential and gave rise to methylene silicon-phosphorus compounds (**II**) with good yields. The reaction of Grignard reagents (**Ia-c**) on "O"-center proceeds with cleavage of C-O bond, *t*-BuCl evolution and subsequent isobutene elimination. Corresponding siloxyderivatives (**III**) were obtained with low yields.



$n=1$ (**Ia**); $n=2$ (**Ib**); $n=3$ (**Ic**); $\text{R}=\text{Alk}, \text{AlkO}, \text{Alk}_2\text{N}, \text{Ph}$.

The influence of *tert*-butoxy groups quantity, substituents volume and nature at phosphorus on these reaction directions was discussed.

The structures of compounds synthesized were proved by ^1H , ^{13}C , ^{31}P and ^{29}Si NMR.

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P18: SIGNIFICANCE OF BENZYL SUBSTITUENTS ON *N*-HETEROCYCLIC CARBENE LIGANDS AS CATALYST

B. Cetinkaya, S. Gulcemal, P.A. Akinci, E. Cetinkaya

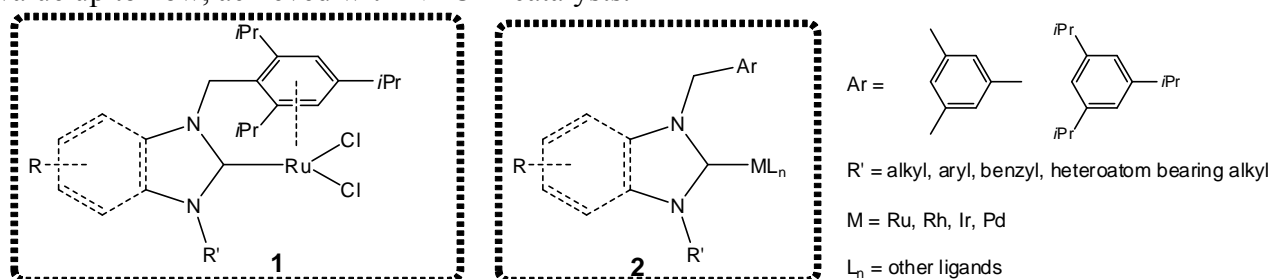
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The ready access to *N*-heterocyclic carbenes (NHCs) has led to a rapid development of homogeneous organic and organometallic catalysts.¹ The electronic and steric parameters of NHC complexes can be modified easily, and they have greater stability toward air, moisture and heating when compared with phosphine analogues.² Thus, Ir, Rh and Ru complexes bearing NHCs have been employed as catalysts for number of catalytic reduction reactions such as, hydrogenation, transfer hydrogenation (TH), and hydrosilylation.^{1,3}

An interesting subclass of such complexes is formed by those species containing electron-donating benzyl substituents (NHC^{Bn}) to give tethered Ru(II) complexes of the type [RuCl₂(η⁶-arene)(η¹-NHC)] (**1**) which display excellent activity in various catalytic reactions.⁴ Prompted by these observation, we decided to expand our studies to the coordination of NHC^{Bn} ligands to the second row transition metals. Tethered NHC complexes (**2**) of Pd(II), Rh(I) or Ir(I) have not been isolated so far. However, NHC^{Bn} ligands coordinated to such metal ions may act as "flexible"

Recently we compared the activity of bulky benzyl (CH₂Mes) and aryl (Mes) substituted Rh-NHCs in TH reaction of acetophenone. It is clear that the introduction of CH₂Mes group to the nitrogen atoms increased the TH performance when compared with their aryl analogues.⁵ NHC complexes of iridium¹ show superior activities when compared with their rhodium¹ analogues.⁶

In this work, [(NHC^{Bn})IrCl(COD)] complexes, bearing bulky 2,4,6-triisopropylbenzyl and 2,4,6-trimethylbenzyl groups on N atom(s) of (5,6-dimethyl)benzimidazole-2-ylidene were synthesized and up to 12.000 h⁻¹ TOF values were obtained in TH of ketones. This is one of the highest TOF value up to now, achieved with NHC-Ir catalysts.



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P19: THE ALUMINUM COMPLEXES BASED ON N,N,O-POLYDENTATE LIGANDS AS INITIATORS OF CYCLIC ESTERS ROP

V.S. Cherepakhin¹, K.V. Zaitsev¹, Y.F. Oprunenko¹, A.V. Churakov², S.S. Karlov¹, G.S. Zaitseva¹, S.V. Kostyuk³, I.V. Vasilenko³

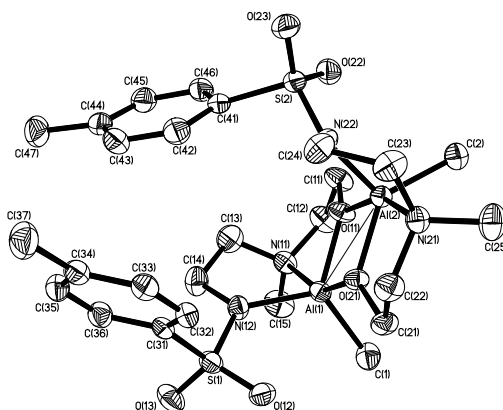
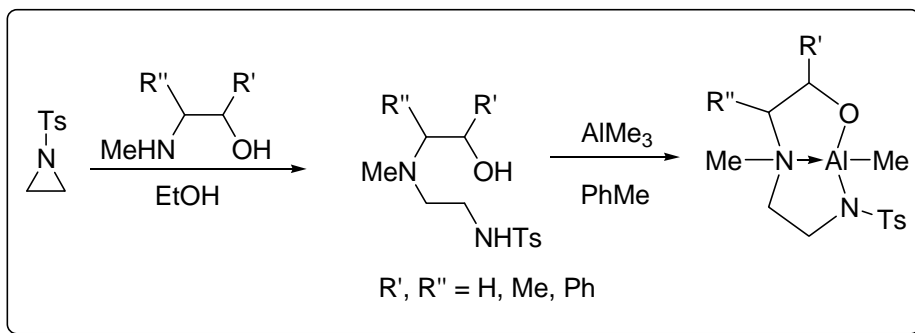
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The materials based on aliphatic polyesters attract great attention due to their biodegradation and biocompatibility. The ring opening polymerization (ROP) initiated by metal complexes is the most used method for the synthesis of such materials due to reproducibility and reaction control [1]. The search for new active initiators for ROP is the actual problem for modern organometallic and polymer chemistry.

In this work we have obtained novel aluminum complexes on the basis of known or new ligands. The structures of the complexes obtained were investigated by multinuclear NMR spectroscopy and in several cases by X-ray analysis.



P20: GOVERNING ROLE OF THE HALOGEN BONDING, STACKING, METALLOPHILICITY AND OTHER WEAK CONTACTS TO THE STRUCTURE OF Au-BIPYRIDINE AND Au-BIPYRIMIDINE COMPLEXES

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Weak contacts, such as metallophilic bonds, halogen bonds, hydrogen bonds, etc. are known to be of a great importance in organometallic chemistry due to their significant influence on the crystal structure of complexes. In the present work we represent the role of number of various weak intermolecular interactions in the structures of Au-bipyridine and Au-bipyrimidine complexes.

In the course of project we synthesized the compounds $[\text{Au}(\text{L})\text{X}_2][\text{AuX}_4]$ (L = bipyridine (bpy), bipyrimidine (bpm); X = Cl, Br) in a single stage from AuX_3 and L and characterized them both in liquid and solid phases using the single crystal X-ray diffraction technique, elemental analysis, IR-spectroscopy, mass-spectrometry and ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. The structure shows the number of intermolecular interactions, such as weak metallophilic interactions with the Au–Au distance of 3.5 – 3.6 Å, wide net of halogen contacts both with 90° and 180° angles, nitrogen–chlorine contact with the distance of 3.0 Å, nitrogen–nitrogen bonding with the distance of 3.0 Å and even halogen– π and Au– π interactions.

Comparing the $[\text{Au}(\text{L})\text{Cl}_2][\text{AuCl}_4]$ and $[\text{Au}(\text{L})\text{Br}_2][\text{AuBr}_4]$ derivatives we found the drastic changes in structure (Fig. 1). In the compound with bromine, which is known to form stronger halogen bonding than chlorine, the halogen bonding, aurophilic contacts and Br– π and Au– π interactions govern the structure while in chlorides hydrogen bonds, weak Au–Cl and Cl– π interactions prevails.

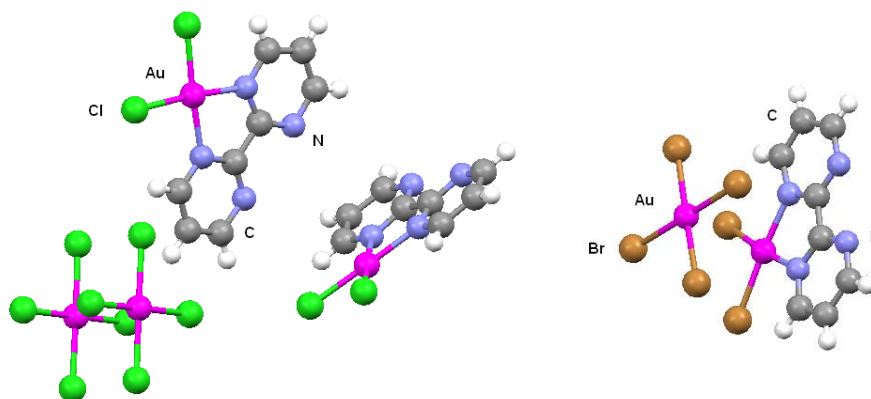


Fig.1 Structures of $[\text{Au}(\text{bpm})\text{Cl}_2][\text{AuCl}_4]$ and $[\text{Au}(\text{bpm})\text{Br}_2][\text{AuBr}_4]$

The shift from $[\text{Au}(\text{bpy})\text{X}_2][\text{AuX}_4]$ to $[\text{Au}(\text{bpm})\text{X}_2][\text{AuX}_4]$ also significantly changes the structure. In $[\text{Au}(\text{bpy})\text{X}_2][\text{AuX}_4]$ the halogen bonding as well as weak Au–X contact dominate. In $[\text{Au}(\text{bpm})\text{Br}_2][\text{AuBr}_4]$ halogen bonding forms a short zigzag of 4 bromines, and each of two inner bromines connects to two other. In $[\text{Au}(\text{bpm})\text{X}_2][\text{AuX}_4]$ the hydrogen bonds and N–N contacts as well as aurophilic interactions determine the structure and change the space group e.g from C2/c for $[\text{Au}(\text{bpy})\text{Br}_2][\text{AuBr}_4]$ to P21/c for $[\text{Au}(\text{bpm})\text{Br}_2][\text{AuBr}_4]$.

We have also carried out the partial reduction of the $[\text{Au}(\text{L})\text{X}_2][\text{AuX}_4]$ compounds in the acetone media to form $[\text{Au}(\text{L})\text{X}_2][\text{AuX}_2]$. These compounds were structurally characterized exhibiting the absence of aurophilic contacts but strong halogen bonding and Au– π and X– π interactions.

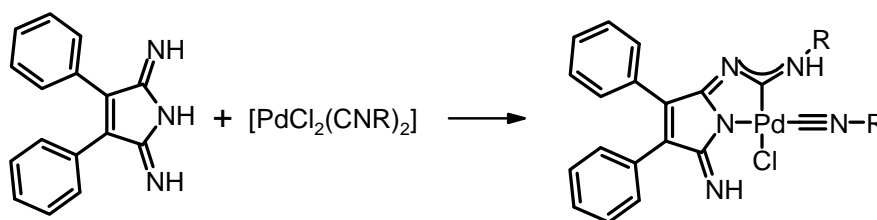
P21: COUPLING BETWEEN 2,5-DIIMINO-3,4-DIPHENYLPYRROLE AND ISOCYANIDES AT A Pd(II) CENTER

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The coupling between *N*-nucleophiles and isocyanides at a Pd(II) center represents an attractive approach for the synthesis of a variety of palladium(II) complexes, which may be used as catalysts for various cross-coupling reactions (e.g., Heck, Suzuki–Miyaura, Sonogashira, Kosugi–Migita, and Stille reactions) [1]. Owing to the reactions of coordinated isocyanides with *N*-nucleophiles (amines, imines, etc.), the so-called nitrogen-acyclic carbene complexes could be easily generated. The past several years has seen the significant development and utilizations of polynucleophiles that can lead to a novel type of carbene ligands [2]. Highly stable nitrogen-acyclic carbene Pd(II) complexes have been synthesized using amidines, 2,6-diaminopyridines, 3-iminoisoindolin-1-ones, and 1,3-diiminoisoindoline [3–5].

We studied the reaction of 2,5-diimino-3,4-diphenylpyrrole and bis(isocyanide)palladium(II) complexes and found that the coupling proceeds with one isocyanide ligand to accomplish the carbene Pd(II) complexes depicted in Scheme.



The obtained palladium(II) species were characterized by X-ray crystallography, IR and NMR spectroscopy, and HRESI mass spectrometry. The molecular structure and the total energy of the carbene palladium(II) complexes were studied by density functional theory (DFT) calculations at the B3LYP/6-31+G(dp) level of theory using CEP-121 for Pd [6]. The transition states of the reactions leading to carbene complexes were calculated.

Acknowledgements The authors thank Saint Petersburg State University for a research grant, the Federal Targeted Program (contract P676 from 20/05/2010), and Russian Fund for Basic Research (grants 11-03-12044-ofm and 12-03-00076-a).

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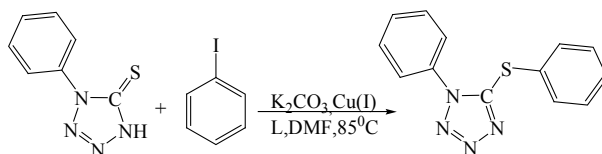
P22: STUDY ON THE COPPER-CATALYZED ARYLATION OF TETRAZOLE-5-THIONES

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The formation of C(aryl)–S bonds is a key step in a synthesis of many molecules that are of biological, pharmaceutical, and material science interest. Tetrazoles and their thio derivatives have attracted a close attention in last years. These fragments were included to many drug molecules compositions for example a β -lactam antibiotics and antihypertensive sartan drug [1, 2]. However universal methods for the preparation of 1-substituted-5-arylsulfanyltetrazoles were absent until now. Recently proposed method for the catalytic arylation of thiotetrazoles can be considered as the most suitable method for the synthesis of these compounds [3].

Continuing the study in the arylation of 1-substituted tetrazole-5-thiones we investigated the effect of ligands and copper salts (CuCl, CuI) on this reaction under thermal heating and microwave activation (MWA). The reaction of 1-phenyltetrazole-5-thione and iodobenzene was chosen as a synthesis model.



Comparison of the action of copper salts to this reaction has shown that in the MWA conditions they are equally effective but CuI is preferable to use at the convectional heating because it gives a more high yields.

In addition, we have studied the effect of various ligands on the arylation reaction. It is determined that the most effective ligands are ethylenediamine and phenanthroline in contrast to the copper catalysed arylation reactions of other substrates such as amines [4]. These ligands give a more high yields and an easier working up of the reaction product.

The results of experiments of arylation reaction are presented in a Table 1.

Table 1. Arylation of 1-phenyltetrazole-5-thione

L	Reaction conditions	Convectional heating		Microwave activation	
		Reaction time, h	Yield, %	Reaction time, h	Yield, %
Ethylenediamine	K ₂ CO ₃ , CuI, DMF 85°C	9.5	73	1.5	85
9. Phenanthroline		2.5	55	1	54
10. N,N,N',N'-Tetramethyl-ethylenediamine		6	23	-	-
N,N'-Dibenzylethylenediamine		5	38	-	-
N,N'-Dimethylethylenediamine		15.5	18	-	-
Diethanolamine		12	19	4.5	35
Without ligand		20	21	8	28

The reaction mixtures were stirred at 85°C until TLC showed complete consumption of starting materials. It should also be noted that MWA reduced the reaction time in 1.5–2 times.

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P23: A NEW EFFECTIVE ONE POT SYNTHESIS OF FUNCTIONALLY SUBSTITUTED 1Z,5Z-DIENES

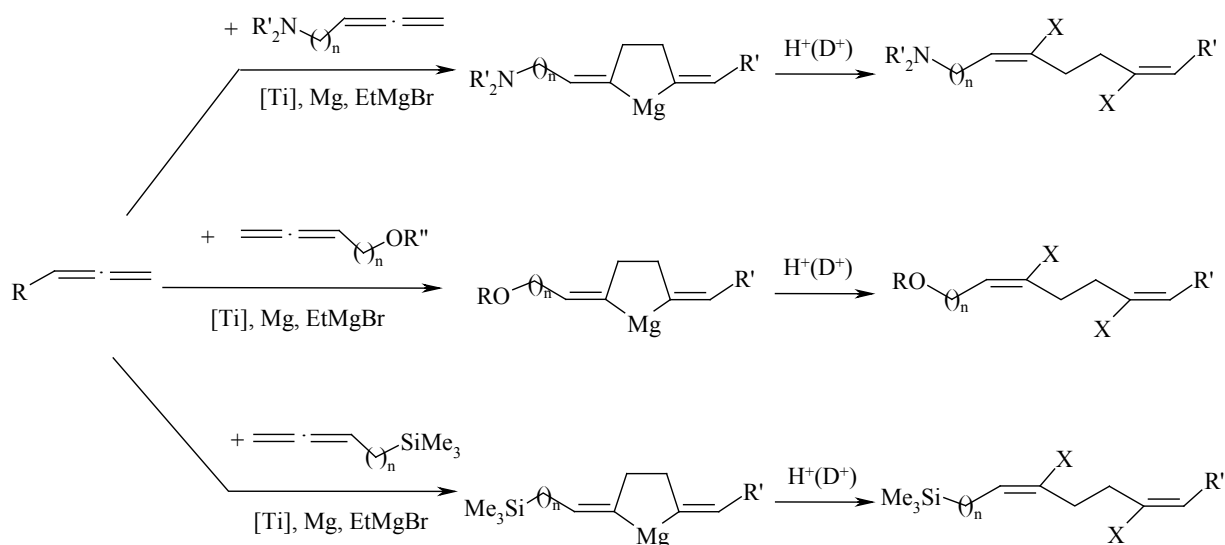
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Widespread distribution of functionally substituted hydrocarbons containing 1Z,5Z-diene moiety in a large number of insect pheromones, as well as natural biologically active compounds and the acetogenin precursors possessing antiviral, bactericidal and antitumor properties are stimulating the development of new approaches to their synthesis.

It was previously shown that the intermolecular cyclomagnesiation reaction of aliphatic 1,2-dienes provides selective formation of hard-to-reach 1Z,5Z-dienes in high yields and can serve as an effective synthetic tool for obtaining these organics [1, 2].

Now we report a new preparative cross coupling method for the synthesis of practically important functionally substituted 1Z,5Z-dienes through cyclomagnesiation of N-, Si-, or O-containing 1,2-dienes with terminal alkyl and aryl substituted allenes in the presence of EtMgBr and the Cp₂TiCl₂ catalyst (aliphatic 1,2-diene:heteroatom-containing 1,2-diene:EtMgBr:Mg:[Ti] = 10:12:40:32:0.5; Et₂O, 6 h, 20–22 °C) to afford exclusively nonsymmetrical organomagnesium compounds. The latters, after acid hydrolysis, gave rise to target 1Z,5Z-dienes in > 80% yield.



[Ti] = Cp₂TiCl₂; R = C₄H₉, C₆H₁₃, C₁₂H₂₅, n = 2–4; R' = Et, i-Pr, -(CH₂)₄-, -C₂H₄-O-C₂H₄-; R'' = THP, Bn; X = H, D.

This work was financially supported by Russian Foundation for Basic Research (Grants 10-03-00046, 11-03-97001, 11-03-00103).

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P24: DISCRIMINATION OF METAL-ORGANIC ARCHITECTURES BEARING AN ARYLHYDRAZONE OF BETA-DIKETONE

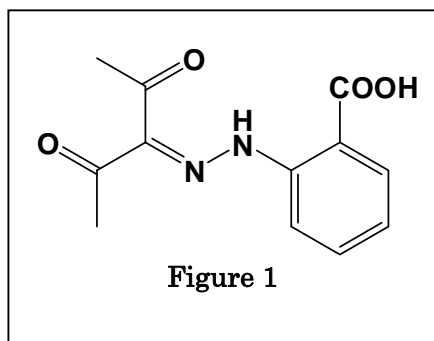
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Arylhydrazones of β -diketones (AHBD) are compounds that combine in their structure the azo- and diketo- motifs which provide a reach organic chemistry and versatility in complex formation. Moreover, they find many attractive applications due a controllable switch between their (*E,Z*)-enol-azo, keto-azo and (*E,Z*)-hydrazone forms.



With the aim of exploring the influence of different metals on the structure, coordination modes, nuclearities and properties of the formed complexes with the same AHBD, we used 3-(2-phenylhydrazono)pentane-2,4-dione (H_2L , Figure 1) as the unique pro-ligand and studied its interaction with a variety of metal ions. We observed that anionic or dianionic derivatives of H_2L created different coordination modes, topologies and nuclearities of a diversity of complexes depending on the metal ions and conditions used for the synthesis. Extensive

intermolecular H-bonds also provided a variety of supramolecular arrangements in 1D chains, 1D chains of the organic anion and 2D networks of metal-aqua aggregates, 2D networks or even 3D frameworks.

Acknowledgements: This work has been supported by the Foundation for Science and Technology (FCT), Portugal.

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P25: SYNTHESIS OF D-GLUCOSOAMINE DERIVATIVES AND THEIR APPLICATION AS CHIRAL LIGANDS IN AN ASYMMETRIC ALKYLATION IN ALLYLIC POSITION

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Carbohydrates as chiral ligand frames in enantioselective reactions are becoming to have more and more important role. Their usefulness comes from accessibility as well as structural and stereochemical variety. During the last years, we have become the witnesses of the development of sugar ligands, for example in the asymmetric allylic nucleophilic substitution reaction [1]. In our research we have focused our attention on Trost's type ligands [2]. These compounds have given us a lot of possibilities in enantioselective formation of new C–C, C–O, C–S, and C–N bonds.

We synthesized benzyl 4,6-O-benzylidene-2-amino-2-deoxy-β-D-glucoside (**1**) in a few simple and efficient stages, using a cheap D-glucosoamine hydrochloride as a starting substrate. The final ligand was synthesized very efficiently in one step starting from compound **1**, and it has been exploited in asymmetric allylic alkylation reaction, catalyzed by palladium complex [Pd(η³-C₃H₅)Cl]₂. For this reason we have used three racemic compound with different steric properties: 1,3-diphenyl-3-acetoxyprop-1-ene, 1,3-dimethyl-3-acetoxyprop-1-ene and 3-acetoxycyclohexene.

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"Carbohydrates as renewable raw materials in the synthesis of products with high added value" no. POIG.01.01.02-14-102/09-02

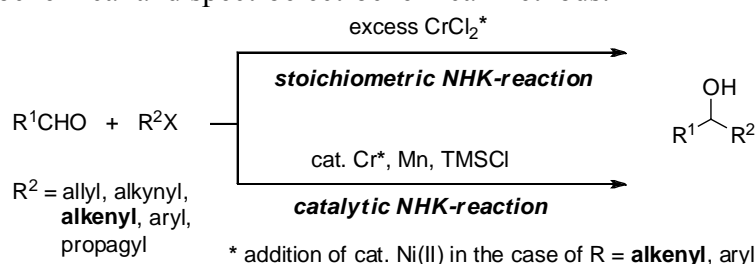
P26: Cr/Ni-CATALYZED VINYLATION OF ALDEHYDES: A MECHANISTIC STUDY ON THE CATALYTIC ROLES OF NICKEL AND CHROMIUM

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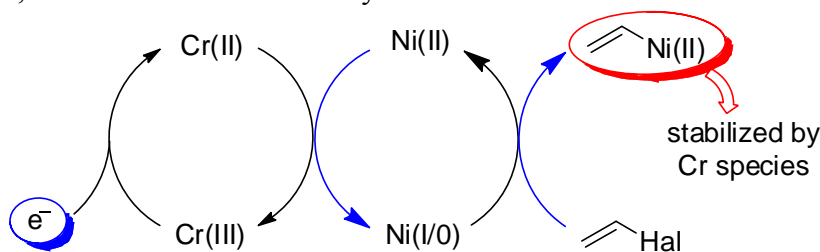
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The roles of nickel and chromium catalysts in the coupling reaction of vinyl halides and aldehydes, the so called Nozaki–Hiyama–Kishi (NHK) reaction (Scheme 1),¹ have been studied by UV/Vis spectroscopy, electrochemical and spectroelectrochemical methods.



Scheme 1. Stoichiometric and catalytic NHK reactions

By using UV/Vis-spectroscopy, cyclic voltammetry and spectroelectrochemistry, we were able to shed light on the roles of the Ni- and Cr-catalysts involved in the reductive coupling of vinyl halides and aldehydes (Scheme 2):² (1) Low-valent Ni from one-electron reduction [formally Ni^{I}], not necessarily Ni^0 activates the vinyl halide by reductive cleavage of the carbon-halogen bond; (2) Cr^{II} does not interact with the vinyl halide; (3) CrCl_2 reduces Ni^{II} to the low-valent Ni-species necessary for vinyl halide cleavage; (4) in the absence of Cr, the initially formed vinyl-Ni species is unstable and decomposes rapidly with dimerization of the vinyl residue; (5) in the presence of Cr, the Ni-vinyl species is stabilized; (6) in the electrochemical reduction of Ni^{II} , the generation of low-valent Ni {specifically $[(\text{bpy})\text{Ni}(\text{COD})]$ } occurs at significantly higher potential when Cr^{III} is present. This points to a catalytic role of Cr^{III} in the generation of low-valent Ni when external chemical reductants are used, as is the case in the "catalytic" NHK-reaction.



Scheme 2. Roles of nickel and chromium in the coupling reaction of vinyl halides and aldehydes.

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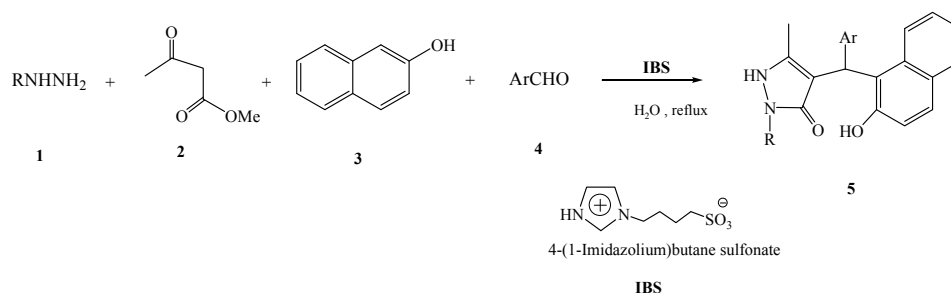
P27: ZWITTERIONIC-TYPE MOLTEN SALT: AN EFFICIENT MILD ORGANOCATALYST FOR SYNTHESIS OF 2-ARYL-5-METHYL-2,3-DIHYDRO-1H-3-PYRAZOLONES BY A FOUR-COMPONENT SEQUENTIAL REACTION IN WATER

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Pyrazolones have gained importance as drug substances in pharmaceutical industry in view of their biological importance. The synthesis of pyrazolones derivatives is currently of much interest, and various methods have been reported for their synthesis. The development of an environmentally benign methodology for the synthesis of pyrazolones derivatives is of great interest [1-5].

In continuation with the search for simple non-hazardous methods and the development of green chemical procedures for the transformations in organic synthesis using, herein we report a highly versatile, efficient, convergent, four-component sequential protocol for the synthesis of 2-aryl-5-methyl-2,3- dihydro-1H-3-pyrazolones (5) from phenyl hydrazine, methyl acetoacetate, aromatic aldehydes and β -naphthol in the presence of catalytic amounts of zwitterionic-type molten salt in water. (Scheme 1)



Scheme 1

The present methodology shows that zwitterionic-type molten salt is an efficient catalyst in the one-pot, convergent, expedient sequential protocol for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1H-3-pyrazolones from the reaction of arylhydrazine, methyl acetoacetate, aromatic aldehydes and β -naphthol in water under mild reaction conditions in good yields.

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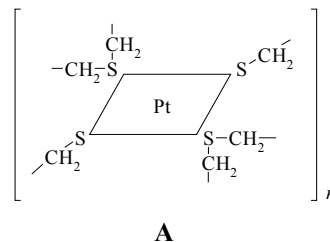
P28: CATALYTIC PROPERTIES OF PLATINUM(II) IMMOBILIZED ON POLYMETHYLENE SULFIDE IN THE HYDROSILYLATION OF ALLYL ETHERS WITH HYDROSILOXANES

M.A. Ilina, M.V. Afonin, D.A. De Vekki, N.K. Skvortsov, S.A. Simanova

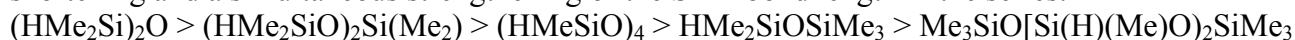
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Despite the successful use of both homogeneous [1–3] and heterogeneous sulfur-containing catalysts of hydrosilylation [4–6], they are often neglected.

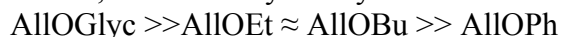
We have developed an efficient way of application of Pt(II) chemisorbed on polymethylene sulfide (complex A) as a catalyst for hydrosilylation of allyl ethers [allyl ethyl (AlIOEt), allyl buthyl (AlIOBu), allyl glycidyl (AlIOGlyc) and allyl phenyl (AlIOPh)] with hydrosiloxanes. One of the advantages of this catalyst is the simplicity of its synthesis [7]. Sulfur atoms that make up the matrix of the sorbent (simultaneously a sulfide and an alkanethiolate ligand) are uniformly distributed throughout the mass and acts as the coordinating atom of a neutral macroligand, which, in addition, prevents dissolution of the immobilized catalyst in the reaction mixture.



Analysis of kinetic data of the catalytic hydrosilylation showed that the reactivity of hydrosiloxanes depends significantly on the electronic and steric characteristics of substituents at the silicon atom. It decreases with increasing effective positive charge on the silicon atom, and it facilitates shortening and a simultaneous strengthening of the Si–H bond length in the series:



In turn, the reactivity of allyl ethers decreases in the series:



The complex of platinum(II) could be reused several times without significant loss of activity and is comparable to the Pt(0)-based catalyst supported on silica containing di(ethylene oxide) units [6]. For example, the conversion of allyl glycidyl ether at first, second and third reuse cycle of complex A is equal to 98.6, 98.5, and 94.5% respectively

The operating temperature range of Pt(II) chemisorbed on polymethylene sulfide in siloxanes under investigation is more than 80°C and depends both on the amount of platinum on the immobilizate (mol/g sorbent) and on the amount of platinum per mole of the reaction mixture.

For the reaction characterized by an induction period, apparently associated with the inaccessibility of platinum and the slow formation of platinum–silicon hydride complex, which is the true catalyst.

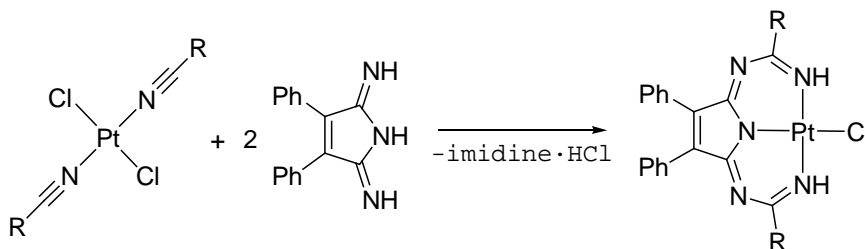
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P29: NUCLEOPHILIC ADDITION OF IMIDINE TO THE TRIPLE CARBON–NITROGEN BOND, ACTIVATED BY Pt(II)

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Interaction of *trans*-[PtCl₂(RCN)₂] (R = Et, Ph, NMe₂, NC₅H₁₀) with 2,5-diimino-3,4-diphenyl-3-pyrroline (imidine) taken in a molar ratio 1:2 in CH₂Cl₂ at 20–25°C results in formation of the unusual adducts (Scheme 1).



Scheme 1

These compounds were characterized by complex of physical and chemical methods (elemental analysis, ESI-MS, IR, ¹H NMR, ¹³C{¹H} NMR spectroscopies). We managed to grow up some crystals, this way the structures of two of compounds in the solid phase were found by X-ray crystallography.

This work was supported by Russian Fund for Basic Research (grant 11-03-00483-a), and the Scientific Council of the President of the Russian Federation (Grant MK-120.2011.3).

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P30: UNSYMMETRIC DIGERMANES: SYNTHESIS, STRUCTURE, PROPERTIES

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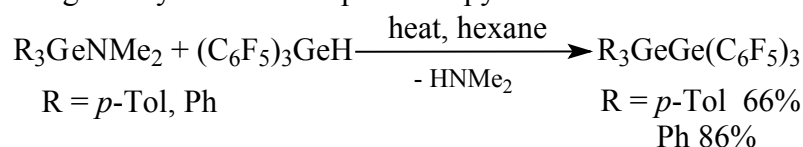
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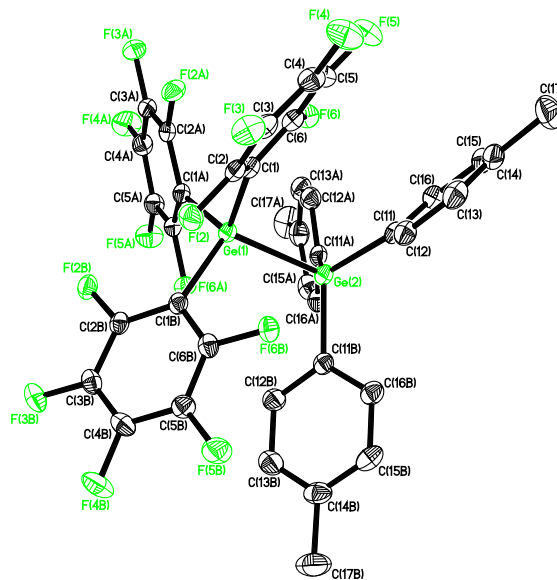
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Oligogermanes may be regarded as models for producing molecular wires. In fact, electrons of single Ge-Ge bond are delocalized across the entire backbone of these molecules [1]. Therefore existence of σ -delocalization in oligogermanes results to appearance of properties similar to unsaturated hydrocarbons (conductivity, thermochromism, non-linear optical properties). It can be assumed that producing unsymmetric digermanes, where each germanium atom has substituents with definite electronic properties, allows obtain compounds with specific features. It may be supposed that most sensible changes in properties appear by introduction of very different substituents (electron-donating or electron-withdrawing) to the end germanium atoms of oligogermane chain.

In the course of this work the number of oligogermanes with unsymmetric substituents were synthesized and investigated by UV/visible spectroscopy.



The composition of the compounds obtained was established on the basis of elemental analysis, and structure was investigated in solution by NMR spectroscopy and in solid state by X-ray analysis.



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P31: SYNTHESIS AND SPECTRAL INVESTIGATION OF SOME NEW HETARYL-SUBSTITUTED HYDROQUINOLINONE DERIVATIVES

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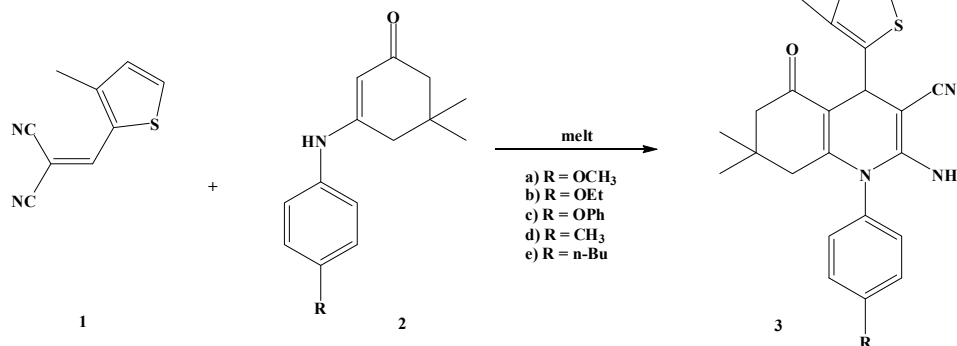
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In recent years, very intensive studies for the synthesizing of heterocyclic compounds have been done because of their important roles as the scaffolds of bioactive substances. Quinoline and its hydro-derivatives are the most popular N-heteroaromatics incorporated into the structures of many pharmaceuticals. It is known that many of hydroquinolinone compounds exhibit a wide spectrum of pharmacological activities, such as antibacterial, antihypertensive, neuroleptic, antipyretic, analgesic, antiphlogistic, antiplasmodial, intrinsic, cytotoxic, antiproliferative, antimalarial, and anticancer activities. Furthermore, these compounds are important precursors in the synthesis of natural products such as alkaloids, azastereoids and toxins^[1].

In this study, the 2-amino-1-aryl-7,7-dimethyl-4-hetaryl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles^[2] **3a-e** (Scheme 1) have been synthesized via condensation of 2-hetarylidenemalononitriles with 5,5-dimethyl-3-arylamino-2-cyclohexanones. The structural elucidation of these compounds were accomplished using IR, mass, elemental analysis, X-ray and 1D (¹H, ¹³C and DEPT), 2D (COSY, HMQC and HMBC) NMR spectroscopic studies at 400 MHz ¹H and 100 MHz ¹³C NMR instrument. The X-ray^[3] analysis reveals that dihydropyridine and cyclohexenone rings adopt boat and envelope conformations respectively (fig.1).



Scheme 1

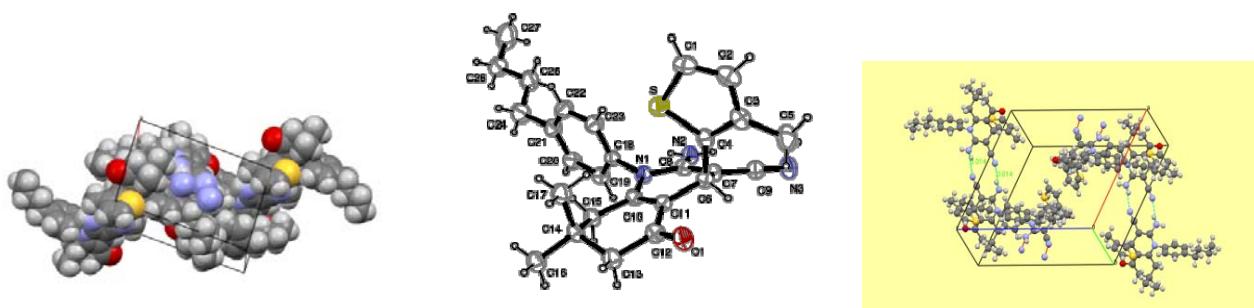


Figure 1

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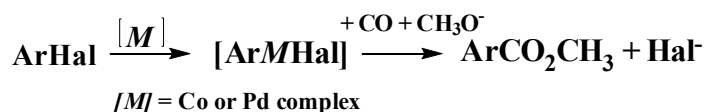
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P32: *ORTHO*-EFFECT IN THE TRANSITION METAL CATALYSED CARBONYLATION OF SUBSTITUTED BROMOBENZENES AS A FUNCTION OF THE METAL NATURE

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An activation of an aryl halide with a transition metal complex named an oxidative addition (OxAdd) is usually a key step in the catalytic cycle of Pd- and Co-catalysed aryl halides methoxycarbonylation [1, 2]:



Therefore, to study the peculiarities of this stage is very important for the effective carbonylation catalysts development.

In this report we have investigated the effect of size and position of substituents on the reaction rate in the carbonylation of various bromoanilines (both unsubstituted and having substituents at the nitrogen atom) using of palladium or cobalt complexes as a catalyst. We have found that the presence of a donor substituent in the benzene ring slows the carbonylation of *meta*- and *para*-bromoanilines for as Pd and Co catalyst systems. The sensitivity to the substituents electronic influence in both cases was close. At the same time the *ortho*-substituent has a fundamentally different effect. The steric hindrance significantly inhibits the process in the case of Pd-catalysed reaction. The reaction slows down the stronger the greater the volume of the substituent in the *ortho*-position to the reaction centre – the bromine atom. When using Co catalyst the situation is reversed: *ortho*-bromoaniline is carbonylated faster than *para*-bromoaniline, and alkyl substituents at the nitrogen atom further accelerate the process.

This dependence of the *ortho*-effect sign from the metal nature can be explained within the concept of several possible ways to activate a halide. A key step of the cobalt-catalysed carbonylation is radical anion non-chain activation of the aryl halide with an anion cobalt complex. In the case of the Pd-catalysed carbonylation the activation of the aryl halide processes via a concerted mechanism (OxIns).

Hence we found an interesting feature can serve as a basis for the catalytic system tuning to a synthetic task.

The authors thank Saint-Petersburg State University for a research grant, the Federal Targeted Program “Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013” (contract P676 from 20/05/2010), and Russian Fund for Basic Research (grant 11-03-00048-a).

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P33: NEW TYPE PALLADIUM(II)-HYDRAZIDOAMINOCARBENE COMPLEXES

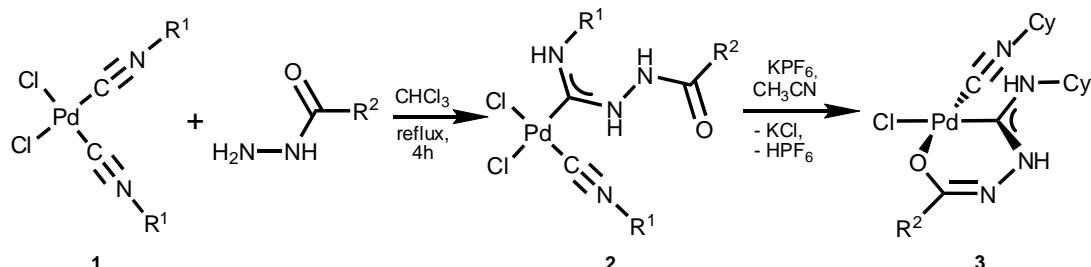
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The coupling of equimolar amounts of the palladium(II)-isonitrile complexes *cis*-[PdCl₂(CNR¹)₂] (R¹ = alkyl) with the various aromatic and aliphatic carbohydrazides R²CONHNH₂ (R² = alkyl, aryl, 12 species) proceeds for ca. 4 h in refluxing CHCl₃. The subsequent workup provides palladium-hydrazidoaminocarbenes **2** in 80–95% isolated yields. Further conversion of the prepared species upon treatment with potassium hexafluorophosphate leads to the intramolecular substitution of the Cl ligands in the metal coordination sphere with the acylhydrazide fragments oxygen atom to form complexes **3** featuring six-membered chelating carbene ligands.



Isolated species were characterized by elemental analyses (C, H, N), ESI⁺-MS, IR, ¹H and ¹³C{¹H} spectroscopies, and two complexes by a single crystal X-ray diffraction.

Prepared carbene complexes exhibit high catalytic activity (TONs up to 9.4×10⁴) in Suzuki–Miyaura cross-coupling of aryl bromides with organoboronic acids (EtOH as environmentally benign solvent, K₂CO₃ as base, 80 °C). Target biaryl species (8 examples) were obtained in high yields (up to 94%). These results are comparable to those previously reported by some of us for the related palladium-diaminocarbenes [1].

This work has been supported by the FTP “Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013” (contract P676 from 20/05/2010), RFBR (grant 11-03-00048-a), and the Fundação para a Ciência e a Tecnologia (FCT), Portugal (including FCT projects PTDC/QUI-QUI/098760/2008 and PTDC/QUI-QUI/109846/2009).

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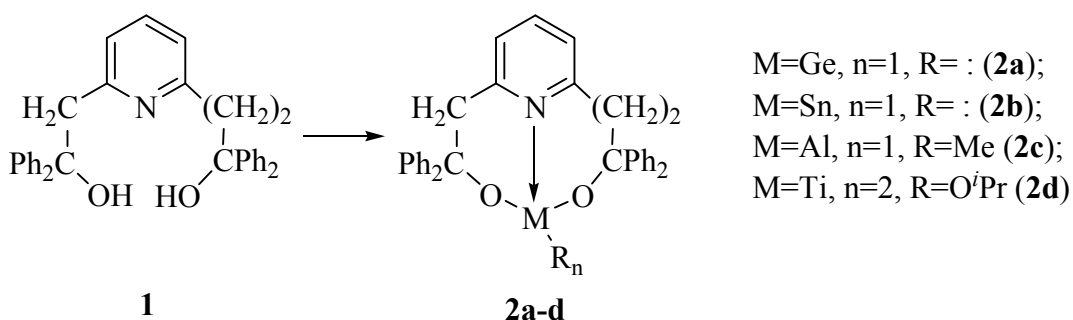
P34: NEW COMPLEXES BASED ON THE NOVEL PYRIDINE-CONTAINING LIGAND

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Dialkanolamines and the related ligands $(\text{RN}(\text{CR}'_2\text{CR}''_2\text{OH})_2)$, $\text{R}=\text{Alk, Ar}$; $\text{R}'=\text{H, Alk, Ar}$; $\text{R}''=\text{H, Alk, Ar}$) are fruitful for the synthesis of a large number of the derivatives of Ge, Sn and Ti [1-4]. Such compounds and also aluminum ones can be regarded as perspective catalysts for many organic transformations (transition-metal germylene (stannylene) complexes for cross-coupling, aluminum and titanium compounds for polymerization reactions). A structure of a catalyst has a great influence on a result of the reaction catalyzed. This led us to expand a series of pyridine-containing ligands. A new ligand (**1**) has been synthesized. The compounds of Ge, Sn, Al and Ti based on the new ligand were obtained.



Structures of the compounds obtained were established by ^1H , ^{13}C and ^{119}Sn (in the case of **2b**) NMR spectroscopy. A composition was confirmed by elemental analysis. The catalytic activity of the compounds in the ring opening polymerization of cyclic esters is under investigation.

Grant of the President of the Russian Federation for state support of young Russian scientists – doctors (MD-3634.2012.3).

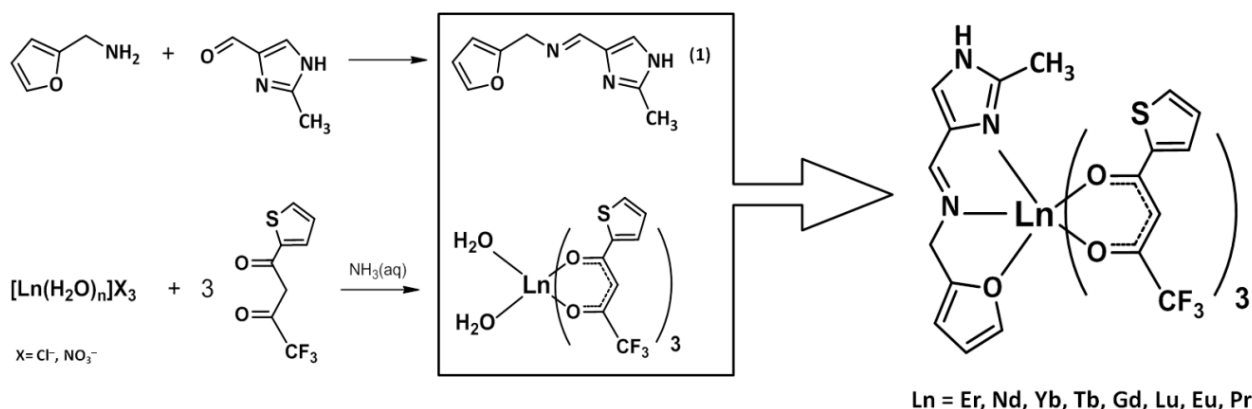
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P35: SHELL LANTHANIDE COMPLEXES CONTAINING NEW POLYTOPIC SCHIFF BASE WITH IMIDAZOLE RING

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New Schiff base (1) was first synthesized by the reaction of furfurylamine and equimolar amount of 2-methyl-1H-imidazole-4-carbaldehyde. The reaction proceeds in dry methanol at room temperature in quantitative yield. The composition and structure of the compound (1) were established by ^1H NMR and IR spectroscopy, mass spectrometry and elemental analysis.



Compound (1) can act as a chelating agent toward the hard Lewis acids. We investigated the reactions of the polidentate ligand (1) with Ln-thenoyltrifluoroacetate complexes ($\text{Ln} = \text{Er}, \text{Nd}, \text{Yb}, \text{Tb}, \text{Gd}, \text{Lu}, \text{Eu}, \text{Pr}$). As a result, 8 new neutral "shell" complexes of rare earth metals were obtained and fully characterized by IR spectroscopy, CHN analysis; ^1H , ^{19}F , ^{19}F - ^{19}F NOESY, ^1H - ^{15}N HMBC NMR spectroscopy; FAB and HR-ESI mass spectrometry.

Luminescence properties of all the species obtained have been also studied. It was found that Europium complex display bright red phosphorescence in solid state and solution, whereas other compounds demonstrate no luminescence in visible region.

The authors greatly appreciate financial support of Saint Petersburg State University research grant 12.37.132.2011

P36: INVESTIGATION OF THE BIOLOGICAL ACTIVITY OF ORGANOMETALLIC COMPLEXES OF PLATINUM

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Complex compounds of platinum are widely used in clinical practice in the treatment of malignant tumors. The most famous include cisplatin, carboplatin (karboplatam) and oxaliplatin, as well as their modification and combination with other pharmaceuticals. It is known that cisplatin ($\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$) slowly and very slightly soluble in water and isotonic sodium chloride solution. Poor solubility of cisplatin and its high systemic toxicity in combination with the lead almost indispensable to the fact that the world attempts to chemical modification to reduce toxicity and improve solubility. Thus, the American approach to the modification of cisplatin is the synthesis of new compounds, where one of the ligands is substituted for the other biogenic ligands or amino acid in order to reduce the overall toxicity of cisplatin.

In the course of studying the properties of binuclear complexes of platinum(II) synthesized by us was investigated antitumor activity of compounds with the α -amino acids (LH) glycine, alanine, valine. Their composition is $[\text{Pt}_2(\text{L})_2(\text{NH}_3)_4](\text{NO}_3)_2$.

The main purpose of *in vitro* studies is to assess the potential direct cytotoxic effect of anticancer drugs and to identify possible differential sensitivity of human tumor cells of various origins to the investigated compounds. The study can be conducted at all stages of the development of new drugs. The system of selection and study of compounds with potential anticancer activity *in vitro* is based on determining the degree of suppression of cell growth under the influence of the test agent. In this case, the following evaluation methods: the method of cell counting, MTT test, ^3H -thymidine test.

Evaluation of antitumor properties of compounds $[\text{Pt}_2(\text{L})_2(\text{NH}_3)_4](\text{NO}_3)_2$ was carried ^3H -thymidine by cells in mastocytoma R815, lymphoma L1210. Cells were seeded at a concentration of 10×10^3 /well were incubated with compounds for 24 hours, 6 hours before the end of incubation, have made a mkKi H^3 -thymidine. At the end of incubation, cells were harvested on glass-fiber filters ("Flow Lab") using the apparatus Harvester ("Titertek"). Results are expressed as imp./min. thymidine incorporation in 10×10^3 cells (average of triplet). The degree of suppression of tumor cell growth under the influence of test compounds was calculated by the formula: $N = (\text{experience} / \text{control}) \times 100\%$. Data on the inhibition of proliferative activity of tumor cells under the influence of the test compounds were obtained with respect to the reference values of proliferative activity of these cells.

All complexes were tested in doses of 0.5 and 5.0 mkg /ml. As the anticancer drug cisplatin comparison, using a dose of 0.5 and 5.0 mkg /ml. Data on the effect of the investigated dinuclear complexes of platinum(II) on the proliferative activity of tumor cells *in vitro* showed that the compound containing valine, at a dose of 0.5 mkg/ml exhibits immunosuppressive properties that are comparable to cisplatin.

P37: REE CYMANTRENECARBOXYLATES, THE NEW ORGANOMETALLIC 3D-4F-HETEROMETALLIC COMPLEXES

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Heterometallic 3d-4f-carboxylates containing transition metal in an organometallic moiety represent the poorly studied class of compounds despite their interesting properties: the possibility to combine specific properties of the organometallic part and of rare earth ion and their potential to be molecular precursors for mixed-oxide functional materials. Until recently only the derivatives of ferrocene (see references in [1]) and the single complex containing Sm^{3+} and a cluster fragment $(\text{CO})_9\text{Co}_3(\mu_3\text{-C-})$ [2] were known. Lately we have obtained and studied 3d-4f-carboxylates containing the cymantrene (cyclopentadienyltricarbonylmanganese) moiety [1].

New binuclear REE cymantrenecarboxylate complexes, $[\text{Ln}_2(\mu\text{-O}, \eta^2\text{-OOCcym})_2(\mu\text{-OOCcym})_2(\text{DMSO})_4]$ ($\text{Ln} = \text{Ce}$ (1), Nd (2), Eu (3), Gd (4), Dy (5); $\text{Cym} = (\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$), $[\text{Ln}_2(\mu\text{-OOCcym})_4(\text{DMSO})_4(\eta^2\text{-NO}_3)_2]$ ($\text{Ln} = \text{Tb}$ (6), Dy (7)) and the polymeric $[\text{Er}(\eta^2\text{-OOCcym})_2(\mu\text{-OOCcym})_4\text{Er}(\text{H}_2\text{O})_4]_n \cdot 3n\text{THF}$ (8) were synthesized and characterized by means of X-ray analysis. Complexes 1–5 are isomorphous; 6 is isostructural with 7. Thermal decomposition of the complexes was studied by means of DSC and TG methods. The final product of thermolysis of 1 in air is the mixture of CeO_2 и Mn_3O_4 ; 2, 3, 4, 5 and 8 under the same conditions afford the mixture of LnMn_2O_5 and Mn_2O_3 , 6 and 7 afford LnMn_2O_5 .

The evaluation of the $\text{Ln-OS}(\text{CH}_3)_2$ bond energy for complexes 1–4 was carried out. It was shown that complex 2 can serve as the catalyst for *trans*-stereoregular polymerization of 2,3-dimethyl-1,3-butadiene under UV irradiation.

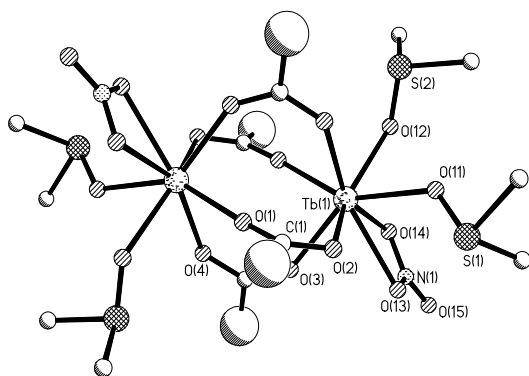


Fig 1. Molecular structure of 6.

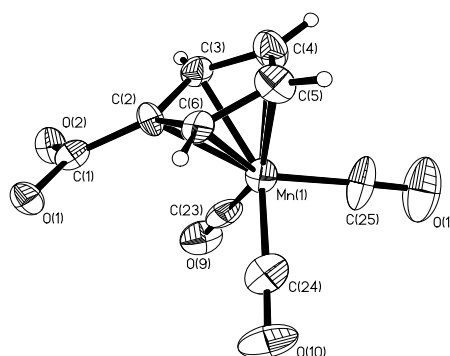


Fig. 2. The structure of CymCOO moiety.

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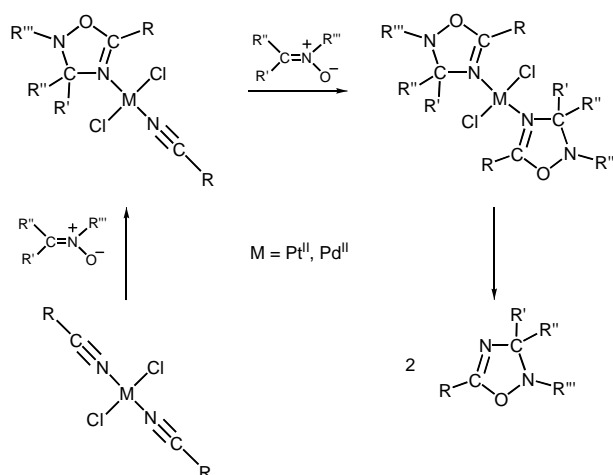
This study was financially supported by the RFBR (project nos. 11-03-00644), the Council on Grants of the President of the Russian Federation (grants, NSh-1670.2012.3), the Ministry for Education and Science of the Russian Federation (SC-P850)

P38: PALLADIUM(II)-MEDIATED CYCLOADDITION OF ACYCLIC NITRONES TO NITRILE LIGANDS

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Metal-mediated 1,3-dipolar cycloaddition (DCA) of nitrones to nitriles is an important route for synthesis of such rare group of heterocyclic compounds as 2,3-dihydro-1,2,4-oxadiazoles. The preparation of 2,3-dihydro-1,2,4-oxadiazoles from the *bis*-nitrile complexes (Scheme) *via* metal-mediated DCA includes a consecutive two-step DCA of the nitrone to each of the nitrile ligands and the liberation of newly formed heterocyclic ligands from the *bis*-dihydrooxadiazoline complexes.



The previous studies demonstrated that the aldonitrones $Z\text{-ArCH=N(O)Alk}$ react with the dialkylcyanamide ligands Alk_2NCN in their Pt^{II} complexes, while the more reactive ketonitrones $\text{Ph}_2\text{C=N(O)C}_6\text{H}_4\text{R}'$ ($\text{R}' = \text{H}, \text{Me}, \text{OMe}, \text{Cl}$) undergo facile DCA to the Pt^{II} -bond species RCN such as dialkylcyanamides ($\text{R} = \text{NMe}_2, \text{NEt}_2, \text{NC}_5\text{H}_{10}$) and even less dipolarophilic alkylnitriles ($\text{R} = \text{Et}$). However, the liberation of the 2,3-dihydro-1,2,4-oxadiazoles can be achieved only by use of NaCN due to very strong σ -donor properties of the heterocycles. In the current work, we found that Pd^{II} center efficiently activates the nitrile ligands toward DCA of the aldo- and ketonitrones. Moreover, the decooordination of the formed heterocyclic ligands can be easily achieved by phosphines or amines.

In addition, we report that a Pd^{II} center activates nitrile ligands toward DCA of nitrones substantially higher than the corresponding Pt^{II} center. We also propose synthetically more favorable method for the decooordination of the heterocycles and provide evidences on the reversibility of Pd^{II} -mediated DCA of the ketonitrones to nitrile ligands (this phenomenon for Pt^{II} -mediated processes was previously discovered in our group).

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P39: STRUCTURE-ACTIVITY RELATIONSHIP OF Pd(II) COMPLEXES WITH N-HETEROCYCLIC LIGANDS

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Palladium(II) complexes with nitrogen donor ligands have received much attention due to their remarkable catalytic and biological activity. Pd(II) complexes are used as active catalyst, particularly, in the carbonylation of aromatic nitrocompounds to carbamates, ureas and amines. Comprehensive investigation on the substituent effects in the pyridine ring on the catalytic activity of PdCl₂(X_nPy)₂ complexes (where Py = pyridine; X = CH₃ or Cl; n = 0–2) for carbonylation of nitrobenzene to ethyl N-phenylcarbamate has been recently conducted by us in Laboratory of the Physicochemical Fundamentals of Chemical Technology at Warsaw University and reported [1]. Here, we applied X-ray characterization, UV-Vis and Time-Dependent Density Functional Theory (TD-DFT) calculations for twelve PdCl₂(X_nPy)₂ complexes (where: Py = pyridine; X = CH₃ or Cl; n = 0–2) in order to investigate substituent effects on their crystal structures and electronic properties and to combine the results with their catalytic activity. PdCl₂(X_nPy)₂ complexes were used as catalysts in reductive carbonylation of nitrobenzene (NB) to aniline (AN) in the presence of CO/H₂O mixture:



Application of mixture CO/H₂O instead of H₂ allows for selective reduction of nitro group even if other functional group are present in aromatic ring of NB.

The structures of complexes PdCl₂(3-MePy)₂, PdCl₂(4-MePy)₂, PdCl₂(2-ClPy)₂, PdCl₂(2,4-Me₂Py)₂, PdCl₂(3,5-Me₂Py)₂ and PdCl₂(2,6-Cl₂Py)₂ have been described for the first time and we compared our results with available data for the whole series of twelve complexes. All compounds exhibit a square planar coordination geometry in which the palladium ion coordinates two nitrogen atoms of pyridine ligands and two chlorine atoms in *trans* positions. For X_nPy the energies of π–π* and n–π* transitions depend on the position and nature of X substituent in X_nPy ring. The UV-Vis spectra of PdCl₂(X_nPy)₂ confirm square planar coordination geometry of complexes **I–XII** and two dπ–π* transitions are expected. With the help of the Time-Dependent Density Functional Theory calculations we proved that dπ–π* transitions in solutions of PdCl₂(XPy)₂ complexes result from MLCT (metal-to-ligand charge transfer) with contribution from chlorine atoms to palladium [2]. We also studied substituent effects on catalytic activity of Pd(II) complexes in reduction of NB to AN by the use of CO/H₂O. Catalytic activity depends on nature and position of substituent in the pyridine ring of PdCl₂(X_nPy)₂ and the rate of the process is accelerated by decreasing electron density on the metal center. PdCl₂ complexes with X_nPy ligands are effective and selective catalysts for reductive carbonylation of NB to AN.

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P40: ALUMINUM COMPLEXES BASED ON PYRIDINE-CONTAINING DIALCOHOLS AS PERSPECTIVE CATALYSTS OF RING-OPENING POLYMERIZATION OF CYCLIC ESTERS

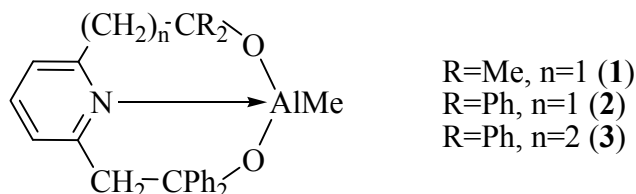
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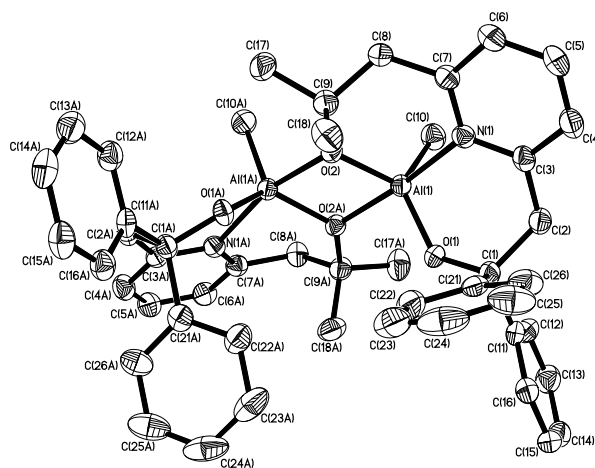
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Polyactides and related materials have been widely used in many applications due to their unique biodegradability and biocompatibility. Ring-opening polymerization initiated by aluminum complexes constitute the most effective and versatile synthetic strategy for preparing polyactides with a wide range of physical, mechanical, and degradation properties. Over the past decade, several aluminum species with N,O-donor ligands have been found to be particularly efficient as ring-opening polymerization catalysts [1].

In the course of this work a series of pyridine-containing tridentate ligands have been synthesized. Reaction of these ligands with AlMe₃ yields the aluminum complexes (1–3).



The crystal structure of the compound **1** was studied by X-ray analysis.



The compounds obtained are under investigation of their catalytic activity in ring-opening polymerization of cyclic esters (*D,L*-lactide, ϵ -caprolactone).

This work is supported by the RFBR (12-03-00206-a) and by President Grant for Young Russian Scientists (MD-3634.2012.3).

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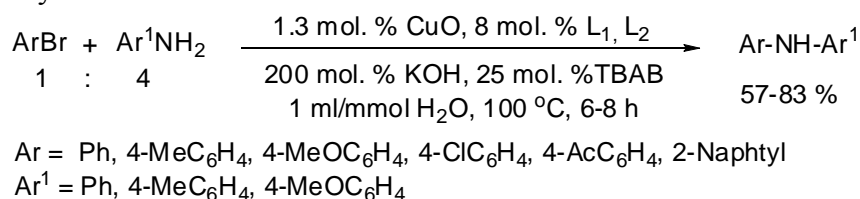
P41: N²-MONOSUBSTITUTED OXALIC ACID BISHYDRAZIDES: NOVEL EFFECTIVE LIGANDS FOR COPPER-CATALYZED CROSS-COUPLING REACTIONS IN WATER

D.V. Kurandina, E.V. Eliseenkov, A.A. Petrov, V.P. Boyarskiy

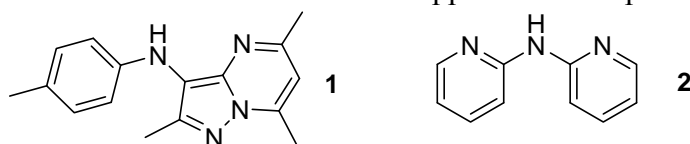
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Transition metal-catalyzed formation of carbon–nitrogen bonds via cross-coupling reactions represents a powerful tool for preparation of numerous important products. During the past decade copper-mediated Ullmann-type processes have attracted much attention due to the low cost of copper and the use of readily accessible ligands. It provides an indisputable advantage over the expensive Pd/ligand systems. N²,N^{2'}-Disubstituted oxalic acid bishydrazides [1] and pyrrole-2-carbohydrazides [2] were found to be effective ligands for copper-catalyzed C–N coupling reaction in water even without inert atmosphere. These coupling reactions required high reaction temperatures (120–140 °C) under microwave heating in closed vessels and high catalyst (5 mol%) and ligands (25 mol%) loadings. Therefore, the goal of our work was to find a more active catalytic system with lower amounts of copper and ligands and to obtain more economically competitive methods that allow reactions to be conducted under milder conditions.

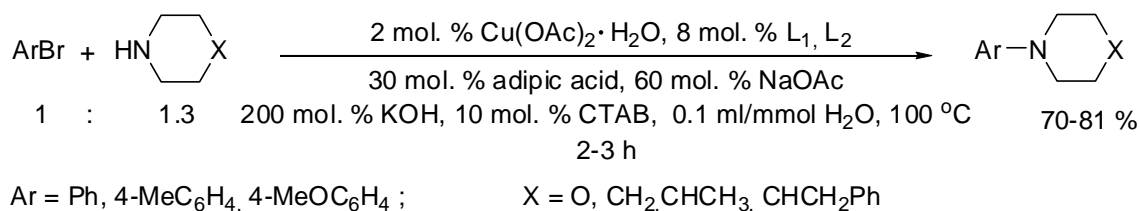
We have studied N²-monosubstituted oxalic acid bishydrazides and found that oxalic acid hydrazide-(N'-phenyl-hydrazide) (L₁) with equimolar amounts of hexane-2,5-dione (L₂) is the most effective ligand that enables to achieve the goal and to develop a reliable and scalable recipe for the preparation of diarylamines.



The procedure for C-N cross-coupling reactions with new catalytic system has been extended with some modifications to hetaryl halogenides – 3-bromo-2,5,7-trimethylpyrazolo[1,5-*a*]pyrimidine and 2-chloropyridine. Amines **1** and **2** were obtained in copper-mediated processes for the first time.



Moreover, our catalytic system (unlike the systems, described in [1, 2]) provides a way to more effective method for N-arylation of hydrophilic secondary heterocyclic amines as well. The optimized reaction conditions differ significantly from that for N-arylation of the anilines mentioned above. The rate enhancement is due to the salting-out effect and the decrease of water content.



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P42: THE RELATIONSHIP BETWEEN THE TYPE OF SOLVATION AND PHOTOPHYSICAL PROPERTIES OF CHLOROPHYLL A IN HOMOLOGOUS SERIES OF ORGANIC SOLVENTS

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Photophysical properties and photocatalytic activity of chlorophyll a (Chl a) in biological and biomimetic redox reactions is highly influenced by the aggregation state of the pigment and the number and nature of axial ligands [1]. The monomeric form of Chl a is known to be efficient in stable excited triplet states formation under visible light irradiation, which are capable of generating reactive oxygen species and provide the electron transfer to acceptor molecules. In contrast, associated species of the pigment possess extremely short lifetime of triplet states and thus are less active in photochemical processes [2]. Both specific and nonspecific solvation determine the functional activity of chlorophyll molecules in photosynthetic pathways, so the study of the correlation between the type of solvation, photophysical properties and photochemical activity of Chl a in different organic solvents (especially within homologous series) is useful for biomimetic modeling and creation of artificial photosynthetic systems.

In homologous series of inert solvents (alkanes, arenes) due to nonspecific solvation the main spectral parameters (position of the absorption bands, molar absorptivity, half-width of the absorption band, the oscillator strength and lifetime of the first singlet excited state) of chlorophyll a were found to be rather similar. In contrast, the interaction of various alcohols with Chl a molecules occurs mainly via specific solvation associated with different nucleophilicity of the homologs, which provides a substantial variation in the values of all spectral parameters. For example, increasing in the extinction coefficient of Chl a in butanol-2 compared with butanol-1 can be attributed to a stronger axial coordination of the solvent molecules due to greater nucleophilicity of the hydroxyl group in the secondary alcohol because of the positive inductive effect of the two alkyl substituents.

The greatest influence on the shape and position of the absorption bands in Chl a spectrum have coordinating solvents such as pyridine, DMSO, DMF, THF and dioxane due to axial coordination to the Mg atom or/and π - π interactions, involving aromatic system of the macrocycle. It was shown that the most nucleophilic solvents from different classes of organic compounds with different polarity and polarizability have similar values of the half-width of the Q-band in a narrow range of wave numbers from 490 to 500 cm^{-1} .

The presence of donor molecules (imidazole, histidine, EDTA) in an aqueous Chl a solution does not significantly alter the position of the absorption band, but increases molar absorptivity in the Q-band, indicating the coordination to the metal atom.

For micellar solutions of different surfactants and biopolymers simulating microheterogeneous environment of Chl a molecules in an intercellular medium the band shape and molar extinction was found to be strongly dependent not only on the charge of the micellar surface, but also on the nature of the solvent.

The obtained correlations contribute to better understanding of the mechanism of intermolecular interactions between the chlorophyll molecules and their biomacromolecular environment in vivo, which allows to establish the correspondence between the type of solvation, molecular organization and photocatalytic activity of the pigment in biomimetic systems and photovoltaic devices.

The work was supported by Grant No MK-227.2011.3 of the President of RF.

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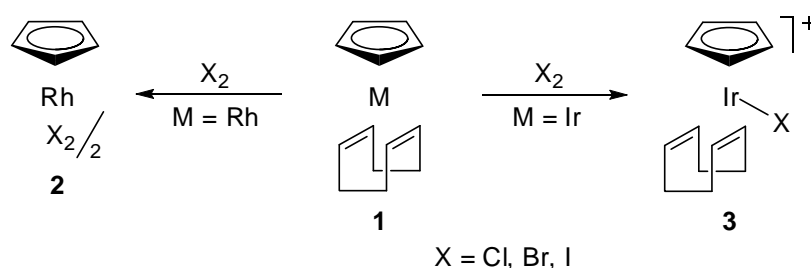
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P43: HALIDE RHODIUM AND IRIIDIUM COMPLEXES AND THEIR SYNTHETIC APPLICATION

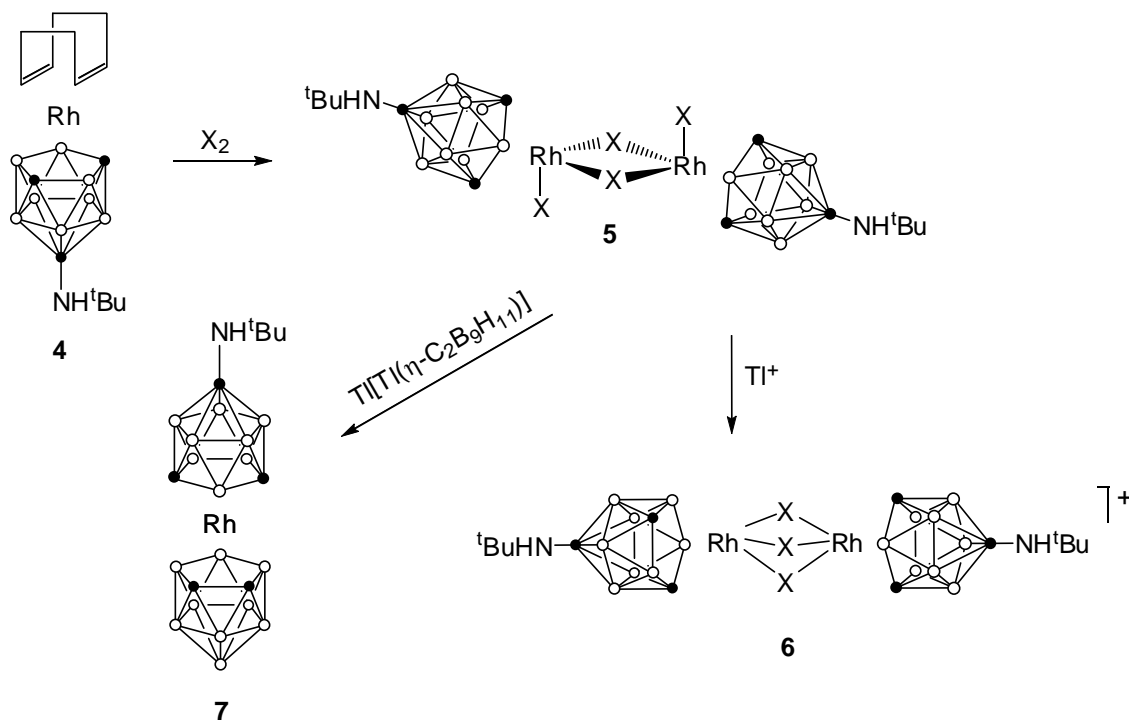
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The pentamethylcyclopentadienyl rhodium and iridium complexes $[\text{Cp}^*\text{MX}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are widely used in organometallic synthesis and homogeneous catalysis. We prepared similar complexes with Cp, indenyl, dicarbollide and tricarbollide ligands. For instance, in the case of rhodium the cyclooctadiene complex **1** reacts with halogens giving dimeric halides **2**. In contrast, analogous reaction of iridium derivative stops on the stage of the formation of cations **3**.



The reaction of **4** with halogens gives the (tricarbollide)rhodium halides **5**, which have dimeric structure. Interaction of **5** with TlBF_4 affords the cationic dinuclear complex **6** as a result of abstraction of one halide anion. The reaction of **5** with $\text{Tl}[\text{Tl}(\eta\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11})]$ leads to the unsymmetrical bis(carborane) complex **7** containing both dicarbollide and tricarbollide ligands.



These and other similar rhodium and iridium halides will be discussed, along with their reactivity and structures.

This work was supported by the Presidium of Russian Academy of Sciences (program P7).

P44: NOVEL PHOTOPHYSICAL APPROACH TO UNRAVELING COORDINATIVE INTERACTION IN HOMOGENEOUS GROUP IV METALLOCENE SYSTEMS

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Early-transition metal metallocenes $(\pi\text{-L})_2\text{MX}_n$ have been a cornerstone in the development of modern coordination organometallic chemistry and catalysis. Despite a number of promising commercial and fundamental applications, a principle relation “structure – properties”, as well as patterns of reactivity of this important organometallic family still remains unresolved.

Recently, we initiated [1–4] a systematic study of photophysics of d^0 group IV metallocenes, possessing rare highly emissive (for Cp_2MCl_2 where $\text{Cp} = \text{C}_5\text{H}_5^-$, $\text{M} = \text{Zr}$ and Hf : $\Phi = 1$ at 77 K), extremely long-lived (τ in the range of milliseconds at 77 K) ligand-to-metal charge transfer (LMCT) excited states. Noteworthy, LMCT states appear to be the less studied type of excited states [1]. Notably, luminescent complexes are particularly useful as the loss of luminescence (quenching) can be a sign that the complex is reacting/interacting with another species rather than undergoing radiative decay and further may be applied, e.g., as fine photosensor tools.

The present contribution will provide an overview of novel experimental and theoretical data on photophysics and photochemistry of d^0 group IV metallocenes with respect their prominent use in homogeneous catalysis and also for phosphorescent devices and photosensors. Namely, we have developed first photophysical approach to estimate orbital nature of rare long-lived LMCT excited states and also coordinative interaction of basic components of catalytic systems for polymerization: group IV metallocene complexes as the catalyst precursors and unsaturated hydrocarbon as the substrates. Our on-going study results provide a new example of triplet energy transfer use for studying intermolecular interactions, in particular, the first example of systematic study of coordination between unsaturated hydrocarbons and d^0 π -complexes by the energy transfer approach. It should be emphasized that the photophysical approach enables studying fine intermolecular interactions in homogeneous systems with catalytic concentrations of metal complexes that cannot be achieved by other conventional (e.g. NMR) physico-chemical methods. The approach to estimate the orbital nature of extremely long-lived LMCT excited states and to reveal coordinative interactions of basic components of polymerization catalysts (d^0 bent metallocenes and unsaturated hydrocarbon substrates) will be overviewed in depth.

In summary, a combined photophysical and theoretical approach made it possible to carry out study of the phenomenon of monomer coordination in practical catalytic or near-practical conditions, that is of crucial importance for understanding mechanism and prediction of a multistage catalytic process of unsaturated compounds polymerization with organometallic complexes, particularly, d^0 metal complexes.

Acknowledgement. The author gratefully acknowledges Professor A.E. Shilov for stimulating discussion and Russian Foundation for Basic Research (grant N 12-03-00984), Presidium of RAS, and Division of Chemistry and Material Sciences of RAS for financial support.

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P45: ASYMMETRIC HYDROGENATION OF KETONES CATALYZED BY IRIIDIUM AND RHODIUM COMPLEXES OF FERROCENYL P,S LIGANDS. REACTIVITY AND MECHANISTIC ASPECTS

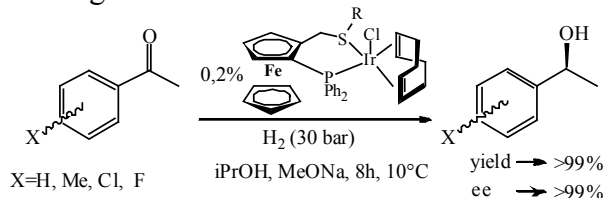
E. Manoury¹, R. Poli¹, J.-C. Daran¹, S. Vincendeau¹, E.M. Kozinets¹, N.V. Belkova², O.A. Filippov², E.S. Shubina², J.M. Hayes³, G. Ujaque³, A. Lledos³

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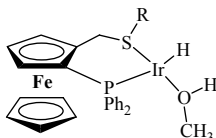
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Iridium complexes of chiral ferrocenyl phosphane-thioether ligands have been successfully used in the asymmetric hydrogenation of unfunctionalized ketones. In the presence of a base, high activities (global TOF up to 250 h⁻¹, TON up to 1500) and good to excellent enantioselectivities (ee up to >99% at 10°C) have been observed [1]. The analogues rhodium complexes have also recently synthesized [2] and proved to be good structural and functional models of these catalysts.



Scheme 1.

Mechanistic proposals based on theoretical calculations for this unprecedented catalytic system, will be also presented. We propose that the catalytic reaction occurs through a heterolytic activation of H₂ via a monohydride-methanol complex.



A stoichiometric investigation of the Rh and Ir precatalyst hydrogenation (1–3 bars H₂) in the presence of alcohol (MeOH, iPrOH), carried out by NMR and UV/Vis spectroscopy in order to identify catalytic species, will be also presented.

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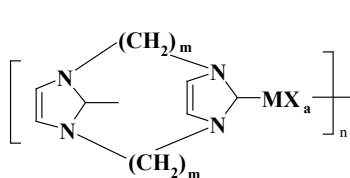
P46: SYNTHESIS AND CATALYTIC ACTIVITY OF BIS- AND POLYCARBENE COMPLEXES OF TRANSITION METALS

K.A. Marichev, N.I. Korotkikh, A.V. Kiselyov, V.S. Saberov, O.P. Shvaika

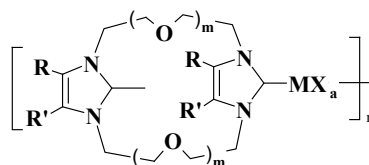
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Among the known polymeric complexes of transition metals conjugated palladium compounds on the basis of biscalrenes were reported earlier [1, 2]. Macrocyclic palladium biscalrene complexes containing calixarene backbone were also synthesized and their catalytic properties in Suzuki cross-coupling were estimated [3]. However, polymeric macrocyclic complexes containing cyclophane- and crown-biscalrene ligands and complexes on the basis of polycarbene have been unknown up to now.

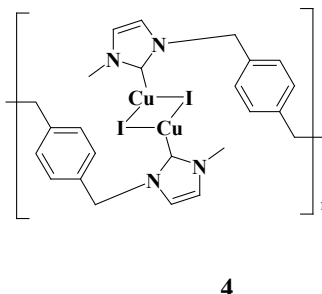
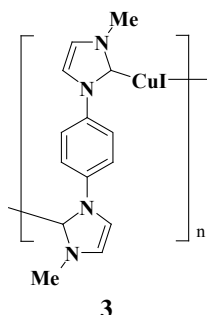
Our research was focused on the synthesis of new types of macrocyclic biscalrene complexes **1–4** of transition metals (copper, palladium and nickel). Polymeric carbene complexes **1a–d**, **2a–c**, **2e** were synthesized *in situ* from the corresponding bisazolum perchlorates and sodium hydride or potassium *tert*-butoxide in the presence of transition metal salts. Carbene complexes of copper(I) **2d** and silver **2f** were obtained from the corresponding crown-bisazolum acetylacetonate under the action of copper(I) iodide or silver nitrate. Bis- and polycarbene complexes **3**, **4** were successfully synthesized from the carbenes, generated *in situ* from the respective bis- and polyazolum salts, and copper(I) iodide (molar ratio 1:1). Molecular weights of the obtained complexes and their precursors were determined by liquid chromatography. The narrow distribution of molecular weights was observed in complex **2d** (M_w 43800; M_n 42400; $M_w/M_n = 1.04$) and polyazolum salt (precursor for complex **4**) (M_w 68800; M_n 63100; $M_w/M_n = 1.09$).



$m=4$, $M=Cu$, $X=I$, $a=1$ (**1a**);
 $m=12$, $M=Cu$, $X=I$, $a=1$ (**1b**);
 $m=4$, $M=Ni$, $X=Cl$, $a=2$ (**1c**);
 $m=4$, $M=Pd$, $X=Cl$, $a=2$ (**1d**)



$m=1$, $R,R'\square=H$, $M=Cu$, $X=I$, $a=1$ (**2a**);
 $m=1$, $R,R'\square=H$, $M=Ni$, $X=I$, $a=2$ (**2b**);
 $m=1$, $R,R'\square=H$, $M=Pd$, $X=Cl$, $a=2$ (**2c**);
 $m=1$, $R,R'\square=(CH)_4$, $M=Cu$, $X=I$, $a=1$ (**2d**);
 $m=2$, $R,R'\square=(CH)_4$, $M=Cu$, $X=I$, $a=1$ (**2e**);
 $m=1$, $R,R'\square=(CH)_4$, $M=Ag$, $X=NO_3$, $a=1$ (**2f**)



Catalytic properties of carbene complexes **1–4** were studied for the reduction of aromatic ketones under the action of 2-propanol in the presence of potassium hydroxide. It was found that complex of copper(I) **2d** is the most effective in this reaction (TON 85000, TOF 32000 h⁻¹).

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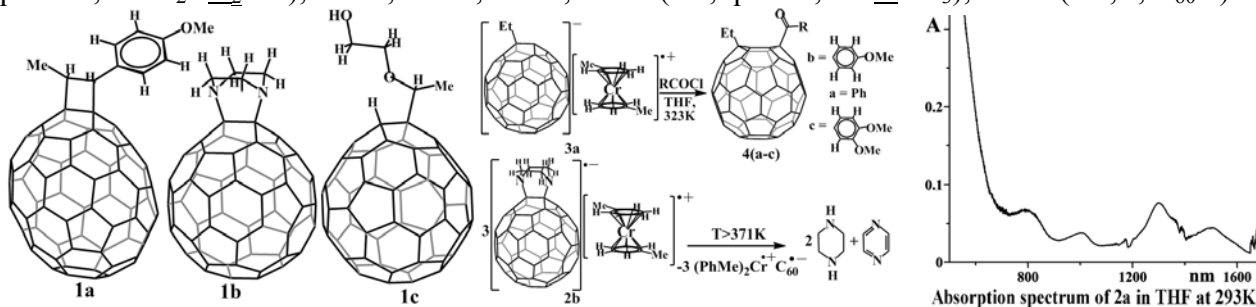
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P47: NEW BIS(ARENE)CHROMIUM FULLERENE DERIVATIVE SALTS

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(PhMe)₂Cr⁰ (**1d**) reacts with (1'-(4-methoxyphenyl)-2'-methylcyclobuta)[3',4':1,2][70]fullerene (**1a**), piperazino[1',4':1,2][60]fullerene (**1b**) and 1-(1-(2-hydroxyethoxy)ethyl)-2-dihydro[60]fullerene (**1c**) at 293K in PhMe to form (1'-(4-methoxyphenyl)-2'-methylcyclobuta)[3',4':1,2][70]fulleride (PhMe)₂Cr⁺(MeOC₆H₄CHCHMeC₇₀)⁻ (**2a**), piperazino[1',4':1,2][60]fulleride (PhMe)₂Cr⁺(N(CH₂CH₂)₂NC₆₀)⁻ (**2b**) and 1-(1-(2-hydroxyethoxy)ethyl)-2-dihydro[60]fulleride (PhMe)₂Cr⁺(HOCH₂CH₂OCHMeC₆₀H)⁻ (**2c**). **2a**, **2b** and **2c** are insoluble in aliphatic solvents, sparingly soluble in aromatic solvents, soluble in THF. UV-vis (THF, 293K) **2a**: 1007, 1300, 1500 (**1a**⁻), **2b**: 480-640, 775, 998 (**1b**⁻), **2c** 991 nm (**1c**⁻). EPR (crystal, 293K) **2a**: single line, satellites, *g* = 1.98586, corresponding to dimer [**1d**⁺]₂[**1a-1a**]²⁻. Above 320K *g* factor changes, at 350 K *g* = 1.98687. **2b**: single line, *g* = 1.99251, Δ*H*=21G, at 120K *g* = 1.99083. EPR **2b** (THF, 293K): *g* = 2.00011 corresponding to **1a**⁻ and a hyperfine line corresponding to **1d**⁺, *g* = 1.98669, *a_H* = 3.65G. **2b** decomposes in THF at 348K to form (PhMe)₂Cr⁺(C₆₀)⁻ (**2d**). Crystalline **2b** begins to decompose above 371K (*P* = 10⁻² Torr) to form piperazine : pyrazine (2:1 molar ratio) and **2d**. Initial **1b** begins to decompose above 463K (*P* = 10⁻² Torr) to form C₆₀ and piperazine. **1d**⁰ reacts with EtC₆₀-C₆₀Et in THF at 314 K to form ethyl[60]fulleride (PhMe)₂Cr⁺(EtC₆₀)⁻ (**3a**). **3a** is insoluble in aliphatic and aromatic solvents, soluble in THF. UV-vis(THF, 293K): 659, 900-1000 nm, EPR(THF, 293K): *g* = 1.98651. **3a** reacts with acid chlorides RCOCl (*R* = Ph, (4-methoxyphenyl), (3,4-dimethoxyphenyl)) at 323 K in THF to form 1-ethyl-4-benzoyl-1,4-dihydro[60]fullerene (**4a**), 1-ethyl-4-(4-methoxybenzoyl)-1,4-dihydro[60]fullerene (**4b**), 1-ethyl-4-(3,4-dimethoxybenzoyl)-1,4-dihydro[60]fullerene (**4c**). NMR ¹H (CDCl₃) **4a** (400 MHz): δ = 1.718, 1.737, 1.756 (3H, t, C₆₀CH₂CH₃), 2.994, 3.009, 3.012, 3.028, 3.046, 3.051, 3.070, 3.088, 3.103, 3.120 (2H, C₆₀CH₂CH₃), 7.611, 7.629, 7.649 (2H, t, arom), 7.701 (1H, m, arom), 8.584 (2H, m, arom). **4b** (200 MHz): δ = 1.696, 1.733, 1.770 (3H, t, C₆₀CH₂CH₃), 3.058, 3.076, 3.094, 3.114 (2H, dd, C₆₀CH₂CH₃), 3.945 (3H, s, OMe), 7.089, 7.134 (2H, d, arom.), 8.720, 8.765 (2H, d, arom.). **4c** (400 MHz): δ = 1.729, 1.748, 1.766 (3H, t, C₆₀CH₂CH₃), 3.027, 3.045, 3.060, 3.063, 3.079, 3.097, 3.115, 3.133, 3.148, 3.152, 3.167, 3.185 (2H, C₆₀CH₂CH₃), 4.020 (6H, s, OMe), 7.066, 7.088 (1H, d, arom.), 8.143, 8.148 (1H, d, arom.), 8.637, 8.643, 8.659, 8.664 ppm (1H, dd, arom.). NMR ¹³C (CDCl₃, 400 MHz) **4c**: 11.437 (C₆₀CH₂CH₃), 35.664 (C₆₀CH₂CH₃), 56.267 (OMe), 60.568 (OMe), 110.450, 112.528, 124.645, 129.661, 137.899 – 158.043, 193.234 ppm (C=O). **1a** has been synthesized by UV-irradiation of C₇₀ in anethole followed by chromatography over silica gel with a decaline as eluent. UV-vis (decaline, 293 K): 213, 235, 364, 399, 445 nm. **1c** has been synthesized by UV-irradiation of C₆₀, 2-ethoxyethanol and PhCOPh in PhH followed by chromatography over silica gel with a PhMe as eluent. NMR ¹H (CDCl₃, 400 MHz): 2.339, 2.354 (3H, d, OCHCH₃), 4.069, 4.079, 4.092 (2H, t, OCH₂CH₂OH), 4.148, 4.160, 4.172, 4.183, 4.196 (2H, doublet of quintets, OCH₂CH₂OH), 5.209, 5.225, 5.241, 5.256 (1H, quartet, OCHCH₃), 6.811 (1H, s, C₆₀H).



This work was supported in part by RFBR (Projects 10-03-00968 and 11-03-97051).

P48: NEW PALLADIUM-DIAMINOCARBENE CATALYST FOR SUZUKI ARYLATION OF CHLOROSUBSTITUTED TRICARBOINDOCYANINE DYES

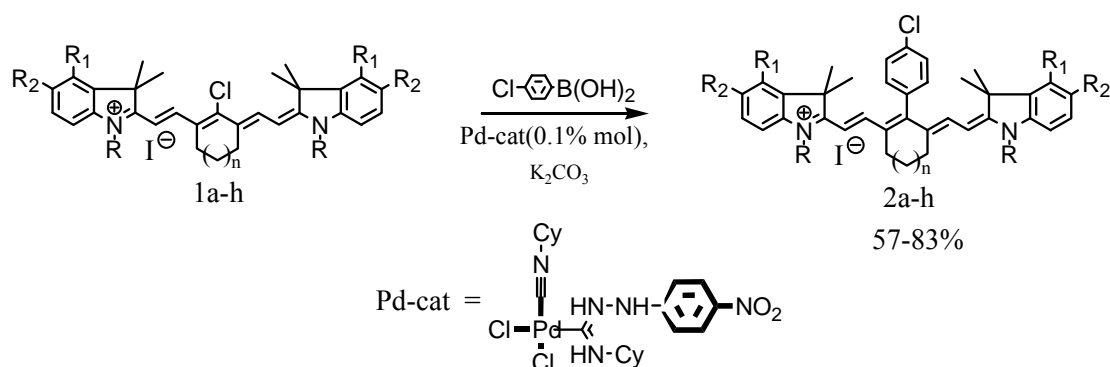
S.A. Miltsov¹, V.S. Karavan¹, V.P. Boyarsky¹, M. Puyol², S. Gomez², J. Alonso²

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2 - Autonomous University of Barcelona, Analytical Chemistry Department, Barcelona, Spain
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Pd-complexes with N-heterocyclic carbenes (NHCs) are widely used as highly efficient catalysts of cross-coupling reactions. Complexes of open-chain analogues of NHCs, prepared by addition of nitrogen nucleophiles to the palladium-coordinated isonitriles also manifested high catalytic activity in Suzuki coupling^{1,2}.

In course of studies on the synthesis of near-infrared absorbing cyanine dyes, suitable for the employment as active components in optical sensors we found that the catalyst of the latter type, prepared by addition of 4-nitrophenylhydrazine to the palladium-cyclohexylisonitrile complex $\text{PdCl}_2(\text{CyN}\equiv\text{C})_2$, can be successively used for Suzuki arylation of *meso*-chlorosubstituted tricarboindocyanine dyes (laser dye IR-780 and its analogues):



Dye	R	R ₁	R ₂	n	λ_{max} (nm)	Yield (%)
2a	Et	H	H	1	764	68
2b	Et		-(CH=CH) ₂ -	1	802	76
2c	Et	H	COOH	1	755	83
2d	Et	H	NHCOCH ₃	1	793	79
2e	Et	H	H	0	795	57
2f	NaO ₃ S(CH ₂) ₄	H	H	1	769	61
2g	Et	H	SO ₃ Na	1	772	65

Complete conversion of dye 1a was achieved in one hour with $5 \cdot 10^{-4}$ eq of catalyst. The stock solution of our catalyst in methanol (0.1 mmol/ml) did not lose its activity within at least three months. The initial complex $\text{PdCl}_2(\text{CyN}\equiv\text{C})_2$ also acts as a catalyst of arylation, but less effective.

The work was supported by SPbU Research Grant, the FT Program (contract P676), RFBR (grants 11-03-00048-a, 11-03-12044-ofim, 12-03-00076-a) and RAS Presidium Subprogram.

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P49: COUPLING OF AZOMETHINE YLIDES WITH NITRILIUM DERIVATIVES OF *CLOSO*-DECABORATE CLUSTERS

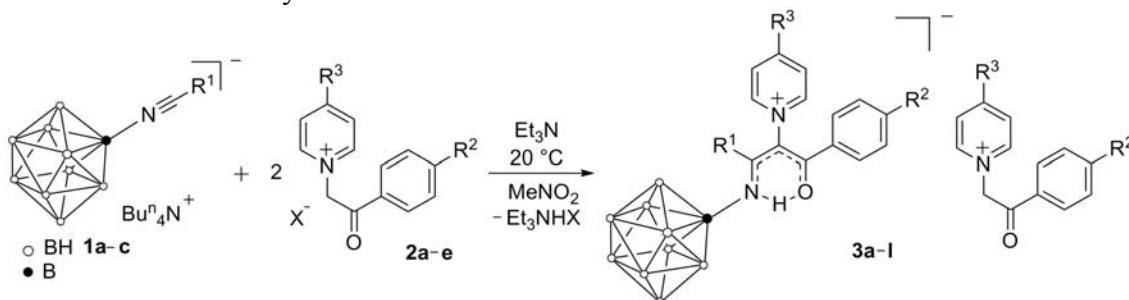
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In contrast to free nitriles, the C≡N bond in the nitrilium derivatives of boron clusters is strongly activated toward addition of various nucleophiles [1,2] and, as we recently reported, toward 1,3-dipolar cycloaddition of nitrones [3]. As an amplification of our studies on the cycloaddition to the borylated nitrile functionality, we performed the reaction between nitrilium *closo*-decaborates **1a–c** and the azomethine ylides $p\text{-R}^3\text{C}_5\text{H}_4\text{N}^+\text{CH}^-\text{COC}_6\text{H}_4\text{R}^2\text{-}p$, obtained *in situ* by treatment of phenacyl pyridinium salts **2a–e** with Et₃N (Scheme). In contrast to our expectation, we found that in this reaction the ylides behave as nucleophiles (rather than 1,3-dipoles), giving a new C–C bond; no products derived from the cycloaddition were detected.



Nos	R ¹	R ²	R ³	Nos	R ¹	R ²	R ³	Nos	R ¹	R ²	R ³	Nos	R ¹	R ²	R ³
3a	Me	H	H	3d	Me	F	H	3g	Et	Me	H	3j	Ph	Me	H
3b	Me	Me	H	3e	Me	Me	Me	3h	Et	F	H	3k	Ph	OMe	H
3c	Me	OMe	H	3f	Et	H	H	3i	Ph	H	H	3l	Ph	F	H

The reactivity of the free and borylated nitriles NCMe and [B₁₀H₉(NCMe)][−] toward the azomethine ylide C₅H₅N⁺CH[−]C(O)Me was studied by theoretical (DFT) methods. This study disclosed that the experimentally observed formation of the nucleophilic addition product instead of the cycloaddition adduct is accounted mostly for by thermodynamic factors rather than by the kinetic arguments. Moreover, theoretical calculations allowed the suggestion of a plausible mechanism for the conversion.

To the best of our knowledge, this transformation is the first example of the addition of a C-nucleophile to the nitrilium group at any of boron clusters. All previously reported examples of the addition of neutral C-nucleophiles belong to RCN species activated by coordination to a metal center [4]. The addition reported here indicates that the nitrile group bound to the *closo*-decaborate anion has a similar effect on the reactivity of the C≡N functionality as coordination of the nitrile group to a high oxidation state metal center [4].

Acknowledgements. The authors thank Russian Fund of Basic Research (grants 11-03-00262) and Saint-Petersburg State University (research grant for 2011–2013) for the support of their studies.

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P50: SCANDIUM COMPLEXES WITH THE TETRAPHENYLETHYLENE AND ANTHRACENE DIANIONS

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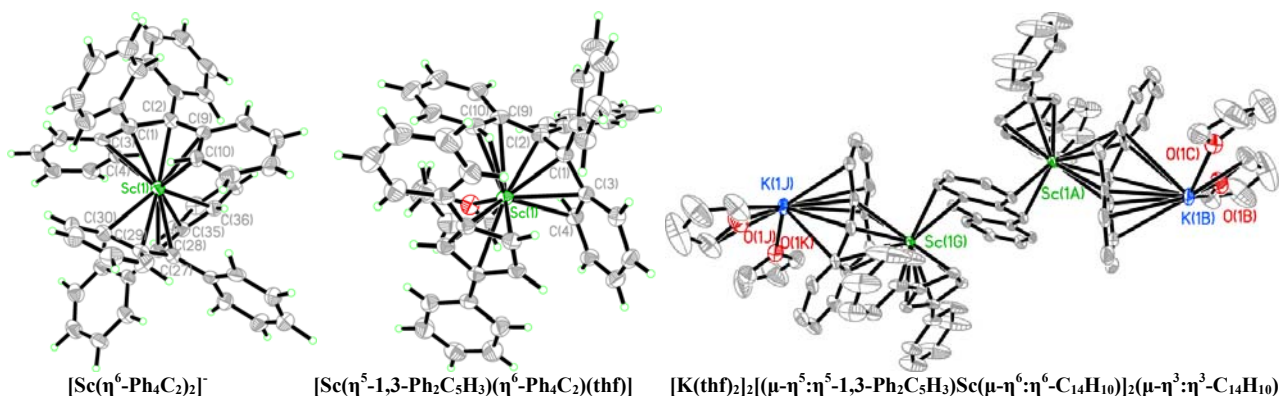
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New organoscandium complexes with the tetraphenylethylene and anthracene dianions have been obtained and studied.

Reactions of ScI_3 or $\text{ScCl}_3(\text{thf})_3$ with disodium- or dipotassiumtetraphenylethylene in THF led to formation of homoleptic *ate*-complexes $\text{M}[\text{Sc}(\text{Ph}_4\text{C}_2)_2]$ ($\text{M}=\text{Na}, \text{K}$). Dynamic behaviour of $\text{M}[\text{Sc}(\text{Ph}_4\text{C}_2)_2]$ in THF solution was investigated by various NMR techniques, including NMR ^{45}Sc . The molecular structure of $[\text{Na}(18\text{-crown-6})(\text{thf})_2][\text{Sc}(\eta^6\text{-Ph}_4\text{C}_2)_2](\text{thf})_2$ has been established by the X-ray structure determination method. The solution and crystal structures of the complex anion $[\text{Sc}(\text{Ph}_4\text{C}_2)_2]^-$ are similar to its yttrium¹ and lutetium² analogs.

Reaction of benzylpotassium with 1,4-diphenylcyclopentadiene-1,3 in THF, followed by reaction with $\text{ScCl}_3(\text{thf})_3$, and then with $\text{Na}_2[\text{Ph}_4\text{C}_2]$, allowed us to obtain $[\text{Sc}(\eta^5\text{-1,3-Ph}_2\text{C}_5\text{H}_3)(\eta^6\text{-Ph}_4\text{C}_2)(\text{thf})]$. Its crystal structure has also been determined, which is similar to $[\text{Lu}(\eta^5\text{-1,3-Ph}_2\text{C}_5\text{H}_3)(\eta^6\text{-Ph}_4\text{C}_2)(\text{thf})]$.³

Formed *in situ* $\text{Sc}(1,3\text{-Ph}_2\text{C}_5\text{H}_3)\text{Cl}_2$ reacts with 2 equivalents of $\text{K}[\text{C}_{14}\text{H}_{10}]$ in THF to give $\text{Sc}(1,3\text{-Ph}_2\text{C}_5\text{H}_3)(\text{C}_{14}\text{H}_{10})$. The crystal structure has not been yet obtained. However, the structure of a by-product $\{[\text{K}(\text{thf})_2]_2[(\mu\text{-}\eta^5\text{:}\eta^5\text{-1,3-Ph}_2\text{C}_5\text{H}_3)\text{Sc}(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{14}\text{H}_{10})]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_{14}\text{H}_{10})\}_\infty$ has been established instead, which is a poorly soluble coordination polymer. This unusual structure incorporates two types of anthracene dianion binding that are common for anthracenide organometallics of rare-earth metals, but have never been previously observed in a single compound.



This work was supported by the US National Science Foundation program (grant CHE-0841014) and by the Russian Foundation for Basic Research (grant 11-03-00043).

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P51: SYNTHESIS AND NMR SPECTRA OF TERT-BUTOXY SUBSTITUTED SILYLMETHYL MAGNESIUM CHLORIDES

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Alkoxy substituted silylmethyl magnesium chlorides of $(\text{AlkO})_n\text{Si}(\text{Me})_{3-n}\text{CH}_2\text{MgCl}$ ($n=1-3$) general formula are of interest because of their implementation in different branches of organic chemistry for synthesis of fullerenes [1], metal complexes [2], steroids [3], phosphorus ligands for supported metal complexes [4], obtaining of insulating resins and films for electronics [5]. However most of these Grignard reagents are unstable and *tert*-butoxy derivatives of this type were practically unknown.

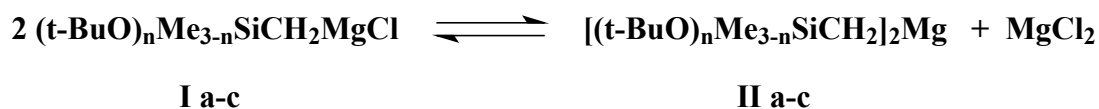
tert-Butoxy substituted silylmethyl magnesium chlorides of $(t\text{-BuO})_n\text{Si}(\text{Me})_{3-n}\text{CH}_2\text{MgCl}$ (**1a–c**, **n=1–3**) general formula were synthesized by reaction of correspondent chlorides with magnesium in boiling THF with up to 95% yields:



The stability of the Grignard reagents (**Ia–c**) was investigated, and these compounds were found to be stable in inert atmosphere at 20 °C from one (**Ia**) to several days (**Ic**).

¹H, ¹³C and ²⁹Si NMR spectra of compounds (I) and (II) in THF were measured.

It was found that these silylmethyl magnesium chlorides (**Ia–c**) were in Schlenk equilibrium with bis[silylmethyl]magnesium derivatives (**IIa–c**) in THF.



It has been proved by variable-temperature nuclear magnetic resonance spectroscopy that the position of the Schlenk equilibrium depends on the temperature and substituents at silicon. For instance, the ratio of compounds (**Ic**):(**IIc**) changes from equimolar at 25 °C to 1:3 at -10 °C, respectively, and is restored when temperature has been risen to 25 °C.

It was found that chemical shifts of methylene groups ^1H nuclei of compounds (I) and (II) were in strong field at -1.48 to -2.05 , which were typical for carbanions [6]. The chemical shifts of methylene groups ^{13}C nuclei of these substances were in strong field too.

It has been found that ^{29}Si chemical shifts of compounds (**I**) and (**II**) strongly depended on substituents at silicon but not on compound type and were observed from 13.3 ppm (**Ia**) to -43.6 ppm (**Ic**).

Assignment of signals for both (I) and (II) in NMR spectra was performed.

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P52: NEW COMPLEXES OF TIN WITH REDOX FRAGMENT BASED ON 2,6-DI-TERT-BUTYLPHENOL IN SULFUR-CONTAINING LIGAND

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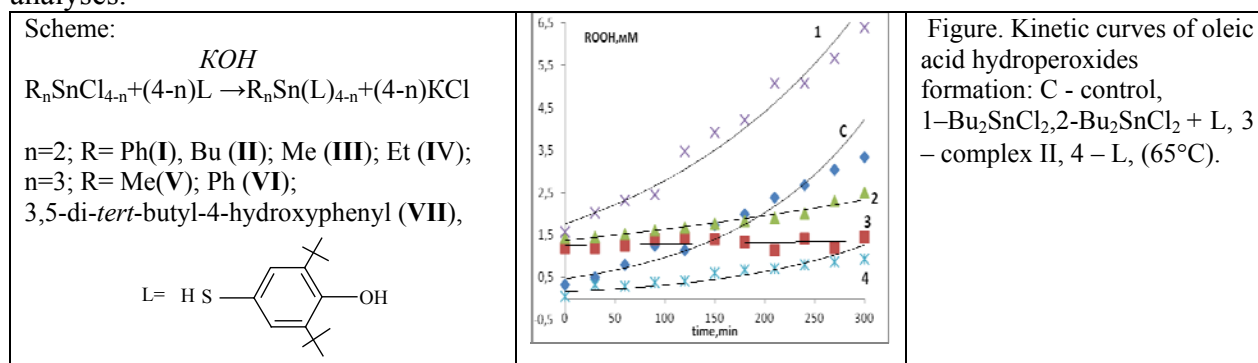
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It is known that the toxicity of the organotin compounds, widely used as biocides, catalysts, stabilizers of polymers, pharmacological preparations, can be related to their cooperating with the HS-groups of the important biosystems. For many molecular complexes of tin, containing covalently connection of Sn–S, anti-tumor activity the mechanism of that is in a great deal unknown is set. Introduction in S-donor a ligand of these complexes easily are oxidation organic groups will allow to investigate them in the redox processes.

The aim of work was a synthesis of new complexes of tin of R_nSnL_{4-n} , containing in S-donor ligand fragment of the sterically hindered phenol, and research of their influence on the process of oxidizing destruction of (Z)-octadec-9-enic (oleic) acid. Complexes of tin R_nSnL_{4-n} **I–VII** were obtained upon interaction of R_nSnCl_{4-n} and 2,6-di-*tert*-butyl-4-mercaptophenol in methanol (scheme). The obtained complexes are described by methods NMR, IR spectroscopy and elemental analyses.



Estimation of influence of complexes **I–VII** in the concentration of 1mM on oxidation of oleic acid conducted by comparison to R_nSnCl_{4-n} separately and jointly with 2,6-di-*tert*-butyl-4-mercaptophenol during 5 h at the constant a thermostatic cell using an air flow at 65 °C. The promoting effect of all organotins R_nSnCl_{4-n} on the oxidation process is established, the concentration $R'OOH$ in 5 hours increased approximately in 2 times in relation to control (fig.). It is marked that *bis*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)tin dichloride showed the inhibitory activity, that is apparently explained by a presence in the structure of the sterically hindered phenol fragment. At joint addition R_nSnCl_{4-n} and 2,6-di-*tert*-butyl-4-mercaptophenol (in correlation 1:2 for the di-organotin derivatives, in correlation 1:1 for the tri-organotin derivatives) level of accumulation $R'OOH$ in oleic acid diminished in relation to control in 1.5 time. Complexes of tin **I–VII** also diminished the level of accumulation $R'OOH$ approximately in 2 times. It is marked that among the synthesized complexes R_nSnL_{4-n} most the inhibitory activity is shown by connection of **VII**, containing four fragments of the sterically hindered phenol in a structure.

Thus, the inhibitory activity of new complexes of tin(IV), containing in S-donor ligand fragment of the sterically hindered phenol in the process of oxidation of oleic acid, is shown. It is set that the increase of amount of fragments of the sterically hindered phenol in the sulfur-containing ligand of complexes of tin(IV) results in the increase of their inhibitory activity.

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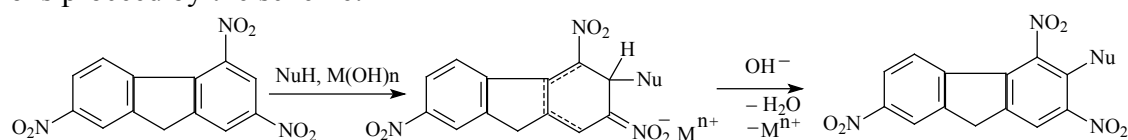
P53: STABILITY OF MOLECULAR COMPLEXES OF 2,4,7-TRINITROFLUOREN (FLUORENONE) WITH DIFFERENT SOLVENTS IN THE PRESENCE OF BASES

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A characteristic feature of polinitroaromatic compounds is their ability to form a sufficiently stable σ -complex with solvent molecules in alkaline media. We have studied the behavior of 2,4,7-trinitrofluoren (A) and 2,4,7-trinitrofluorenon (B) in alkaline solutions in various solvents (ethanol, acetone, acetonitrile, DMF) in the presence of metal salts. Formation of σ -complexes (complexes Yanovsky–Meyzengeymer) fixed by the appearance of the electronic absorption spectra of TNF and TNF on new absorption bands in the 24000–2000 cm^{-1} , and by ^1H NMR spectra.

Reactions proceed by the scheme:



It is shown that the use of polar solvents (acetone, DMF) σ -complex stand in the crystalline state. Recrystallization or prolonged contact with the solvent leads to the release of solvent addition products to the initial substances.

The interaction of TNF and TNFon with solvents was studied under different conditions: a presence of different metal cations, in various solvents, in an ammonia presence.

The reactions order and the activation energy of σ -complex formation were calculated using the spectrophotometric data of the progress of the reaction at different conditions: temperature, ratios of TNF (TNFon): NaOH, solvents (acetone, DMF). According to calculations, the time dependence of α ($\alpha = \frac{A_x}{A_\infty}$) is linear for all experiments, regardless of the ratio of the components (in a large

excess of alkali). The formation of σ -complex is the reaction of pseudo-first order, then there is the nucleophilic addition of only one group. The activation energy for all complexes is the same and is 30 ± 5 kJ / mol.

To determine the direction of nucleophilic attack carried out quantum-chemical calculations of the stability of the anions formed ab initio. It is shown that the attack for the TNF is preferably 1 or 3 carbon atoms of nitrofluoren cycle, for TNFon – mostly attack in position 9 (confirmed by RSA).

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P54: SYNTHESIS AND STRUCTURE OF THE NOVEL BISCHELATE COMPLEX OF PENTACOORDINATE SILICON

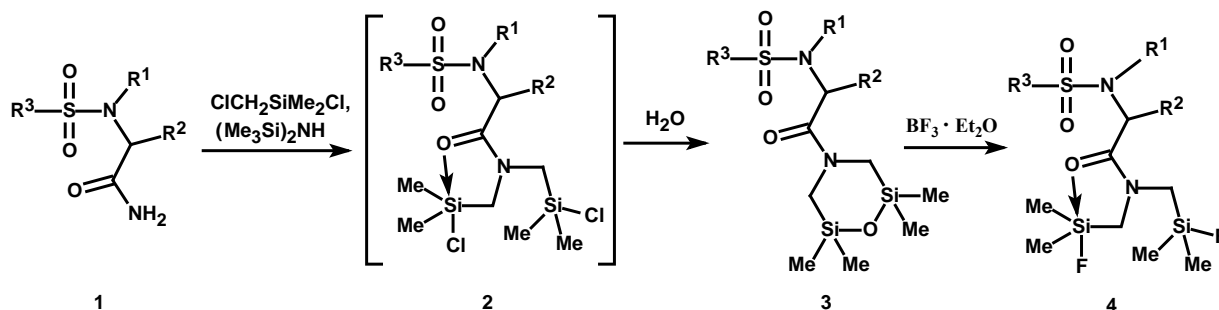
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Silicon-containing heterocyclic compounds are very important because of their specific reactivities, biological activity, and also an opportunity for their practical application [1, 2].

2,6-Disilamorpholines, containing a fragment of sarcosine (**3a**) or proline (**3b-c**), which were unknown earlier, was prepared. It was obtained as a result of hydrolysis of *N,N*-bis(dimethylchlorosililmethyl)amides (**2**), formed "in situ" from nonsubstituted amides (**1**) and system $\text{ClCH}_2\text{SiMe}_2\text{Cl}/(\text{Me}_3\text{Si})_2\text{NH}$. Compounds **3** were involved in reaction with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to form difluorides **4**.



$\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$ (a); $\text{R}^1, \text{R}^2 = (\text{CH}_2)_3$, $\text{R}^3 = \text{Me}$ (b); $\text{R}^1, \text{R}^2 = (\text{CH}_2)_3$, $\text{R}^3 = 4\text{-MeC}_6\text{H}_4$ (c)

The structure of formed compounds was established based on spectral methods (IR, NMR ^1H , ^{13}C , ^{19}F , ^{29}Si), elemental analyses and X-ray data.

Acknowledgment: The work was supported by RFBR (project 10-03-00824).

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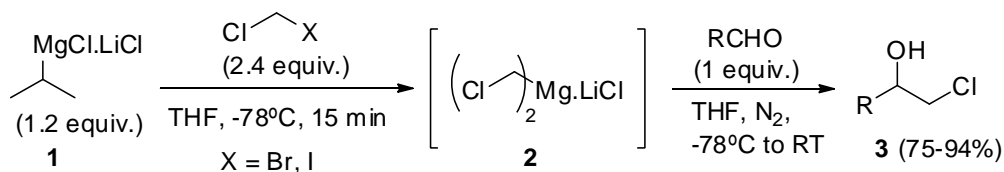
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P55: (ClCH₂)₂Mg•LiCl: AN EFFICIENT REAGENT FOR THE SYNTHESIS OF CHLOROHYDRINS

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The preparation of functionalized molecules by using organometallic intermediates is of great interest since allows the rapid synthesis of various compounds that present biological activity. Organolithium reagents, although widely used, suffers from several drawbacks (low functional group compatibility, low metalation temperature, unselective reactions of the resulting lithium reagent).¹ These advantages can be overcome by alternative preparation of the corresponding arylmagnesium compounds. Such organometallics combine a satisfactory reactivity with good functional group compatibility and their preparation is possible via direct insertion or halogen metal exchange reactions. Due to its special reactivity, *i*-PrMgCl.LiCl (**1**) has emerged as the reagent of choice for halogen magnesium exchange reactions.² In this work, we have investigated the preparation of mixed magnesium-lithium reagents of type (XCH₂)₂Mg.LiCl, through the direct reaction of **1** with methylene dihalides in THF, and their reaction with aldehydes. (ClCH₂)₂Mg.LiCl (**2**) appeared to be the best reagent and led to the formation of the corresponding halohydrins (**3**) in good yields (Scheme). It is a very selective reagent and the reaction works well with aromatic substrates substituted with electron withdrawing and electron donating groups. In addition, it could be employed in the synthesis of some intermediates of HIV protease inhibitors.



Authors thank FAPESP and CNPq for financial support.

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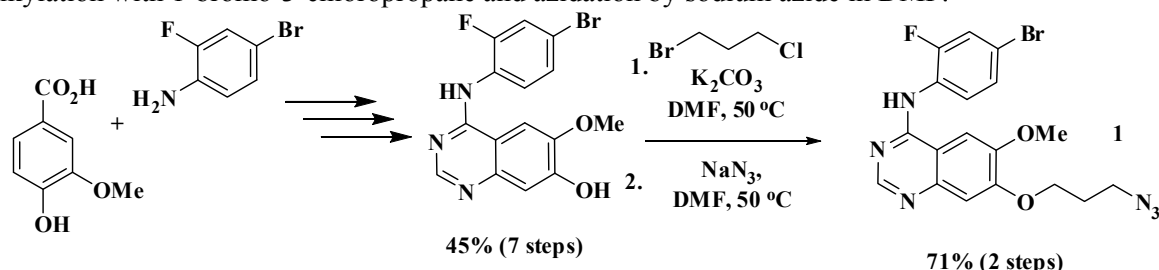
P56: SYNTHESIS OF CHLORIN-*e*₆-VEGFR LIGAND CONJUGATE

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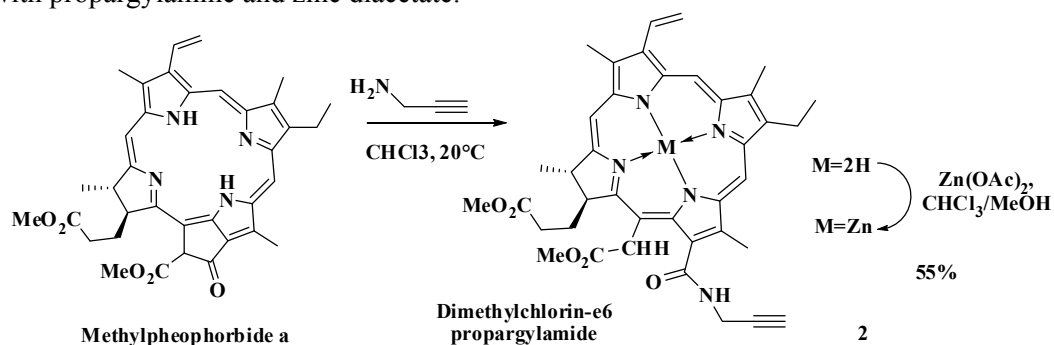
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The last two decades were marked by an active search for drug delivery systems and carrier-linked prodrugs. In the past years, numerous efforts were concentrated on conjugation of the anticancer drugs with a wide spectrum of carriers including sugars, growth factors, vitamins, peptides, antibodies, polysaccharides, lectines, synthetic polymers and liposomes.^[1]

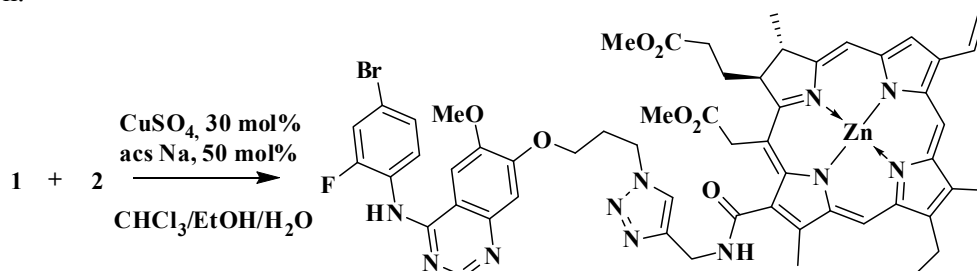
In this project low-molecule antitumor quinazoline-chlorin conjugate was synthesized. Quinazoline part of antitumor hybrid is responsible for the selective delivery of therapeutic molecule to tumor tissue due to the affinity to VEGFR over expressed on the rapidly growing neoplasm.^[2] Quinazoline-type VEGFR ligand was synthesized from vanilic acid and 2-fluoro-4-bromoaniline with 45% overall yield. This ligand was modified via alkylation with 1-bromo-3-chloropropane and azidation by sodium azide in DMF.



Chlorins reveal powerful photodynamic effect which is used intensively for the treatment of some kinds of cancer.^[3] Dimethylchlorin-*e*₆ propargylamide zinc complex was synthesized from methylpheophorbide *a* by reaction with propargylamine and zinc diacetate.



The desired conjugate was synthesized from azido-containing VEGFR ligand 1 and chlorin-type alkyne 2 via click-reaction.



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P57: CATALYTIC AEROBIC PRODUCTION OF IMINES EN ROUTE TO MILD, GREEN, AND CONCISE DERIVATIZATIONS OF AMINES

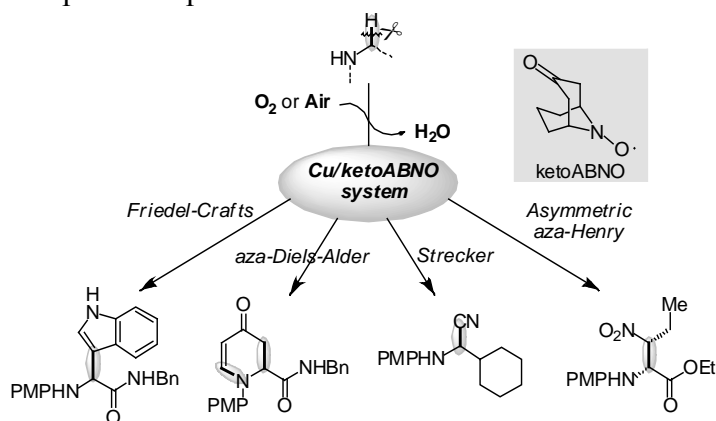
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The recent worldwide concern for the environment has inspired chemists to utilize aerobic oxygen as a stoichiometric oxidant in artificial chemical reactions aimed at environmentally benign, streamlined complex molecule synthesis.^[1] Continuous escalation of the oxidation level of synthetic intermediates contributes to the minimal use of protective groups that are not included in target compounds.^[2] Molecular oxygen is the most ideal stoichiometric oxidant for such oxidative transformations, because it is abundant and produces H₂O as the sole side product.

Amines are primordial structures ubiquitously observed in bioactive molecules. Classically two methods are used to elaborate complex amines; 1) nucleophilic addition to imines or iminium ions and 2) *N*-alkylation or cross coupling. The reactions occur at the nitrogen atom. Alternatively, *direct aerobic oxidative transformation of amines* is the α -position of a substituent on the nitrogen atom is modified via C–C bond-formation with generated transient imine intermediates from amines by aerobic oxidation. The method will provide a new entry to amine synthesis.

We will present a general and synthetically useful catalytic aerobic dehydrogenation of amines to imines using the combination of a sterically less-demanding and electron-deficient new *N*-oxyl radical (ketoABNO) and copper(I) salt.^[3] This mild transformation allowed for extension to a direct α -derivatization of secondary amines involving sequential C–C bond-formation to the resulting imines, including a catalytic asymmetric variant. Mechanistic insight into this novel catalytic system will be also the scope of our presentation.



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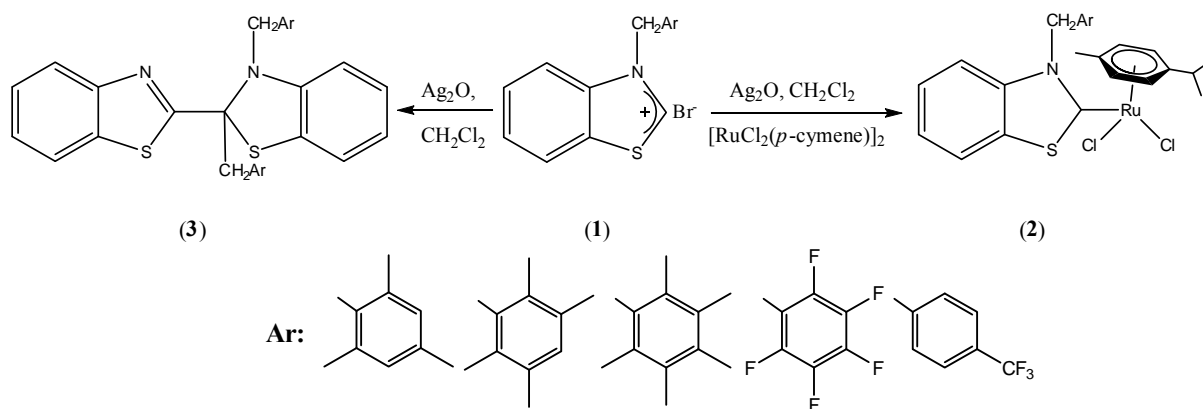
P58: BENZOTHAZOLE-2-YLIDENERUTHENIUM(II) COMPLEXES AND THEIR CATALYTIC PROPERTIES

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Benzothiazole derivatives have been studied since the 1950s as biological activities of compounds and still continues to work in this direction.^[1,2] However, benzimidazolium derived N-heterocarbene complexes have been relatively neglected. Ru(II) complexes of a series of powerful and efficient catalysts in organic transformations have been reported recently.^[3]

Benzothiazolium salts (**1**) were prepared from the reaction of benzothiazole with substituted benzyl bromides. When we tried to isolate Ag-carbene compound we obtained (**3**) as a result of 1,3 sigmatropic rearrangement, as shown in Scheme 1.^[4] However, the reaction of salts (**1**) with Ag₂O and [RuCl₂(*p*-cymene)]₂ in situ at room temperature gave ruthenium(II) carbene complexes (**2**).



Scheme 1

The new Ru(II) complexes have been employed as catalyst for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source and results were compared with related compounds.

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P59: REACTION BETWEEN FUROXANS AND CHROMIUM(0) COMPLEXES: CATALYTIC FUROXAN-RING OPENING

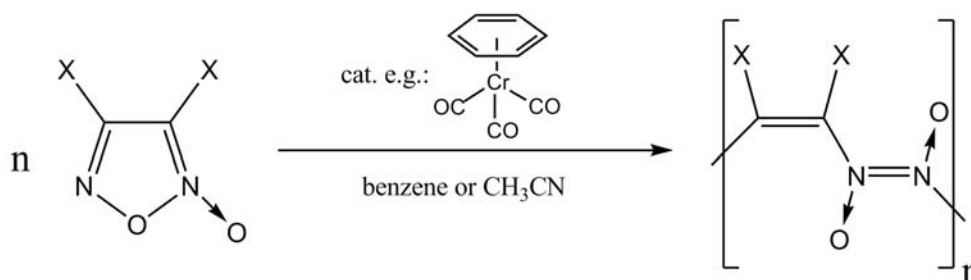
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Organometallic complexes are versatile tools in inorganic and organic synthesis and widely used in various fields of chemistry as reagents and catalysts. Their chemical behavior depends strongly on both the central atom and the coordinating ligands, and can be finely tuned by varying these constituents. Introducing new ligands is thus important and may open the door for novel applications.

The original aim of the present research was to investigate the complex formation between furoxans (1,2,5-oxadiazole 2-oxides) and transition metals in low oxidation state. Furoxans are well known aromatic molecules, what, in principle, can coordinate to a Lewis acid as π - or n-donor ligands using the π -system or lone electron pairs of nitrogen and oxygen atoms, respectively. Such furoxan complexes, however, are not known to date. Chromium(0) was selected as the central metal atom in our first study, because it is known to form complexes with π - and/or n-donor ligands and these complexes usually obey the '18 electron rule'. Considering substitution reactions, our aim was to synthesize chromium(0)-furoxan complexes by reacting furoxans (namely the parent furoxan, dimethyl-furoxan, dihalo-furoxans, and benzofuroxan) and chromium(0)-complexes (namely $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_3(\text{NCCH}_3)_3$, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)$), and to investigate the structure and formation mechanism of these complexes by theoretical means.

Our preparative work has indicated fast and exothermic reaction between furoxans and stoichiometric amounts of chromium(0)-complexes with the formation of oligomers and amorphous brownish black polymeric materials, which latter are not soluble in water and common organic solvents. Optimization of these reactions has revealed that catalytic amounts of chromium(0) complexes are sufficient to convert the whole amounts of furoxans to oligomers and polymers. These polymers decompose, according to TG analysis, around 200 °C, and release partially their monomer furoxans. The identity of these polymeric materials is still unknown and we tentatively suggest the structure provided in Scheme 1.



Scheme 1

Theoretical calculations at the B3PW91/6-311+G(d,p) level have been performed to predict the structure and stability of target complexes, and the energetics of complex formations. Calculations have predicted the formation of n-donor complexes, but indicated furoxan-ring opening in hypothetical π -donor mode, leading to dinitrosoethylene-derivatives. These latter might be key compounds in polymer formation. Structures of these latter dinitrosoethylene complexes and energetics of their formation reactions have also been calculated.

Acknowledgment: Hungarian Scientific Research Fund (OTKA T049148 and T101164)

P60: NOVEL METAL COMPLEXES OF CHROMEN-2-ONES (COUMARINS)

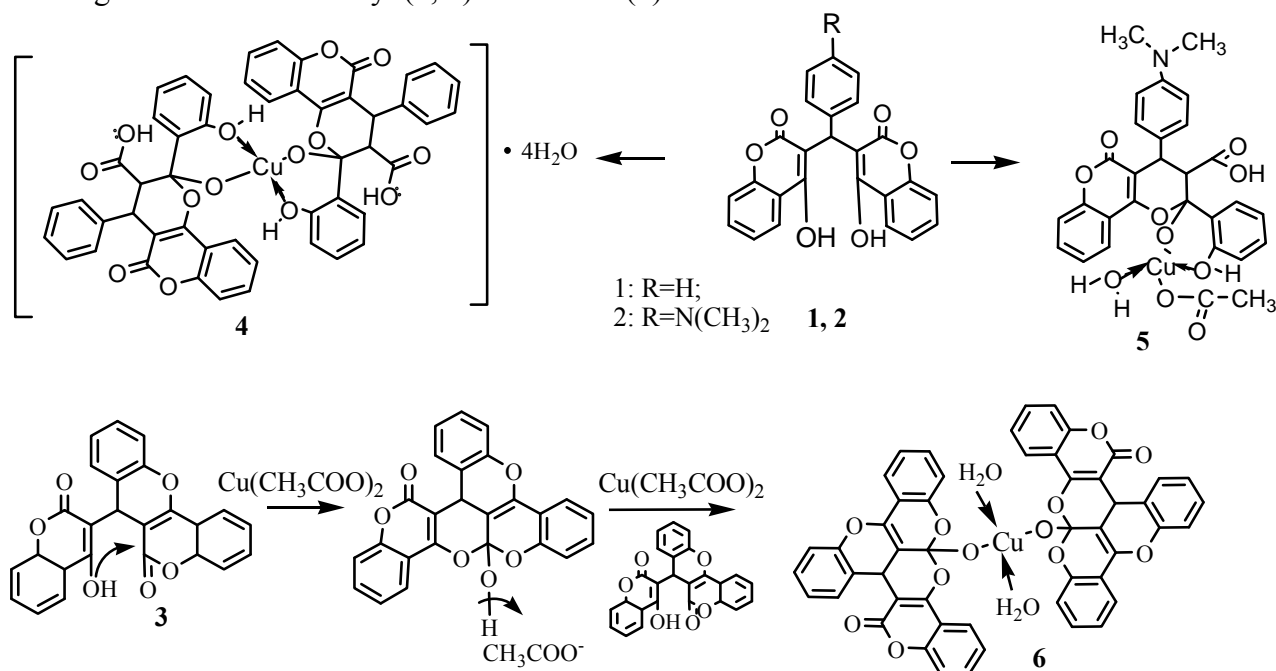
A.G. Platonova, O.A. Mazhukina, O.V. Fedotova, R.I. Kuzmina

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The rapid development of the coordination chemistry of the d-series transition metals has led to accumulation of plenty of information on the composition, structure, and physicochemical properties of their complexes with organic ligands. However, no reactions of 3-substituted 2*H*-chromen-2-ones with transition metal salts are described in the literature, which would enable significant expansion of our knowledge not only of their reactivity but also of opportunities of their practical application, including biological activity in the coordinated state.

Palladium complexes were synthesized by changing the ligand environment of copper(II) acetate in an ethanol solution.

Substrates **1**, **2**, and **3** with one or two 4-hydroxychromen-2-one fragments in their structure have the common trend to hemiketalization (promoted by the medium acidity) and subsequent complex formation with similar reactive centers involved, namely, the enolic group at C₄ of the chromen-2-one fragment and the carbonyl (**1**, **2**) or lactonic (**3**) function.



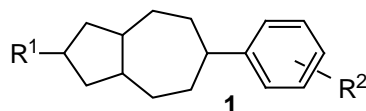
The composition and structure of the complexes obtained have been verified by means of differential thermal and spectral data. In the ¹H NMR spectrum of complexes **4** and **6**, unlike structure **5**, doubling the proton signals is noted due to the formation of the binuclear structure of the complex and no signal of a hydroxylic function around 11 ppm (for product **6**), peculiar to the substrate. The synthesized complexes are promising for the formation of nanosized catalysts to implement oil hydrocarbon conversion and in ecological catalysis.

P61: Zr/Ni-MEDIATED HYDROAZULENE CORE FORMATION

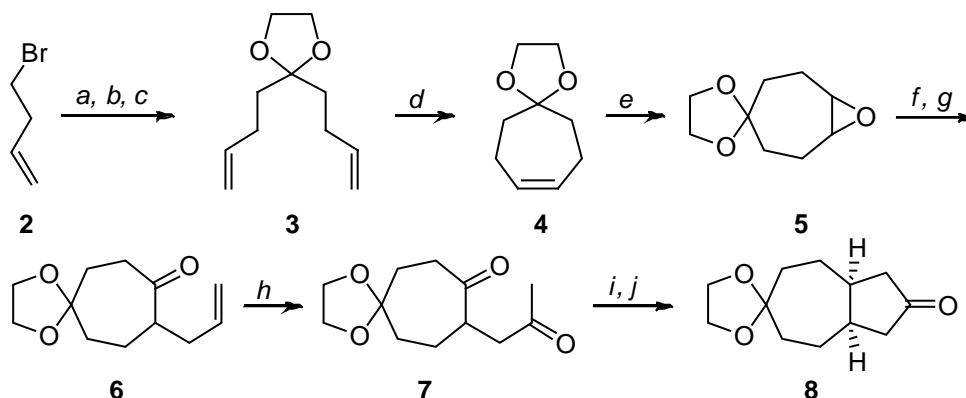
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The synthesis of a new class of mesogenic compounds, the perhydroazulenes, carrying substituents in their *para*-positions (HAZ-derivatives, **1**), has been already described [1]. The new liquid crystalline materials display a broad enantiotropic nematic mesophase slightly above room temperature without any additional smectic phase.

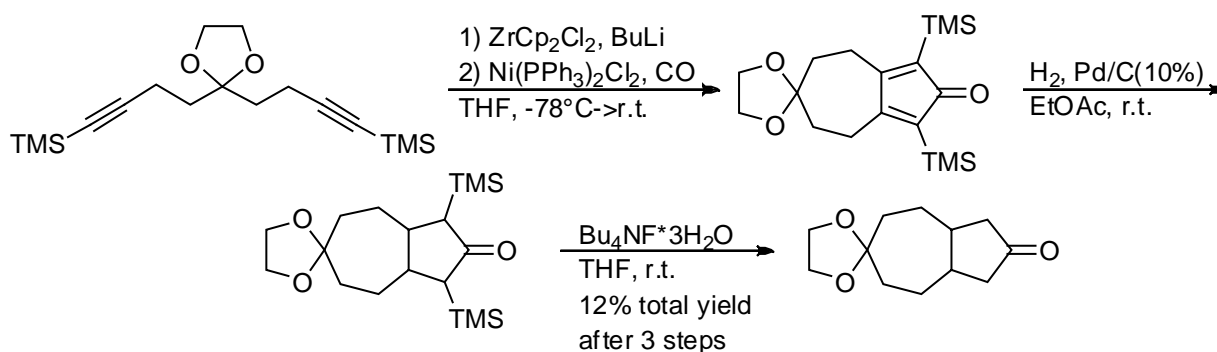


The published approach includes sequential ring building of the perhydroazulene moiety, the construction of the seven-membered ring followed by that of the five-membered ring.



a) Mg, r.t., then HCO₂Et, 0 °C, Et₂O, 89%; b) Jones Reagent (2.67 M), acetone, 0 °C, 98%; c) Ethyleneglycol, p-TsOH, H₂O (cat.), benzene, reflux, 99%; d) Grubbs cat. I, 2% mol., 1,2-dichloroethane, 40 °C, 30 h, 93%; e) MCPBA, CH₂Cl₂, 0 °C, 91%; f) Allylmagnesium bromide, THF, 50 °C, 4 h, 82%; g) Pyridinium chlorochromate, CH₂Cl₂, 0 °C, 91%; h) O₂, PdCl₂ (0.25 eq), CuCl (1 eq.), DMF:H₂O = 6:1, r.t., 81%; i) KOH, MeOH/H₂O, 65 °C, 90%; j) H₂, Pd/C, EtOAc, r.t., 99%

We have now attempted to build the perhydroazulene core in three stages using a Zr/Ni-mediated cyclization of corresponding substituted diacetylenes.



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P62: FIRST PLATINUM-(ACYCLIC AMINOCARBENE) CATALYSTS FOR THE HYDROSILYLATION OF TERMINAL ALKYNES

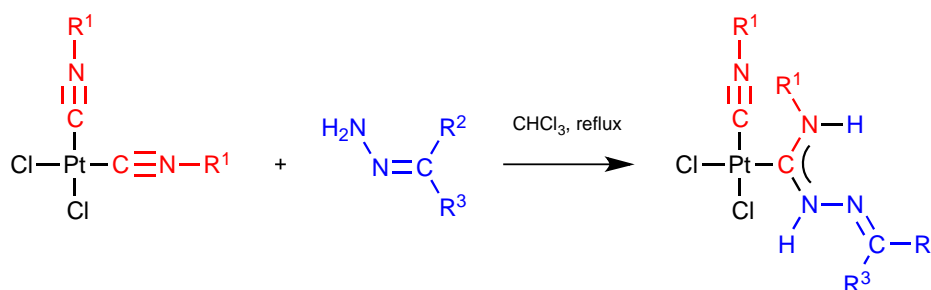
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Coupling between the platinum(II)-isocyanide complexes *cis*-[PtCl₂(CNR¹)₂] [R¹ = cyclohexyl (Cy), 2,6-Me₂C₆H₃ (Xyl), 2-Cl,6-MeC₆H₃] and the hydrazones H₂N–N=CR²R³ [R², R³ = Ph; R²/R³ = 9H-fluorenyl; R² = H, R³ = 2-(OH)C₆H₄] afforded the platinum-(acyclic aminocarbene) species *cis*-[PtCl₂{C(N(H)N=CR²R³)=N(H)R¹}(CNR¹)] (9 examples, **Scheme 1**) in good (75–85%) isolated yields.



Scheme 1

Catalytic properties of the thus prepared complexes in the hydrosilylation of terminal alkynes (4 substrates) with organosilanes (6 substrates) giving corresponding vinyl silanes, were evaluated. High efficiencies (yields up to 99% and TONs up to 4.0x10⁴) with various sterically demanding substrates were observed. This system was not sensitive to air and moisture and performed successfully in the absence of solvent, thus, being environmentally benign. This study represents the first report on successful application of platinum complexes with acyclic aminocarbene ligands as catalysts for the hydrosilylation of terminal alkynes.

Acknowledgements: This work has been supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (including FCT projects PTDC/QUI-QUI/098760/2008 and PTDC/QUI-QUI/109846/2009) and RFBR (project 11-03-12044-ofim).

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P63: CYANOSILYLATION OF ALDEHYDES CATALYZED BY MAGNETIC NANOPARTICLES Fe_3O_4 -IMMOBILIZED GUANIDINE

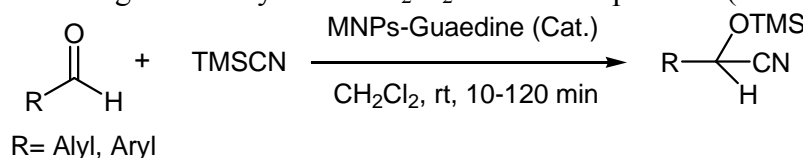
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In recent years, the synthesis and applications of magnetic nanoparticles (MNPs) have attracted increasing interest in catalysis research [1]. Among the various magnetic nanoparticles under investigation, Fe_3O_4 nanoparticles are arguably the most extensively studied as the core magnetic support for catalysts because of their simple synthesis, low cost, and relatively large magnetic susceptibility Fe_3O_4 [2].

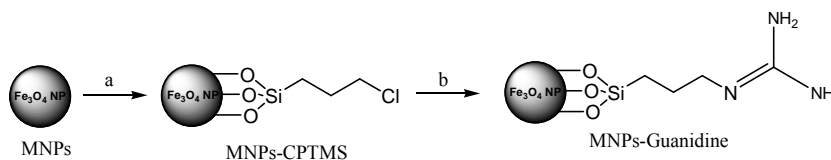
Cyanohydrin trimethylsilyl ethers are versatile intermediates because they can be transformed into a number of important building blocks such as α -hydroxyacids and β -hydroxyamines [3]. One of the common methods to prepare silylated cyanohydrins is the addition reaction of trimethylsilylcyanide (TMSCN) to aldehydes in the presence of various catalysts [4].

In this study, we present for the first time catalytic applications of magnetic nanoparticle-supported guanidine (MNPs-Guanidine) as a novel magnetically heterogeneous nanocatalyst for cyanosilylation of wide range of aldehydes in CH_2Cl_2 at room temperature (Scheme 1).



Scheme 1

The MNPs-Guanidine was prepared according to the procedure shown in Scheme 2. The catalyst has been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR) are shown in Figure1 and thermogravimetric analysis (TGA).



Scheme 2. a) (3-chloropropyl)-triethoxysilane, ethanol/water, 40 °C, 8 h; b) guanidine, toluene, 28 h, reflux

In conclusion, we have prepared the first MNPs-guanidine as robust and efficient catalyst for cyanosilylation of aldehydes with good to high yield of products under mild conditions. The characteristic aspects of this nanocatalyst are rapid, simple and efficient separation by using an appropriate external magnet, which minimizes the loss of catalyst during separation and reusable for several cycles. In addition, it couples the advantages of heterogeneous and homogeneous systems, which make them as promising materials for industrial.

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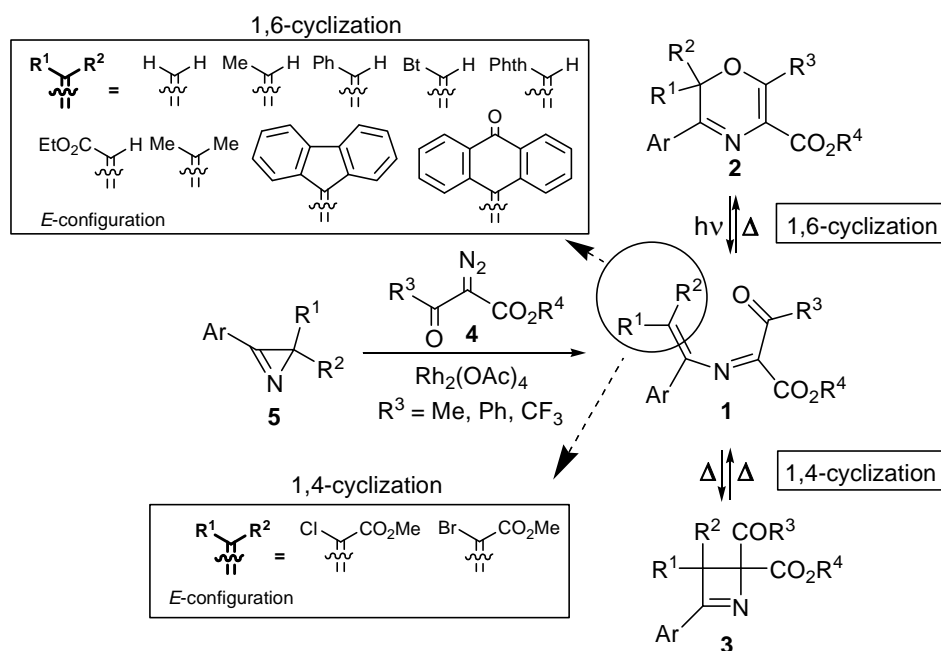
P64: REACTIVITY OF 1-ACYL-2-AZABUTA-1,3-DIENES DERIVED FROM 2H-AZIRINES AND Rh(II)-CARBENOID: 1,6- vs 1,4-ELECTROCYCLIZATION

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Electron-poor 2-azabuta-1,3-dienes are widely used as building blocks for synthesis of various 5- and 6-membered nitrogen heterocycles. They can act as the diene components in Diels-Alder reactions, C₂-components in 1,3-dipolar cycloadditions, and electrophiles in nucleophile-promoted cyclizations [1]. At the same time there are practically no examples of nitrogen ring construction by electrocyclizations with the participation of 2-azabuta-1,3-diene system.

We have shown that the introduction of acyl group in position 1 of 2-azabuta-1,3-diene-1-carboxylate system **1** makes it susceptible for electrocyclizations of two types: 1,6-cyclization to 2H-1,4-oxazines **2** and 1,4-cyclization to 2,3-dihydroazetes **3**. Thus, 1-acyl-2-azabuta-1,3-dienes **1** can be easily generated by Rh₂(OAc)₄-catalyzed reaction of alkyl 2-acyl-2-diazoacetates **4** with 2H-azirines **5** (84 °C, DCE). Depending on substitution pattern, the formation of either 2H-1,4-oxazine or 2,3-dihydroazete derivative can occur under the reaction conditions or at slightly higher temperatures.



The structure—reactivity relationship as well as stereoselectivity and reversibility of electrocyclization of azadienes **1** will be discussed with the use of experimental data and the results of quantum-chemical calculations.

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This work was supported by the Russian Foundation for Basic Research (grant No. 11-03-00186), the Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract no. 16.740.11.0442), and St. Petersburg State University (grant No. 12.38.78.2012).

P65: THE SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES USING H₂O₂ IN THE PRESENCE OF MAGNETIC NANOPARTICLES SUPPORTED N-PROPYLSULFAMIC ACID (MNPS-PSA) AS A NANOCATALYST

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Magnetic nanoparticles have recently emerged as efficient alternatives for the immobilization of homogeneous catalysts and as catalysts themselves. More important, magnetic separation of the magnetic nanoparticles is more effective than filtration or centrifugation, simple, economical and promising for industrial applications [1].

Selective oxidation of sulfides to sulfoxides is a very important reaction in organic synthesis, since they are useful synthetic intermediates for the construction of various chemically and biologically significant molecules, especially drugs and natural products [2]. A number of catalysts have been reported for oxidation of sulfides to sulfoxides using H₂O₂[3]. Grafting of chlorosulfuric acid on the amino-functionalized Fe₃O₄ nanoparticles afforded *N*-propyl sulfamic acid-functionalized magnetic Fe₃O₄ nanoparticles (MNPs-PSA) as a novel organic-inorganic hybrid heterogeneous catalyst, which is characterized by SEM, XRD and FT-IR (Fig.1).

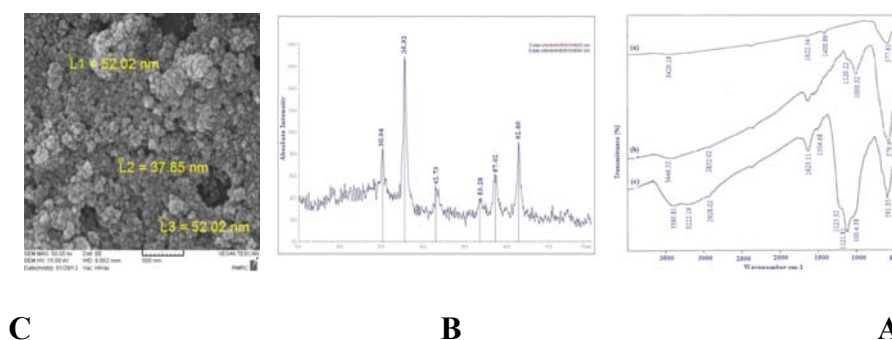
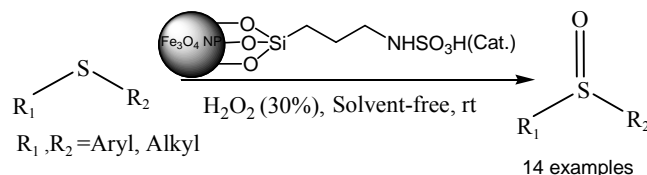


Fig. 1. (A) SEM images of MNPs-PSA, (B) the XRD pattern of MNPs-PSA (C) the comparative FT-IR spectra for (a) MNPs, (b) MNPs-APTMs and (c) MNPs-PSA.

In this study, we employ MNPs-PSA as a recyclable catalyst for the selective oxidation of sulfides to sulfoxides using hydrogen peroxide under mild and solvent-free conditions at room temperature (Scheme 1).



Scheme 1

This method offers several advantages including high yield, short reaction time, chemoselective, and ease of separation, also the recycled catalyst was used for up to 10 runs with little loss of activity.

References

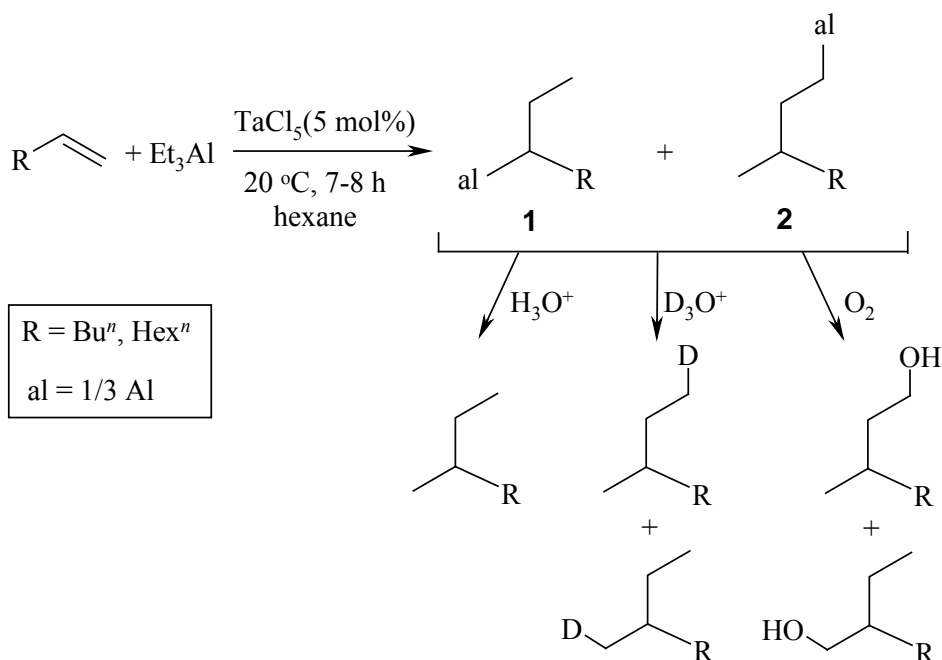
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P66: UNUSUAL TANTALUM-CATALYZED CARBALUMINATION OF 1-ALKENES WITH TRIETHYLALUMINUM

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It is well-known that 1-alkenes enter into the cycloalumination reaction with triethylaluminum (Et_3Al) in the presence of Cp_2ZrCl_2 as a catalyst giving rise to aluminacyclopentanes [1]. Herein, we report findings from our first study of the Ta-catalyzed reaction between Et_3Al and 1-alkenes. Thus, the interaction between Et_3Al and 1-hexene (or 1-octene) in the presence of catalytic amounts of TaCl_5 in hydrocarbon solvent (hexane, benzene) was shown to afford the carbalumination products as a mixture of regioisomeric 2R-substituted **1** and 3R-substituted **2** butylaluminums (~1:1 molar ratio) in high yields (75–85%).



The simultaneous formation of two types of organoaluminum compounds is also in good accordance with the mechanistic scheme proposed for the carbalumination reaction. In situ generated tantalacyclopentanes are discussed as the key intermediates.

The structures of the synthesized compounds **1** and **2** were proved using chemical transformations.

This work was financially supported by the Russian Foundation for Basic Research (Grant 10-03-00046).

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P67: IR AND QUANTUM CHEMICAL STUDY OF THE DEPENDENCE OF ELECTRONIC STRUCTURE AND VIBRATIONAL SPECTRA OF GERMANIUM COMPOUNDS WITH INTRAMOLECULAR Ge•••N BONDING ON THE NUMBER OF COORDINATION CYCLES

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Ge-hydroxyderivatives of pentacoordinated germanium are of great synthetic, theoretical, and practical interest. They comprise 1-germatranol (I), 1,1-quasigermatranol (II) and hypogermanetriol (III) with general formula $(\text{HO})_{4-n}\text{Ge}(\text{OCH}_2\text{CH}_2)_n\text{NR}_{n-3}$ ($\text{R}=\text{H}, \text{Me}; n=1-3$).

The first of these compounds is of substantial synthetic interest and exhibits a specific biological activity. Its analogs containing two and three hydroxy groups are less studied.

Hydroxyderivatives I–III were synthesized by the interaction of GeO_2 with tris-, bis-, monohydroxyethylamines $(\text{HOCH}_2\text{CH}_2)_n\text{NR}_{3-n}$ ($n=1-3$). Molecular structure of compounds I and II is defined by X-ray diffraction. In this communication experimental IR spectra of compounds I–III are reported and they are compared with the theoretical spectra of monomers and dimers obtained by the DFT B3LYP/aug-cc-pVDZ method. The existence of hydrogen bound species in the solid phase of compounds I and II is revealed by X-ray diffraction. The structure of dimeric species of III is predicted by quantum chemical methods.

The assignment of the solid state IR spectra of compounds I–III is based on their theoretical vibrational spectra. The absence of the GeOH group bands predicted for free (monomeric) molecules I–III and the presence of corresponding bands in the spectral ranges predicted for dimeric species confirm oligomeric H-bonded structure of I–III solids. Quantum chemical data evidence the substantial shortening of the Ge•••N dative bond on going from germatranol (I) to hypogermatranol (III). However, this effect hardly can be traced out in vibrational spectra because vibrations with significant contribution of the Ge•••N bond stretch are strongly mixed with other vibrations of the germatrane frame.

These researches were carried out by Russian Foundation of Basic Researches (№ 12-03-00383)

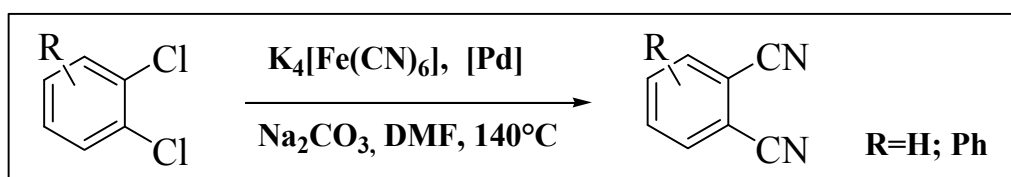
P68: PALLADIUM-CATALYZED CYANATION OF ARYL CHLORIDES

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Transition metal-catalyzed cyanation of aryl halides with $K_4[Fe(CN)_6]$ is a convenient and prospective method to obtain substituted aryl nitriles [1]. From an environmental point of view and for applications in the chemical industry it is efficient to use inexpensive and readily available aryl chlorides (and *o*-dichlorides to get phthalodinitriles and phthalocyanines).

Recently we reported a procedure for cyanation of aryl dichlorides using inexpensive and non-toxic $K_4[Fe(CN)_6]$ in the presence of less than 5 mol% of commercially available Pd-catalyst, e.g. $Pd(PPh_3)_4$ [2]. Surprisingly, in all cases the aryl dinitriles were obtained, but never monocyano monochloro arenes:



To study the reason of such reactivity we have investigated the effect of the substituents on the reaction rate. A number of different chloroarenes were reacted under standard conditions. It was found that the activation of aryl chloride in the Pd-catalyzed cyanation is accelerated by introduction of electron withdrawing groups ($\rho = 2.3 \pm 0.06$):

Table 1. Relative rate constants of the Pd-catalyzed cyanation of substituted chlorobenzenes

Substrate	k_{rel}
4-chloroanisole	0.23
4-chlorotoluene	0.44
chlorobenzene	1.0
1,4-dichlorobenzene	2.9 ^a
1,3- dichlorobenzene	7.6 ^a
4-chlorobenzonitrile	35
1,2- dichlorobenzene	3.2 ^a
2-chlorobenzonitrile	43

^aStatistically corrected

Hence, the reason for the predominant dinitrile formation could be the high sensitivity of the Pd-catalyzed cyanation to electron substitution effect and the slight rate dependence of steric hindrances.

Acknowledgements: The authors thank the Federal Targeted Program “Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013” (contract P676 from 20/05/2010), Russian Fund for Basic Research (grant 11-03-00048-a), and German–Russian Interdisciplinary science center (G-RISC).

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P69: Ni-CATALYZED (3+2+2) CYCLOADDITION OF ALKYLIDENECYCLOPROPANES

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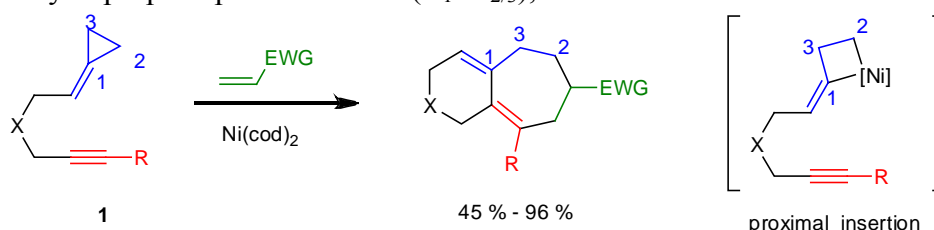
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Alkylidenecyclopropanes (ACPs) are interesting reactive units in organic synthesis due to the presence of an exocyclic C–C double bond and a strained three-membered carbocycle. Recently, we and others reported different types of Pd- and Rh-catalyzed (3+2+2) cycloadditions of ACPs like **1**, cycloadditions that proceed by cleavage of the distal bond of the ACP.^[1] Here, we present a new type of Ni-catalyzed (3+2+2) cycloaddition of ACPs that provide products resulting from the formal cleavage of the cyclopropane proximal bond (C₁–C_{2/3}), instead of the distal one.^[2]

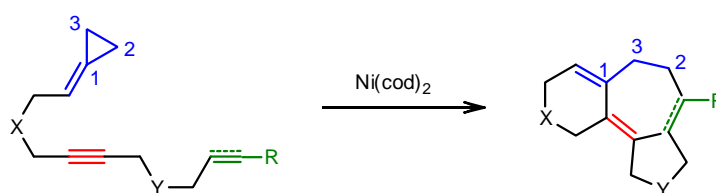


X = C(CO₂Et)₂, NTs

R = Me, CO₂Et, OTBS, OAc

In addition, we will show experimental and theoretical mechanistic information which confirm that the (3+2+2) cycloaddition takes place by cleavage of a proximal bond of the cyclopropanic ring. A mechanistic proposal compatible with this data will be also presented

Finally, we will introduce a fully intramolecular (3+2+2) cycloaddition that allow to directly obtain, from simple acyclic precursors, a variety of interesting tricyclic systems containing six, seven and five membered-fused rings.



X = C(CO₂Et)₂, CH₂, O, NTs

Y = C(CO₂Et)₂, O

R = H, EWG

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P70: DIPHOSPHITES FOR ISOMERIZING HYDROFORMYLATION OF OLEFINS

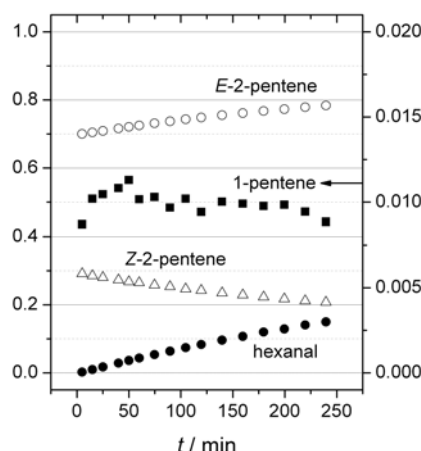
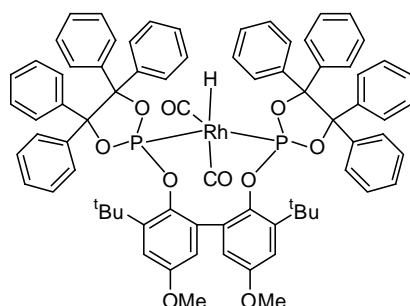
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A benzpinacol substructure has been included into several diphosphite ligands used in Rh-catalyzed hydroformylation. This structural motif reduces the activity of the catalyst towards the undesired hydroformylation of internal olefins. With 1-octene, an i/b aldehyde ratio of 124 is achieved. A remarkable regioselectivity of 99% *n*-hexanal is also obtained in the consecutive isomerization hydroformylation reaction of 2-pentene. Regioselectivity as well as activity are significantly influenced by the chain length of the olefinic substrate. The distribution of C₈ as well as C₅ olefin isomers is far from the thermodynamically determined one for the full reaction time. The constant low concentration observed for the 1-olefins and the depletion of *cis*-2-isomers points to their highest reactivity in hydroformylation and isomerisation, respectively. High pressure NMR and FTIR spectroscopic and theoretical results verify a predominant bisequatorial diphosphite coordination in the *tbp* structured hydrido complex resting state of the regioselective catalyst. In the solid state, the complex is exclusively crystallized as the P∩P axial, equatorial isomer. The catalyst can be formed from Rh acetyl acetonates as well as from precursors containing an ortho-metallated ligand. Due to the straightforward synthesis of the new ligand it has the potential of broad application in academic and industrial hydroformylation.



P∩P: *eq,eq* in solution; *eq,ax* in solid state (X-ray)

D. Selent, R. Franke, C. Kubis, A. Spannenberg, W. Baumann, B. Kreidler, A. Börner, *Organometallics* **2011**, 30, 4509.

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P71: THE NEW MOLYBDENUM COMPLEX WITH TRYPTOPHAN AS MODEL OBJECT IN NEUROSCIENCE

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Soluble Mo(VI) complexes, containing dimeric oxo-cations stabilized by oxygen-containing ligands, such as amino-acids, are known as convenient models of different homogenous catalysts of metabolic processes in protein biosynthesis [1]. On the other hand, it is known that an essential amino-acid Tryptophan acts as building block in protein biosynthesis in brain. It functions as a biochemical precursor for a neurotransmitter **serotonin**, which can be converted to a neurohormone **melatonin**. Recent clinical research has shown promising results with respect to Tryptophan's containing compounds as the excellent treatment of depression, aggression and a variety of other conditions typically associated with low serotonin levels in human brain [2]. Tryptophan is a routine constituent of most dietary proteins of milk, yogurt, red meat, eggs, fish, poultry, bananas. It is supposed that organometallic molybdenum soluble compound with Tryptophan can be recommended as a dietary supplement by Canada's Food Guide to Healthy Eating.

The new effective synthesis of the soluble μ -oxo-(μ -L-tryptophan-O,O')-bis-[hydroxodioxomolybdenum(VI)] by the modified solution-based co-precipitation technique have been reported by us earlier [3]. Solvation state of this organometallic compound with the concentration ~ 0.1 M in solution had been characterised by ^1H NMR investigations. The characteristic feature of the spectrum of DMSO solutions of the compound to compare with water solutions is the **complexity** of the part corresponding to the area of the appearance of the signals of the CHn ligand groups, connected directly both to deprotonated carboxy- and protonated amino-groups, that is located closely to the Mo atoms. This fact, along with the appearance of the low intensity signal at 5.40 ppm, corresponding to released water molecule's protons, revealed the occurrence of polymerization process with water removal in DMSO solution. It is found out that the heat treatment of the compound at 110–130°C also results in further growth of polymeric molecular chains. Moreover, being initially diamagnetic, after heat treatment the compound resembles paramagnetic properties. It is supposed that the partial reduction of Mo(VI) to Mo(V) by the indole group of the ligand leads to the formation of magnetic change-valence clusters which is confirmed by the observation of nonlinear static magnetic susceptibility at low temperatures (20–120K). The investigation of the molecular structure and properties of Mo(VI) binuclear complex with Tryptophan both in solution and in solid state may be useful in understanding the chemical pathways that will give new research directions for psychiatry dietology, psychological medicine and neuroscience alone.

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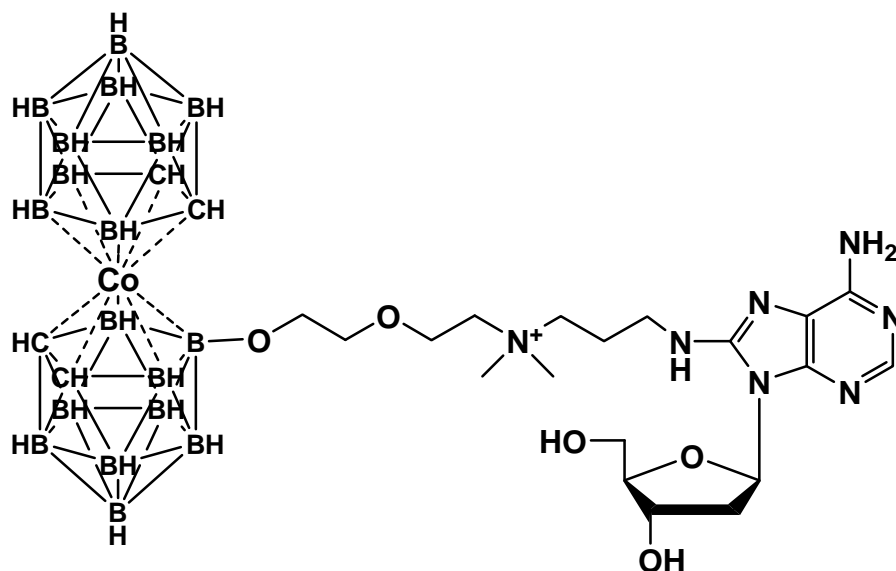
P72: NOVEL CONJUGATES OF BIS(DICARBOLLIDE)COBALT AND CLOSO-DODECABORATE WITH NATURAL NUCLEOSIDES. SYNTHESIS AND BIOLOGICAL INVESTIGATIONS

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Synthesis of bis(dicarbollide)cobalt and *closo*-dodecaborate bearing nucleosides focuses growing attention in recent time^{1,2}. Some of these compounds were prepared by cleavage reactions of cyclic oxonium derivatives of bis(dicarbollide)cobalt and *closo*-dodecaborate using canonic nucleosides as nucleophiles^{3,4}. However, in these compounds boron cluster was linked to the nucleoside via amino and imido groups of the nucleobase. These groups are responsible for the hydrogen bonding in DNA helix, so attaching boron cluster via them makes incorporation of boronated nucleoside into DNA problematic.

Now we would like to present synthesis of novel conjugates of *closo*-dodecaborate and bis(dicarbollide)cobalt with purine nucleosides, where amino or imido groups of the nucleoside remain free. We have found that desoxy/adenosine (dAdo/Ado) can be easily modified introducing 2-(N,N-dimethylalmino)-ethylamino or 3-(N,N-dimethylalmino)-propylamino groups as nucleophilic centres into 8th position. These compounds readily react with oxonium derivatives of *closo*-dodecaborate and bis(dicarbollide)cobalt, leading to a novel conjugates with excellent yields. The in vitro cytotoxic activity of synthesized dAdo derivatives was analyzed against a primary skin fibroblast cell line by a MTT assay. The deoxyadenosine was used as positive control. Results of cell-viability tests revealed that compounds were well tolerable in range of concentrations from 0.1 μ M to 100 μ M.



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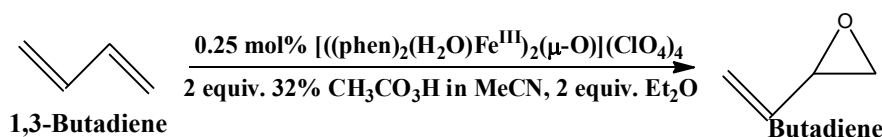
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P73: HOMOGENEOUS CATALYTIC ASYMMETRIC EPOXIDATION OF 1,3-BUTADIENE TO BUTADIENE MONOXIDE CATALYZED BY μ -OXO-BRIDGED DIFERRIC COMPLEXES

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Asymmetric epoxidation of olefins has become an important reaction to obtain epoxides. Epoxides are widely used as raw material in pharmaceuticals, pesticides, painting, or as an intermediates in organic synthesis.¹⁻² Epoxidation in homogeneous catalytic asymmetric reaction has been done by many researchers with using various catalyst systems such as sharpless system, porphyrin system, salen or salphen system, etc. with resulted in high yields.³ In here, we synthesized butadiene monoxide from 1,3-butadiene with using 0.25 mol% of μ -oxo-bridged diferric complexes $[(\text{phen})_2(\text{H}_2\text{O})\text{Fe}^{\text{III}}]_2(\mu\text{-O})(\text{ClO}_4)_4$ as a catalyst⁴, 2 equiv. of 32 wt% peracetic acid as an oxidant in acetonitrile medium and 2 equiv. of diethyl ether as cosolvent (scheme 1).



Scheme 1. Synthetic Route of Butadiene Monoxide

The effects of reaction temperature from -10°C to -40°C , reaction time from 5 min to 120 min, and the effect of diethyl ether as cosolvent in a reaction to the butadiene monoxide yield has been investigated. Butadiene monoxide yield is calculated by using gas chromatography (GC) with decane as an internal standard. The highest yields of butadiene monoxide are 91% at -40°C , 120 min in acetonitrile medium without cosolvent, 92% at -30°C , 20 min in acetonitrile medium without cosolvent (volume of acetonitrile increased 3 times), 96% at -40°C , 90 min with cosolvent in a reaction, and 89% at -10°C , 5 min in acetonitrile medium with cosolvent (volume of acetonitrile increased 2 times) in a reaction.

Acknowledgement: This work is supported by Korean Research Foundation. Grant funded by the Korean Government (KRF-2011-0002834).

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P74: STRUCTURAL PECULIARITIES OF DIBENZOBARRELENE-BASED PCP PINCER IRIIDIUM COMPLEXES

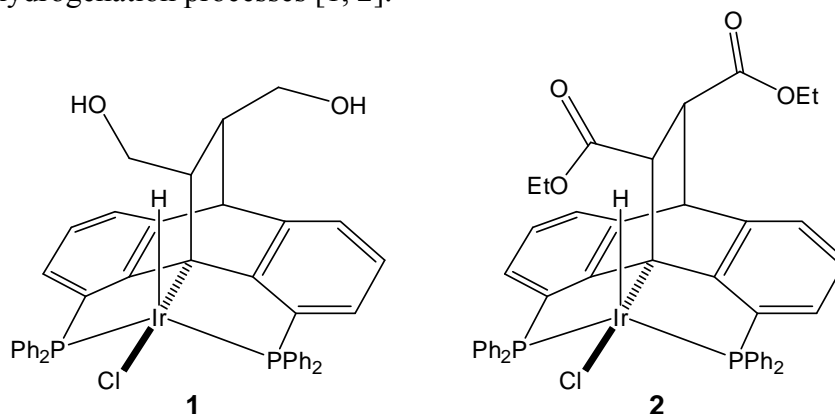
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Cooperative ligands participating in reversible structural transformations of catalytic species over the course of a catalytic cycle are increasingly used in recent years to develop novel efficient catalysts of (de)hydrogenation processes [1, 2].



In the course of a mechanistic investigation of acceptorless dehydrogenation of alcohols catalysed by a bifunctional iridium hydride complex **1** we cognized the diversity of its structure. In order to shed more light on the peculiarities of the geometry of the C_{sp3}-metalated pincer compounds based on the dibenzobarrelene scaffold, the detailed structural investigation of complexes **1–2** was carried out. For this purpose variable temperature IR and NMR spectroscopy studies were combined with computational calculations at the DFT/B3PW91 level.

The calculations revealed four basic structures (isomers) of **1** which have the distorted tetragonal pyramidal geometry around the metal center and differ by the mutual arrangement of C, P, H and Cl atoms. The experimental data obtained are in full agreement with the theoretical ones. It was established that the structural transformations between isomers become possible in the presence of bases/coordinating reagents such as DMSO, pyridine, acetonitrile and triethylamine, some of which have been used as auxiliary base in catalysis [3]. The first results on the structure effect on the catalytic activity of complex **1** in alcohol dehydrogenations have been obtained and will be presented.

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P75: SYNTHESIS AND BIOLOGICAL EVALUATION OF INDOLE-CONTAINING ALLOCOLCHICINOIDS

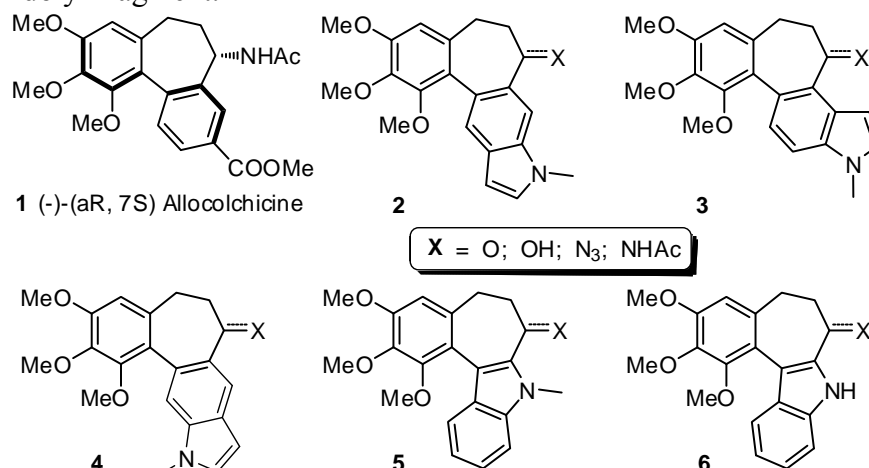
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(–)-Colchicine, the major alkaloid from *Colchicum autumnale*, is known for decades as an efficient antimitotic agent able to inhibit microtubule formation (tubulin polymerization) in living cells, thus causing mitosis arrest in the metaphase. While high toxicity has prevented its use as an antitumor agent, colchicine still represents an important lead structure for drug discovery. Allocolchicine (**1**) is a constitutional isomer of colchicine bearing a six membered aromatic C-ring instead of the tropolone moiety. Allocolchicine itself as well as its analogues show promising biological activities similar to colchicines. Herein we report the synthesis of a series of novel allocolchicine analogs **2–6** containing *1H*-indolyl fragment.



The fused four-membered carbocyclic skeleton in compounds **2**, **3** and **4** was constructed via Suzuki–Miyaura cross-coupling reaction and subsequent Friedel–Crafts annulation. In turn, Weinreb ketone synthesis and subsequent direct intramolecular C–H arylation reaction gave access to compounds of type **5**. The key ring forming steps for type **6** compounds were aldol condensation and direct intramolecular C–H arylation.

Preliminary biological screening of compounds **2**, **3** on BJAB tumor cell line revealed high antimitotic and apoptose-inducing activity (nanomolar or subnanomolar concentration range) along with particularly low unspecific cytotoxicity as determined by LDH-release assay.

	colchicine	2 (X = O)	3 (X = O)	2 (X = OH)	3 (X = OH)	2 (X = NHAc)	3 (X = NHAc)
IC ₅₀ [μ M]	0.02	0.0025	< 0.001	0.03	0.008	0.08	0.03
AC ₅₀ [μ M]	0.03	0.005	< 0.001	0.1	0.01	0.5	0.05

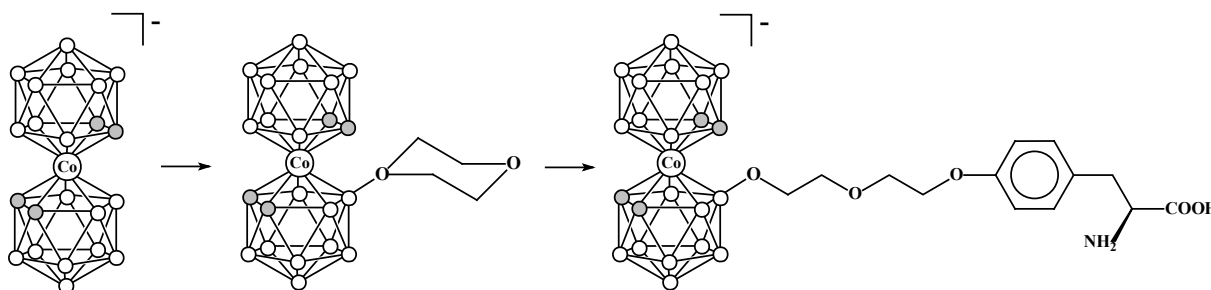
Acknowledgements – this work was supported by the German Academic Exchange Service (DAAD № A/08/79551), Russian Federal Target Program (16.740.11.0476 and 14.740.12.1382), Russian Foundation for Basic Research (12-03-00214-a)

P76: BORON HYDRIDE CLUSTERS AS ANALOGUES OF THE TRANSITION METALS IN ACTIVATION OF ORGANIC MOLECULES

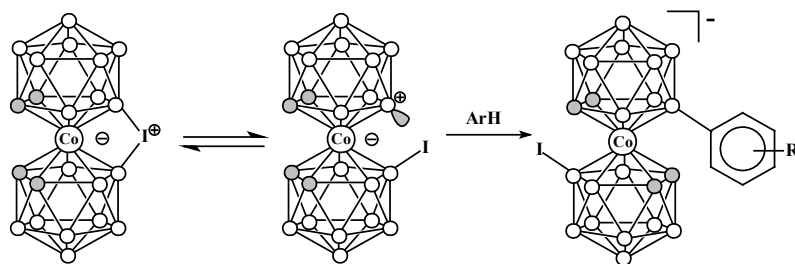
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The role of the transition metals in activation of organic molecules as ligands [1] and activation of C–H bond [2] is well recognized. Polyhedral boron hydrides, including carboranes and metallocarboranes, are capable to abstract hydride ion on the treatment with Lewis or Brønsted acids resulting in formation of quasi-borinium cations which act strong electrophiles and give stable complexes with amines, nitriles, ethers, etc. [3]. The coordination of nitriles and ethers results in extremely strong activation of the last ones toward nucleophilic attack and nowadays the nucleophilic disclosure of cyclic oxonium derivatives became one of main strategies of functionalization of boron hydrides [4].



More recently we have found that the quasi-borinium cations are able to activate aromatic C–H bonds under rather mild conditions to give the corresponding aryl derivatives [5].



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P77: THE INFLUENCE OF COMPLEXES $\text{Ph}_3\text{Sb}(\text{Cat})$ AND $[\text{Ph}_3\text{Sb}(\text{Cat})]\text{O}_2$ ON THE PROCESS OF LIPID PEROXIDATION *IN VIVO*

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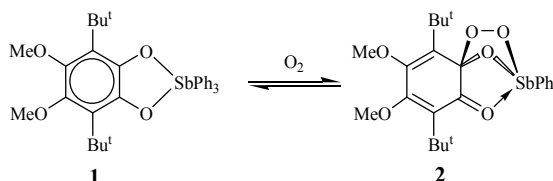
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Earlier it was found that catecholates complexes of triphenylantimony(V) $\text{Ph}_3\text{Sb}(\text{Cat})$ show antiradical activity in experiments in vitro [1]. Such behavior is unusual for organometallic derivatives of heavy metals. Complexes interact with free radicals and oxygen due to the presence of redox-active catecholate fragment. Under aerobic conditions complexes $\text{Ph}_3\text{Sb}(\text{Cat})$ with donor groups in catecholate ligand fix molecular oxygen reversibly that leads to the formation of cyclic endoperoxide [2].



In present work we have investigated the influence of triphenylantimony(V) catecholate (**1**) as well as its endoperoxide form (**2**) on lipid peroxidation process (LP) of inbred mice of BALB/c line. The compounds were injected once in peroral way, 5 days in week during 28 days ($C = 10 \text{ mg/kg}$) in olive oil solution. The oil solution was preliminarily heated up to 60°C in case of the first compound because it is necessary to prevent the formation of (**2**). The concentration of TBARS in blood serum was studied: the enzymatic and non-enzymatic ascorbate-dependent LP; in case of tissue homogenates, the initial level of MDA was measured. In the first group of animals (complex **1**) the level of TBARS in blood serum decreases by 40–45% in comparison with control animals, while the results for the second group (complex **2**) point out a weak promotion effect of endoperoxide. The values of TBARS concentration (as initial concentration of malonic aldehyde) in tissue homogenates of liver, kidneys, heart are represented in table.

Groups	C_{TBARS} , nmol/g		
	Liver homogenate	Kidneys homogenate	Heart homogenate
Control	2.62 ± 0.09	2.78 ± 0.36	2.6 ± 0.16
1	1.95 ± 0.17	2.64 ± 0.19	1.5 ± 0.37
2	2.74 ± 0.15	3.01 ± 0.27	3.97 ± 0.10

The first substance has inhibitory effect on LP which is more pronounced in the case of liver and heart homogenates whereas the second compound displays promotion action that appears in increasing concentration of TBARS. Growth of C_{TBARS} at 150% for the heart homogenate supposes cardiotoxic properties of endoperoxide (**2**) that is in the agreement with known data. Consequently, activity of complexes (**1,2**) in the LPO depends on availability of the catecholate ligand and varies from antioxidant for the first compound to prooxidant for the second.

Acknowledgements: we are grateful to RFBR (12-03-00513, 12-03-31026 11-03-00389), grants President of RF (MK-1156.2011.3, MK-614.2011.3), for financial support of this work.

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P78: FERROCENES: BIOCHEMICAL PRODUCTS AND MEDICINAL APPLICATIONS

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During the past two decades ferrocene compounds as novel class of antitumor drug candidates have attracted considerable attention due to their unique properties [1]. So, therapeutic indexes $TI=LD50/ED$ for these ferrocene compounds are significant bigger than for the drugs used in clinical practice. Our current interest in these ferrocene compounds is connected with mechanistic aspects responsible for the specific pharmacological effects and medicinal applications [2]. The preparative pathways for the synthesis of the series of novel ferrocene-modified nucleobases, azoles and amino acids from heterocycles and ferrocenyl carbinols according to simple and suitable methods were realized (Scheme 1).

In experiments *in vivo* and *in vitro* it was demonstrated that ferrocene compounds with heterocyclic systems are effective against some animal solid tumors and human tumors [2, 3], they are also displayed DNA synthesis inhibitory effects. These results are principally important for the investigation of ferrocene-modified compounds as potential prospective drugs for antitumor polychemotherapy,

This work was financially supported by the Russian Academy of Sciences (Presidium Program 'Fundamental Sciences – for Medicine'), by the Department of Chemistry and Materials Science (Program 'Medicinal and Biomolecular Chemistry') and by the Russian Foundation for Basic Research (RFBR No 09-03-00535).

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P79: CARBENE LIGANDS INCORPORATED TO β -CYCLODEXTRINS – 1,2,3-TRIAZOLYLIDENE DERIVATIVES

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The triazoles are compounds which can be easily obtained via Scharpless “click” chemistry reaction [1]. On the other hand, the most important issue of cyclodextrin derivatization is its’ selective substitution. Although several solutions had been proposed, the best ways for obtaining mono- and the bis-derivatized products was elaborated by Bitmann et al. [2] and Pearce and Sinay [3] respectively.

Triazoles are used as ligands in organometallic complexes. In 2008 Albrecht group introduced triazoles as precursors for abnormal carbene ligands for transition metals [4]. Comparing to coordination complexes, the advantage of such compounds is the stability of the interaction between metal and ligand are much stronger.

Here we present an example of combining these methods in order to create new functional hybrids which can hypothetically behave like artificial enzymes. Therefore, we formed a library of β -cyclodextrin derivatives, containing α -amino acid derivatives as side-chains on either primary and secondary site of the cyclodextrin rim. We will present our attempts in metal incorporation to described hybrids.

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"Carbohydrates as renewable raw materials in the synthesis of products with high added value" no. POIG.01.01.02-14-102/09-02

P80: METAL COMPLEXES WITH PHOSPHORUS-CONTAINING LIGANDS IN ORGANIC SYNTHESIS

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Hydroalkoxycarbonylation of olefins with carbon monoxide and alcohols under conditions of homogeneous catalysis with transition metal complexes allows facile one-step synthesis of practically useful carbon acid esters. Many of them have biological activity and are constituents of drugs or valuable intermediate products in drug synthesis.

New efficient technologies for preparation of drugs are based on isovaleric acid esters – “Novovalidolum”, “Ethyl ester of α -bromisovaleric acid” and “Corvalolum–K” (further Medicines) – were worked out.

Novovalidolum – is a spasmolytic (sedative) medicine, an analogue of the widely used medicine “Validolum”; it is 23–25% solution of menthol in menthylisovalerate. It has a sedative effect on the nervous system and a moderate reflex vaso-dilating effect. “Ethyl ester of α -bromisovaleric acid” possesses sedative and spasmolytic properties and in larger doses provides light soporific action. It is included in Corvalolum-K composition and may be used for producing other medicines. Corvalolum-K (is analogous to medicines Corvalolum and Valocordinum) is a combined medicine and consists of ethyl ester of α -bromisovaleric acid, phenobarbital, sodium hydroxide, peppermint oil, ethyl alcohol and water. Corvalolum-K possesses anesthetic and spasmolytic properties.

The technologies for obtaining of the Medicines are based on catalytic hydroethoxycarbonylation and hydromenthoxycarbonylation of isobutylene with carbon monoxide and ethanol (l-menthol) in the presence of metalcomplexes with phosphorcontaining ligands. The proposed technologies may be used for commercial production of the Medicines.

Due to the more advanced technology of production the Medicines will have better qualitative characteristics. The cost of production of the Medicines with the use of new technology is 2–4 times lower as compared to similar medicines produced by existing at the present traditional technologies.

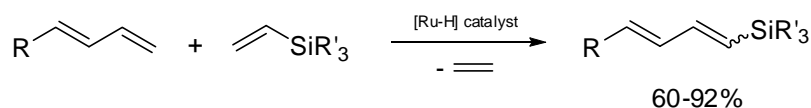
P81: EXTENDING THE SILYLATIVE COUPLING: HIGHLY SELECTIVE SYNTHESIS OF SILYL-SUBSTITUTED BUTA-1,3-DIENES

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Silyl substituted 1,3-dienes are versatile building blocks that have significant potential in stereoselective synthesis [1]. Silylated 1,3-butadienes have been demonstrated as useful building blocks to construct cyclic compounds *via* Diels–Alder reaction and can be used for allylation and desilylation reactions [1]. They can be readily transformed into a wide variety of functional molecules, such as a silyl-substituted cyclohexene skeleton, allylsilane system or functionalized (halogen-, aryl-, acyl-substituted) diene moiety.

In the last two decades, we have developed the silylative coupling of olefins with vinyl-substituted organosilicon compounds occurring in the presence of complexes containing initially or generating in situ M–H and M–Si bonds [2]. In the communication we present that silylative coupling of olefins with vinylsilanes may be successfully extended for systems based on conjugated dienes. Selective synthesis of silyl-substituted 1,3-butadienes is reported by exploitation of catalytic silylative coupling reactions of functionalized (*E*)-buta-1,3-dienes that comprise aryl and alkoxy groups as well as organic moieties containing nitrogen with alkyl-, alkoxy- and siloxy-substituted vinylsilanes in the presence of ruthenium-hydride complexes.



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P82: ORGANOMETALLIC CATALYSTS BASED ON RUTHENIUM FOR ALKYLATION OF AMINES WITH ALCOHOLS

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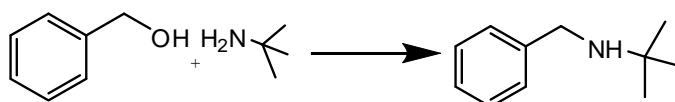
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The direct alkylation of amines with alcohols has been known since the beginning of the 20th century. The use of alcohols as direct alkylating agents for amines is generally limited due to the poor electrophilicity of most alcohols, although such a procedure is appealing since the only reaction byproduct is water. The alkylation of amines with alcohols is therefore potentially an atom economical and less hazardous process than the use of conventional alkylating agents.[1]

The alcohol is activated by oxidation to give an aldehyde or ketone, which then undergoes a condensation reaction with the amine nucleophile. Subsequent hydrogenation of the resulting imine with the initially generated hydrogen yields the desired amine product.

The first examples of homogeneous catalysts for the alkylation of amines by alcohols were published independently by Grigg and Watanabe [2, 3] and there have been several ruthenium [4] and iridium [5] catalysts reported subsequently. Many of these catalysts require forcing conditions. Herein we report the synthesis of some organometallic catalysts based on ruthenium such as $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ and $\text{CpRuCl}(\text{PPh}_3)_2$ and applying them in amination of alcohol in moderate conditions. Ruthenium catalysts were found to be inactive in the absence of a phosphine ligand, Hence a number of bidentate ligands such as bis(diphenylphosphino)ferrocene (dppf) diphenylphosphinopropane (dppp) and Xantphos were tested.

The reaction of benzylalcohol with *t*-butylamine was chosen as a model for establishing a competent catalyst for the alkylation of amines with alcohols. $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ was selected as a readily available catalyst precursor, and the reaction was examined in the presence of dppf.



Primary amines have been converted into secondary amines, and secondary amines into tertiary amines. Secondary alcohols require more forcing conditions than primary alcohols but are still effective alkylating agents in the presence of these catalysts. Subsequently, it was discovered that the addition of additives such as molecular sieves and base had beneficial effect on these reactions and were therefore placed in our investigation. $\text{CpRuCl}(\text{PPh}_3)_2/\text{dppf}$ gave same product as well as the other catalyst but the combination of $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ and dppf appeared to be the most effective in this reaction.

Taking the $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2/\text{dppf}$ combination, we decided to explore its activity with different phosphine ligands in order to determine a trend of reactivity for the different ligands.

Excellent yields were obtained by heating a equivalent solution of the alcohol and amine at reflux in toluene in the presence of 2.5 mol% of $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$, 5 mol% dppf 10 mol% K_2CO_3 and 3Å MS for 24 hours under argon atmosphere. The reactions were monitored by GC-MS in order to study the alkylation process in detail.

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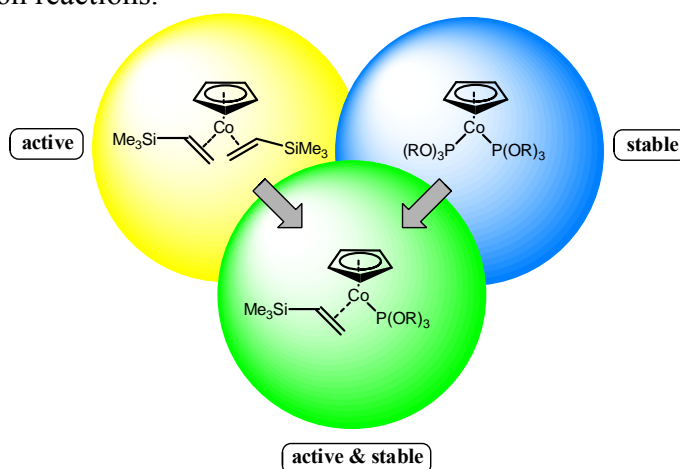
P83: LIGAND INFLUENCE ON THE STABILITY AND ACTIVITY OF NOVEL COBALT COMPLEXES FOR [2+2+2] CYCLOADDITION REACTIONS

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Transition metal-catalyzed [2+2+2] cycloaddition reactions are a convenient method for the synthesis of benzene or pyridine derivatives in a highly atom-economical manner.^[1] As work from our group previously showed, cobalt complexes of the type $[\text{CpCo}(\text{olefin})_2]$ are excellent catalysts for these cycloaddition reactions. Especially $[\text{CpCo}(\text{H}_2\text{C}=\text{CHSiMe}_3)_2]$ proved to be not only an excellent catalyst but also a great precursor for the convenient synthesis of a variety of different $[\text{CpCo}(\text{olefin})_2]$ -complexes.^[2]

One drawback of $[\text{CpCo}(\text{H}_2\text{C}=\text{CHSiMe}_3)_2]$ (**1**) is its thermal instability and the rapid degradation of the complex above -40°C , which makes the handling of the catalyst somewhat tricky. To improve the stability of precatalyst **1** without interfering too strongly with its capability to rather easily generate the catalytically active species, we set out to prepare CpCo(I) -complexes, which have one of their olefin ligands substituted for a ligand that would be able to provide sufficient stability as well as reactivity. In due course we synthesized room temperature-stable complexes of the general type $[\text{CpCo}(\text{H}_2\text{C}=\text{CHSiMe}_3)(\text{phosphite})]$ as well as $[\text{CpCo}(\text{phosphite})_2]$ and screened their respective activities in cyclotrimerization experiments of diynes with nitriles. Here the mixed olefin-phosphite complexes exhibit an excellent combination of thermal stability and high activity in [2+2+2] cycloaddition reactions.^[3]



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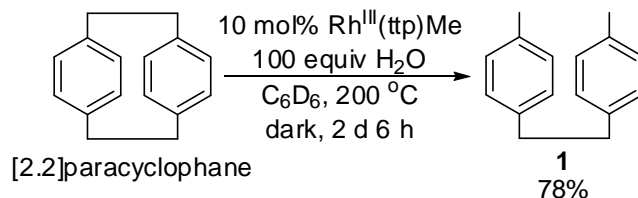
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P84: CATALYTIC CARBON–CARBON BOND HYDROGENATION WITH WATER CATALYZED BY RHODIUM PORPHYRINS

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Hydrocracking of fossil fuels increases the fuel quality by bringing up the H/C ratio, however in harsh and acidic conditions of temperature about 400 °C and pressure over 50 bar.¹ Making such process milder can reduce the energy input and hence negative environmental impacts. Water is a cheap and attractive hydrogen source via water splitting.² Recently, we have reported the selective carbon-carbon bond activation of cyclooctane.³ Now we successfully achieved the catalytic carbon-carbon bond hydrogenation under neutral medium, using water as the hydrogen source. The benzylic carbon-carbon bond of [2.2]paracyclophane was catalytically cleaved and hydrogenated to produce 4,4'-dimethylbibenzyl **1** in good yield.



Acknowledgement

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P85: PRODUCTION OF DIMERIZED LINOLEIC ACID

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Dimers of fatty acids are used in the production of polyamides, polyesters, polyurethanes, special paints and cosmetics [1]. Process of fatty acids dimerisation in U.S. is carried out by heating at 230–250°C for several hours under pressure and in the presence of catalysts, viz. montmorillonite clay. The main component of fatty acids is linoleic acid. In the linoleic acid, the hydrogen atoms of methylene groups associated with the two ethylene systems have increased activity, which facilitates the migration of the double bond both prototropic mechanism, and through formal elimination-addition of hydride ion. As a result, the migration of double bonds in the reaction mixture will accumulate the most stable of the possible products, i.e. linoleic acid with conjugated double bonds. These acids react readily diene synthesis (Diels–Alder reaction) with other unsaturated compounds. Dienophiles may be natural linoleic acid, oleic acid and other unsaturated compounds. Dimerisation of tall oil fatty acids by thermal oxidation in Soviet Union was performed. The process was carried out in a reactor in which the tall oil or fatty acid were heated to temperature $195 \pm 5^\circ\text{C}$ with continuous air bubbling. Under the action of oxygen fatty acid molecules formed free radicals. These radicals can react with another molecule having a double bond to form a linear dimer, or isomerize to conjugated system, which in turn readily reacts to Diels–Alder reaction with other unsaturated molecules, forming a cyclic dimer.

The disadvantages of using thermal oxidation method of dimerisation include the formation of low molecular weight gaseous products, hard-controlled oxidation process and complicated structure of the oxidized product. The thermal method under the action of catalysts (U.S. method) requires high temperature, imported (for Russia) catalyst, and sometimes requires pre-activation of the catalyst. Temperature decreasing in fatty acids dimerisation by using more effective catalysts is the most perspective method to avoid above mentioned disadvantages.

Author of the article proposed a method of obtaining fatty acids dimers by using boron trifluoride. Linoleic acid was heated at a temperature 140°C for 7 hours in the presence of boron trifluoride. The product was examined by ^1H NMR spectroscopy methods and mass spectrometry. It is shown that in the reaction product dimers and trimers of linoleic acid are formed.

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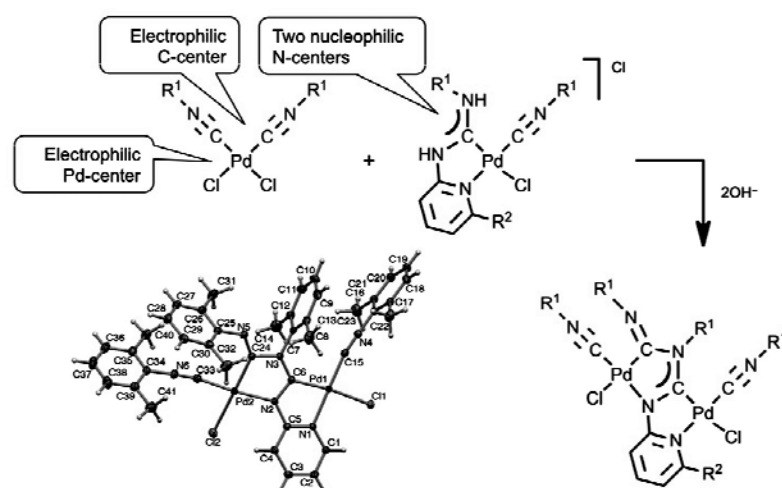
Acknowledgments The author acknowledges Center for Community Use, Department of Chemistry, RGPU im. A.I. Herzen for their assistance in performing the ^1H NMR experiment.

P86: Pd-MEDIATED COUPLING BETWEEN ACYCLIC DIAMINOCARBENES AND ISOCYANIDES LEADING TO DINUCLEAR SPECIES

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In the past decade, metal-aminocarbenes have gained special attention in both organometallic and organic chemistry.¹ Most work in this field has been devoted to the preparation of novel metal-aminocarbenes, optimization of the electronic and steric effects of the carbenes in their complexes, understanding the nature of the metal–C_{carbene} bond, and, what is also very important, the application of carbene metal species as catalysts in organic syntheses.^{2–4} Although metal-aminocarbenes have long been prepared, the reactivity modes of aminocarbene ligands are practically unknown.



We found that chelated diaminocarbenes under certain conditions could behave as nucleophiles and be involved in a cascade reaction with metal-activated isocyanides to furnish dinuclear species (Scheme). We report herein on the novel reactivity mode of diaminocarbene ligands.⁵

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P87: GOLD DEPOSITION ON POROUS MAGNETIC CARBONIC COMPOSITES FROM GOLD-CHLORIDE SOLUTION

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In this paper we present a study of the sorption process of gold from HAuCl_4 solution on porous composites for the purpose of possible creation of gold catalysts and use of these magnetic composites in gold mining industry for efficient recovery of precious metals.

It is known that one of the most effective ways of synthesis of gold catalysts, as well as recovery of precious metals from gold-bearing solution is the deposition on support/sorbent surface of various forms of $[\text{Au}(\text{OH})_x]\text{Cl}_4-$, which interact with hydroxyl, carbonyl and other groups on the surface.

Synthesized magnetic carbonic microporous samples with the surface area of 1000–1350 m^2/g were obtained from the wood sawdust modified chlorides of iron and zinc, at different temperatures, and they were taken as the supports. Sorption activity of the composites obtained at the temperatures of 400 °C and 800 °C was determined for gold extraction from aqueous solution of chloroauric acid.

It was shown that maximum sorption capacity of samples by gold from HAuCl_4 solution consists 3–5 g/g and depends on the temperature of carbonization of synthesized composite. It was noted that the amount of adsorbed gold correlate with the content of magnetite in the sample. With XRD and electron microscopy, it was revealed that high-temperature sample contains smaller gold particles than low-temperature sample.

DTA of samples with and without add of gold was carried out in air media. It showed that addition of gold promoted the flow of the sample oxidation and reduced exothermic effect observed at temperatures of 400–600 °C.

It was also found that majority of gold in the sample can be easily desorbed from synthesized composite by washing in hydrochloric acid solution.

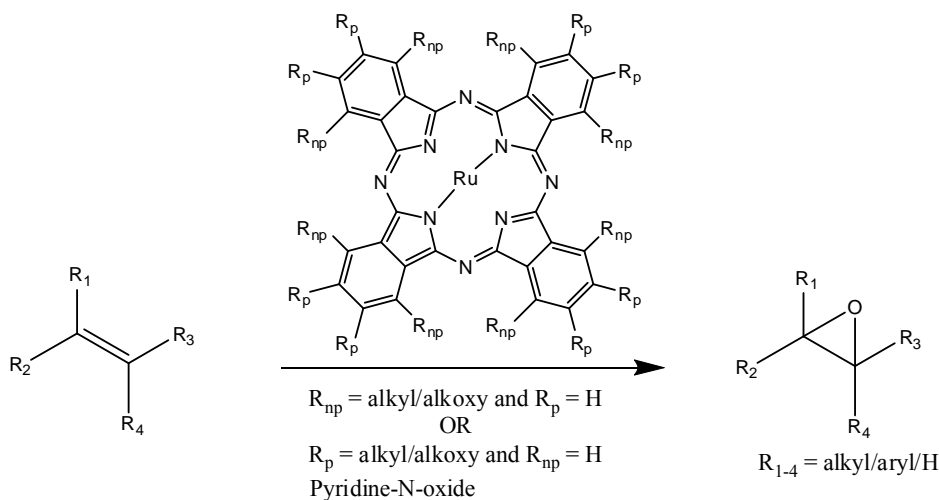
P88: SUBSTITUTED RUTHENIUM PHTHALOCYANINES AS NEW EPOXIDATION CATALYSTS

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While epoxidation represents an extremely powerful tool in synthetic organic chemistry, catalytic processes for this transformation are often hampered by low product yields, long reaction times, limited scope, and catalyst deactivation. While the utilisation of porphyrins [1] and salen type complexes [2] in the epoxidation of alkenes are well documented for a variety of oxidants, only a few examples [3] do exist in literature where the very similar phthalocyanines containing Fe, Mn and Co have been investigated as catalysts in epoxidation reactions. Furthermore, many of these reactions were based on the utilization of a sacrificial oxidant, aldehyde or similar compound, that would give rise to unwanted side products like the carboxylic acid.

Due to the multi-step, low-yielding, synthetic route for obtaining the substituted versions of these macrocycles utilizing known procedures [4], new methodology for the preparation of symmetrical peripherally and non-peripherally alkyl and alkoxy-substituted phthalocyanines was developed. The availability of these compounds allowed for the assessment of their relative potential towards effecting the epoxidation of aryl substituted, cyclic, linear, internal and terminal olefins with pyridine-N-oxides, that could be regenerated by oxidation, as stoichiometric oxidant.



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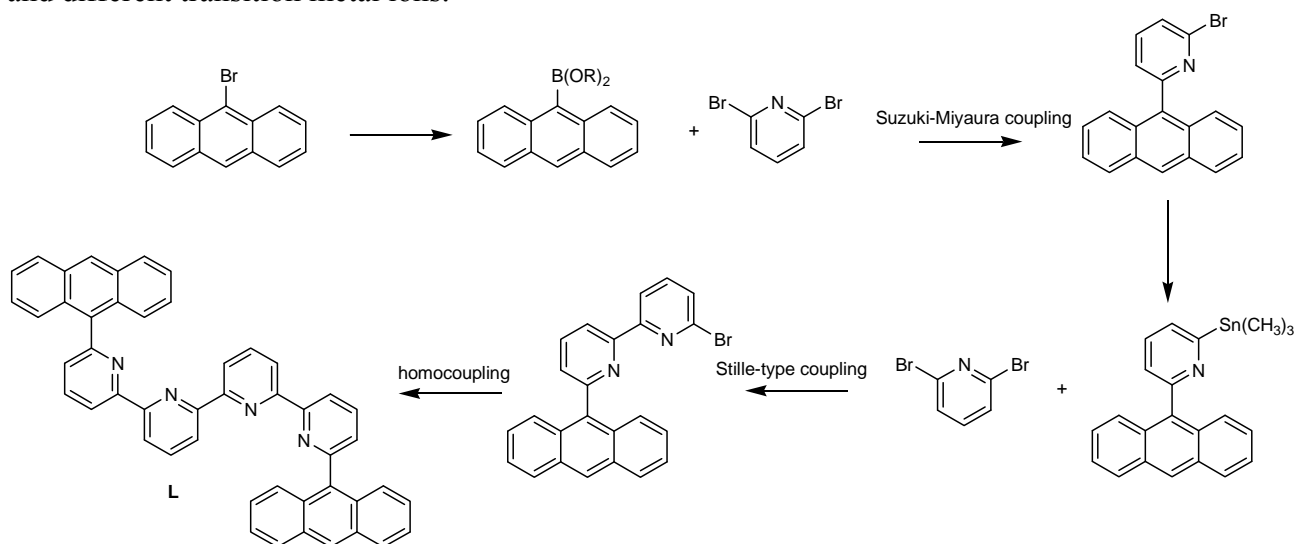
P89: SUZUKI-MIYaura AND STILLE-TYPE COUPLING REACTIONS IN SYNTHESIS OF NEW N-HETEROCYCLIC LIGAND

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The cross-coupling of organic halides and related electrophiles with organometallic reagents constitutes one of the most direct methods for the formation of C–C bonds [1]. Reactions such as Sonogashira, Stille, Negishi and Suzuki-Miyaura cross-coupling are commonly employed in synthetic routes of natural products, advanced materials and therapeutic agents. Organotin and organoboron compounds are readily available and quite air and moisture stable and tolerate many functional groups. Due to Suzuki-Miyaura and Stille-type coupling reactions are one of the most important coupling reactions used for synthesis of N-heterocyclic ligands.

Quaterpyridine ligands are known to form many types of supramolecular architectures such as mononuclear complexes, dinuclear helicates [2] and polynuclear architectures [3]. The ligand **L** (scheme 1) has been obtained in a multistep synthesis via Pd(0)-catalysed Suzuki-Miyaura and Stille-type coupling reactions. Supramolecular complexes have been obtained by self-assembly of **L** and different transition metal ions.



Scheme 1 Synthesis of the ligand **L**

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Project supported by: grant IP2011 058871 from the Polish Ministry of Higher Education and Science

P90: APPLICATION OF SILYLATIVE COUPLING IN THE SYNTHESIS OF UNSATURATED STARBURST COMPOUNDS WITH BORON ATOM IN THE CORE

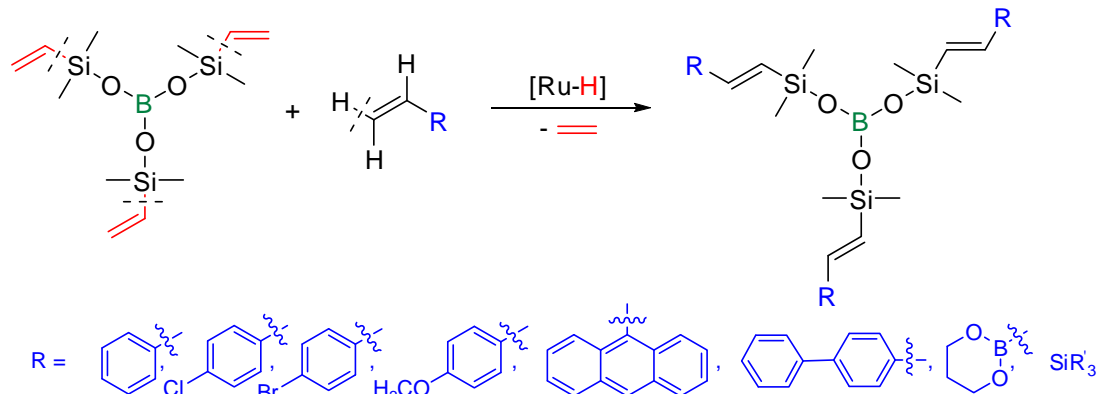
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Over the last few decades a new class of dendrimers, called metallodendrimers, containing main group elements and transition metals has attracted much attention because of their unique chemical and physical properties. Metallodendrimers can be used in many branches of chemistry, biology, medicine and materials science [1]. There are known only a few examples of dendrimers containing boron atom in the core or at the ends of dendrimer arms, which were applied i.e. in the neutron capture therapy, as active Lewis acid catalysts for hydrosilylation of ketones or as new materials due to the fact that boron and silicon atoms in the structure enhance thermal and mechanical properties and can be therefore used as precursors for new type of ceramic or optoelectronic materials [2–3].

In the communication the highly effective method for regio- and stereoselective synthesis of unsaturated starburst compounds with boron atom in the core via discovered in our group silylative coupling reaction [4] of selected olefins with boron tris(dimethylvinylsiloxide) catalyzed by $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ is described. Such products can be used as potential precursors for new, highly branched materials with unique mechanical, thermal and optoelectronic properties. The mechanism of this catalytic process is also discussed [5].



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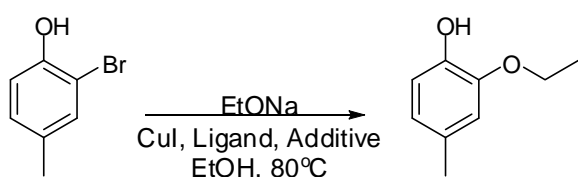
Acknowledgement: This work was supported by the Ministry of Science and Higher Education of Poland (Grant NN 204265538).

P91: OBSERVING OF THE ACTIVITY OF SOME LIGANDS IN THE COPPER MEDIATED COUPLING OF BROMOPHENOLS AND SODIUM ETHOXIDE

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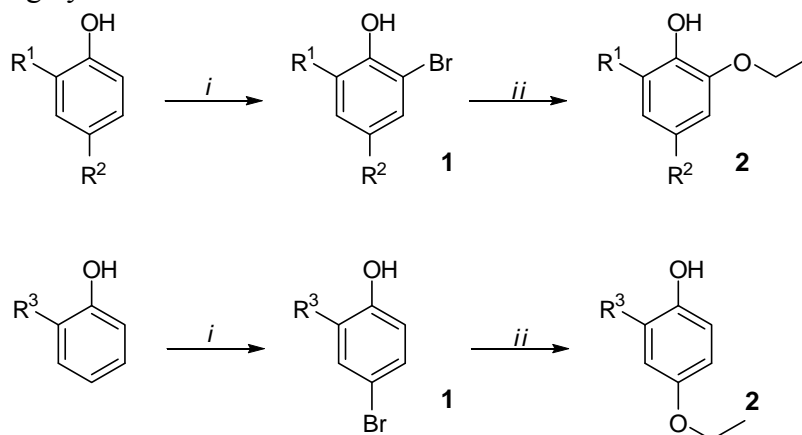
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The formation of carbon–heteroatom bonds by transition metal catalysed cross-coupling reaction has been the subject of significant interest during the past years. Copper-catalysed coupling of alcohols (or alkoxides) and arylhalogenides (Ullmann condensation) is a very useful method of phenol derivatives synthesis.



Ligands		Additive
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$	DMF
$\text{Me}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NMe}_2$	$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$	or
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOH}$	$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$	DMA

In this work we present results of testing of some ligands and some optimization for Cu-catalyzed coupling of bromophenols and sodium ethylate. Compounds **1a–k** were converted to derivatives **2a–k** in high yields with TMEDA as a ligand. O-, S- and Se-substituted derivatives can be obtained by this method in high yield too.



$\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ (a); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Me}$ (b); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{t-Bu}$ (c); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{t-Bu}$ (d);
 $\text{R}^1 = \text{t-Bu}$, $\text{R}^2 = \text{Me}$ (e); $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$ (f); $\text{R}^1 = \text{t-Bu}$, $\text{R}^2 = (\text{CH}_2)_3\text{SBu}$ (g); $\text{R}^1 = \text{Cy}$,
 $\text{R}^2 = (\text{CH}_2)_3\text{SBu}$ (h); $\text{R}^1 = \text{t-Bu}$, $\text{R}^2 = (\text{CH}_2)_3\text{SeBu}$ (i); $\text{R}^1 = \text{H}$, $\text{R}^2 = (\text{CH}_2)_2\text{OH}$ (j);
 $\text{R}^1 = \text{H}$, $\text{R}^2 = (\text{CH}_2)_3\text{OH}$ (k); $\text{R}^3 = \text{Me}$ (l); $\text{R}^3 = \text{t-Bu}$ (m). i: Br_2 , CHCl_3 , r.t.;
 ii: EtONa, CuI, TMEDA, DMF, EtOH, 80 or 90°C

This work was supported by the grant of the Novosibirsk City Hall.

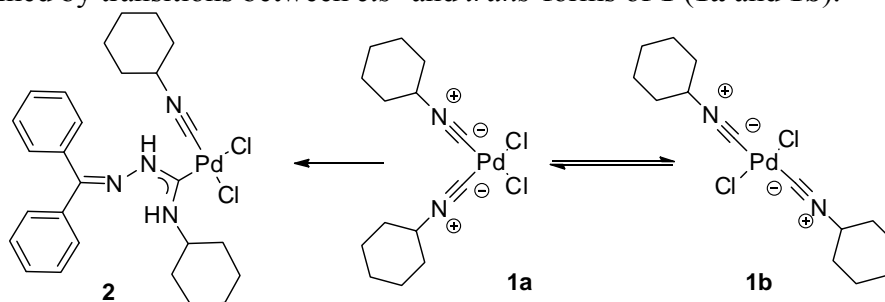
P92: THE STRUCTURE AND BEHAVIOR OF BIS-(CYCLOHEXYLISONITRILE)PALLADIUM(II) DICHLORIDE IN SOLUTIONS

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Recently acyclic diamino-carbene (ADC)Pd complexes have come into use as catalysis for different cross-coupling reactions. One of the methods applied to produce such catalysts is the reaction between *bis*-isonitrile complexes of palladium(II) chloride with N-nucleophiles [1]. This is the reason for a great and increasing interest to *bis*-isonitrile complexes, like mentioned above, and their properties.

The present study is devoted to the structure and behavior of *bis*-(cyclohexylisonitrile)palladium(II) dichloride in solution. This complex normally crystallizes as *cis*-isomer (**1a**). However, we observed that complex **1** shows two different sets of signals in ^1H NMR spectra in solution, which could be explained by transitions between *cis*- and *trans*-forms of **1** (**1a** and **1b**).



This isomerization was studied by IR and ^1H NMR spectroscopy. The equilibrium between two forms is reached at room temperature in 10 days in CDCl_3 , the ratio of **1a** and **1b** being 2:1. The isomerization is strongly accelerated upon heating; taking only 30 min for the equilibrium to be established at 50 °C. Temperature effect on the isomers equilibrium ratio was also investigated.

It was shown that complex **1** in solution exists as a mixture of isomers **1a** and **1b**. On the other hand, ADC complexes between **1** and N-nucleophiles are formed very rapidly with an almost quantitative yield of the pure *cis*-form of Pd-ADC **2**, according to our X-ray data. We suggest that this contradiction is due to the influence of N-containing bases on the isomerization rate. We studied the behavior of complex **1** in solution in the presence of N-bases (such as pyridine or 4-pycoline) which cannot react with **1** generating ADC's. The isomerization rate increases greatly in the presence of a base (from 10 days to 3 hours at room temperature and 7 mol% pyridine). Furthermore, the heating up to 50 °C in the presence of N-containing bases affects the equilibrium constant, shifting the equilibrium towards *trans*-isomer **1b**.

Hence, our data imply the possibility of *cis*-Pd-ADC **2** formation from a mixture of *cis*-/*trans*-isomers of parent isonitrile complex **1** due to the rapid establishment of the equilibrium in the presence of a nucleophile.

Acknowledgements: The authors are grateful to Saint-Petersburg State University for a research grant, the Federal Targeted Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013" (contract P676 from 20/05/2010), and Russian Fund for Basic Research (grant 11-03-00048-a).

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P93: MODIFIED ALUMINUM COMPLEXES BASED ON IMINOPHENOLS: NEW STRATEGY OF CATALYSIS

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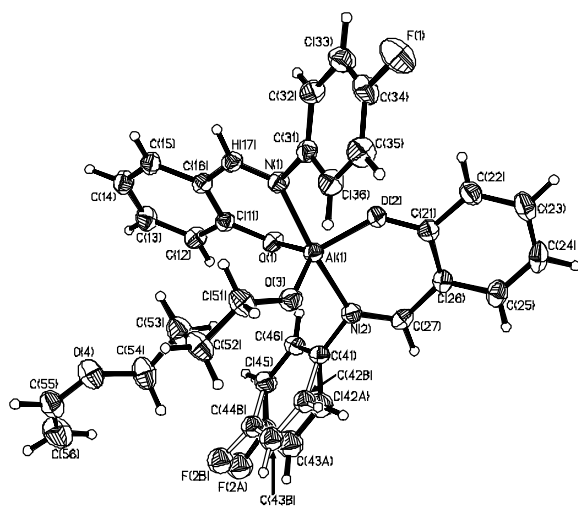
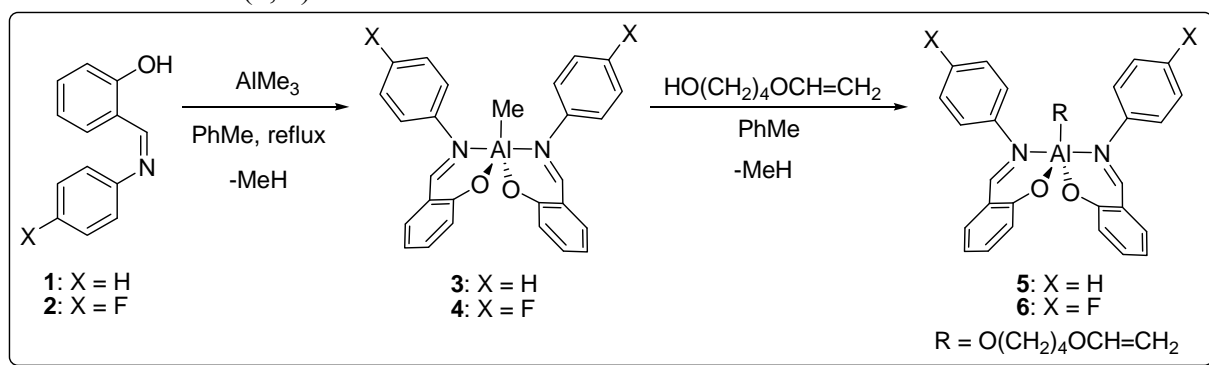
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Development of the efficient initiators of ring-opening polymerization (ROP) of cyclic esters (lactide, glycolide, ϵ -caprolactone) is one of the important trends of modern chemistry [1]. Usually organometallic compounds used as initiators of this process. Aluminum complexes based on phenolate ligands are easily accessible, their catalytic behavior in ROP is studied in detail. In accordance with coordination/insertion mechanism of ROP [2], the fragment of alcohol originally present in molecule of initiator is transferred to the end of the polymer chain. In this respect we proposed that application of aluminum complexes containing at Al atom fragments of unsaturated alcohols as initiators of ROP will results to macromonomers, which may be used as precursors of more complicated biodegradable polymer structures (brushes, stars etc.)

In this work we describe the synthesis of several aluminum complexes containing fragments of unsaturated alcohols (**5**, **6**).



The compounds **5**, **6** were investigated by multinuclear NMR spectroscopy and X-ray analysis. Compounds **5**, **6** have high activity in ROP of *D*, *L*-lactide and ϵ -caprolactone. The corresponding macromonomers were obtained with high functionality.

This work is supported by the RFBR (12-03-90020-Bel_a) and by President Grant for Young Russian Scientists (MD-3634.2012.3).

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P94: HYDROGENATION OF ACETYLENE ALCOHOLS OVER METAL-POLYMER CATALYSTS SUPPORTED ON ZINC OXIDE

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Macromolecule-metal complexes are promising catalysts for organic synthesis because polymers are widely used as stabilizers for metal nanoparticles which show high catalytic activity in many types of reactions. Hydrogenation of long-chain acetylene alcohols is one of the basic reaction for producing medicines, fragrances and bioactive substances. The catalysts were modified with polyethylene glycol (PEG) and fixed on ZnO. Catalytic properties were tested in the reaction of 3,7,11,15-tetramethyldodecine-1-ol-3 (C_{20}) hydrogenation under mild conditions. The results are presented in the Table.

Hydrogenation of C_{20} acetylene alcohol on 1%Cu-PEG/ZnO, 1%(Pd-Cu)/ZnO and 1%Pd-PEG/ZnO

Metal phase in 1%Me-PEG/ZnO catalysts	$W \cdot 10^{-2}$, mol/sec	$S_{C=C}$	TON
Cu	0.08	-	-
Pd:Cu = 1:3	0.27	70.9	-
Pd:Cu = 1:1	0.40	74.0	800
Pd:Cu = 3:1	1.88	81.0	7800
Pd	13.06	83.3	12000
Conditions: 0.05 g catalyst; $T=40^{\circ}C$; $P=1$ atm; ethanol - 20 ml, 2.2×10^{-3} mol C_{20}			

Hydrogenation rate on the copper catalyst is very low. Replacement of 0.25% Cu for Pd in 1%Cu-PEG/ZnO leads to the increase of activity of the bimetallic catalyst. Higher activity, selectivity and stability is observed for the 1%Cu-Pd-PEG/ZnO catalysts with the metal ratio of Pd:Cu = 3:1. The maximum activity and TON shows Pd-PEG/ZnO catalyst. However, the selectivity to olefin alcohol close to the obtained on the 1%(Cu-Pd)-PEG/ZnO. Catalysts prepared without PEG were less active.

According to TEM study, modification of the catalysts with PEG leads to the formation of uniformed nanoparticles of the active phase on the surface of the support.

Thus, modification of palladium catalysts with copper and PEG leads to the formation of active supported catalysts with nanoparticles of active phase of metals.

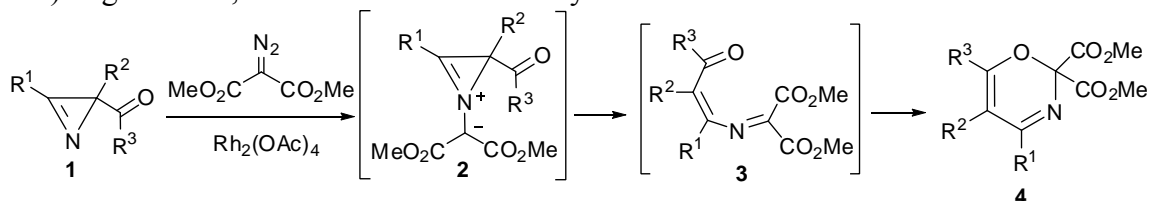
P95: Rh(II)-CATALYZED REACTIONS OF DIAZO ESTERS WITH 2-ACYL-2H-AZIRINES AND ISOXAZOLES

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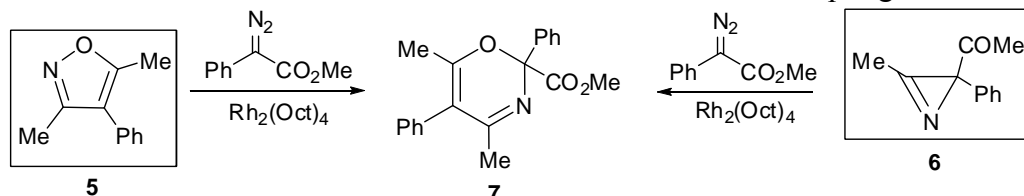
Rh(II)-catalyzed reaction of alkyl 2-phenyl-2-diazoacetates and dialkyl diazomalonates with 3-aryl- or 2,3-diaryl-2H-azirines is a facile route to stable electron-poor 2-azabuta-1,3-dienes [1]. 1-Acyl-2-azabuta-1,3-dienes, derived from 2-acyl-2-diazoacetates are unstable compounds, which undergo fast 1,6-electrocyclization into 2H-1,4-oxazines [2]. It is considered that the 2-azabuta-1,3-diene system results from ring opening of intermediate azirinium ylide.

We have shown that the formyl or acetyl group, introduced in the 4 position of 2-azabuta-1,3-diene by reaction of 2-formyl- or 2-acyl-2H-azirine with diazo compounds, also can be involved into 1,6-electrocyclization to give new 2H-1,3-oxazine derivatives. Thus, the reaction of 2-acyl-2H-azirines **1** with dimethyl diazomalonate in the presence of Rh₂(OAc)₄ proceeds sequentially via azirinium ylides **2** and 4-acyl-2-azabutadienes **3**, which undergo 1,6-cyclization under reaction conditions (84 °C, DCE) to give 2H-1,3-oxazines **4** in moderate yields.



R¹ = Ph, 4-ClC₆H₄, 4-MeOC₆H₄, 4-MeC₆H₄, Me; R² = H, Me, Ph; R³ = H, Me

Earlier the formation of the compounds **4** was observed in the Rh(II)-catalyzed reaction of α-diazo esters with isoxazoles, and two possible mechanisms of the process were suggested: a) ring opening of transient isoxazolium ylide to 2-azabuta-1,3-diene followed by 1,6-cyclization and b) [1,2]-sigmatropic shift in isoxazolium ylide [3]. We have found that the Rh₂(Oct)₄-catalyzed reaction of methyl 2-phenyl-2-diazoacetate with both isoxazole **5** and azirine **6** give one and the same product, 2H-1,3-oxazine **7**. This result as well as quantum-chemical calculations of the reaction routes indicates in favor of “azadiene” mechanism of isoxazole – diazo ester coupling.



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P96: HYDROFORMYLATION OF OLEFINS OVER HYBRID MESOPOROUS SILICATE-ANCHORED Rh-P COMPLEX

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Hydroformylation of olefins with syngas is an important homogeneous process which produces aldehydes with one more carbon than the initially employed olefin. However, the recycle of homogeneous catalysts is quite troublesome. The increasing awareness of green chemistry and atomic economy require the catalysts being recyclable. Mesoporous silicates thus offer us the significant opportunities to heterogenize metal complexes via multi-step assemble [1]. Here we report the immobilization of a Rh-phosphine complex into hybrid SBA-15 or MCM-41 (hereafter Rh-P(Ph₂)-(CH₂)_n-SBA-15 or Rh-P(Ph₂)-(CH₂)_n-MCM-41, n=1~11) and their application in C₆~C₁₀ olefins hydroformylation.

SBA-15 and MCM-41 was synthesized according to the literature methods [2,3], using TEOS as silicate source. The chloro-alkylation of the surface of SBA-15 or MCM-41, the connection of -PPh₂ and the coordination with Rh were carried out in turn under Schlenk operation, and the detailed procedures are shown in the literatures [4]. The preparative procedures were also monitored by Fourier-Transform Infrared Spectroscopy (FT-IR). In addition, the prepared catalysts were characterized by isothermal nitrogen adsorption, powder X-ray diffraction (XRD). Metal content was determined by inductive coupling plasma-atomic emission spectroscopy (ICP-AES).

Hydroformylation of C₆~C₁₀ olefins was carried out in a 100mL autoclave under the conditions of 393 K, 5 MPa syngas (H₂/CO = 1) and 2.5 h (using 5.0 mL olefin substrate and 15.0 mL toluene as a solvent). The resulting mixture was analyzed by a gas chromatograph equipped with an SE-30 capillary column. In the catalyst recycle experiments, the separated catalyst was washed by toluene under ultrasonic washing.

FT-IR monitoring showed that Rh-P complex was successfully anchored onto modified SBA-15 or MCM-41 via coordination bonding through flexible alkyl chain spacer with different carbon numbers. XRD patterns and nitrogen adsorption isotherms revealed ordered mesoporous structures of the prepared immobilized catalysts, indicating the preparative procedures of the catalysts did not ruin the support structure and revealing the good solvothermal stabilities of SBA-15 and MCM-41. The reaction results showed that the prepared immobilized catalysts reveal activities and remarkable selectivity to nonyl aldehydes in the recycle hydroformylation of 1-octene. The length of the alkyl spacer has a drastic effect on the specific activity (TON) of the immobilized catalysts. Rh complex immobilized through longer spacer revealed comparatively stable activity in light of no obvious decrease in substrate conversion. The catalyst prepared by longest alkyl spacer (C₁₁) revealed a specific activity comparable to the homogeneous counterpart. The immobilized catalysts showed remarkable low Rh leaching along with successful catalyst cycles. In addition, lower olefin (1-hexene) was more easily activated and the hydroformylation of 1-hexene gave the highest turnover number of substrate. On the contrary, the hydroformylation of 1-decene gave lowest TON level among the C₆~C₁₀ linear olefins.

Acknowledgments: This work is supported by China NSF (No. 20673064).

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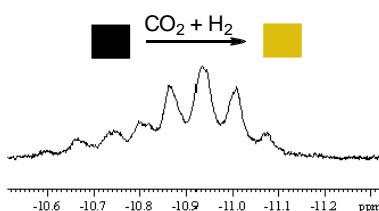
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P97: CATALYTIC HYDROGENATION OF CARBON DIOXIDE AND BICARBONATES WITH A WELL-DEFINED COBALT DIHYDROGEN COMPLEX

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Using a well-defined cobalt dihydride catalyst, we have shown [1] that it is possible to hydrogenate bicarbonates and CO₂ in high yields and TONs. Applying this active catalyst, significantly improved TONs for hydrogenation of bicarbonates and CO₂ compared to other non-precious metal-based catalysts have been achieved. Our cobalt complex is competitive or even superior in comparison with many known precious metal systems for the hydrogenation of CO₂. Notably, it is possible to perform reductions of carbon dioxide at comparably low pressures of H₂ and CO₂ (5 bar), giving the best TONs so far reported under such mild conditions. This represents a good starting point to further improve the hydrogenation at more ambient conditions with low-cost metals. Based on high pressure NMR and catalysis experiments with different kind of hydrid spezies of the complex, we propose that mixing of the PP₃ ligand and the cobalt precursor Co(BF₄)₂·6H₂O resulted in a defined dihydride complex [Co(H₂)PP₃]⁺BF₄⁻ which participates in the catalytic cycle.



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P98: LOW-TEMPERATURE SKELETAL ISOMERIZATION OF PARAFFINIC HYDROCARBONS IN THE PRESENCE OF A HOMOGENEOUS CATALYST SYSTEMS BASED ON ALUMINUM CHLORIDE

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Isohydrocarbons - the basis of modern petrochemistry, oil refining and the production of motor fuels. Today, the process of isomerization mastered less than half of the largest Russian plants.

We suggest the use of catalytic systems based on AlCl_3 in the isomerization of normal paraffins to produce isobutane, isopentane, isohexane and higher boiling hydrocarbons, required for the synthesis of monomers for synthetic rubber industry (isobutane–isobutylene, isopentane–isoprene), as well as high-octane additives to motor fuels.

Modern types of catalysts, including low-temperature chlorinated catalysts have some disadvantages: very high sensitivity to impurities of sulfur, nitrogen, moisture, corrosion of equipment, the need to neutralize the alkaline scrubber effluent gases. Moreover, the relatively high temperature of the process 120–160 °C are firstly, to increase energy expenditure, and secondly due to the thermodynamic limit in the working temperature zone the depth of isomerization of pentanes and hexanes is insufficient.

The process of skeletal isomerization of n-pentane and n-hexane in the presence of an ionic liquid based on AlCl_3 was studied. The optimum ratio of the components of the catalyst complex, the temperature at which the highest yields of the target isoparaffins are reached, were determined. As activating additives to the ionic liquid were investigated copper salts of different nature and their effect on the conversion of the starting hydrocarbon composition and yield of the products of isomerization.

It is shown that at the reaction temperature 20 °C proceeds efficiently isomerization of n-pentane, the conversion reaches 60–70% with selectivity of isoparaffins to 95%, the total yield of isoparaffins $\text{C}_4\text{--C}_8$ is 70%. This fact shows the effectivity of the investigated ionic liquid as a catalyst for the isomerization of hydrocarbon fractions in order to obtain the components of motor fuels.

The process takes place at low temperatures (20–40 °C), that are significantly lower than of the temperature conditions in which the industrial bifunctional catalysts isomerization of paraffinic hydrocarbons are working. This singularity of the catalytic properties of ionic liquids leads to increase in the yield of desired products and is a clear technological advantage of these catalysts.

The work was performed as part of the Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" for 2009-2013, FC № 14.740.11.0383.

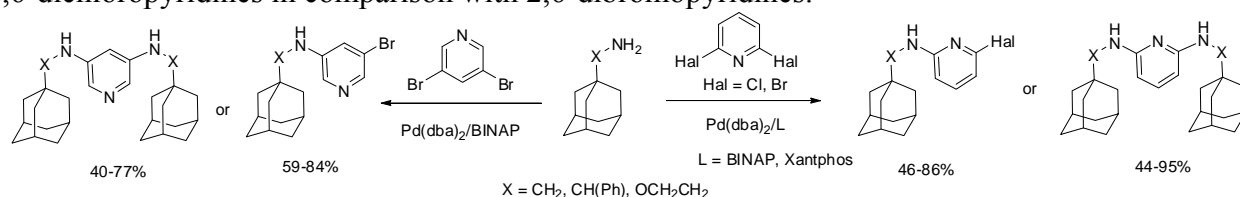
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P99: PALLADIUM-CATALYZED AMINATION OF DIHALOGENO SUBSTITUTED PYRIDINES AND QUINOLINES WITH ADAMANTANE-CONTAINING AMINES

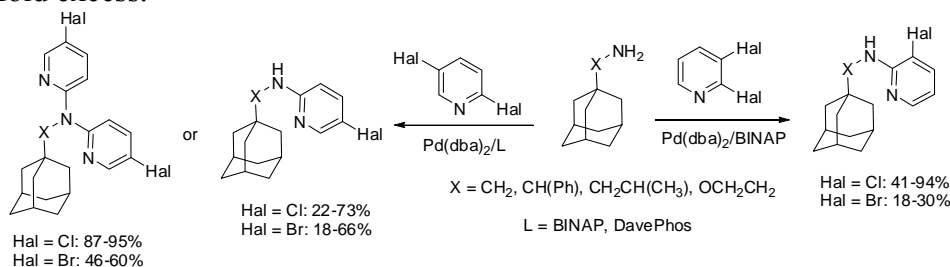
A.S. Abel¹, A.D. Averin¹, E.N. Savelyev², B.S. Orlinson², I.A. Novakov², I.P. Beletskaya¹

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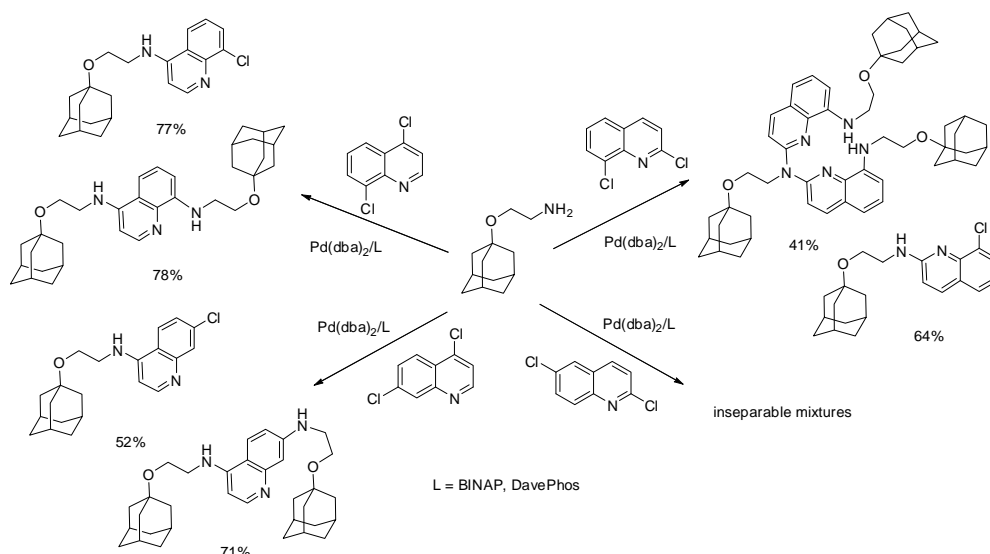
Symmetrical 2,6- and 3,5-dihalopyridines successfully produced mono- and diamino derivatives depending on the stoichiometry of starting compounds. Generally, better results were obtained with 2,6-dichloropyridines in comparison with 2,6-dibromopyridines.



The catalytic substitution of the halogen atom at α -carbon atom of pyridine in 2,3- and 2,5-dihalopyridines was in many cases successful, and better results were achieved with less active dichloropyridines. The most interesting fact is the possibility to synthesize *N,N*-bis(5-halopyridin-2-yl) derivatives of adamantane-containing amines in yields up to 95% using 2,5-dihalopyridines taken in a 4-fold excess.



Diamination of 4,7- and 4,8-dichloroquinolines with the excess of 1-(2-ethoxy)adamantane afforded diaminosubstituted quinolines in high yields while diamination of 2,6- and 2,8-isomers was not selective.



The work was supported by the RFBR grant 10-03-01108.

P100: VINYLIDENE COMPOUNDS OLYGOMERIZATION CATALYZED EXCHANGE RESINS, AS A METHOD FOR CLEANING OCTENE-1

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The major areas of application higher olefins are the production linear low density polyethylene (LLDPE), in which α -olefins are comonomers, and also surface-active agents (surfactants) different classes, oil additives, etc.

The basic requirements for quality α -olefins relate content vinylidene olefin structures that separation by rectification is impossible because of close boiling point. That vinylidene isomers, being the most active and reactive, especially in the reaction. However, their branched structure not give the expected properties of products derived from α -olefins.

The chosen method of treating the fraction of α -olefins C_8 of JSC "Nizhnekamskneftekhim" is based on a highly reactive hydrocarbons vinylidene double bonds. Cleaning is the selective oligomerization reaction olefins with tertiary carbon atom, followed by stripping unreacted α -olefins.

The catalyst of oligomerization was used sulfonic Lewatit K-2425, which is a macroporous catalyst with high content of SO_3H -groups, pore diameter 240 Å, the total exchange capacity of 5.20 mq/g. Studies have shown that the initial rate of the reaction of oligomerization is more dependent on the reaction temperature, and to a lesser extent on the concentration of catalyst.

The values of the initial velocities of the oligomerization reaction, depending on the temperature and the concentration of catalyst.

Temperature, °C	Catalyst concentration, wt%.		
	5	10	15
	Initial velocity, mol / l·s $\times 10^5$		
60	0,41	0,83	0,75
80	2,08	1,85	1,7
100	2,17	2,07	2,01

Optimal conditions of the selective oligomerization vinylidene hydrocarbons C_8 on sulphocationite Lewatit K-2425: $T = 80$ °C, the concentration of the catalyst 10 wt %. Response time 3 hours. The conversion vinylidene hydrocarbons in these conditions was 94.66%, and their content was reduced from 1.8 to 0.096 wt%.

Isomer content in a fraction of C_8 α -olefins.

Isomers	Parent fraction	Purified fractions
Linear α -olefins,% wt..	97,31	98,99
Vinylidene hydrocarbons,% wt.	1,8	0,096
With the inside of the double bond,% wt.	0,89	0,914

The work was performed as part of the Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" for 2009-2013, FC № 14.740.11.0383.

P101: NOVEL CHIRAL AMINOCARBENE COMPLEXES DERIVED FROM THE COUPLING OF AMINO ACID ESTERS WITH ISONITRILES

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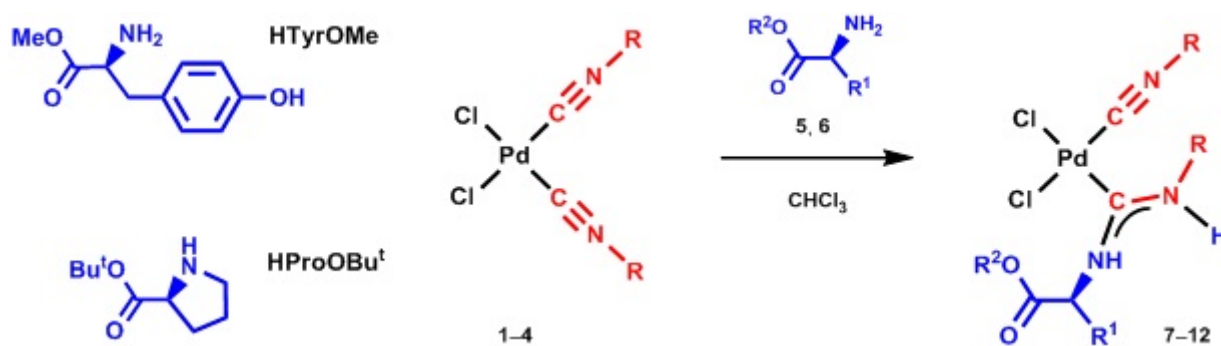
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Metal-mediated coupling between one isonitrile ligand in *cis*-[PdCl₂(CNR)₂] [R = C₆H₃(2,6-Me₂) **1**, C₆H₃(2-Cl,6-Me) **2**, C₆H₁₁ **3**, *t*-Bu **4**] and optically active amino acid esters *L*-HTyrOMe **5** and *L*-HProO(*t*-Bu) **6** proceeds under mild conditions (CHCl₃, 20–25 °C) giving chiral aminocarbene species *cis*-[PdCl₂(CNR)(C(*L*-TyrOMe)NHR)] [R = C₆H₃(2,6-Me₂) **7**, C₆H₃(2-Cl,6-Me) **8**], *cis*-PdCl₂(CNR)(C{*L*-ProO(*t*-Bu)}NHR) [R = C₆H₃(2,6-Me₂) **9**, C₆H₃(2-Cl,6-Me) **10**, C₆H₁₁ **11**, *t*-Bu **12**].



All compounds were fully characterized by elemental analyses (C, H, N), ESI-MS, IR, 1D (¹H and ¹³C{¹H}) and 2D (¹H, ¹H-COSY, ¹H, ¹³C-HMQC/¹H, ¹³C-HSQC, ¹H, ¹³C-HMBC) NMR spectroscopic techniques, and by X-ray diffraction for five complexes. The set of analytical methods indicated that the absolute configuration of the chiral component remains the same in the reaction [1].

Generated aminocarbene complexes were employed as precatalysts for the symmetric Suzuki-Miyaura coupling of aryl bromides BrC₆H₄R-4 with phenylboronic acid giving biaryl species and demonstrated catalytic activity (yields about 50%, TONs up to 5•10⁴) under mild conditions (80 °C, Na₂CO₃, EtOH). Preliminary results showed that compound **9** possess a catalytic activity (yield about 50%, TON about 40) under extremely mild conditions (25 °C, Na₂CO₃, toluene). The catalytical properties of all the obtained chiral carbene species in the asymmetric processes will further be explored and compared to those for previously reported chiral NHC complexes [2].

This project has been supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (Projects PTDC/QUI-QUI/098760/2008 and PTDC/QUI-QUI/109846/2009 and Ph.D. Grant for TBA SFRH/BD/81459/2011). The authors thank Russian Fund for Basic Research for a grant (11-03-12044-ofim).

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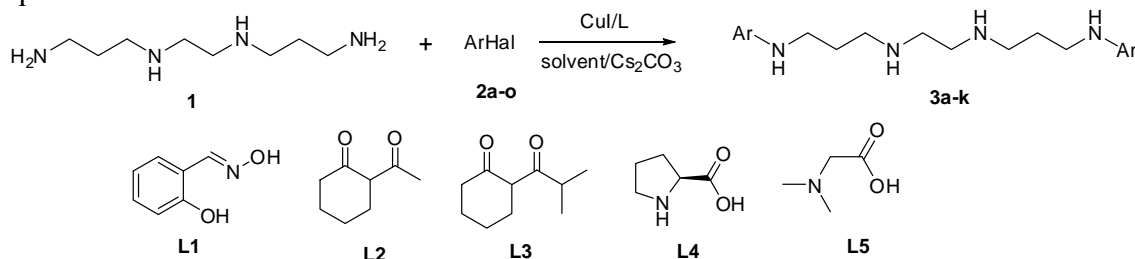
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P102: Cu(I)-CATALYZED ARYLATION AND HETEROARYLATION OF POLYAMIN

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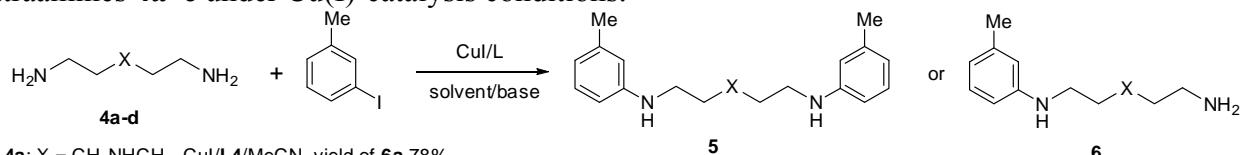
Cu(I)-catalyzed *N,N'*-diarylation of tetraamine **1** with a variety of aryl halides **2a–o** provided corresponding compounds **3a–k** in yields up to 68%, aryl iodides being more reactive than aryl bromides. The reaction conditions were adjusted to favor selective arylation of primary amino groups.



2a: PhBr, CuI/L4/MeCN, yield of **3a** 65%
2b: PhI, CuI/L4/MeCN, yield of **3a** 59%
2c: *m*-bromotoluene, CuI/L4/MeCN, yield of **3b** 55%
2d: *m*-iodotoluene, CuI/L4/MeCN, yield of **3b** 67%
2e: 3,5-dimethyliodobenzene, CuI/L2/DMF, yield of **3c** 54%
2f: 1,3-dibromobenzene, CuI/L2/DMF, yield of **3d** 28%
2g: 1-bromo-3-iodobenzene, CuI/L4/EtCN, yield of **3d** 27%
2h: 1,3-diiodobenzene, CuI/L4/EtCN, yield of **3e**, 24%

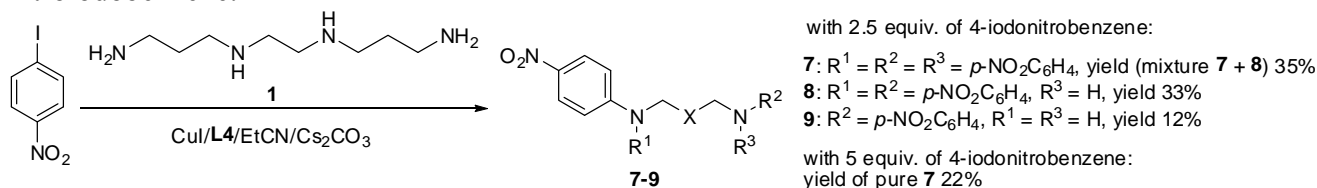
2i: 4-bromobiphenyl, CuI/L1/toluene, yield of **3f** 27%
2j: 4-iodobiphenyl, CuI/L4/MeCN, yield of **3f** 43%
2k: 4-acetoxy-4'-iodobiphenyl, CuI/L4/EtCN, yield of **3g** 68%
2l: *N,N*-diethyl-3-iodobenzamide, CuI/L4/EtCN, yield of **3h** 58%
2m: 2-bromonaphthalene, CuI/L3/DMF, yield of **3i** 28%
2n: 4-iodoanisole, CuI/L4/EtCN, yield of **3j** 52%
2o: 4-iodochlorobenzene, CuI/L4/EtCN, yield of **3k** 42%

m-Iodotoluene was used as a model reagent for the investigation of the reactivity of tri- and tetraamines **4a–c** under Cu(I)-catalysis conditions.

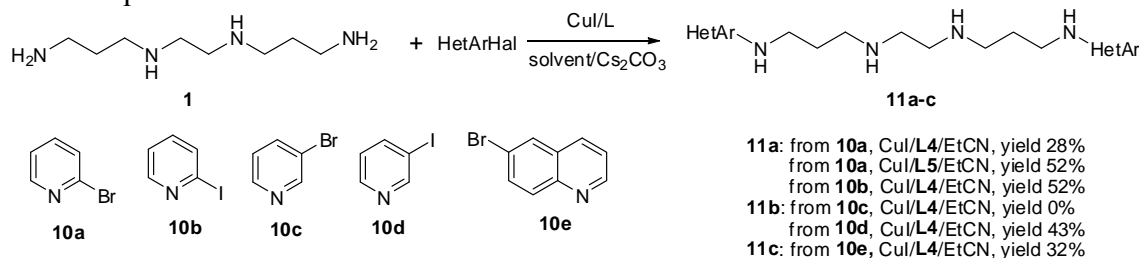


4a: X = CH₂NHCH₂, CuI/L4/MeCN, yield of **6a** 78%
4b: X = NHCH₂CH₂CH₂NH, CuI/L4/EtCN, yield of **5b**, 35%
4c: X = CH₂NHCH₂CH₂CH₂NHCH₂, CuI/L4/EtCN, yield of **5c**, 18%

The possibility of *N,N*-diarylation of primary amino groups was demonstrated when using *p*-nitroiodobenzene.



N,N'-diheteroarylation reactions of tetraamine **1** was carried out using bromo- and iodosubstituted pyridines and quinoline.



The work was supported by the RFBR grant N 12-03-00796.

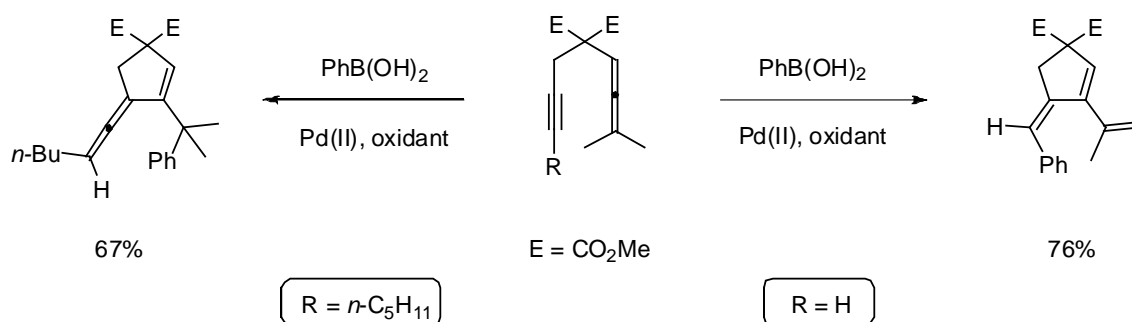
P103: PALLADIUM-CATALYZED OXIDATIVE ARYLATIVE CARBOCYCLIZATION OF ALLENYNES

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Transition metal-catalyzed cyclizations of allenynes provide efficient and atom-economical routes to polyunsaturated carbo- and heterocycles.^[1] An oxidative protocol was developed allowing for the palladium-catalyzed synthesis of arylated carbocyclic structures under mild and insensitive conditions.^[2] Using palladium acetate as catalyst and 1,4-benzoquinone as oxidant, a wide range of arylboronic acids is suitable for the cyclization reactions of 1,5-allenynes.

Employing these conditions cross-conjugated trienes were obtained in the case of a terminal or an aryl-substituted alkyne-moiety. However, with alkyl-substituents access to vinylallenenic products is provided. Two possible mechanisms were suggested to rationalize the formation of the two different products.



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P104: CARBOHYDRATE-DERIVED PHOSPHORAMIDITE LIGANDS FOR ENANTIOSELECTIVE Cu-CATALYZED 1,4-CONJUGATE ADDITION OF DIETHYLZINC TO ENONES

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The enantioselective copper-catalyzed conjugate addition is one of the most important methods for the formation of new stereogenic center. Leading role among chiral ligands used for this reaction play phosphoramidite ligands based on the atropisomeric binaphthols and chiral amines. There are only single examples of phosphoramidite ligands based on carbohydrate-derived amines, all other are mixed phosphonic-phosphoramidite ligands. Having in mind that most of successful phosphoramidite ligands were based on a single phosphorous atom, we decided to synthesize carbohydrate-derived ligands having the structure **I** (Figure 1), in which one can control the asymmetric induction by varying steric demands of protecting group R–R’.

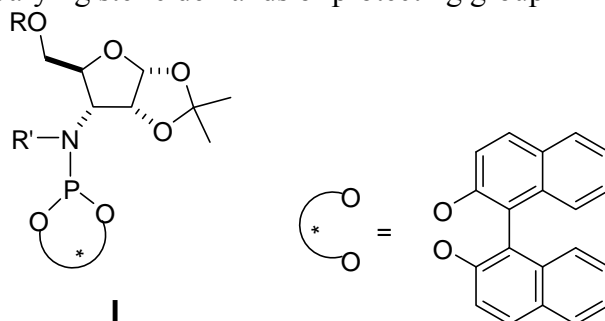


Fig. 1

We have synthesized library of ligands with various protecting group R and R’ (hydrogen or alkyl) and used them for the enantioselective conjugate addition of Et₂Zn to chalcone and cyclohexenone. Best results were obtained for ligands with *tert*-butyldimethylsilyl as the R group and benzyl (77% ee for chalcone) or cyclohexylmethyl (57% ee for cyclohexenone) as R’ groups. This results position our ligands among the best sugar-derived ligands for copper-catalyzed conjugate addition.

P105: HETEROGENEOUS CATALYSIS WITH IMMOBILIZED PALLADIUM NANOPARTICLES ON METAL-ORGANIC FRAMEWORKS (PD@MOF)

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Due to the growing need for sustainable development, enormous efforts to develop environmentally friendly and efficient catalytic systems have been made. In this context, heterogeneous catalysis offers great advantages from an industrial and environmental point of view. Heterogeneous catalysts can be separated from the reaction media, they can be recycled more easily than homogeneous catalysts, and the production of waste can be minimized. We describe here our latest results on the synthesis and characterization of a novel heterogeneous catalyst that consists of palladium nanoparticles incorporated in a functionalized metal-organic framework (MIL-101(Cr), Figure 1). [1]

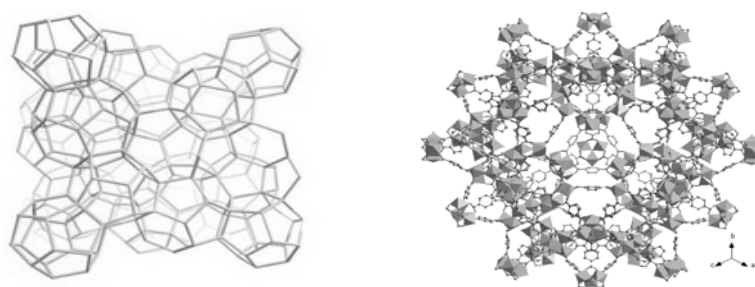


Figure 1. Zeotype architecture of MIL-101(Cr) (left) and structure of the large cage (right).

We also present the catalytic activity of the palladium catalyst (Figure 2) in the aerobic oxidation of alcohols. [2]

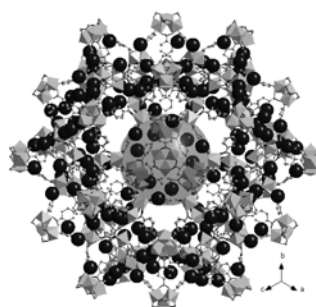


Figure 2. Palladium nanoparticles inside functionalized MIL-101(Cr).

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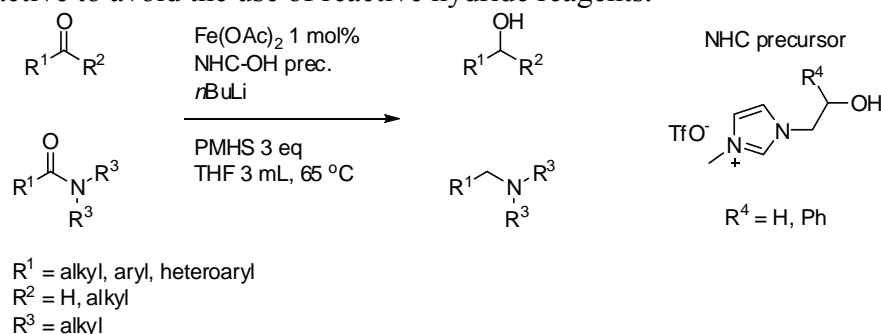
P106: DIRECT AND EFFECTIVE IRON/NHC CATALYZED HYDROSILYLATION OF ALDEHYDES, KETONES AND TERTIARY AMIDES

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The reduction of carbonyl compounds to alcohols is a common and most useful method for the formation of alcohols. There are numerous transition metal catalyzed methods for this transformation, but most catalysts today are derived from heavy or rare metals and the toxicity and high price of those are drawbacks for large scale synthesis. There is a demand for the use of non-toxic and less expensive metals, and iron, which has a high natural abundance, is environmentally and biologically benign and inexpensive has become one of the most interesting alternatives. In particular, a number of iron catalyzed hydrosilylation protocols have been presented during the last years.[1]

Here we show a new iron/N-heterocyclic carbene (NHC) catalyzed hydrosilylation protocol, where an active catalyst was formed in situ from structurally simple hydroxyethyl imidazolium salts together with an iron source, and the inexpensive and benign silane polymethylhydrosiloxane (PMHS).[2] The potentially bidentate ligand shows an enhanced catalytic activity to similar systems, and the scope of the reaction is very wide. The highly active hydroxyethyl NHC system was also proven to work well for the reduction of tertiary amides to amines, a transformation where it is highly attractive to avoid the use of reactive hydride reagents.



Scheme 1 Direct hydrosilylation of carbonyl compounds catalyzed by in situ generated iron/NHC complexes

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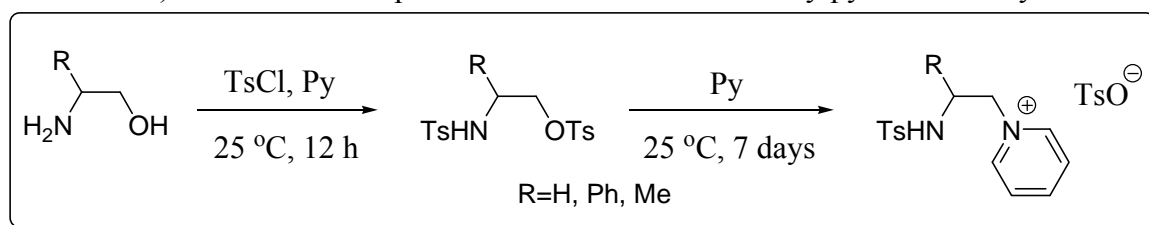
P107: UNEXPECTED FORMATION OF *N*-ALKYLPYRIDINIUM SALTS AS AN ALTERNATIVE WAY TO ETHANOLAMINE TOSYLATION IN PYRIDINE

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The ligands based on ethanolamines widely used in organometallic and coordination chemistry [1]. The tosylation reaction of ethanolamines results to semiproducts in synthesis of such ligands. The classical method of tosylation of monoethanolamines usually results in *N,O*-ditosylation [2]. However, in some cases the alcohol tosylation gives the products with substitution of TsO group by nucleophiles present in reaction medium [3]. In this study we have established that tosylation of monoethanolamines in a medium of pyridine under increased reaction time (compared to the classical method) leads to the unexpected formation of novel *N*-alkylpyridinium tosylates.



The structure of the compounds obtained was established by multinuclear NMR spectroscopy and X-ray analysis ($\text{R} = \text{H}$).

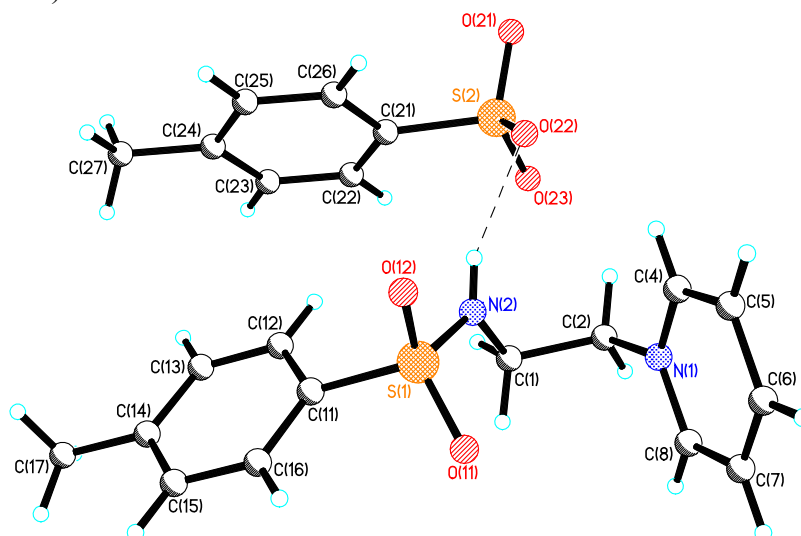


Figure. Molecular structure of the compound ($\text{R} = \text{H}$).

This work is supported by the RFBR (12-03-00206-a) and by President Grant for Young Russian Scientists (*MD-3634.2012.3*).

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P108: FACILE AND SOLVENT FREE SYNTHESIS OF XANTHENES AND BENZOXANTHENE DERIVATIVES USING SIMPLE IONIC LIQUIDS

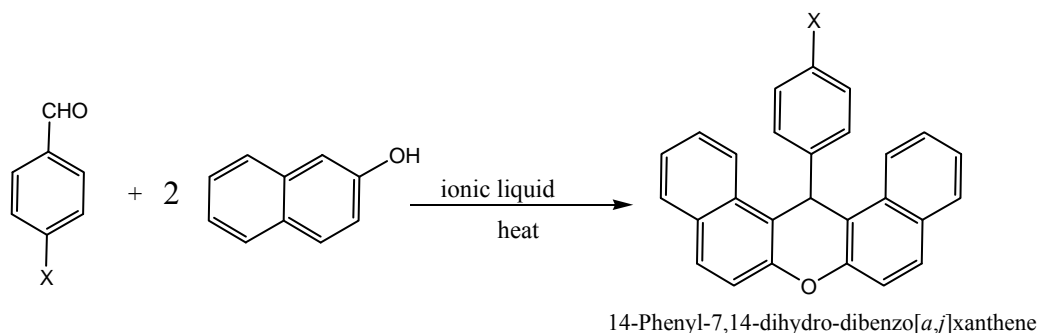
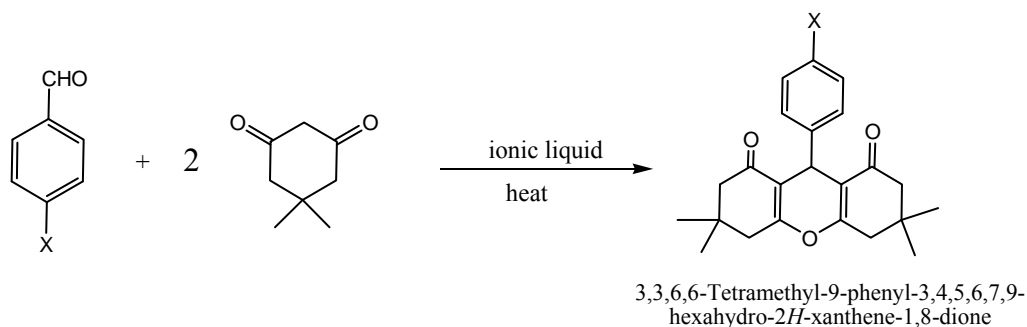
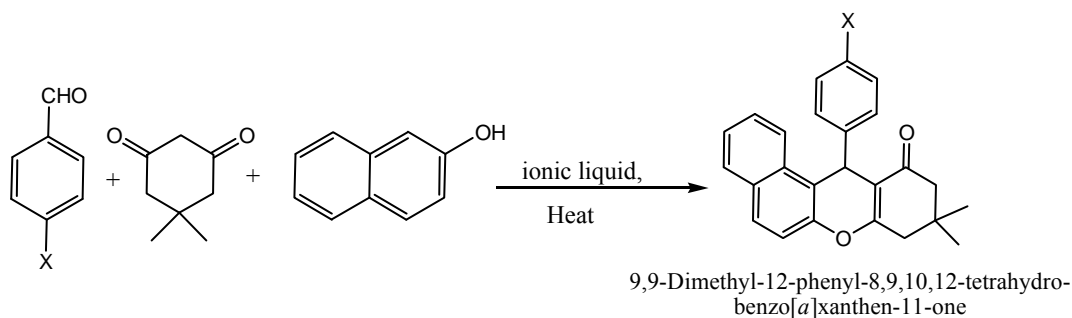
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The synthesis of xanthenes, especially benzo xanthenes has attracted great interest in recent years due to their wide range of biological and pharmaceutical properties such as antiviral, antibacterial, and anti-inflammatory activities as well as sensitizers in photodynamic therapy.

A facile, efficient and environment-friendly protocol for the synthesis of 9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one, 3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione and 14-Phenyl-14H-dibenzo[a,j]xanthene by a one-pot condensation of 2-naphthol, 5,5-dimethyl-1,3-cyclohexadione and aromatic aldehydes promoted by simple ionic liquid under solvent-free conditions is reported.

The synthetic approach offer the advantages of clean reaction, simple methodology, short reaction time, high yield, easy purification, and easy preparation of the catalysts.

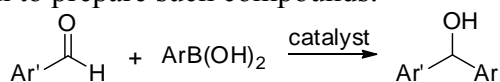


P109: CHIRAL NHC-RHODIUM(I) COMPLEXES AND THEIR APPLICATIONS IN THE ARYLATION OF ALDEHYDES

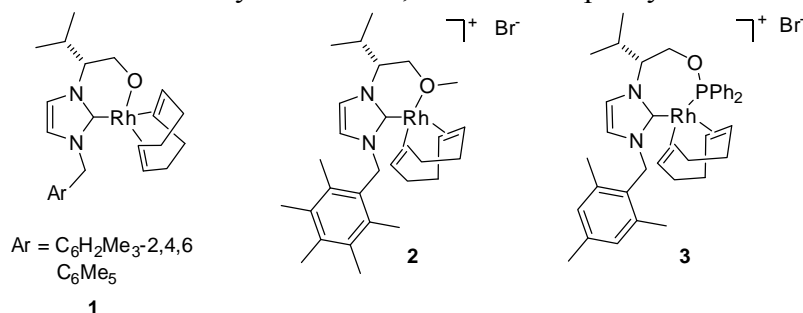
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Diarylmethanols are important structural motives for the synthesis of biologically and pharmaceutically active compounds.¹ The addition of organometallic reagents to aryl aldehydes has been the general method to obtain the diarylmethanols. Organolithium, organomagnesium, organozinc and organocopper compounds are the most frequently used organometallics. However, limitations to their applications arise from the nature of the reagents, which are usually toxic and sensitive to air and moisture.² Therefore, 1,2-addition of boronic acids to aldehydes catalyzed by various metal complexes has attracted considerable attention following the seminal report by Miyaura et. al. in 1998.³ Since then several catalysts have been developed and NHC complexes, has become a very useful approach to prepare such compounds.⁴



With regard to the synthesis of chiral diarylmethanols, the asymmetric arylation of aldehydes with boronic acids in the presence of chiral NHC complexes has attracted much attention.⁵ Chiral neutral (1) and cationic NHC-Rh(I) complexes (2, 3) were prepared and characterized by spectroscopic techniques. These were used as catalysts for the 1,2-addition of phenylboronic acid to aldehydes.



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P110: HIGHLY ENANTIOSELECTIVE ORGANOCATALYTIC TRIFLUOROMETHYL CARBINOL SYNTHESIS – A CAVEAT ON REACTION TIMES AND PRODUCT ISOLATION

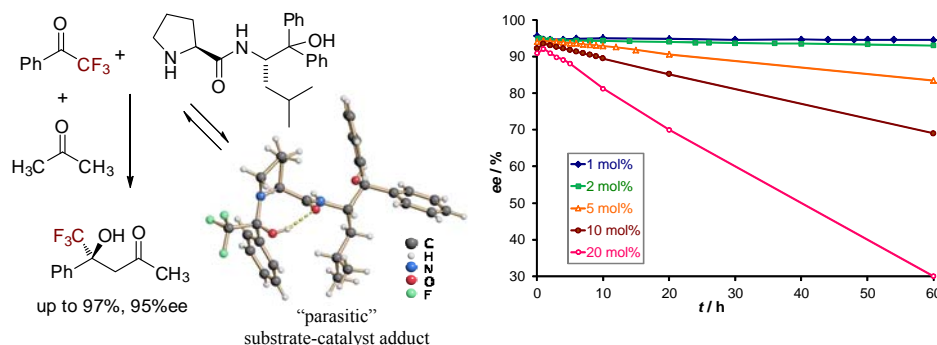
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The asymmetric organocatalytic aldol reaction serves as one of the most powerful carbon-carbon bond forming methods, providing access to β -hydroxycarbonyl compounds in an enantio-selective fashion.¹ Herein, we describe aldol reactions with trifluoroacetophenones as acceptors, yielding chiral α -aryl, α -trifluoromethyl tertiary alcohols, valuable intermediates in organic synthesis. Of the various organocatalysts examined, Singh's catalyst [(2*S*)-N-[(1*S*)-1-hydroxydiphenylmethyl]-3-methylbutyl]-2 pyrrolidinecarboxamide] was found to efficiently promote this organocatalytic transformation in a highly enantioselective manner.² Detailed reaction monitoring (¹⁹F-NMR, HPLC) showed that up to full conversion, the catalytic transformation proceeds under kinetic control and affords up to 95 % ee in a time-independent manner.³ At longer reaction times, the catalyst effects racemization. For the product aldols, even weak acids (such as ammonium chloride) or protic solvents can induce racemization, too. Thus, acid-free workup, at carefully chosen reaction time, is crucial for the isolation of the aldols in high (and stable) enantiomeric purity. As evidenced by ¹⁹F-NMR, X-ray structural analysis, and independent synthesis of a stable intramolecular variant, Singh's catalyst reversibly forms a catalytically inactive ("parasitic") intermediate, namely a N,O-hemiacetal with trifluoroacetophenones. X-ray crystallography also allowed the determination of the product aldols' absolute configuration (*S*).



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P111: CATALYTIC CYCLOALUMINATION AS A NEW APPROACH FOR STEROID MODIFICATION

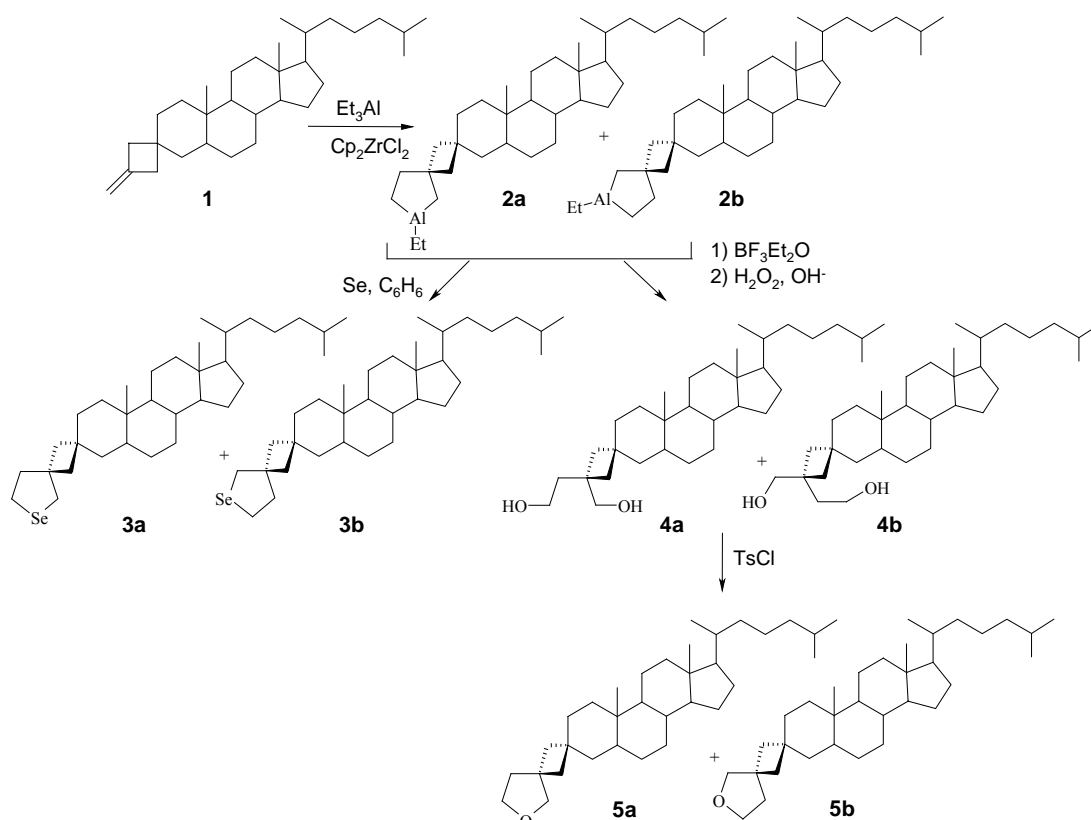
V.A. Dyakonov, R.A. Tuktarova, I.I. Islamov, U.M. Dzhemilev

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The development of new modification methods for natural and synthetic steroids remains actual problem in organic chemistry since the resulting derivatives may possess various types of biological activities.

We believe that the cycloalumination reaction of unsaturated compounds, which was developed in our laboratory and was found wide application in synthesis of mono- and bifunctional hydrocarbons as well as carbo- and heterocyclic compounds, is one of approaches for incorporation of carbo- and heterocyclic fragments or functional groups in a steroid molecule [1,2].

In this report, this new approach for steroid modification is demonstrated on the example of 3'-methylene-spiro[(5 α)-cholestane-3,1'-cyclobutane] **1**, which enters into the Cp₂ZrCl₂-catalyzed cycloalumination reaction with Et₃Al to afford diastereomeric pair of spiro[(5 α)-cholestane-3,2'-(6'-ethyl-6'-alumina-spiro[3.4]octane)] **2a** and **2b**. The latters undergo transformations to both selenophane derivatives **3a,b** when treated with Se in benzene solution and tetrahydrofurane derivatives **5a,b** through oxidation with hydrogen peroxide followed by cyclization of resulting diols **4a,b**.



This work was financially supported by Russian Foundation for Basic Research (Grants 10-03-00046, 11-03-00103, 11-03-97001).

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P112: GOLD(I)-CATALYZED INTERMOLECULAR CYCLOADDITIONS OF ALLENAMIDES

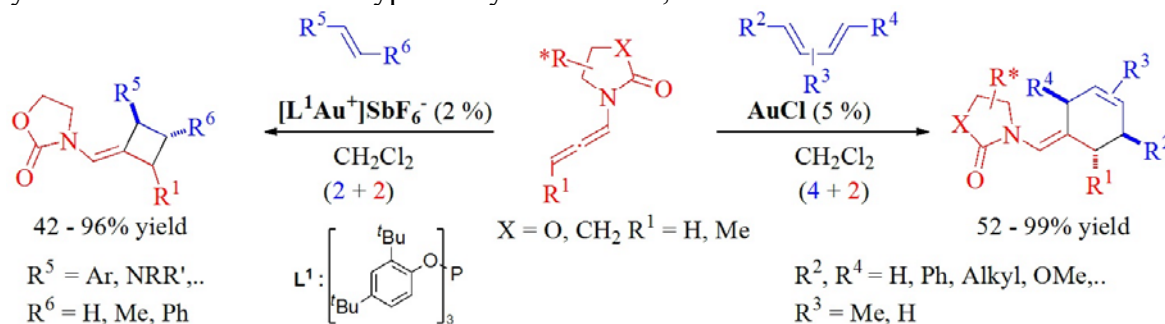
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In recent years there have been extraordinary advances in the development of Au-catalyzed processes. [1] In this context, our group has recently demonstrated the possibility of using allenes as three or two carbon components in intramolecular Au-catalyzed [4C+3C] and [4C+2C] cycloadditions.[2]

Herein, we describe our results on the development of Au-catalyzed (4 + 2) intermolecular cycloaddition between a variety of dienes and allenamides, which is efficiently catalyzed by AuCl.^[3] Curiously, in some cases, (2 + 2) cycloadducts were also detected as minor side products. On these bases, and considering the synthetic and medicinal relevance of these cyclobutanic systems, we specifically pursued the development of a Au-catalyzed intermolecular (2 + 2) cycloaddition. As a result, we found that these (2 + 2) cycloadditions between allenamides and alkenes can be efficiently achieved using a gold complex incorporating a bulky phosphite ligand, providing excellent yields of a variety of (2 + 2) adducts, with complete regio-, chemo- and stereo-selectivity.^[4] Analysis of their scopes, possible mechanistic scenarios as well as the development of asymmetric versions of these types of cycloadditions, will also be discussed.



HF acknowledges FCT for a doctoral fellowship SFRH/BD/60214/2009.

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P113: NEW CHIRAL NHC LIGANDS FOR THE COPPER-CATALYZED ASYMMETRIC CONJUGATE ADDITION OF GRIGNARD REAGENTS

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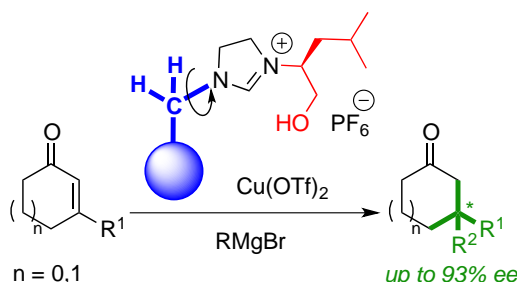
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Since asymmetric conjugate additions (A.C.A.) represent a powerful methodology allowing direct access to enantioenriched ketones, we kept our attention on some specific remaining challenges.[1] At this time, only few copper-catalysed nucleophiles were able to be introduced selectively on trisubstituted enones, promoted by various types of NHC's chiral ligands.[2] This work discloses recent advances in the A.C.A. of the highly desirable Grignard reagents to β -substituted cyclic enones.[3]

Several ligands have been synthesized in high yields and involved in catalysis for the addition of ethylmagnesium bromide leading to chiral 3,3-cyclohexanone (up to 93% *ee*). The best ligand was then engaged in optimized conjugate additions of various Grignard reagents allowing for the formation of quaternary centers with high level of regio- and enantioselectivity with only 0.75mol % of catalyst loading. Noteworthy is the addition of alkylmagnesium bromide for the construction of 3,3-cyclopentanone (up to 86% *ee*), highlighted by useful chiral synthon synthesis. Such level of selectivity for A.C.A. of alkylmagnesium bromide to 5-membered rings is unprecedented.



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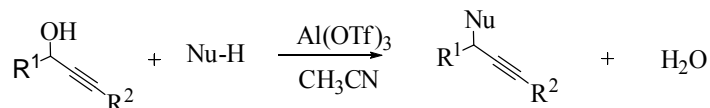
P114: Al(OTf)₃: AN ENVIRONMENTALLY BENIGN CATALYST FOR DIRECT NUCLEOPHILIC SUBSTITUTION OF THE HYDROXY GROUP OF PROPARGYLIC ALCOHOLS

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Substitution of the hydroxy group of propargylic alcohols by nucleophiles gives access to functionalized alkynes which can be readily converted into a variety of other functional groups. [1] As a result of the wide synthetic applicability associated with the alkyne functional group, the propargylic alcohol substitution reaction has played a major role in organic synthesis. In this regard, the most useful methodologies are based on transition-metal, [2] Lewis [3] and Brønsted acid [4] catalyzed/ mediated substitution reactions. Many of these and other methods [5] are, however, hampered by the cost and availability of the catalysts, excessive catalyst loading and/or limited nucleophile applicability. While a few catalyst systems (FeCl₃ in CH₃CN, MoCl₅ in DCM, and phosphomolybdic acid on silica) have been reported for propargylic alcohol substitution reactions in decent yields [6], none of these allow for C–C bond formations. In view of the synthetic importance of these propargylic synthons, the development of a general and convenient method for their synthesis is desired.

In this presentation we would like to disclose our results with regards to the Al(OTf)₃-catalyzed direct substitution of propargylic hydroxy groups with various aromatic and heteroatomic nucleophiles including indole to afford the corresponding products in excellent yields.



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P115: RUTHENIUM COMPLEXES OF 1,10-PHENANTHROLINE DERIVATIVES AND THEIR CATALYTIC PROPERTIES

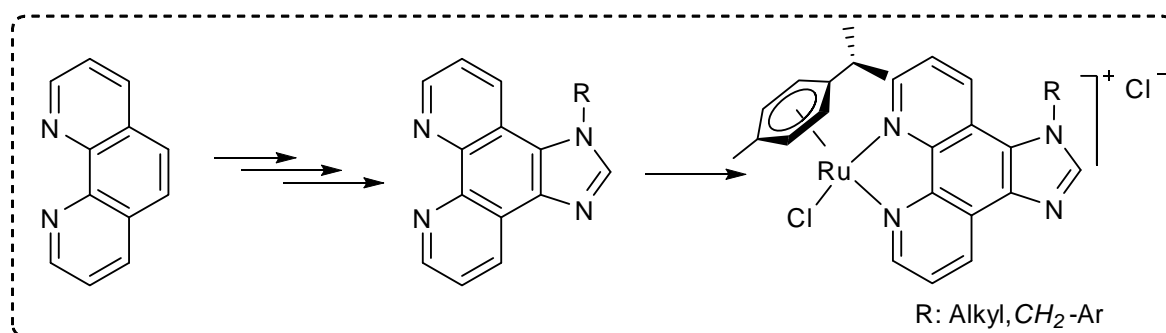
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(η^6 -Arene)ruthenium(II) complexes have been subject to intensive studies for many years due to their interesting coordination chemistry and catalytic properties.^[1] Furthermore interest in the chemistry of half-sandwich (η^6 -arene)-ruthenium(II) complexes received considerable attention owing to their interesting anti-tumor activity.^[2]

The reduction of ketones using catalytic hydrogenation transfer conditions with 2-propanol as hydrogen source has been largely investigated in the last years and several ruthenium complexes have proven to be efficient catalyst precursors in transfer hydrogenation.^[3]

We have studied and catalytic properties of five new complexes (Scheme 1) isolated from the reaction between $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ dimers and derivatives of 1,10-phenanthroline.



Scheme 1. Reaction steps of Ru(II) complexes

Firstly, starting from phenanthroline 1,10-phenanthroline-5,6-dione was synthesized afterwards benzimidazole derivatives, 1*H*-imidazo-[4,5-*f*][1,10]phenanthroline formed by ring closing process by means of NH_4OAc and formaldehyde, interaction with this ligand and the alkyl halide in basic medium, afforded *N*-substituted benzimidazole derivatives, 1-*R*-1*H*-imidazo[4,5*f*][1.10]phenanthroline was synthesized. Reaction of obtained ligands with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ gave water soluble ruthenium complexes according to the steps are shown in Scheme 1.

The new ruthenium(II) complexes have been employed as catalyst for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source and results were compared.

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P116: METAL-FREE ARYLATION OF OXYGEN NUCLEOPHILES WITH DIARYLIODONIUM SALTS

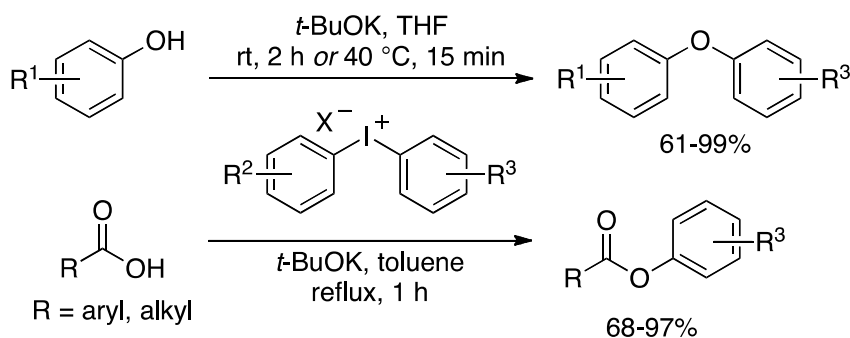
N. Jalalian, T.B. Petersen, B. Olofsson

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Diaryl ethers and aryl esters are common structural motifs in pharmaceuticals and agrochemicals.¹ Many natural products containing the diaryl ether substructure have received considerable attention, including vancomycin and other glycopeptide antibiotics, as well as anti-HIV agents like chloroceptin. Despite an immense focus on the synthesis of these compound classes, *ortho*-substituted diaryl ethers and sterically hindered aryl esters remain difficult to obtain for applications in life science and the polymer industry.²

We have developed methodology for the electrophilic arylation of phenols, carboxylic acids and sulfonic acids with diaryliodonium salts. The reaction conditions are mild, metal-free, and avoid the use of halogenated solvents, additives or excess reagents.

The arylated products are obtained in good to excellent yields in short reaction times. Sterical hindrance is very well tolerated, both in the nucleophile and in the diaryliodonium salt. The scope includes bulky *ortho*- and halo-substituted products, which are difficult to obtain by metal-catalyzed protocols. Many functional groups are tolerated, including carbonyl groups, heteroatoms and alkenes.³⁻⁵



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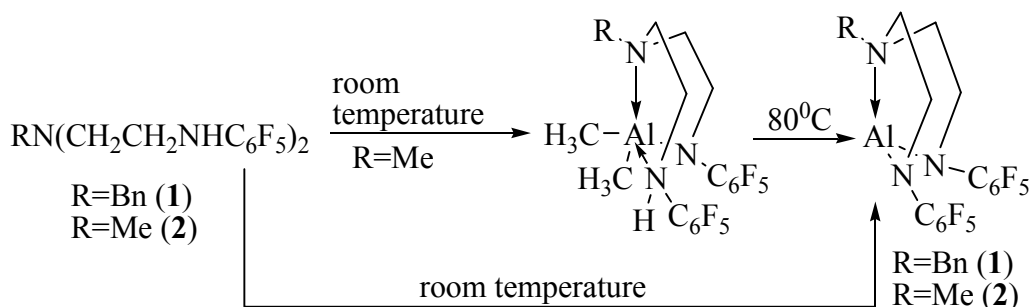
P117: ALUMINUM COMPLEXES BASED ON TRIDENTATE NITROGEN DONOR LIGANDS AS PERSPECTIVE CATALYSTS OF RING-OPENING POLYMERIZATION OF HETEROCYCLES

M.M. Kireenko¹, K.V. Zaitsev¹, Y.F. Oprunenko¹, A.V. Churakov², S.S. Karlov¹, G.S. Zaitseva¹

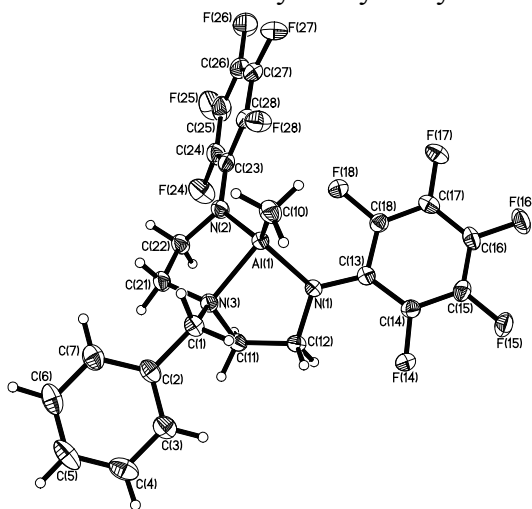
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Biodegradable and biocompatible materials are of great importance today [1]. The most convenient and efficient method to obtain such materials is the ring opening polymerization (ROP) of cyclic esters. There has been particular attention over the past decade on the development of new catalytic systems for this process. Tetracoordinated group 13 derivatives are promising catalysts for the ring-opening polymerization of heterocycles (propylene oxide and (*D, L*)-lactide) [2]. Tridentate nitrogen donor ligands (RN(CH₂CH₂NHR')₂) can be used for stabilizing four-coordinate aluminum center [3]. We synthesized novel complexes of aluminum based on the related ligands. It has been shown that replacement of alkyl substituent at one nitrogen atom in the ligand has a great influence on the course of the reaction.



The crystal structure of compound **1** was studied by X-ray analysis.



This work is supported by the RFBR (12-03-00206-a) and by President Grant for Young Russian Scientists (MD-3634.2012.3).

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P118: PALLADIUM-CATALYZED AMINATION IN THE SYNTHESIS OF MACROTRICYCLIC CRYPTANDS

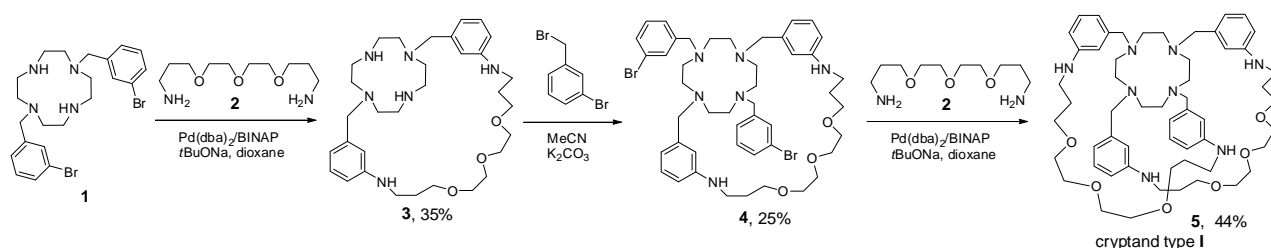
S.M. Kobelev¹, A.D. Averin¹, F. Denat², R. Guillard², I.P. Beletskaya¹

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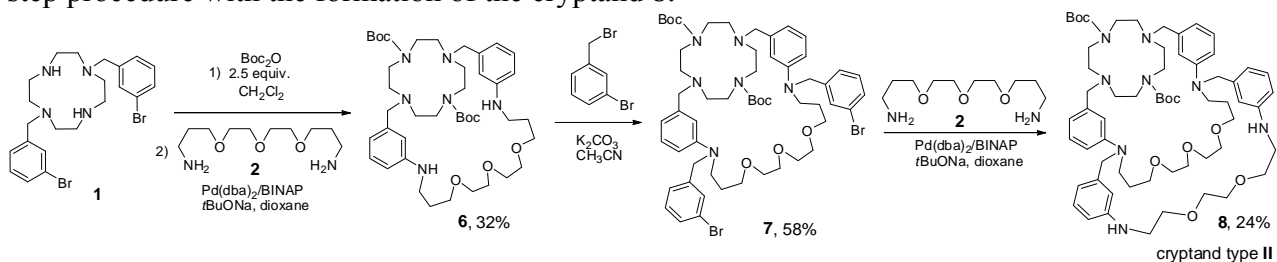
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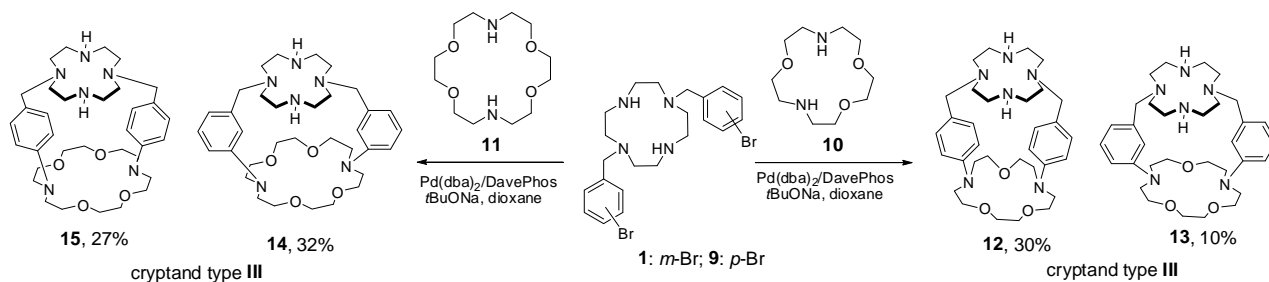
We have proposed various approaches to macrotricyclic cryptands using Pd-catalyzed amination at the macrocyclization steps. Cryptands of type **I** (spherical) were synthesized from 1,7-bis(3-bromobenzyl)-cyclen **1** in three steps by constructing the second macrocycle in compound **3**, modifying it with two *m*-bromobenzyl substituents with the formation of tetrabenzyl cyclen unit in compound **4**, and furnishing the third macrocycle at the last step (cryptand **5**).



Cryptands of type **II** were obtained by protecting two nitrogen atoms in 1,7-bis(3-bromobenzyl)-cyclen **1** with BOC groups and introducing the resulting compound in a similar three-step procedure with the formation of the cryptand **8**.



Cryptands **12-15** of type **III** (cylindrical) were synthesized *via* one-step procedure from 1,7-bis(bromobenzyl) substituted cyclens **1** and **9** and diazacrown ethers **10** and **11**.



P119: VISIBLE LIGHT INDUCED M–C BOND FORMING REDUCTIVE ELIMINATION OF HETERODINUCLEAR ORGANOPLATINUM-MANGANESE COMPLEX

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Heterodinuclear organotransition metal complexes attract considerable interests in relation to cooperative effects of different transition metals in catalysis. Use of light energy in selective chemical reactions and catalysis are also unsolved important subject in these fields. Heterodinuclear (2,2'-bipyridine)- or (4,4'-di-tert-butyl-2,2'-bipyridine)triorgano-platinum-manganesepentacarbonyl complexes (t-Bu₂-bpy)₃Pt-Mn(CO)₅, which have been prepared by the simple metathetical reactions of the corresponding triorgano(nitrato)platinum(IV) complexes with sodium pentacarbonylmanganate in THF, were found to show facile Mn–Me bond forming reductive elimination on visible light irradiation under ambient conditions.¹ No significant effects of the added t-Bu₂bpy ligand, [Mn(CO)₅][–] anion, and radical scavenger on both rates under dark and irradiation of light were observed, excluding possible mechanisms involving prior ligand dissociation and heterolytic Pt–Mn bond cleavage processes. This visible light irradiation would cause electron promotion from the HOMO (Pt–Mn bond) to the LUMO (bpy p*), leading to facile methyl transfer reaction from Pt to Mn.

Synthesis and mechanistic insights of light induced reductive elimination of heterodinuclear organoplatinum-manganese complexes will be discussed.

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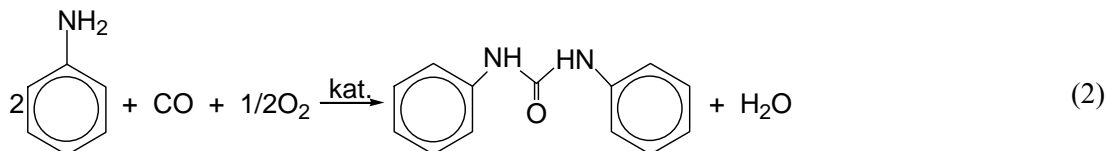
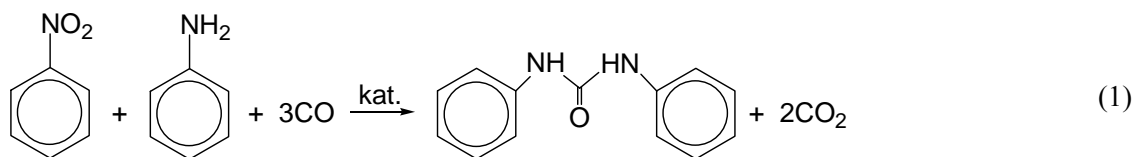
P120: THE ROLE OF OXIDIZING AGENT ON THE MECHANISM OF CATALYTICAL CARBONYLATION OF ANILINE

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Carbamates and ureas are industrially important products and intermediates (in the synthesis of isocyanates, pesticides, pharmaceuticals) traditionally prepared through the so-called phosgene route. The use of extremely toxic phosgene is major disadvantage of this reaction, therefore, new alternative methods are still being explored. Among possible catalytical alternatives, processes of amines carbonylation in the presence of various oxidants have a potential for a large scale. Palladium(II) complexes with N-donor ligands are considered as good catalysts for the carbonylation reactions [1]. There is a general agreement that catalytic activity of metal complexes with nitrogen containing ligands depends on electron density on the palladium atom and a strategy to design (and to obtain) more active catalysts is based on incorporation of new ligands to manipulate the steric and electronic effects around the palladium center.

In our work we carried out several syntheses of palladium(II) complexes of general structure $\text{PdCl}_2(\text{X}_n\text{Py})_2$ and we investigated the relationships between the structure and electronic properties of X_nPy and catalytic activity of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ complexes in carbonylation of aniline (model amine). We studied substituent effect in X_nPy on the rate determining step of aniline (AN) carbonylation carried out in presence of two oxidizing agents: nitrobenzene (process 1) and molecular oxygen (process 2).



Electron withdrawing/donating properties of X_nPy ligands were correlated with activities of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ complexes in presence of Fe/I_2 as co-catalyst. We observed an increase of conversions and yields with increasing X_nPy ligand basicity in the system employing NB as oxidant whereas the opposite tendency was noticed when NB was replaced with O_2 . On the basis of presented results we propose two different mechanisms of AN carbonylation [2,3]. We optimized reaction conditions in order to obtain high catalyst selectivity toward N,N'-diphenylurea.

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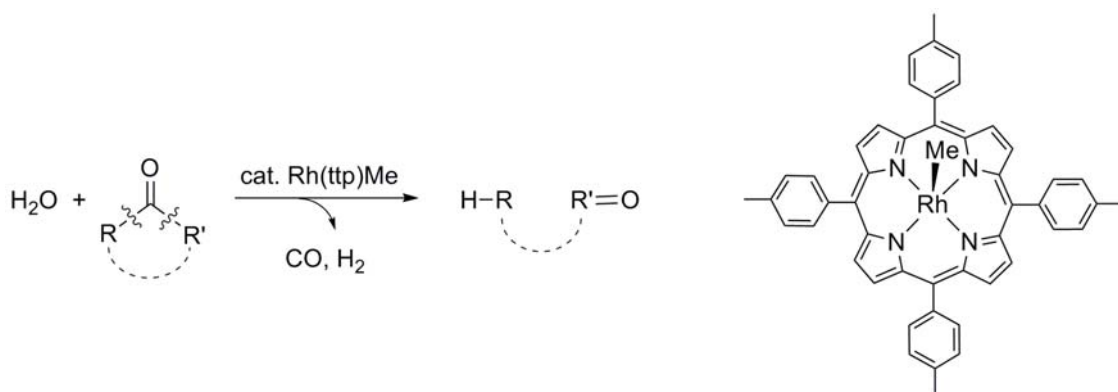
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P121: PHOTOCATALYTIC CARBON–CARBON BOND ACTIVATION OF KETONES BY RHODIUM(III) PORPHYRINS

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Catalytic cleavage of unactivated carbon–carbon bond is an attractive yet very challenging aspiration in organometallic chemistry. Traditionally, the catalytic carbon carbon bond activation (CCCA) was accomplished under thermal conditions. However, the high temperature required is energy-intensive and it introduces the selectivity problems. Recently, the goal has been achieved with the help of the abundant natural resources: light and water. To pursue a mild, selective and catalytic bond cleavage, light has been introduced into the reaction. We discovered the selective CCCA of unstrained ketones by rhodium(III) porphyrins to yield the corresponding O-incorporated organics. In the presence of water, the photocatalysis was achieved under ambient conditions with good turnovers. Through mechanistic studies, we propose Rh(tpp)OH as a key intermediate and water acts as an oxidizing agent.



Structure of Porphyrin, Rh(tpp)Me

Acknowledgement

We thank the Research Grants Council of Hong Kong for financial support.

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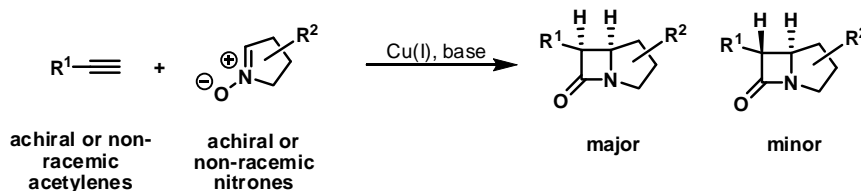
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P122: AN ENTRY TO CARBAPENAMS VIA ASYMMETRIC KINUGASA REACTION INVOLVING CYCLIC NITRONES DERIVED FROM SUGARS AND TERMINAL ACETYLENES

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The copper(I) mediated reaction of nitrones and terminal acetylenes, which is known as Kinugasa reaction, represents an attractive method of direct formation of the β -lactam ring.^{1,2} This reaction can be performed in many ways including diastereo- and enantioselective versions. In most cases, as 1,3-dipoles simple acyclic nitrones have been used.³ Number of reactions involving cyclic ones is limited.



Herein, we present our recent studies on Kinugasa reaction involving cyclic nitrones readily available from hydroxy acids or pentoses and terminal acetylenes either achiral or bearing a stereogenic center.⁴ All investigated reactions proceeded in good yield and with high diastereoselectivity providing an attractive entry to carbapenams of a potential biological activity.⁵ The stereochemical pathway of the reaction and influence of geometry and substitutions in one or both reactants on direction and magnitude of asymmetric induction will be discussed.

This project was financed by the European Union within the European Regional Development Fund, project POIG. 01.01.02.-14-102/09

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P123: NEW METHOD OF SYNTHESIS OF COMBRETASTATIN A-4 ANALOGS

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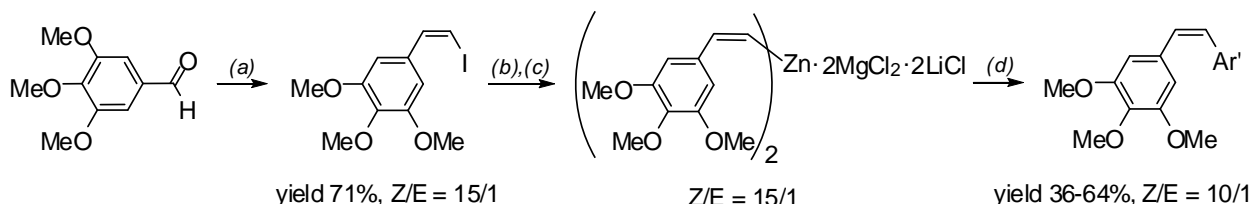
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Combretastatin A-4 (CA-4), isolated from South African tree *Combretum caffrum*, is one of the most potent antivasular and antimitotic agents acting at the colchicine binding site of tubulin, that has shown excellent activity against multidrug resistant cancer cells. Due to their unique anticancer properties and simple structures, these *Z*-stilbenes have drawn significant attention of medicinal chemists as lead structures for the design of novel antitumour agents. It has been demonstrated that *Z*-combretastatins manifest much higher biological activity than the corresponding *E*-isomers. However, CA-4 and its analogs are prone to thermal *Z/E*-isomerisation, even during the course of synthesis. This indicates a strong need for the development of convenient, mild and stereoselective methods for preparation of such electron-rich *Z*-stilbenes.

We have developed mild and stereoselective approach to *Z*-stilbenes, using palladium-mediated Negishi cross-coupling reaction of *Z*-alkenylzinc reagents with different arylhalogenides. Proposed method permits to synthesize CA-4 analogs, bearing different substitution pattern in good yield (36-64%) and high stereoselectivity (*Z/E* = 10:1) *via* the sequence of three-step one-pot reactions (Scheme 1). Newly prepared compounds manifested good cytotoxicity against HBL100 epithelial cell lines (IC_{50} = 0.022 - 10.3 μ M).



Scheme 1. Synthesis of combretastatin A-4 analogs. *Reagents and conditions*: (a) $^{-}IPh_3P^{+}CH_2I$, NaHMDS, THF, -20 °C – 45 min, -78 °C – 3 h, 71% (*Z/E* = 15:1); (b) *i*-PrMgCl·LiCl solution in THF, -40 °C, 15 min, (*Z/E* = 15:1); (c) ZnCl₂ solution in THF, NMP, -40 °C, 1 min, (*Z/E* = 15:1); (d) Ar'X, (A-^{ta}Phos)₂PdCl₂ (2 mol %), rt, 0.5-17 h, (*Z/E* = 10:1) (e) At the stage of the cross-coupling reaction phenolic groups were protected as TBS-ethers, free amino groups as Boc-amides.

Acknowledgements. This work was supported by German Academic Research Service (A/08/81119), Federal Targeted Programme “Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009-2013” (16.740.11.0476).

P124: CHEMOENZYMATIC ENANTIOSELECTIVE TOTAL SYNTHESIS OF THE NORLIGNANS HYPERIONE A AND B

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In 2010, Mu *et al.* reported on the isolation of two novel diastereomeric norlignans from *Hypericum chinese*, a herb which has broad application in traditional chinese medicine. [1] Their structure has been proposed to consist of a central tetrahydrofuran core flanked by two piperonyl-containing substituents in 2- and 4-position, however, the absolute configurations remained unknown.

Here, we present the first enantioselective synthesis of Hyperione A and B based on a lipase-catalyzed desymmetrization. [2] Biocatalytic conversion of a prochiral piperonyl-substituted allenic diol produced the axially chiral key intermediate in enantiopure form. In the following steps, silver-catalyzed cycloisomerization and grignard-addition selectively furnished the 2,4-disubstituted tetrahydrofuran moiety, which was finally transformed to the natural products. [3]

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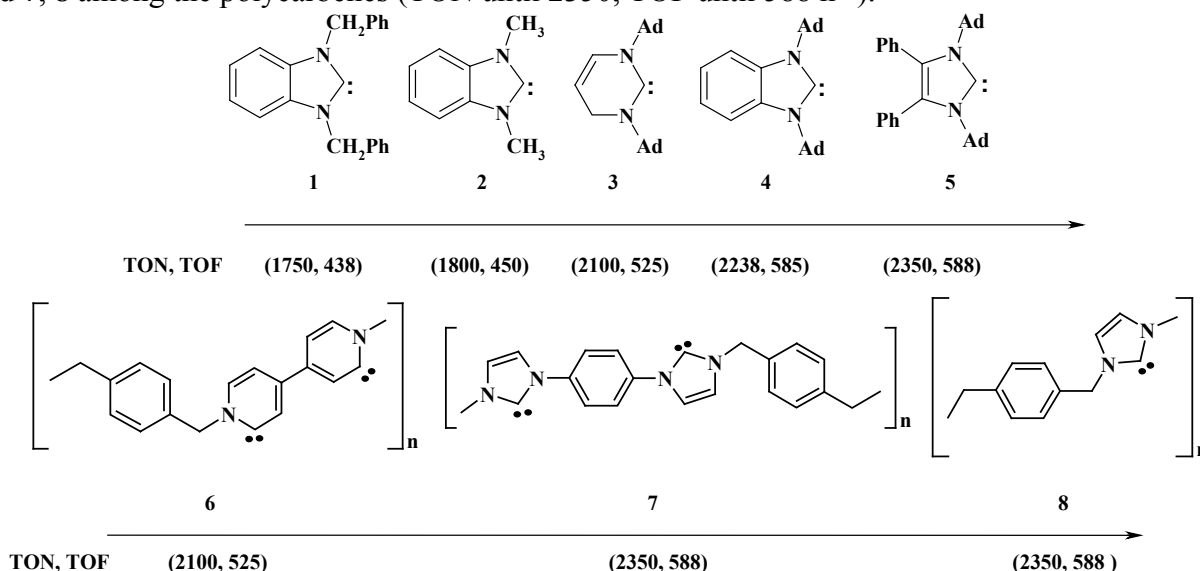
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P125: CATALYSIS OF TRANSESTERIFICATION AND BENZOIN CONDENSATION BY *N*-HETEROCYCLIC CARBENES

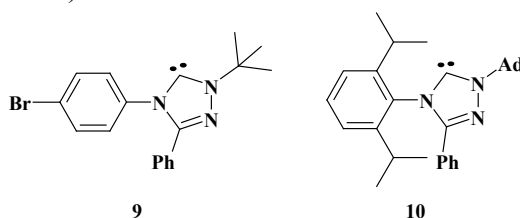
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Transesterification is one of the interesting reactions catalyzed by *N*-heterocyclic carbenes, mild and effective method for the preparation of esters, particularly, for producing of biodiesel fuel. It was found that the transformation of esters successfully proceeds in alcohol excess in the presence of 1,3-disubstituted imidazole-2-ylidenes using 4.4 mol% of carbene catalyst with maximum yield in 85% [1]. High yields were also achieved in the presence of molecular sieves and excess quantities of esters [2]. But the catalytic efficiency of the indicated carbenes was sufficiently low (TON until 60, TOF until 30 h⁻¹). We studied the catalytic properties of a series of mono-, bis- and polycarbenes in the model transesterification of ethylbenzoate to methylbenzoate in the tenfold methanol excess at room temperature (23 °C). The reaction was carried out for 4 h using 0.04 mol% of catalyst [3]. The most efficient carbene catalysts are found to be **4**, **5** among the monocarbenes and **7**, **8** among the polycarbenes (TON until 2350, TOF until 588 h⁻¹).



Another organocatalytic reaction involving *N*-heterocyclic carbenes is the benzoine condensation of aldehydes. The transformations of benzaldehyde into benzoin and furfural into furoin were chosen in our research as model. It should be noted insufficient catalytic efficiency of carbenes **9**, **10**. Nevertheless, it was achieved good efficiency in the experiments using 1–5 mol% of compounds **4**, **5** (TON until 62, TOF until 6.5 h⁻¹).



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P126: VINYL ACETALS TO BETA-ALKOXY KETONES BY TEBBE METHYLATION AND ACID-INDUCED REARRANGEMENT

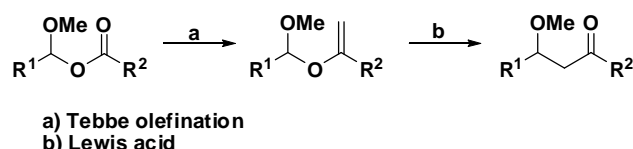
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Titanium carbenoids are useful reagents for transformation carbonyl groups into alkenes. They are small and nonbasic, but above all because they will convert carboxylic acid derivatives into the corresponding hetero-substituted alkenes.¹ A range of titanium carbenoids have been used to methylenate esters, but the reagent used by Tebbe, has particular advantages: □ it is easy to prepare and the workup following reaction often involves simple precipitation of the titanium-containing side products.

One application of titanium carbenoids is in the Petasis–Ferrier rearrangement.² It involves methylenation of a 1,3-dioxan-4-one with Tebbe or Petasis reagent to give an enol ether, which rearranges under Lewis-acidic conditions to give a 2,6-*syn*-disubstituted tetrahydropyranone. Surprisingly, rearrangement of linear vinyl acetals, which would be expected to provide a route to β-alkoxy ketones, has not been reported.

We developed a method that allows easy conversion of vinyl acetals into β-hydroxy ketones, which are important building blocks in the synthesis.



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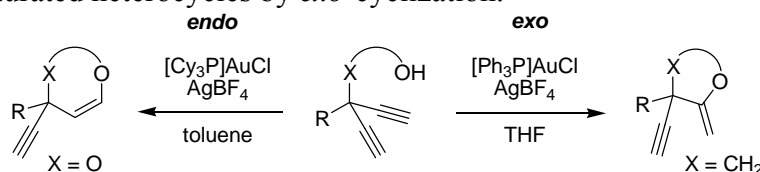
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P127: ANION-INDUCED ENANTIOSELECTIVE CYCLIZATION OF DIYNAMIDES TO PYRROLIDINES BY CATIONIC GOLD COMPLEXES

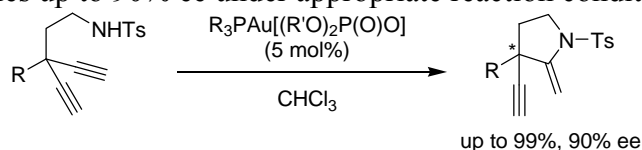
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In recent years, gold complexes have been employed extensively for the activation of alkenes, alkynes, and allenes towards the attack of various *O*-, *N*-, *S*-, or *C*-nucleophiles.^[1] These transformations occur with high chemoselectivity, high functional group tolerance, and mild reaction conditions to allow access to a variety of new compound classes such as aromatic and aliphatic, saturated and unsaturated heterocycles. In stark contrast to this increasing number of applications for gold catalysts in method development and applications in complex natural product synthesis, corresponding enantioselective processes employing optically active gold complexes as well as mechanistic investigations aiming at an understanding of the fundamental reasons for stereoselectivity are more limited in number.^[2] In this context, gold complexes employing chiral phosphine ligands and chiral phosphate anions have been demonstrated as effective and selective catalysts for the transformation of allenes, alkenes, and enynes. In contrast, stereocontrol in the case of diynes has proven difficult so far, in particular in the case of terminal alkynes. In the past, we have focussed on the development of a new method for the gold-catalyzed desymmetrization of 1,4-diynes.^[3] Herein, we have shown that intramolecular, nucleophilic cyclization of 3-alkoxy-1,4-diynes results in selective *endo*-cyclization, whereas 3-alkyl-1,4-diynes provide access to the corresponding unsaturated heterocycles by *exo*-cyclization.



Initial studies showed that for the desymmetrization of terminal 1,4-diynes neither chiral phosphine nor carbene ligands led to gold catalysts which permitted highly enantioselective ring closure to unsaturated heterocycles.^[4] It was shown however that gold complexes incorporating chiral anions derived from BINOL were successfully employed in the desymmetrization of diynamides to pyrrolidines in selectivities up to 90% ee under appropriate reaction conditions.



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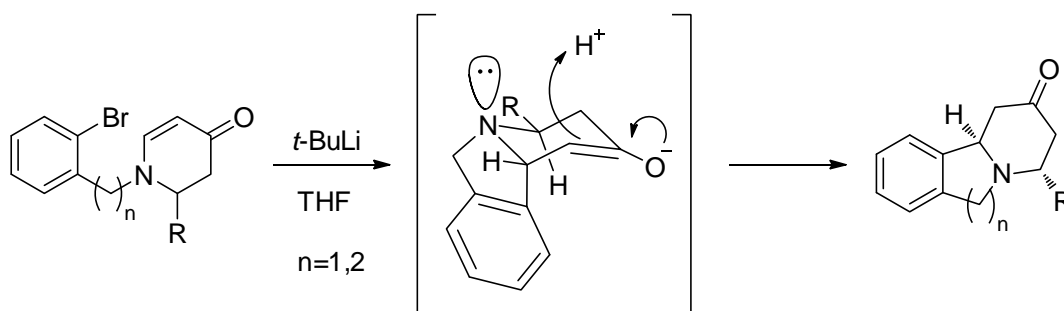
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P128: LITHIUM – HALOGEN EXCHANGE INITIATED INTRAMOLECULAR ARYL LITHIUM ADDITIONS TO DIHYDROPYRIDONES

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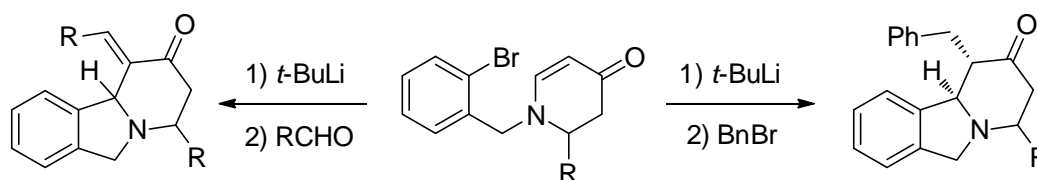
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We have discovered a new method of synthesis of benzoquinolizidines and related homologues based on the lithium – halogen exchange initiated conjugate addition of aryllithium to dihydropyridones (Scheme 1).



Scheme 1.

The mechanism suggests that the enolate intermediate is protonated on the top face (axial addition). When we made a tandem reaction with the enolate trapped by a different electrophile (BnBr), the product is also that of axial attack, while the reaction with aldehydes to give the corresponding enones (Scheme 2).



Scheme 2.

P129: SYNTHESIS OF FLUORESCENT COUMARIN-SACCHARIDE CONJUGATES

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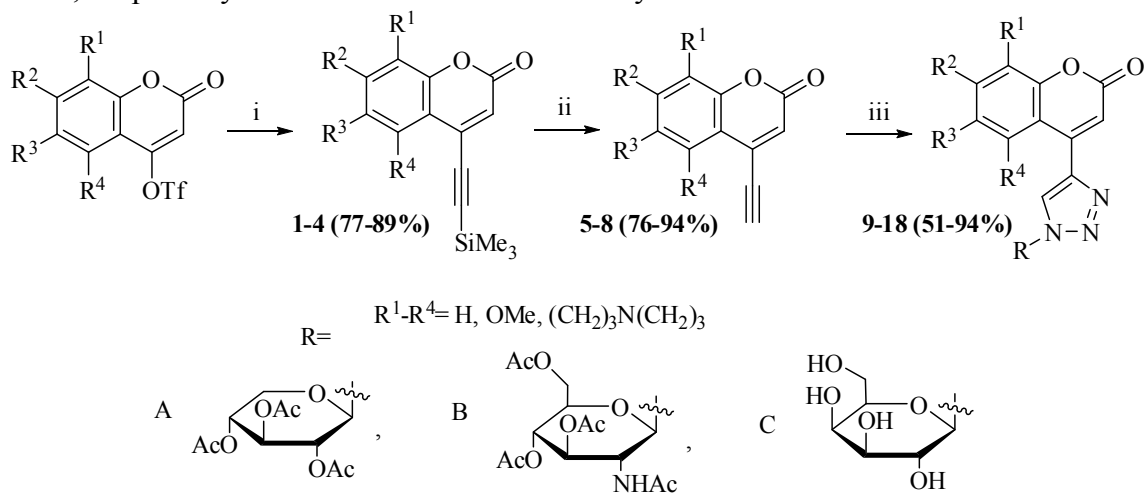
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Coumarins are present in plant, microorganism, and animal sources and manifest a wide range of pharmacological activities, including antitumor, antibacterial and antiviral properties.¹

Compounds **9–18** can serve as good models for the fluorescent detection of carbohydrate receptors on the surface of pathogens, for example, for the recognition some types of cancers² using binding of galactose, glucose, or xylose residues to corresponding receptors on the targeted pathogen.

A series of coumarin triazolylglycosides were synthesized³ starting from 4-trifluoromethanesulfonates coumarins in good yields via Sonogashira cross-coupling and copper-mediated 1,3-dipolar cycloaddition reactions of carbohydrate azides.



Scheme 1. Reagents and conditions: (i) Me_3SiCCH (1.1 equiv.), $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.05 equiv.), CuI (0.1 equiv.), $i\text{-Pr}_2\text{NEt}$ (2 equiv.), MeCN , rt, 2 h; (ii) Bu_4NF in THF , rt, 15 min; (iii) **4a–d** (1.1 equiv.), CuI (0.2 equiv.), $\text{THF/EtOH/H}_2\text{O}$ (1:1:1), 60 °C, 15 h.

Several of the products show strong luminescence [relative quantum yield (Rhodamine 6G as standart) near 0.7] in the 490–560 nm region and are compatible with surface imaging applications.

A standard cytotoxic assay with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT assay)⁴ showed no toxic effects of water soluble compound **11** ($R^1-R^4 = (\text{CH}_2)_3\text{N}(\text{CH}_2)_3$, $R = \text{C}$) in micromolar concentrations on HeLa cells. In this connection fluorophore **11** may be of interest and is compatible with surface imaging applications.⁵

This work was supported by Federal Targeted Programme ‘Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013’ (16.740.11.0476 and 14.740.12.1382) and the Russian Foundation for Basic research (№ 12-03-00214-a).

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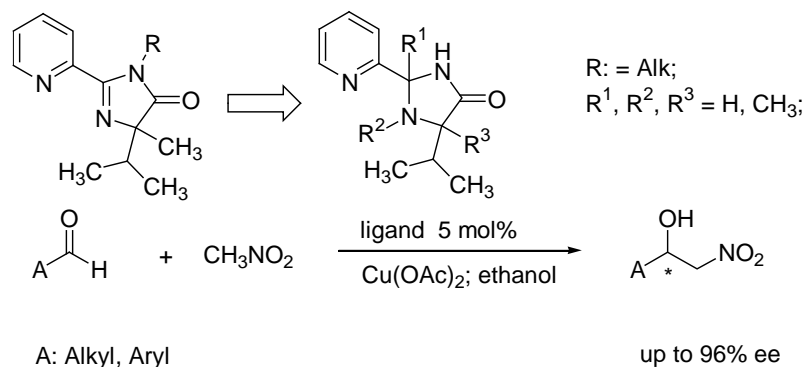
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P130: HIGHLY ENANTIOSELECTIVE NITROALDOL REACTIONS CATALYZED BY COPPER(II) COMPLEXES DERIVED FROM SUBSTITUTED 2-(PYRIDIN-2-YL)IMIDAZOLIDIN-4-ONE LIGANDS

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The nitroaldol (Henry) reaction represents one of the basic processes in organic synthesis for producing a carbon-carbon bond and is a key step in the synthesis of many significant compounds. The asymmetric variant of the Henry reaction plays a significant role in the synthesis of pharmaceutical precursors, in particular. The general procedure of this asymmetric synthesis requires the application of a suitable optically pure chiral ligand, often in combination with metal ions. In the case of the nitroaldol reaction, complexes with Cu(II) have proven particularly useful. The Cu(II) complexes derived from 2-(pyridin-2-yl)-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-ones, which we prepared earlier, were also efficient catalysts for Henry reaction.¹ However, in the case of these complexes, the resulting enantioselectivity was only low (maximum 19% ee). Thanks to the *sp*³ configuration at the 2-carbon atom, the imidazolidin-4-ones are less rigid than the substituted 4,5-dihydro-1*H*-imidazol-5-ones.² A similar example was encountered in the catalysis of the Henry reaction in the case of Cu(II) complexes derived from substituted pyridylimidazolidines as compared with the Cu(II) complexes derived from pyridylimidazolines.



We acknowledge financial support from Project M3MT ČR – MSM 0021627501

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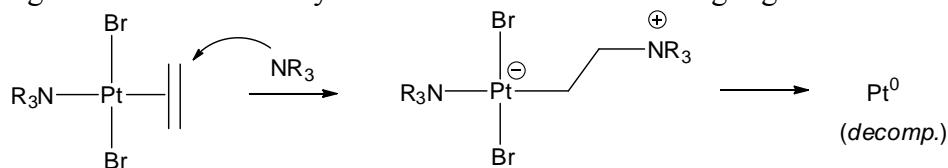
P131: CATALYZED OLEFIN HYDROMINATION BY SIMPLE PLATINUM SALTS: NEW MECHANISTIC FEATURES

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The intermolecular addition of an N-H bond across the C–C double bond in non activated olefins is a current economical and scientific challenge. Our group has introduced one of the best and especially simplest catalytic systems, consisting of bromide-activated platinum(II) salts, for the addition of anilines to ethylene and higher olefins.¹ Experimental and computational studies have elucidated the mechanism of the catalytic cycle.² A puzzling point of this catalytic system is the effect of Brønsted basicity on catalytic activity: while more basic anilines yield lower TON, the catalyst decomposition to metallic Pt is also shown to be accelerated by stronger bases. DFT calculations yield similar barriers for the addition of PhNH₂ and Et₂NH to C₂H₄, while the latter yields no hydroamination product at all.³ The decomposition seems to occur after formation of the zwitterionic intermediate resulting from the amine addition to the coordinated olefin (scheme). Recent studies into the catalyst decomposition mechanism and ways to prevent it will be reported. The effect of ligands on the selectivity of the reaction will also be highlighted.



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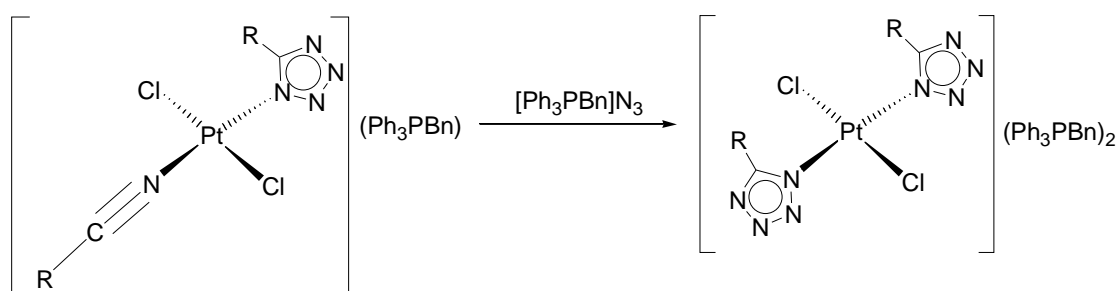
P132: QUANTITATIVE ESTIMATION FOR REACTIVITY OF NITRILES COORDINATED TO Pt(II) IN REACTIONS WITH AZIDES

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It has been shown that the coordination of RCN to the metals of the platinum group considerably increased the nitrile reactivity in reactions with azides [1]. In this work kinetic of azidation of nitriles coordinated to Pt(II) was studied by gas chromatography method. The synthesis was carried out with triphenylbenzylphosphonium azide in nitromethane at 1–10 °C (Scheme).



R = Me, Et, Ph

Scheme

Rate constants for the second-order reactions were determined in range 0.1–0.4 l·mol⁻¹sec⁻¹. It has been founded that rate of reactions with Pt(II) in some times higher than classical 1,3-dipolar cycloaddition. Considering the significant acceleration of the process, it is presumable that the azidation mechanism of nitriles coordinated to platinum may be distinct from that of the noncoordinated nitriles.

Popova E. A., Bokach N. A., Haukka M., Trifonov R. E., Ostrovskii V. A. *Inorg. Chim. Acta.* **2011**, 375, 242.

P133: SYNTHESIS OF OPTICALLY ACTIVE WARFARIN

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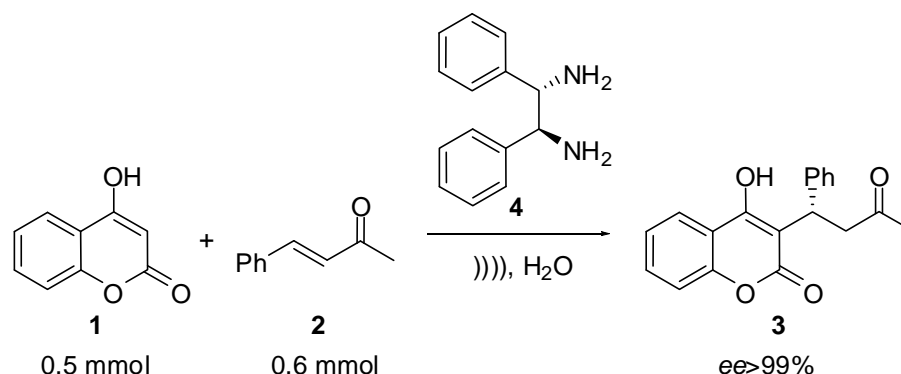
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Warfarin (**3**) is a Vitamin K antagonist, inhibiting Vitamin K epoxide reductase and thereby decreasing blood coagulation by preventing the Vitamin K-dependent synthesis of blood-clotting proteins. In the form of its sodium salt it is one of the most widely prescribed anticoagulants for prevention of thrombosis and embolism. Although currently prescribed as the racemate, activity and metabolism are markedly dissimilar for the two enantiomers, the (*S*) enantiomer being more active than the (*R*) enantiomer by a factor of 2–5. Efficient asymmetric syntheses of warfarin are therefore of great interest.[1] The methods of synthesis without metal complexes are more desirable for future therapeutical applications.

Here we present an example of the straightforward synthesis of chiral warfarin via Michael addition of 4-hydroxycoumarin (**1**) to benzylideneacetone (**2**) on water using commercially available primary amine (**4**) as a catalyst. After one crystallization from hexane we obtained optically pure warfarin.[2]



Water is a desirable solvent for catalysis with respect to environmental concerns, safety, and cost. The variety of interactions between water and substrates (hydrogen bonding or interactions related to polarity, acidity, hydrophobicity, etc.) make water interesting from an industrial as well as laboratory perspective. In this regard, processes using water as a reaction medium have recently attracted a great deal of attention.[3]

Sonication enables the rapid dispersion of solids on water surface allowing better contact between water and reactants. The use of ultrasounds as a means of accelerating reactions is an important technique and one which is rapidly developing for green processes.[4]

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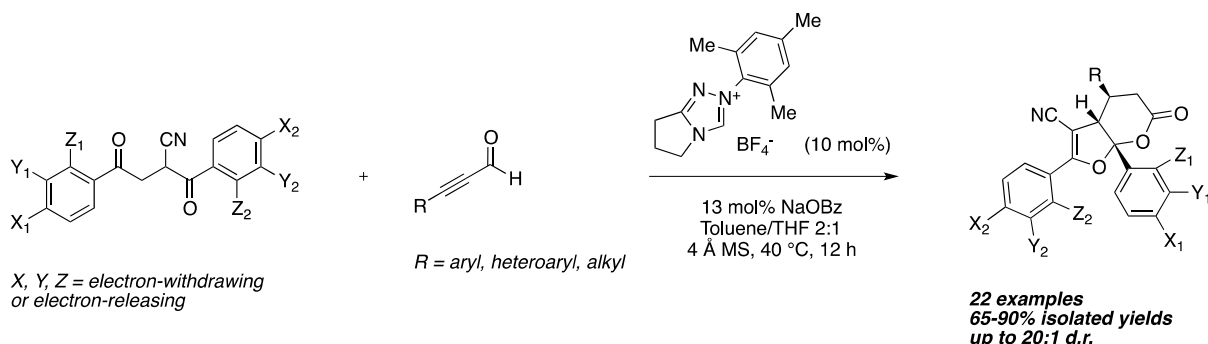
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P134: CYANO-1,4-DIKETONE PRONUCLEOPHILES: NHC-CATALYZED CYCLOADDITION REACTION WITH YNALS

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Recently, N-Heterocyclic Carbenes (NHCs) have emerged as remarkably powerful catalytic entities in the field of synthetically relevant organic transformation. Besides being reputed as powerful σ -donor ligands for transition metals, these divalent carbon nucleophiles also behave as versatile organocatalysts of their own right. Thereby, numerous metal-free, NHC-catalyzed transformations, shedding light on the multiple facets of NHC reactivity, have been reported over the past years.

Herein, we disclose the first highly diastereoselective cycloaddition reaction between α -cyano-1,4-diketones and ynals, mediated by catalytic amounts of a triazolium salt precatalyst and co-catalytic amounts of a weak carboxylate base. The title transformation proceeds smoothly under mild reaction conditions and generates 3 contiguous stereogenic centers, one of which is quaternary. This reaction tolerates a wide variety of electronically distinct substituents on both reaction partners, and affords privileged cyclic ketal scaffolds in 65-90% isolated yields and with up to 20:1 diastereomeric preference. The obtained compounds are interesting candidates for the synthesis of the ginkgolide class of monoterpenoids.

Research on the development of an enantioselective variant of this transformation is ongoing actively in our lab.

P135: CONFORMATIONAL FLEXIBILITY OF A PCP PINCER IRIDIUM HYDRIDE CATALYST OF ALCOHOL DEHYDROGENATION

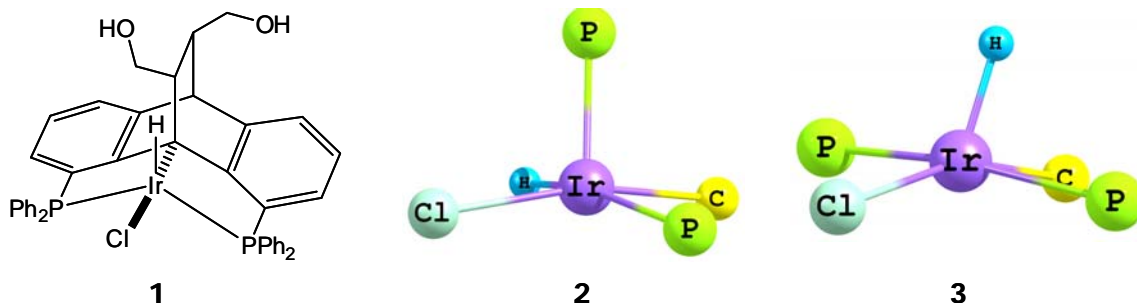
G.A. Silantyev¹, O.A. Filippov¹, S. Musa², D. Gelman², N.V. Belkova¹, L.M. Epstein¹, K. Weisz³, E.S. Shubina¹

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Recently, a new class of bifunctional dibenzobarrelene-based pincer complexes has been demonstrated to exhibit catalytic activity in various processes [1]. In this communication we present the first results of combined variable temperature IR and NMR spectroscopic as well as DFT studies on the PC(sp³)P pincer iridium hydride complex **1**, being a catalyst of acceptorless alcohol dehydrogenation [2].



The detailed spectroscopic and computational analysis showed the existence of three basic isomers having different geometry around the metal center: **2** and two isomers of type **3** with a *syn*- and *anti*-position of the hydride ligand. Due to the flexibility of the –CH₂OH sidearms each isomer can form several conformers which feature different intramolecular interactions, e.g. dihydrogen bonding of the hydride ligand with the proton of CH and OH groups. Rupture of these bonds and formation of stronger hydrogen bonds with more acidic/basic centers was demonstrated upon addition of trifluoroethanol or NEt₃ in dichloromethane. The equilibrium between isomers shifts in the presence of different bases/coordinating reagents (pyridine, acetonitrile, DMSO, NEt₃), some of which were used as auxiliary base in catalysis [2]. It was established that NEt₃ stabilizes the catalytically active conformer whereas pyridine addition leads to the formation of the non-active species.

This work was financially supported by the Russian Foundation for Basic Research (project No. 11-03-01210) and by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD) (projects No. C-2011b-4 and C-2012a-4).

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P136: SYNTHESIS OF INDOLE-DERIVED ALLOCOLCHICINE ANALOGS EXHIBITING STRONG APOPTOSIS-INDUCING ACTIVITY

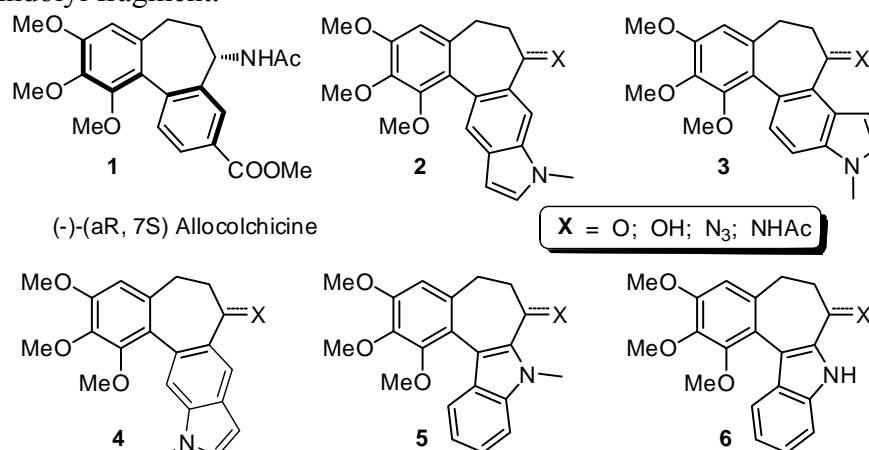
N.S. Sitnikov¹, A.V. Sinzov¹, A.S. Kokisheva¹, J. Velder², L. Abodo³, A. Prokop³, H.-G. Schmalz², A.Yu. Fedorov¹

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(-)-Colchicine, the major alkaloid from *Colchicum autumnale*, is known for decades as an efficient antimitotic agent able to inhibit microtubule formation (tubulin polymerization) in living cells, thus causing mitosis arrest in the metaphase. While high toxicity has prevented its use as an antitumor agent, colchicine still represents an important lead structure for drug discovery. Allocolchicine (**1**) is a constitutional isomer of colchicine bearing a six membered aromatic C-ring instead of the tropolone moiety. Allocolchicine itself as well as its analogues show promising biological activities similar to colchicines. Herein we report the synthesis of a series of novel allocolchicine analogs **2–6** containing 1*H*-indolyl fragment.



The fused four-membered carbocyclic skeleton in compounds **2**, **3** and **4** was constructed via Suzuki–Miyaura cross-coupling reaction and subsequent Friedel–Crafts annulation. In turn, Weinreb ketone synthesis and subsequent direct intramolecular C–H arylation reaction gave access to compounds of type **5**. The key ring forming steps for type **6** compounds were aldol condensation and direct intramolecular C–H arylation.

Preliminary biological screening of compounds **2**, **3** on BJAB tumor cell line revealed high antimitotic and apoptose-inducing activity (nanomolar or subnanomolar concentration range) along with particularly low unspecific cytotoxicity as determined by LDH-release assay.

	colchicine	2 (X = O)	3 (X = O)	2 (X = OH)	3 (X = OH)	2 (X = NHAc)	3 (X = NHAc)
IC ₅₀ [μM]	0.02	0.0025	< 0.001	0.03	0.008	0.08	0.03
AC ₅₀ [μM]	0.03	0.005	< 0.001	0.1	0.01	0.5	0.05

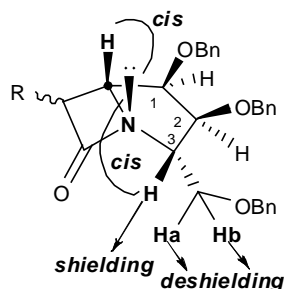
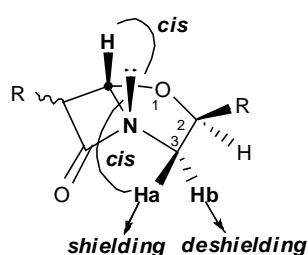
Acknowledgements to German Academic Exchange Service (DAAD № A/08/79551), Russian Foundation for Basic Research (12-03-00214-a) and Russian Federal Target Program (16.740.11.0476 and 14.740.12.1382).

P137: A SIMPLE METHOD FOR THE ASSIGNMENT OF THE RELATIVE STEREOCHEMISTRY OF CLAVAMS AND CARBAPENAMS

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We propose a simple method for determination of the relative stereochemistry of 2-substituted clavams¹ and carbapenams based on nuclear Overhauser effect (NOE) experiments and assignment of the diastereotopicity of protons attached to the C-3 atom.



This project was financed by the European Union within the European Regional Development Fund, Project POIG.01.01.02.-14-102/09.

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P138: β -CYCLODEXTRIN WITH α -AMINO ACID DERIVATIVES – NEW POTENT CHIRAL HYBRIDS

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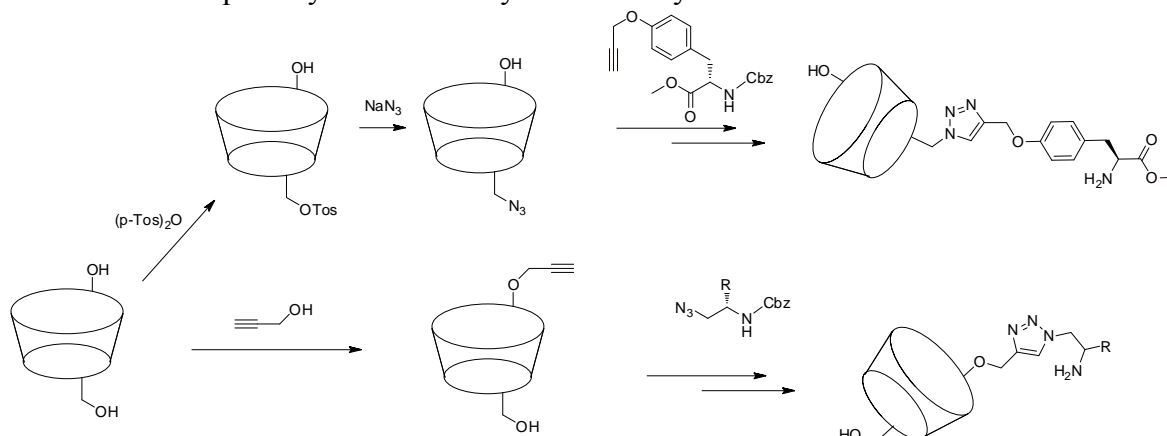
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The problem of cyclodextrin derivatization has been solved 14 years ago, since Bittman et al. [1] presented efficient and selective approach to mono-6-substituted β -cyclodextrin; obviously as the new challenge appeared the issue of selective bis-derivatization. Although several solutions had been proposed, the best way for obtaining the single bis-derivatized products was elaborated by Pearce and Sinay [2]. On the other hand, introduction of highly specific coupling – Sharpless' click chemistry – gives an opportunity to combine compounds with many functional groups (often not orthogonal).

Here we present an example of combining these two methods in order to create new functional hybrids which can potentially behave like molecular carriers as well as artificial enzymes. Therefore, we formed a library of β -cyclodextrin derivatives, containing α -amino acid derivatives as side-chains on either primary and secondary site of the cyclodextrin rim.



Some examples of application of these compounds as molecular recognition vessels are to be reported.

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"Carbohydrates as renewable raw materials in the synthesis of products with high added value" no. POIG.01.01.02-14-102/09-02

P139: SYNTHESIS OF BIOLOGICAL ACTIVE ISOVALERIC ACID ESTERS BY HYDROALKOXYCARBONYLATION OF ISOBUTYLENE

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Hydroalkoxycarbonylation of isobutylene, a product of oil refining, with carbon monoxide and an alcohol in the presence of homogeneous metal complexes catalysts makes it possible to synthesize easily and conveniently in one step isovaleric acid esters, which possess biological activity and are components of pharmaceutical compositions or valuable intermediates for their synthesis. Some isovalerate esters possess a characteristic odor and are used as fragrance compounds in the manufacture of perfumes, cosmetics, and food essences.

We applied hydroalkoxycarbonylation of isobutylene with carbon monoxide and mono(noly)hydric alcohols in the presence of catalytic systems based on the phosphinopalladium complexes ($\text{Pd}(\text{PPh}_3)_4\text{-PPh}_3\text{-TsOH}$, $\text{Pd}(\text{Acac})_2\text{-PPh}_3\text{-TsOH}$) to prepare of biological active isovaleric acid esters: l-menthylisovalerate (possesses spasmolytic properties; it used as main active component of the spasmolytic medicine "Validolium"), ethylisovalerate (possesses aromatic (fruit) odor; intermediate product for obtaining sedative and spasmolytic medicines "Ethyl ester of α -bromisovaleric acid" and "Corvololium"), cyclohexylisovalerate (bactericide activity (against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*); antifungus activity (against *Candida albicans*)), benzylisovalerate (bactericide activity (against *Escherichia coli*, *Staphylococcus aureus*)) and monoglyceride of isovaleric acid (bactericide activity (against *Escherichia coli*, *Pseudomonas aeruginosa*); antifungus activity (against *Candida albicans*)).

The reaction were performed in a stainless-steel autoclave (20 atm, 100°C, 4 h). The reaction was performed without solvent. The [alcohol]:[isobutylene]:[Pd]:[PPh₃]:[p-TsOH] ratio was 435:565:1:7:12. The autoclave at room temperature was charged with the catalytic system and alcohol. The autoclave was hermetized, purged in duplicate with carbon monoxide for deaeration, and charged with olefine, after which required carbon monoxide pressure was effected, and stirring and heating were started. The reaction products were isolated by fractional distillation. The yields of the target products were 14.7–96.0%. The selectivity in linear reaction products was 100%. Such a high regioselectivity is apparently provided both by the structure of the starting alkene (isobutylene) and by the reaction mechanism. The most probable is a hydride mechanism. Evidence for this proposal comes from the observation of an exceptionally strong effect of the p-TsOH addition, which being a proton donor, facilitates formation of the primary active hydride complexes of the catalytic cycle.

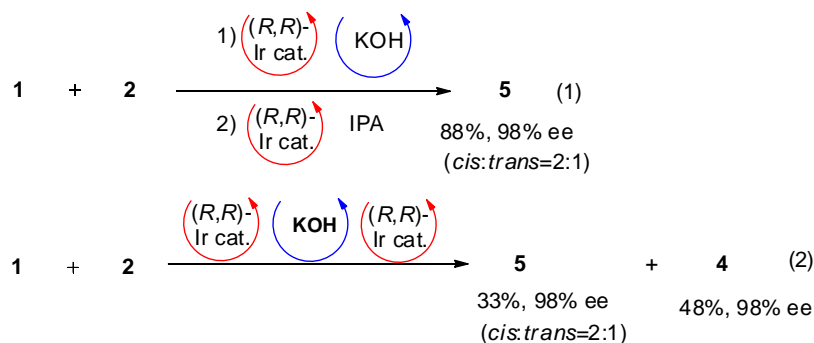
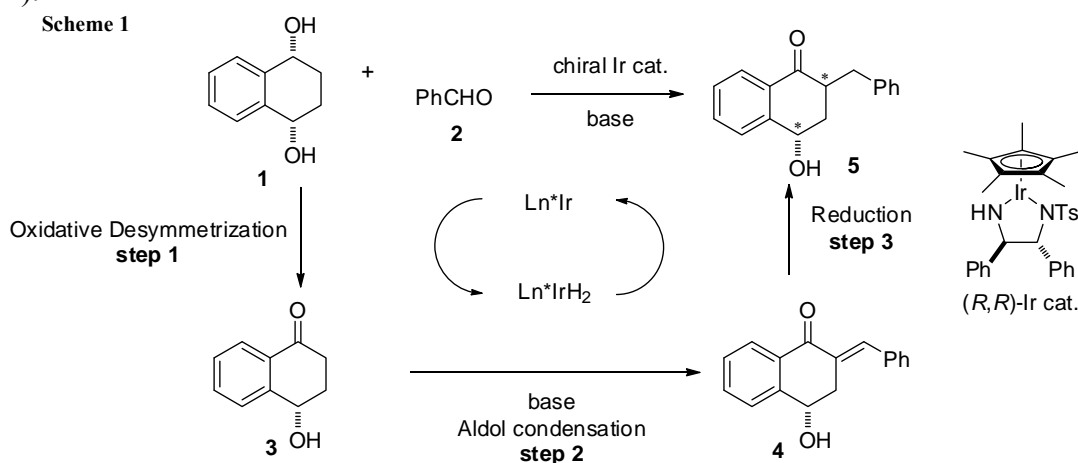
P140: IRIIDIUM-CATALYZED ASYMMETRIC TANDEM REACTION OF MESO-DIOLS AND ALDEHYDES

T. Suzuki, Y. Ishizaka, K. Ghazati, D.Y. Zhou, K. Asano, H. Sasai

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The development of tandem catalyst processes is one of the main properties for the modern synthetic organic chemistry. They lead to reduce the solvent, reagent, purification steps for green chemistry.¹ Recently we have reported oxidative desymmetrization of *meso*-diols using chiral iridium complex catalysts.² The reaction is safe and environmentally friendly process without use of stoichiometric amount of heavy metals. We also applied this reaction for the synthesis of otteliones, tubulin polymerization inhibitors.³ We report here that asymmetric tandem coupling of *meso*-diols and aldehyde using chiral Ir catalyst. This tandem reaction consists of oxidative desymmetrization of *meso*-diols (Scheme 1, step1), aldol condensation with aldehyde (step 2), reduction of enone (step 3).

A mixture of *meso*-diol **1**, benzaldehyde **2**, chiral Ir complex (10 mol %) and KOH (50 mol %) in dioxane was stirred for 1 h at 50 °C, then 2-propanol (IPA) was added and the mixture was further stirred at the same temperature. After 2 h. the desired benzyl ketone **5** was obtained with 98% ee in 88% yield (eq 1). Asymmetric hydrogen autotransfer reaction without additional hydrogen donor such as IPA gave **5** with 97% ee in 33% yield together with enone **4** with 98% ee in 48% yield (eq 2).



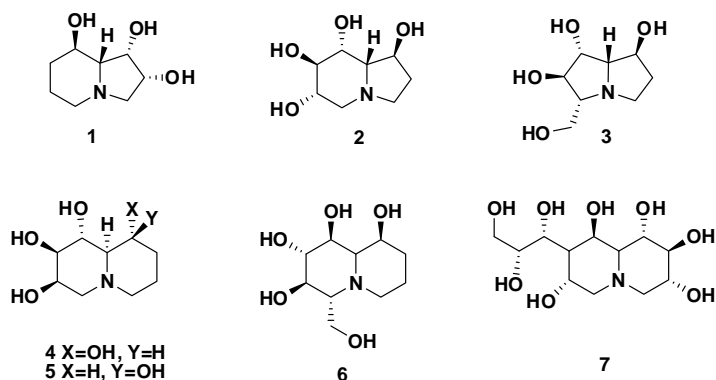
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P141: DIRECT CHEMOSELECTIVE SYNTHESIS OF POLYHYDROXYLATED QUINOLIZIDINE ENAMINONES FROM INERT SUGAR-DERIVED LACTAMS

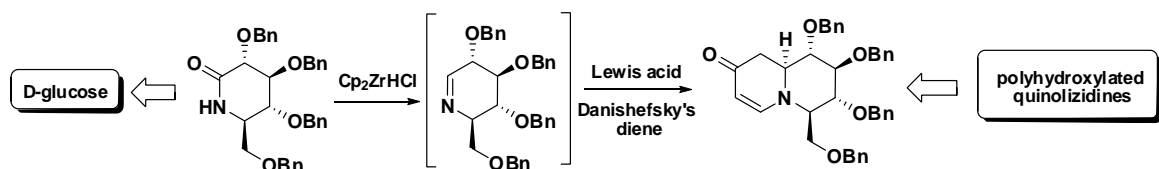
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The synthesis of polyhydroxylated indolizidine, pyrrolizidine and quinolizidine is well visible trend in current carbohydrate chemistry. [1] Among these iminosugars, swainsonine (**1**), [2] castanospermine (**2**), [3] and alexine (**3**) [4] and fully synthetic polyhydroxylated quinolizidines **4-6** [5] have attracted significant interest due to their biological activities as glycosidase inhibitors.



Based on our previous experience we proposed a new method for the synthesis of polyhydroxylated quinolizidine enaminones starting from 6-membered cyclic imines derived from commercially available sugars.



This project was financed by the European Union within the European Regional Development Fund, Project POIG.01.01.02.-14-102/09.

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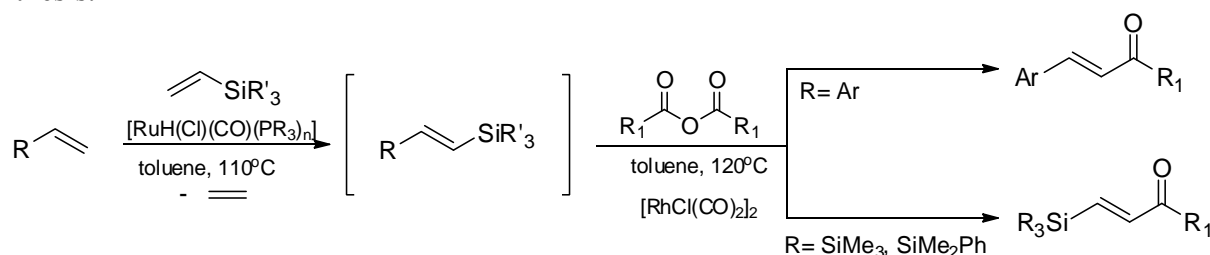
P142: NEW CATALYTIC ROUTE TO (*E*)-UNSATURATED KETONES

J. Szudkowska-Fratczak, P. Pawluc, G. Hreczycho, B. Marciniec

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α,β -Unsaturated ketones have been widely applied as useful key reagents in organic synthesis. Their use as substrates for a number of reactions such as Michael addition, hydrogenation, epoxidation, cycloaddition, Morita-Baylis-Hillman reaction etc., has stimulated their synthetic advancements [1]. In the past two decades, we have developed the silylative coupling of olefins with vinyl-substituted organosilicon compounds occurring in the presence of complexes containing initially or generating in situ M–H and M–Si bonds [2]. The ruthenium-catalyzed silylative coupling in combination with subsequent rhodium-catalyzed desilylative acylation (Narasaka coupling) appears to be a valuable step to provide functionalized unsaturated carbonyl compounds.

In the communication, we present our recent results on the synthetic applications of the catalytic silylative coupling reaction for the stereoselective synthesis of α,β -unsaturated ketones such as (*E*)-styryl ketones [3] and (*E*)- β -silylvinyl ketones [4] which are interesting building blocks in organic synthesis.



Acknowledgment. Financial support from the Ministry of Science and Higher Education (Poland); NN 204 148540 is gratefully acknowledged.

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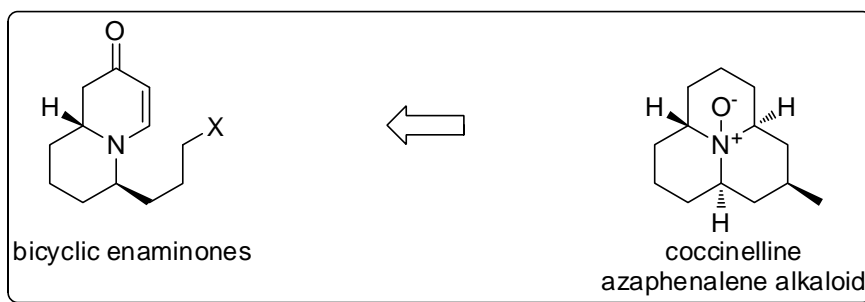
P143: BICYCLIC ENAMINONES AS BUILDING BLOCKS IN THE SYNTHESIS OF AZAPHENALENES AND RELATED COMPOUNDS

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Enaminones are versatile starting materials for the synthesis of many classes of organic compounds [1]. Use of Danishefsky's diene with imines led to generate bicyclic enaminones from easily available azaheterocyclic compounds as precursors of imines [2]. Our ongoing program is aimed on usage of these moieties in further transformations resulting in tricyclic skeleton of azafenalene alkaloids, which are common defensive substances of ladybird beetles family (*Coccinellidae*) [3]. due to their interesting structure and potentially beneficial biological activities this class of natural compounds is of interest of our research group.

This project was financed by the European Union within the European Regional Development Fund, project POIG. 01.01.02.-14-102/09



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P144: CONVERSION OF ALCOHOLS INTO AMINES USING HOMOGENOUS RUTHENIUM CATALYSTS

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Amines are conventionally synthesized by the alkylation of alkyl halides with ammonia or amines, but over-alkylations are common leading to mixtures of primary, secondary, tertiary amines as well as quaternary ammonium salts. [1]

The direct alkylation of amines with alcohols has been known since the beginning of the 20th century.[2] This is an attractive and promising alternative method to traditional alkylating procedures due to several factors, it is a safer and non-toxic procedure which generates water as a by-product and avoids production of wasteful products, alcohols are inexpensive and more readily available than the corresponding toxic halides or carbonyl compounds and the selectivity of the reaction can be controlled with the catalyst.[3,4]

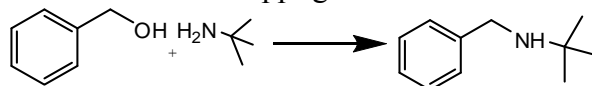
The alcohol is activated by oxidation to give an aldehyde or ketone, which then undergoes a condensation reaction with the amine nucleophile. Subsequent hydrogenation of the resulting imine with the initially generated hydrogen yields the desired amine product

This method had been extensively explored using different homogenous and heterogeneous catalysts. The disadvantages of the known homogeneous catalysts similarly to heterogeneous systems, are the high temperatures and long reaction times to obtain optimum yields which are not desired for industrial processes.

In this paper, we investigated synthesis of amines by the amination of alcohol applying organometallic catalysts based on ruthenium in moderate conditions. Ruthenium catalysts were found to be inactive in the absence of a phosphine ligand, Hence a number of bidentate ligands such as bis(diphenylphosphino)ferrocene (dppf) diphenylphosphinopropane (dppp) and Xantphos were tested.

Primary amines have been converted into secondary amines, and secondary amines into tertiary amines, using primary alcohols. Secondary alcohols require more forcing conditions than primary alcohols but are still effective alkylating agents in the presence of these catalysts. Subsequently, it was discovered that the addition of additives such as molecular sieves and suitable base had beneficial effect on these reactions and were therefore placed in our investigation.

The reaction of t-butylamine and benzyl alcohol with $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ was chosen as a model reaction, among the ligands it was found that dppf gave the best conversions.



Excellent yields were obtained by heating a equivalent solution of the alcohol and amine at reflux in toluene in the presence of 2.5 mol% of $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$, 5 mol% dppf 10 mol% K_2CO_3 and 3Å MS for 24 hours under argon atmosphere. The reactions were monitored by GC-MS in order to study the alkylation process in detail.

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P145: RARE EARTH COMPLEXES FOR SYNTHESIS OF BIODEGRADABLE AND BIOCOMPATIBLE POLYMERS

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New multidentate tethered amidine-phenol pro-ligands $\{4,6-t\text{Bu}_2\text{C}_6\text{H}_2\text{O}-(2-\text{C}(\text{N}-\text{R})=\text{N}-\text{R})\}_2\text{H}_2$ ($\{\text{LON}^{\text{R}}\}_2\text{H}_2$, $\text{R} = i\text{Pr}$, cyclohexyl (Cy), 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (Ar)). Amine elimination reactions between $\{\text{LON}^{i\text{Pr}}\}_2\text{H}_2$ or $\{\text{LON}^{\text{Cy}}\}_2\text{H}_2$ and $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ afforded the corresponding phenoxy-amidinate amides $\{\text{LON}^{\text{R}}\}_2\text{LnN}(\text{SiMe}_3)_2$ ($\text{Ln} = \text{Y}$, $\text{R} = i\text{Pr}$, **1**; $\text{R} = \text{Cy}$, **2**; $\text{Ln} = \text{Nd}$, $\text{R} = \text{Cy}$, **3**), whereas the same reaction between $\{\text{LON}^{\text{Ar}}\}_2\text{H}_2$ and $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$, under various conditions, always yielded the homoleptic tris(phenoxy-amidinate) complex $\{\text{LO}^{\text{H}}\text{N}^{\text{Ar}}\}_3\text{Y}$ (**4**). Amido complexes **1**, **2** and **3** are effective initiators for the ring-opening polymerization (ROP) of *racemic* lactide (*rac*-LA), giving atactic or heterotactic-enriched (P_r up to 76%) polymers with high molecular weights (M_n up to 158,800 $\text{g}\cdot\text{mol}^{-1}$), but broad molecular weight distributions ($M_w/M_n = 1.5\text{--}2.8$). Effective immortal ROP of *rac*-LA was feasible by combining complex **1** with 5–50 equiv. of isopropanol or benzyl alcohol, affording PLAs with well controlled molecular weights and narrow polydispersities ($M_w/M_n = 1.11\text{--}1.38$).

The reactions of $\text{Ln}(\text{BH}_4)_3(\text{THF})_2$ with an equimolar amount of the dilithium derivative of a bridged bis(amidine) containing a conformationally rigid naphthalene linker afforded heterobimetallic *ansa*-bis(amidinate) lanthanide borohydrides $[1,8\text{-C}_{10}\text{H}_6\{\text{NC}(t\text{Bu})\text{N}-2,6\text{-Me}_2\text{-C}_6\text{H}_3\}_2]\text{Ln}(\text{BH}_4)(\mu\text{-BH}_4)\text{Li}(\text{THF})_2$ ($\text{Ln} = \text{Nd}$, **5**; Sm , **6**). Compounds **5** and **6** are active in the ring-opening polymerization (ROP) of *racemic* lactide at 20 °C, acting as single-site diinitiators with the two borohydride groups operative, and providing polymers with a slight heterotactic bias ($P_r = 0.54\text{--}0.62$), controlled molecular weights and relatively narrow polydispersities ($M_w/M_n = 1.5\text{--}1.7$).

A series of borohydrido $[o\text{-C}_6\text{H}_4\{\text{NC}(t\text{Bu})\text{NC}_6\text{H}_2\text{-2,6R}_2\}]\text{Ln}(\text{BH}_4)(\text{THF})_2$ ($\text{R} = \text{Me}$, $i\text{Pr}$; $\text{Ln} = \text{Y}$, Nd , Sm) and alkoxy $[o\text{-C}_6\text{H}_4\{\text{NC}(t\text{Bu})\text{NC}_6\text{H}_2\text{-2,6R}_2\}]\text{Ln}(\text{OtBu})(\text{L})_n$ ($\text{R} = \text{Me}$, $i\text{Pr}$; $\text{Ln} = \text{Y}$, Nd , Sm ; $\text{L} = \text{THF}$, $n=2$; $\text{L} = \text{DME}$, $n = 1$) rare earth complexes supported by *ansa*-bis(amidinate) ligand system with conformationally rigid *o*-phenylene linker was synthesized and structurally characterized. These complexes proved to be efficient initiators of ring-opening polymerization of *rac*-lactide.

Bis(guanidinate) alkoxy complexes $\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NPr}^i)_2\}_2\text{LnOtBu}$ ($\text{Ln}=\text{Y}$ (**7**), Lu (**8**)) were estimated as initiators for ring-opening polymerization of *rac*-lactide at 130°C in bulk to give atactic polylactides with M_n up to 33000 g/mol . Total conversion of 500 equivalents of monomer was reached in 2 h when **7** was used as an initiator. Complex **7** allows conversion of up to 2500 equivalents of monomer within 8 h. The obtained polylactides demonstrate monomodal molecular mass distribution with rather narrow polydispersities $M_w/M_n=1.46\text{--}1.84$. The experimental molecular weights are noticeably (3–11 times) lower compared to calculated values.

Acknowledgements

This work is supported by the Russian Foundation for Basic Research (Grant No 11-03-00555-a)

P146: GAS PHASE STUDIES OF THE COMPLEXATION OF NICKEL(II) IONS BY PHENYLPYRIDINES

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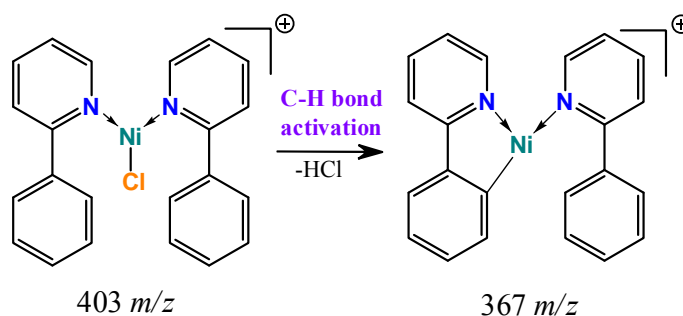
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Despite the considerable progress in organometallic chemistry, there are major gaps in our understanding of mechanistic details, especially in comparison with classical organic chemistry. Complexes of late transition metals with organic molecules are a particularly attractive field of study as they are encountered in different kinds of metal-mediated transformations¹.

ESI-MS, ion mobility and CID experiments were performed for ions generated from dilute solutions of 2-, 3- and 4-phenyl pyridines with NiCl₂ in methanol.

Electrospray ionization mass spectra show the generation of Ni(II) complexes with phenyl pyridines (both singly and doubly charged). Of the regioisomeric phenylpyridines, 2-phenyl pyridine behaves in a drastically different way, compared to 3- and 4-phenyl pyridines.

Furthering this observation, ion mobility studies of the complex at m/z 403 ([NiCl(phpy)₂]⁺) were performed, in combination with calculations using density functional theory methods. CID measurements show the occurrence of C-H bond activation, which is most pronounced in the case of 2-phenyl pyridine.



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P147: SYNTHESIS OF POROUS MAGNETIC CARBONIC MATERIAL FROM MODIFIED WOOD SAWDUST

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Synthesis of porous composites with magnetic properties from renewable natural resources and its processing waste is of great importance for solution of some problems in ecology (oil-spill recovery, water purification and etc.), biomedicine, electronics, metallurgy and catalysis. In this paper the study of magnetic porous materials preparation from modified sawdust is presented and possible using of them for noble metals extraction and catalysis.

Wood sawdust was used as a starting material in order to synthesize the porous magnetic materials. The sawdust was impregnated with different reagents (FeCl_3 , ZnCl_2 , KOH , H_3PO_4) and their mixtures. Obtained composites were shaped in pills and then undergone a thermal treatment at 200–800°C. Some of theirs were washed with water. The sample modified with chlorides of iron and zinc was found to be the best obtained mixture for porous magnetic material synthesis.

It was established that the maximum surface area ($1350 \text{ m}^2/\text{g}$) of charcoal obtained from this starting mixture was observed during carbonization at 400°C and accompanied with exothermic process and zinc ferrite formation. Moreover, the water-washed charcoals obtained during carbonization up to 300–600°C have three orders greater specific surface area than non-washed.

An analysis of charcoals by X-ray shown that low-temperature sample (400°C) contains crystalline phase of magnetite such as $(\text{Zn}_{0,29} \text{Fe}_{0,71})\text{Fe}_2\text{O}_4$; high-temperature sample (800°C) contains zinc-free magnetite and maghemite.

A magnetic hysteresis was observed during the magnetic test of synthesized samples. The magnetic parameters (coercive force, saturation magnetization, residual magnetization) were calculated using the hysteresis loop. Obtained values were close to magnetic parameters of zinc ferrite.

The sorption capacity of synthesized materials during the extraction of gold, palladium and platinum from chloride solutions was found to be higher than the sorption capacity of manufactured nonmagnetic sorbent. It was detected also that the sorption capacity of charcoals depended strongly on the temperature of carbonization of the starting material. The best sorption of gold was observed at samples treated at 400°C, and platinum and palladium – at 800°C.

Thus, modified sawdust with chlorides of iron and zinc was selected as sorbent with the most successful combination of porosity and magnetic properties. Treatment temperature influences the magnetic properties of the material; zinc-containing fragments remove from the charcoal with a temperature rise, and a content of iron oxides in the product go up. It is supposed that synthesized materials can be used for recovery of noble metals by magnetic separation because of its magnetic properties and high adsorption capacity.

P148: NANO-PALLADIUM ON AMINO-FUNCTIONALIZED MESOCELLULAR FOAM: AN EFFICIENT CATALYST FOR SUZUKI REACTIONS AND TRANSFER HYDROGENATIONS

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Nanoparticles have recently attracted an increasing amount of interest because of their unique properties and numerous applications in a variety of fields.^[1] In chemistry, heterogenous catalysts based on transition metal nanoparticles have shown to be efficient and selective for a wide range of organic transformations under mild conditions. Particularly in the large-scale synthesis of pharmaceuticals, highly stabilized nanoparticle catalysts can provide solutions to many practical problems.

Recently, we have developed a novel heterogenous catalyst based on Pd nanoparticles immobilized on amino-functionalized siliceous mesocellular foam (Pd(0)-AmP-MCF) (Fig 1).^[2] Herein, we report on its use in Suzuki cross-coupling reactions and in transfer hydrogenations of alkenes using microwave irradiation.

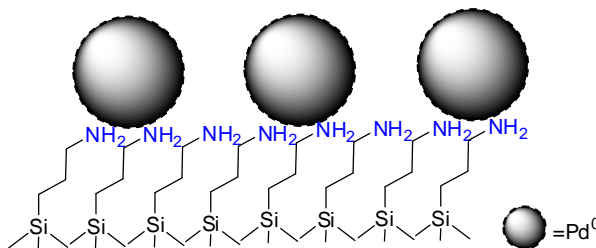


Figure 1: Schematic representation of the Pd(0)-AmP-MCF.

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P149: SYNTHETIC, STRUCTURAL AND REACTIVITY INVESTIGATIONS OF ALUMINIUM BISTRIFLATE COMPLEXES

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A diverse range of compounds containing triflate (OTf) ligands, such as LiOTf^1 , $\text{Zn}(\text{OTf})_2^2$ and $\text{Sc}(\text{OTf})_3^3$, have been employed as successful Lewis acid catalysts or stoichiometric reagents in various organic transformations. However, the use of classical organic-based ligands with these triflate-containing complexes has been scarce and predominantly investigated *in situ*⁴ providing a very limited amount of structural information on the active species. The importance of structural features of these triflate-containing Lewis acids could be of immense importance when attempting to improve their activities. Therefore, we set our goal on investigating the synthesis, structural features and reactivity properties of various ligand-supported aluminium bistriflate complexes with a general formula $\text{LAl}(\text{OTf})_2$ (L = terphenyls, amidinates, β -diketiminates etc.).

The preparation of the targeted aluminium bistriflate complexes is best achieved by first synthesizing the coresponding dihalopresoursors LAlCl_2 followed by the chloride-for-triflate ligand exchange using AgOTf .⁵ Structural investigations of several target compounds $\text{LAl}(\text{OTf})_2$ demonstrated the ligand importance in designing these complexes.

Lastly, we investigated potential catalytic activities of the target aluminium bistriflate complexes as alternatives for more expensive Au-based Lewis acids in several organic transformations.

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P150: SUPRAMOLECULAR COMPLEXES OF NEW N4-DONOR LIGAND CONTAINING AN ANTHRACENE MOIETY WITH POTENTIAL APPLICATIONS AS CATALYSTS

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Investigation on metal organic complexes represents one of the most active areas of material science and chemical research. Supramolecular complexes exhibit interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, host-guest chemistry, ion exchange, nonlinear optics, etc. They also can have catalytic properties in many chemical reactions [1]. For example dinuclear Pd(II) complex with quaterpyridine ligand has application in asymmetric allylic substitution reactions [2]. Complexes of Co(II) and Ni(II) with N₆-donor ligand containing quaterpyridine moiety are effective catalysts for ethylene oligomerisation reaction [3].

Quaterpyridine ligands are known to formation many types of supramolecular architectures such as mononuclear complexes, dinuclear helicates [4] and polynuclear architectures [5]. The ligand **L** (figure 1) have been obtained in a multistep synthesis via Pd(0)-catalysed Suzuki–Miyaura and Stille-type coupling reaction. Supramolecular complexes have been obtained by self-assembly of **L** and different transition metal ions. Catalytic properties of obtained compounds in different reactions have investigated.

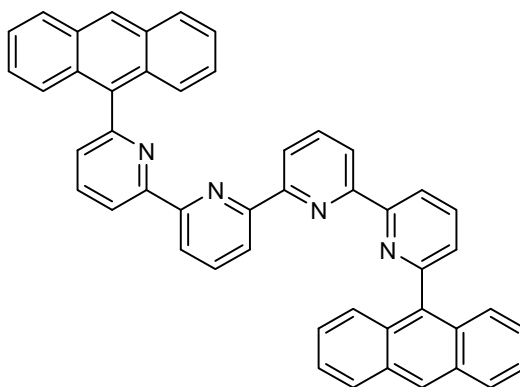


Figure 1 The ligand **L**

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Acknowledgments:

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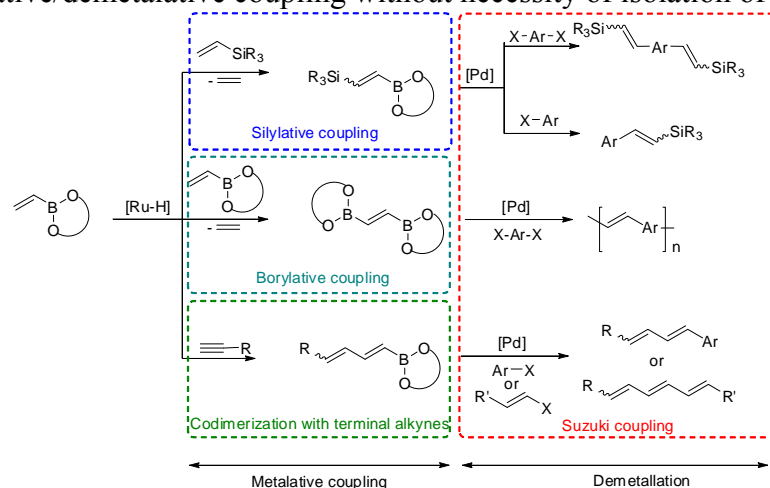
P151: METALATIVE COUPLING / SUZUKI COUPLING – SEQUENTIAL REACTION IN THE SYNTHESIS OF π -CONJUGATED UNSATURATED ORGANIC MOLECULAR AND MACROMOLECULAR COMPOUNDS

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Main group substituted olefins constitute an indispensable tool in modern organic synthesis. The diversity of the reaction, which allows the substitution of i.e. silyl, boryl or stannyl moieties with broad range of functional groups cause a continuous increase in application of such unsaturated compounds [1]. These organometallic reagents have found application in palladium catalyzed C–C bond formation reactions (Suzuki, Hiyama, Sonogashira), which play an important role in the synthesis of complex organic molecules, natural compounds analogous or pharmaceuticals [2].

In the communication we present our recent results on the synthetic application of vinylboranes in organometallic and organic synthesis. The application of transition metal catalyzed processes discovered in our group [3]: silylative and borylative coupling [4] as well as codimerization of vinylboronates [5] with terminal alkynes in combination with demetalative reactions (Suzuki coupling) provide highly π -conjugated organic molecular and macromolecular compounds. The appropriate choice of the process conditions allowed for regio- and stereoselective formation of desired products. The increased emphasis on economy in organic reactions (reduction of the time-consuming and expensive product isolation steps, the amount of used solvents etc) imposes on chemist to run reactions in tandem or longer sequences. The processes presented in the communication can be successfully applied in sequential, one pot formation of desired conjugated products via metalative/demetalative coupling without necessity of isolation of intermediates.



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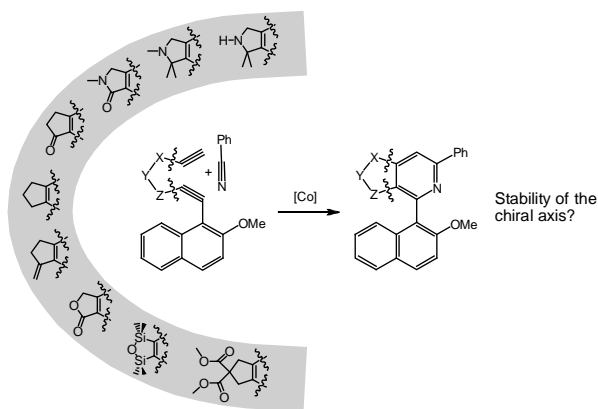
P152: APPLICATION OF COBALT-CATALYZED [2+2+2] CYCLOADDITION REACTIONS

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The transition metal-catalysed [2+2+2] cycloaddition reaction is a very useful and valuable member of the synthetic chemists toolbox for the construction of complex organic structures.¹ Access to a significant increase of molecular complexity is granted by the concurrent or successive formation of several bonds leading to the cyclic products. This opportunity has been seized recently, e.g. in several elegant natural product syntheses.

Cobalt complexes belong to the first generation of catalyst systems for cyclotrimerisation reactions, which have been evaluated in complex synthetic endeavours. Photochemical energy input allows the use of mild reaction conditions and sensitive chiral substrates as well as the direct conversion of gaseous coupling partners like acetylene.² Here, the application of chiral Co-catalysts for the successful selective preparation of atropisomeric biaryls starting from nitriles and diynes will be discussed. The investigation details the structural requirements of the coupling partners as well as the chiral biaryl products.^{3,4} Interestingly, the formed biaryl products show a distinct behaviour concerning the stability of the biaryl axes with the formation of different ring sizes and their substitution pattern. Furthermore, the reaction of chiral diynes with nitriles using achiral catalysts under different conditions furnishes diastereomeric atropisomers, which turned out to be separable easily via chromatography. The features of the cycloaddition reaction as well as the follow-up chemistry will be discussed.⁵



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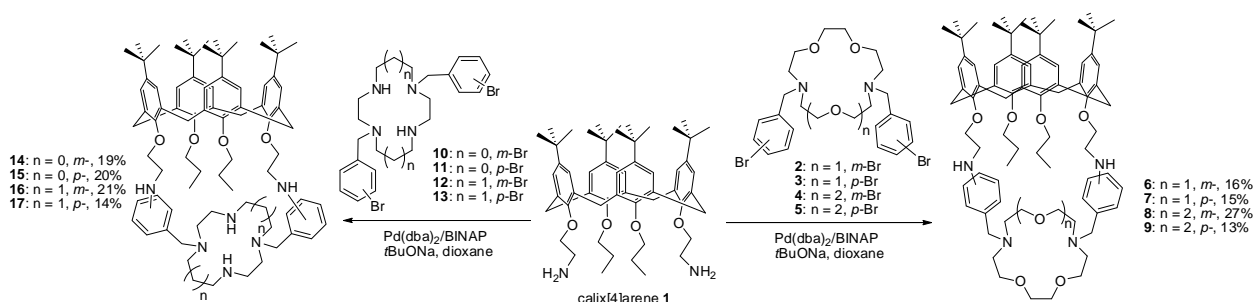
P153: PALLADIUM-CATALYZED AMINATION IN THE SYNTHESIS OF HYBRID POLYMACROCYCLIC SYSTEMS

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I.P. Beletskaya¹

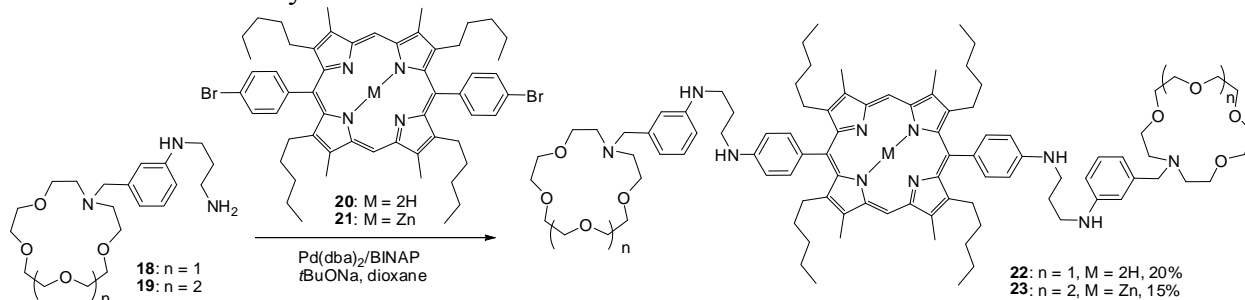
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Pd-catalyzed amination was successfully applied to the synthesis of hybrid macrotricyclic systems by reacting diaminocalix[4]arene **1** with a variety of bis(bromobenzyl) substituted diazacrown ethers **2–5**, cyclens **10**, **11** and cyclams **12**, **13**. Macrotricycles **6–9** comprising diazacrown moieties were obtained in 13–27% yields whereas their analogs with tetraazamacrocycles **14–17** in 14–21% yields.



Bis(bromophenyl)substituted porphyrins are valuable substrates in the Pd-catalyzed amination as they can be modified with linear and cyclic oxadiazines. E.g., the reaction of a free-base bis(3-bromophenyl)porphyrin with excess trioxadiazine afforded bis(trioxadiazine) derivative in 30% yield, while mono(4-bromophenyl) substituted porphyrin reacted with the same diamine only in the form of its Zn complex. Azacrown ethers modified with diaminobenzyl substituent (**18** and **19**) were introduced in the Pd-catalyzed reactions with bis(4-bromophenyl)porphyrin **20** and its Zn complex **21** and produced hybrid tris macrocyclic compounds **22** and **23** comprising porphyrin and two azacrown macrocycles.



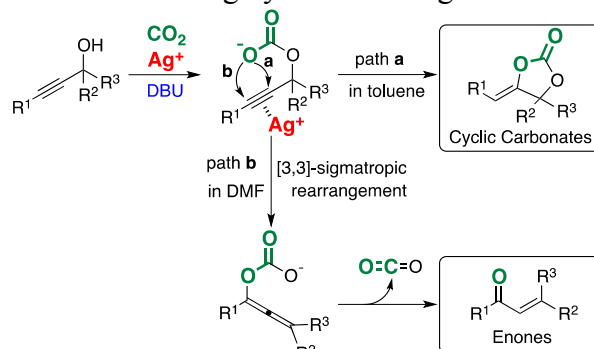
The work was supported by the RFBR grant 12-03-00796.

P154: SILVER-CATALYZED CARBON DIOXIDE INCORPORATION REACTIONS ON ALKYNE DERIVATIVES

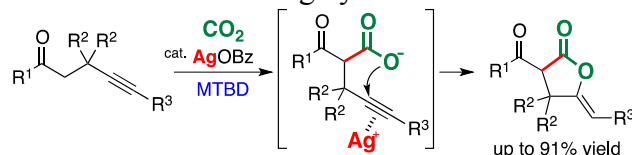
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A silver/DBU system was developed for the effective catalyst to activate alkyne derivatives as π -Lewis acid. The reaction of carbon dioxide with propargylic alcohols and propargylic amines afforded the corresponding cyclic carbonate and oxazolidinone, respectively, in high yields under mild conditions (Scheme 1, path **a**)^[1]. In a polar solvent, such as DMF, the [3,3]-sigmatropic Meyer-Schuster-type rearrangement of the propargylic alcohol was mediated by carbon dioxide to afford the corresponding α,β -unsaturated carbonyl compounds in high yields (Scheme 1, path **b**)^[2]. The silver salt combined with the chiral Schiff base ligand could be applied to enantioselective carbon dioxide incorporation into various bispropargylic alcohols to produce the corresponding cyclic carbonate *via* desymmetrization in high yields with high enantioselectivity.^[3,4]



Based on these observations, the present catalyst system was successfully applied to ketone derivatives containing an alkyne group at an appropriate position in the presence of base. It was found that the carbonate intermediate derived from the enolate and carbon dioxide in the presence of MTBD (7-methyl-triazabicyclo[4.4.0]dec-5-ene) was cyclized on alkyne by AgOBz catalyst to afford the corresponding lactone derivative in high yield under mild conditions.



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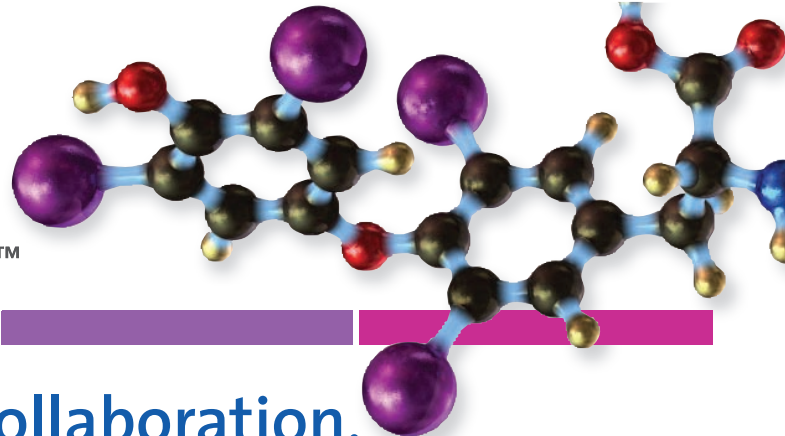
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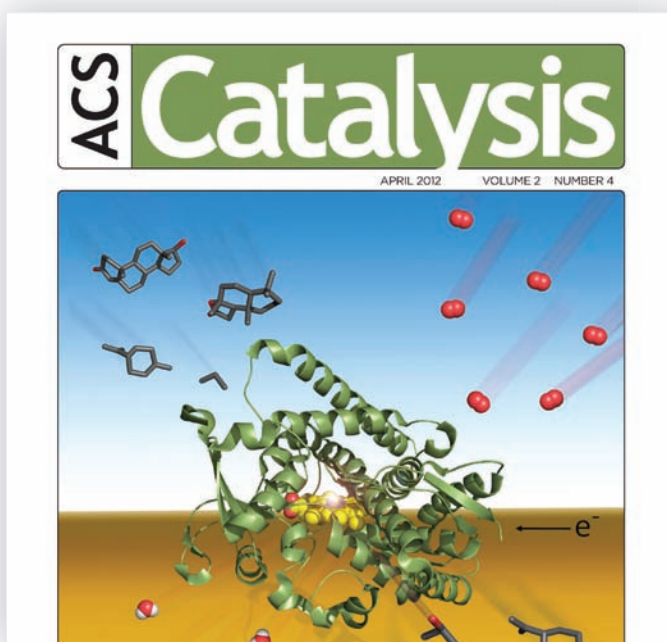
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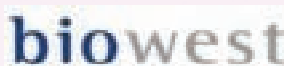
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- Весь спектр расходных материалов для хроматографии со склада в Москве, в том числе пластины для ТСХ, силикагель для колоночной хроматографии, колонки для ГХ и ВЭЖХ, фильтры, виалы.
- Лабораторное и мерное стекло из Германии.
- Все для ЯМР — ампулы, крышки, растворители на складе в Москве.
- Лабораторная мебель.
- Подбор оптимального варианта по критерию «цена-качество».
- Бесплатная доставка по регионам России в короткие сроки.





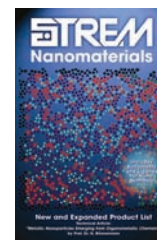
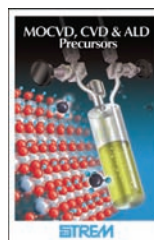
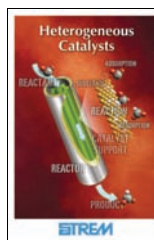
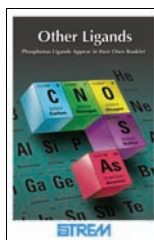
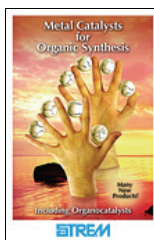
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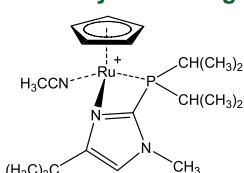
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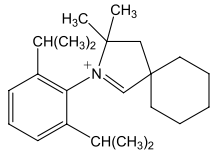
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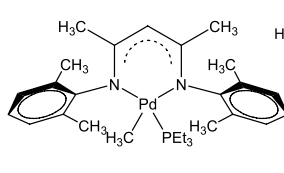
New Catalysts and Ligands



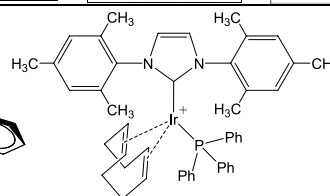
44-0017



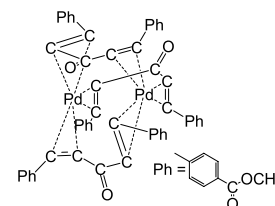
07-0550 Cyclohexyl-CAAC



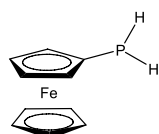
46-0230



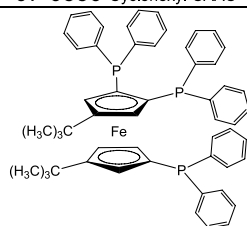
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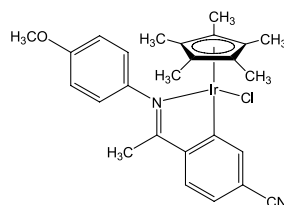
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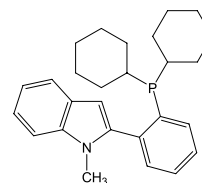
26-3620



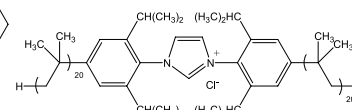
26-0318 HiersoPHOS-2



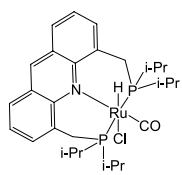
77-0424 Iridicycle-CN



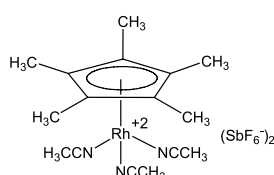
15-1088 CM-Phos



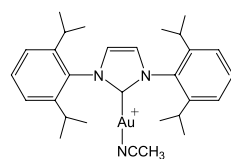
07-4050 PIB-NHC



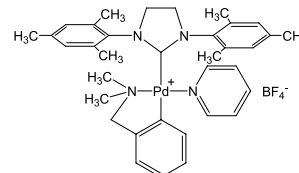
44-0525 Milstein Acridine



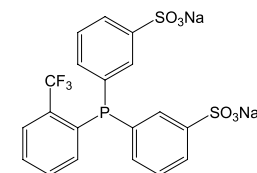
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79-0300

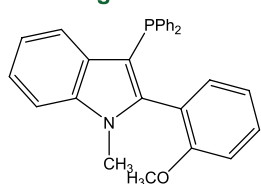


46-0224 PACCTM

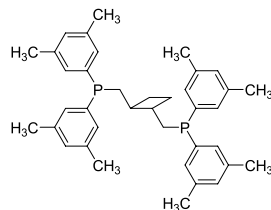


15-0577 o-DANPHOS

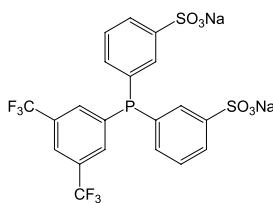
New P Ligands



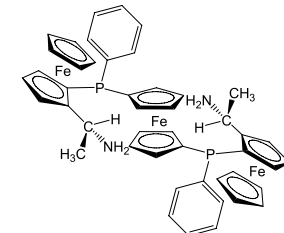
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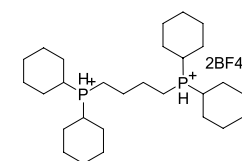
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15-0570 DANPHOS

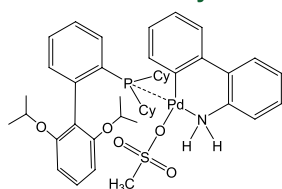


26-1261 Trifer

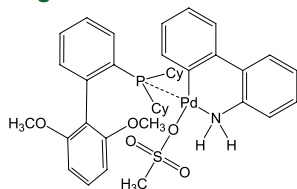


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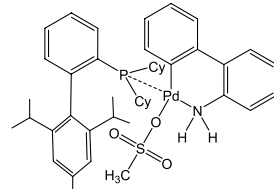
Buchwald Catalysts and Ligands



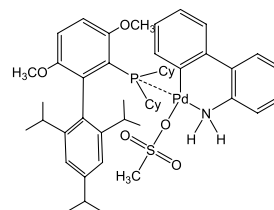
46-0314 from RuPhos



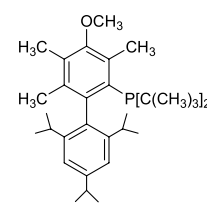
46-0318 from SPhos



46-0320 from XPhos

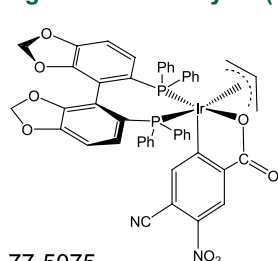


46-0322 from BrettPhos

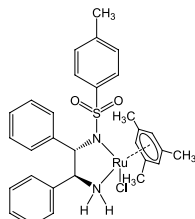


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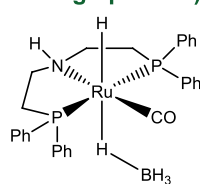
Ligands and Catalysts (Manufactured under license of Takasago patents).



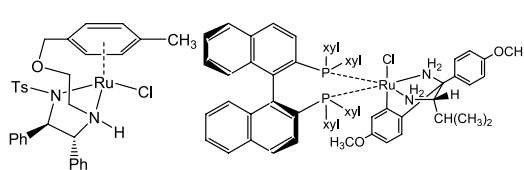
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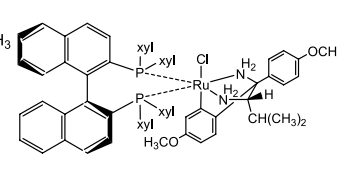
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