CRC International Symposium

in Moscow

Cross-Coupling & Organometallics

Organizers:

Zelinsky Institute of Organic Chemistry
Russian Academy of Science
Russian Foundation for Basic Research

Hokkaido University, Japan

Catalysis Research Center, Hokkaido Univeristy, Japan

Co-Organizers:

Moscow State University

Japan Interaction in Science & Technology Forum (JIST)

Sigma-Aldrich Corporation

The Chemical Society of Japan, Hokkaido Branch

Hokkaido University GCOE Program Catalysis & Materials Science

The CRC International Symposium in Moscow

Program

09:00 – 10:00	-	Registration on the CRC Symposium
10:00 – 10:10	-	Opening Ceremony: **Tamotsu Takahashi** (Hokkaido Univ., Japan)
10:10 – 10:50		**Ei-ichi Negishi** (Purdue Univ., USA)
		Transition Metal-Catalyzed C-C Bond Formation: Cross-Coupling and Carbometalation that Have Revolutionized Organic Synthesis
10:50 – 10:55	-	Questions/Discussion
10:55 – 11:35		**Irina P.Beletskaya** (Moscow State Univ., Russia)
		Some Aspects of Green Chemistry Principles Application to Transition Metal Catalysis
11:35 – 11:40	-	Questions/Discussion
11:40 – 12:10	-	Coffee-break 1
12:10 – 12:50		**Akira Suzuki** (Hokkaido Univ., Japan)
		Cross-Coupling Reactions of Organoboron Compounds
12:50 – 13:00	-	Questions/Discussion
13:00 – 15:00		Lunch
		Poster Presentations
15:00 – 15:40		**Yuri Belokon** (INEOS RAS, Russia)
		Binuclear Lewis Acids in Asymmetric Catalysis: Success and Unexpected Problems
15:40 – 15:45	-	Questions/Discussion
15:45 – 16:15	-	Coffee-break 2
16:15 – 16:55		**Paul Knochel** (Univ. of Munich, Germany)
		New Chemoseletive and Regioselective Cross-Couplings with Functionalized Organometallics
16:55 – 17:00	-	Questions/Discussion
17:00 – 17:40		**Tamejiro Hiyama** (Kyoto Univ., Japan)
		Invention of Transition Metal-Catalyzed Carbon-Carbon Bond Forming Reactions for Organic Synthesis
17:40 – 18:00	-	Closing Remarks
19:00 – 21:00	-	Gala dinner

Plenary
Lectures

Ei-ichi NEGISHI

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Birth: July 14, 1935

Ei-ichi Negishi, H. C. Brown Distinguished Professor of Chemistry, Purdue University, grew up in Japan and received his Bachelor's degree from the University of Tokyo (1958). He then joined a chemical company, Teijin. In 1960 he came to the University of Pennsylvania on a Fulbright-Smith-Mund All-Expense Scholarship and obtained his Ph.D. degree (under Prof. A. R. Day) in 1963. He returned to Teijin but decided to pursue an academic career. In 1966, he joined Professor H. C. Brown's Laboratories at Purdue as a Postdoctoral Associate and began investigating various C—C bond forming reactions of organoboranes. He was appointed Assistant to Professor Brown in 1968. It was during the following few years that he began feeling the need for some catalytic ways of promoting organoborane reactions.

Negishi went to Syracuse University as Assistant Professor in 1972 and began his life-long investigations of *transition metal-catalyzed organometallic reactions for organic synthesis*. His initial and largely unsuccessful attempts to develop a Cu-catalyzed conjugate addition or substitution reaction of organoboranes soon led him to adopt a then novel strategy of considering all 60 or so non-radioactive metals as components of both stoichiometric reagents and catalysts. During the 1976-1978 period he published about 10 papers describing the Pd- or Ni-cataiyzed cross-coupling reactions of various organometals including those of Mg, Zn, B, Al, Sn, and Zr. Today, those involving Zn, Al, and Zr are called the *Negishi coupling*. His success in developing the Pd- or Ni-catalyzed alkenylzirconiums was the beginning of many series of his subsequent investigations of organozirconium chemistry leading to the discoveries and developments of the Zr-catalyzed alkyne carboalumination often called the *Negishi alkyne carboalumination* (1978-), the Zr-catalyzed asymmetric alkene carboalumination (*ZACA reaction*) (1995-), and the chemistry of low-valent zirconocenes generated via "Bu_2ZrCp_2 and other dialkylzirconocenes widely known as *the Negishi reagents* (1985-).

Negishi was promoted to Associate Professor at Syracuse University in 1976 and invited back to Purdue University as Full Professor in 1979. In 1999 he was appointed the inaugural H. C. Brown Distinguished Professor of Chemistry. Various awards he has received include Guggenheim Fellowship (1987), the 1996 A. R. Day Award, a 1996 Chemical Society of Japan Award, the 1998 ACS Organometallic Chemistry Award, a Humboldt Senior Researcher Award, Germany (1998 - 2001), the 2000 RSC Sir E. Frankland Prize Lectureship, and the 2007 Yamada-Koga Prize . At Purdue University, he was the recipient of the 1998 McCoy Award and the 2003 Sigma Xi Award.

Negishi has published over 400 publications including two books, one of which is *Handbook of Organopalladium Chemistry for Organic Synthesis*, 2 Vols., Negishi, E., Ed., Wiley-Interscience, New York, **2002**, 3279 pp., and several patents. Collectively, these publications have been cited about 18,000 times (h-Index of 66). Negishi has been cited in Marquis Who's Who in American and Marquis Who's Who in the World. The Negishi coupling has been cited in Merck Index.

Transition Metal-Catalyzed C-C Bond Formation: Cross-Coupling and Carbometalation that Have Revolutionized Organic Synthesis

Ei-ichi Negishi

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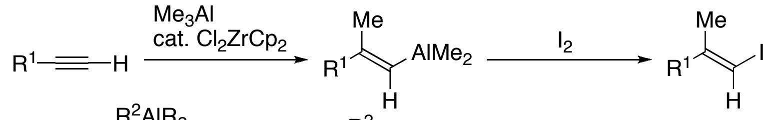
Recognition and explorations of the only several discrete processes that transition metals can undergo for C-C (and C-X) bond formation including (1) **reductive elimination** producing coupling products, (2) **carbometalation**, (3) **migratory insertion**, and (4) **nucleophilic and electrophilic attack on ligands** have led to the discoveries and developments of a number of synthetically useful reactions.

In particular, **Pd-catalyzed cross-coupling** discovered in the mid-1970's has emerged as arguably the most versatile method for C-C bond formation by coupling (Eq. 1). Significantly, it is mostly complementary with the conventional uncatalyzed Grignard and organoalkali metal reactions and has thus overcome the major deficiencies associated with the latter. Indeed, the great majority of all conceivable types of cross-coupling can be efficiently and selectively carried out.

$$R^1M + R^2X \xrightarrow{\text{cat. PdL}_n} R^1\text{-}R^2 + MX \qquad \text{(Eq. 1)}$$

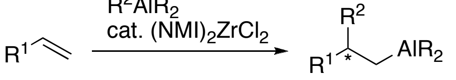
The progress in the Pd-catalyzed cross-coupling has made it desirable to be able to synthesize as many conceivable types of R^1M and R^2X. For the preparation of structurally most intricate and varied alkenyl and alkyl (especially chiral alkyl) reagents, hydrometalation, carbometalation, metallometalation, as well as seemingly contrathermodynamic halo- and other hetero-metalation of alkynes and alkenes have proven to be efficient, selective, and collectively versatile. Many of these processes, especially those involving carbometalation, heavily rely on transition metal catalysis, as exemplied by Zr-catalyzed carboalumination of alkynes, especially methylalumination (ZMA, Eq. 2), Zr-catalyzed asymmetric carboalumination of alkenes (ZACA, Eq. 3) as well as carbopalladation and acylpalladation.

ZMA Reaction



(Eq. 2)

ZACA Reaction



(Eq. 3)

Efforts towards the goal of being able to synthesize any types of alkenes through the combined use of Pd-catalyzed cross-coupling and various addition reactions mentioned above are still ongoing but the progress to date has been very fruitful.

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Irina Beletskaya received her Diploma degree in 1955, her Ph.D. degree in 1958, and her Doctor of Chemistry degree in 1963 from Moscow State University. The subject for the latter was Electrophilic Substitution at Saturated Carbon. She became a Full Professor at Moscow State University in 1970, and in 1974 she became a Corresponding Member of the Academy of Sciences (USSR), of which she became a full member (Academician) in 1992. She is currently Head of the Laboratory of Organoelement Compounds, Department of Chemistry, Moscow State University. Irina Beletskaya is Chief Editor of the Russian Journal of Organic Chemistry. She was President of the Organic Chemistry Division of IUPAC from 1989 to 1991. She was a recipient of the Lomonosov Prize (1979), the Mendeleev Prize (1982), the Nesmeyanov Prize, (1991), the Demidov Prize (2003), and the State Prize (2004). Tarrant distinguished visiting professor of organic chemistry, University of Florida (2004), Honorary Doctor of Royal Institute of Technology, Stockholm (2006), the International Arbuzov Award (2007). She is the author of more than 600 articles and 4 monographs. Her current scientific interests are focused on (i) transition metal catalysis in organic synthesis, (ii) organic derivatives of lanthanides, and (iii) carbanions and nucleophilic aromatic substitution.

Some Aspects of Green Chemistry Principles Application to Transition Metal Catalysis

I. P. Beletskaya.
Moscow State University, Moscow

Several important trends in two types of transition metal catalysed reactions – substitution (cross-coupling reaction, the Heck reaction, carbonylation) and addition (element – element and element – hydrogen bonds addition to triple bond) will be considered.

These trends include the usage of green solvents like water, “ligandless” palladium, palladium on soluble polymers, the possibility of recycling of catalysts, the use of Ni- and Cu-complexes instead of palladium, nanosized catalysts.

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Birth: September 12, 1930

Education:

1954	BS in Chemistry	Hokkaido University
1959	PhD in Chemistry	Hokkaido University
1963-1965	Postdoctoral	Purdue University (Prof. Herbert C. Brown)

Professional Career:

1959-1961	Research Assistant, Hokkaido University
1961-1973	Associate Professor, Hokkaido University
1973-1994	Professor, Hokkaido University
1994-1995	Professor, Okayama University of Science
1995-2002	Professor, Kurashiki University of Science and Arts
1988	Invited Professors, University of Wales, UK
2001	Invited Professors, Purdue University, USA
2002-2003	Invited Professors, National Taiwan University and Academia Sinica, Taiwan

Publications

342 Research Articles in Chemistry to International and Internal Journals (by April 2009).

Memberships

Chemical Society of Japan (Vice-president, Director, and Editorial Member of the Bulletin of the Chemical Society of Japan). Society of Synthetic Organic Chemistry, Japan (Director and President of Tohoku-Hokkaido Branch). American Chemical Society.

Awards and Honors

Weissberger-Williams Lectureship Award, 1986 (Eastman Kodak Co.,USA). Testimonial, 1987 (Korean Chemical Society). Chemical Society of Japan Award, 1989 (Chemical Society of Japan). Professor Emeritus, 1994 (Hokkaido Univ.). Dow Elanco Lectureship Award, 1995 (Ohio State Univ., USA). Herbert C. Brown Lecturer Award, 2000 (Purdue Univ., USA). Weissberger-Williams Lectureship Award. 2001 (Eastman Kodak Co., USA). Distinguished Lecturer Award, 2001 (Queen's University, Canada and Pfizer Co., USA). Honorary Member, Argentine Organic Chemistry Society, 2001 (Argentina). Synthetic Organic Chemistry Japan Special Award, 2004 (Society of Synthetic Organic Chemistry, Japan). Japan Academy Award, 2004 (Japan Academy). Honorary Member of Chemical Society of Japan, 2005, and Honorary Member of Synthetic Organic Chemistry, Japan, 2005. Distinguished Professor, 2006 (Graduate School of Engineering, Hokkaido University). Honorary Professor, 2006 (Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China). P. Karrer Gold Medal, 2009 (Zürich University, Switzerland). Fellow of the Royal Society of Chemistry, 2009 (UK).

Research Field

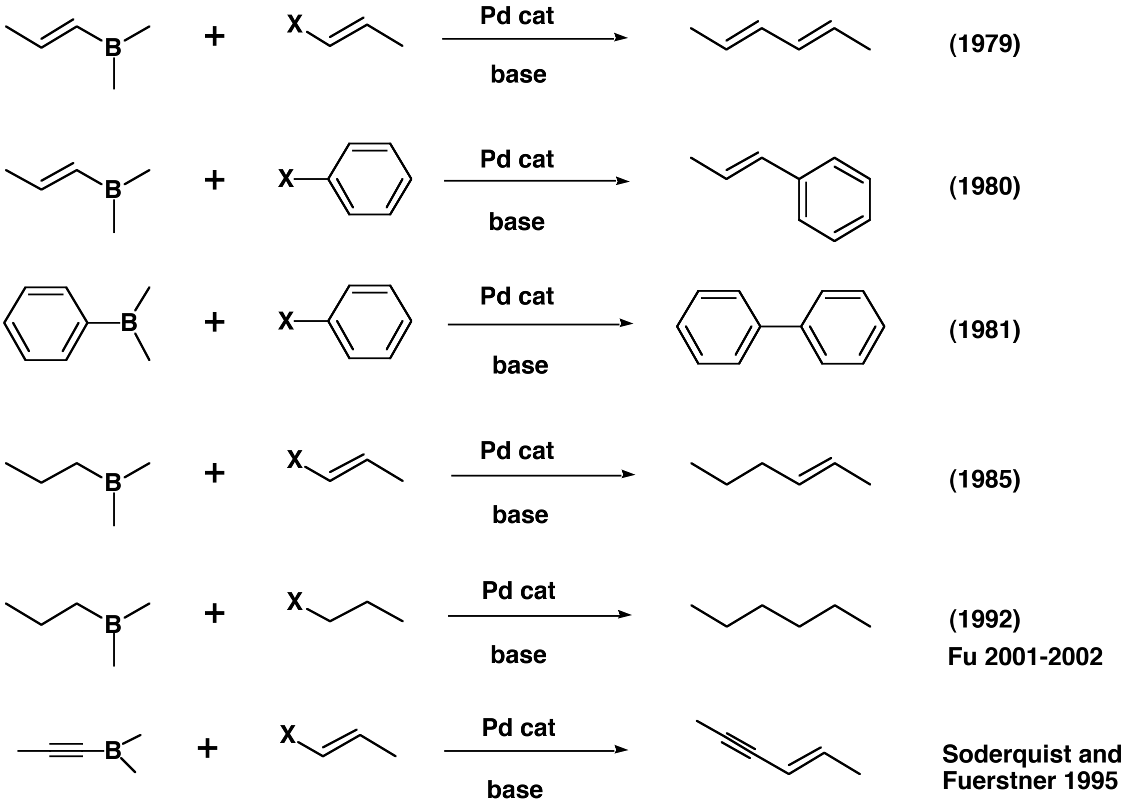
Synthetic Organic Chemistry

Cross-Coupling Reactions of Organoboron Compounds

Akira Suzuki

Professor Emeritus, Hokkaido University, Sapporo, Japan

The palladium-catalyzed cross-coupling reaction between different types of organoboron compounds and various organic electrophiles including halides or triflates in the presence of base provides a powerful and general methodology for the formation of carbon-carbon bonds. The (sp^2)C-B compounds (such as aryl- and 1-alkenylboron derivatives) and (sp^3)C-B compounds (alkylboron compounds) readily cross-couple with organic electrophiles to give coupled products selectively in high yields. Recently, the (sp)C-B compounds (1-alkynylboron derivatives) have been also observed to react with organic electrophiles to produce expected cross-coupled products.



(1979)

(1980)

(1981)

(1985)

(1992)
Fu 2001-2002

Soderquist and
Fuerstner 1995

Such coupling reactions offer several advantages: (1) ready availability of reactants; (2) mild reaction conditions; (3) water stability; (4) easy use of the reaction both in aqueous and heterogeneous conditions; (5) toleration of a broad range of functional groups; (6) high regio- and stereoselectivity of the reaction; (7) insignificant effect of steric hindrance; (8) use of a small amount of catalysts; (9) application in one-pot synthesis; (10) nontoxic reaction; and (11) easy separation of inorganic boron compound.

These coupling reactions have been actively utilized not only in academic fields but also in industrial processes.

In this lecture, the overview of the coupling reaction will be discussed to understand the outlines.

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Education:

1961-1965	BS, Dept. of Synthetic Chemistry, Kyoto University
1965-1967	Master Degree, Kyoto University
1967-1970	Doctor course work, Kyoto University
1971	Dr. Eng., Kyoto University (Prof. M. Kumada)

Academic Experience:

1970-1987	Assistant Professor, Kyoto University, Faculty of Engineering
1973-1974	PD Fellow: State Univ. of New York at Binghamton (J. J. Eisch)
1987-1993	Associate Professor, Kyoto University, Faculty of Engineering
1993-2005	Professor, Kyoto University, Institute for Chemical Research
2000-2002	Director of Institute for Chemical Research, Kyoto University
2002-2004	Visiting Professor: Kyushu University
2003-2005	Director: International Research Center for Elements Science, Institute for Chemical Research, Kyoto University
2003-2005	Visiting Professor: Nagoya University
2005	Emeritus Professor, Kyoto University
2005-2007	Visiting Professor: Hokkaido University
2005-2008	Director, RIKEN Frontier Research System
2007-present	Unit Leader, Functional Elemento-Organic Chemistry Unit
2008-present	Director, RIKEN Advanced Science Institute
2008-present	Visiting Professor: Gunma University

Awards and Honors:

1977	The Chemical Society of Japan Award for Young Chemists
1994	Fellow of the Royal Society of Chemistry, FRSC CChem
1999	The Chemical Society of Japan Award
2002	The American Chemical Society, Frederic Stanley Kipping Award
2002	The Toray Science & Technology Prize
2003	The Asahi Prize (Asahi News Paper Culture Foundation)
2004	Honor with Purple Ribbon
2007	Japan Academy Prize
2008	Honorary member of The Chemical Society of Japan
2008	The Society of Silicon Chemistry Award

Research Field:

Organometallic Chemistry, Synthetic Organic Chemistry, Organosilicon Chemistry,
Main Group Materials Science: 250 original papers and 35 reviews (and 50 reviews in Japanese)

Scientific Service and Membership:

2000-2004	Leader of Center of Excellence (COE) Grant, entitled "Elements Science" supported by the Ministry of Education, Science, Sports and Culture, Japan
2004-2008	Editor-in-Chief of *Bull. Chem. Soc. Jpn.*
2004-2006	President: The Society of Silicon Chemistry, Japan
2005	Vice President: The Chemical Society of Japan
2005-2011	Member of Science Council of Japan

Nickel-Catalyzed Cross-Coupling Reaction between Grignard Reagents and C(sp^2) Halides: A Brief Historical Survey and Some Recent Developments[*]

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The Ni-catalyzed cross-coupling reaction between Grignard reagents and C(sp^2) halides, reported in 1972 independently from France and from Japan,[1] together with Kochi's Fe-catalyzed cross-coupling reaction reported in 1971,[2] has opened up the new field of "Cross-Coupling Reaction", which includes various Pd-catalyzed cross-coupling reactions.[3] This lecture will present a brief historical survey of the Ni-catalyzed cross-coupling reaction[4] and some recent developments in comparison with similar Pd-catalyzed reactions, which include the following topics.

(1) The first proposal of the most plausible catalytic cycle which consists of the oxidative-addition/transmetallation/reductive-elimination sequence, as a guiding principle for development of various types of cross-coupling reactions thereafter.

(2) The first introduction of the concept of "molecular catalysis" in this field by using some nickel-phosphine complexes as catalysts, demonstrating the great dependence of the catalytic activity on the nature of the phosphine ligands.

(3) The most outstanding point of the Ni-phosphine catalyzed cross-coupling reaction is that the alkyl-Grignard reagents containing the β-hydrogen atom(s) can couple with the C(sp^2) halides without the β-hydride elimination.

(4) Another characteristic feature of the Ni-phosphine catalyzed cross-coupling reaction is that aryl chlorides and even aryl fluorides can be used as the coupling partners.

(5) Some recent developments may include the Ni- and Pd-catalyzed cross-coupling reaction of polyfluoro-arenes,[5a] the Pd-catalyzed cross-coupling of aryl-triazenes with arylboronic acids[5b] or aryl-trifluorosilanes,[5c] and a common key role of Lewis acid to activate the strong Aryl-F and Aryl-N bond in these cross-coupling reactions.[5,6]

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   (b) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.
2. Tamura, M.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1487.
3. *E.g.*, (a) Tamao, K. In "*Comprehensive Organic Synthesis*", Trost, B. M.; Fleming, I.; Pattenden, G., Ed.; Pergamon Press: Oxford, 1991, Vol. 3, pp. 435-480. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (c) 30 Years of Cross-Coupling Reaction (Eds.: Tamao, K.; Negishi, E.-i.; Hiyama, T.), *J. Organomet. Chem.* **2002**, Vol. 653. (d) Metal-Catalyzed Cross-Coupling Reactions, 2nd Ed. (Eds.: de Meijere, A.; Diederich, F.), Wiley-VCH, Weinheim, 2004. (e) Negishi, E.-i. *Bull. Chem. Soc. Jpn.* (Vol. 80 Commemorative Accounts) **2007**, *80*, 233.
4. Tamao, K. *J. Organomet. Chem. (Cross-Coupling issue)*, **2002**, *653*, 23.
5. (a) Saeki, T.; Takashima, Y.; Tamao, K. *Synlett* **2005**, 1771. (b) Saeki, T.; Son, E.-C.; Matsunaga, T.; Tamao, K. *Org. Lett.* **2004**, *6,* 617. (c) Saeki, T.; Matsunaga, T.; Son, E.-C.; Tamao, K. *Adv. Synthesis and Catalysis* **2004**, *346*, 1689.
6. *Cf.,* Yoshikai, N.; Mashima, H.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 17978.

[*] This lecture is dedicated to the late Prof. Makoto Kumada who passed away on June 28, 2007. All research results presented in this lecture have been obtained in Kyoto University where the author worked for 35 years until 4 years ago.

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Birth: 09. 11. 1938, Moscow, Russia

Dr. of Sciences, Professor,
Head of the Laboratory of Asymmetric Catalysis.

Education and Professional Career:

1960	Institute of Gas and Oil Industry
1968	Ph.D., (degree at the Institute of Organoelement Chemistry in Moscow under the supervision of Dr. V. M. Belikov)
1980	D.Sc., (Nesmeyanov Institute of Organoelement Chemistry)
1990	Full Professor

Scientific Interests:

Asymmetric catalysis by chiral complexes of transition metals
Asymmetric organic catalysis
Use of enzymes for the synthesis of optically pure compounds
Stoichiometric asymmetric synthesis of amino acids using complexes of transition metals
Catalysts of olefin plymerization
Chiral complexes of alkali metal ions as catalysts of asymmetric C-C bond formation.
Asymmetric synthesis of 18F-labeled radiotracers for PET diagnostics

Experience:

1960-1962	Junior Researcher, Institute of Petrochemical Synthesis
1962-1990	Junior Researcher, Senior Researcher, Leading Researcher, Institute of Organoelement Chemistry
1990-present	Head of Laboratory

Awards:

On 27-Oct, 2001	Jointly with other four European scientists he was awarded a Descartes Prize.

Binuclear Lewis Acids in Asymmetric Catalysis: Success and Unexpected Problems

Yuri N. Belokon
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The development of chiral single site catalysts constitutes one of the most important and burgeoning fields of the contemporary industrial technology of organic synthesis. Many such catalysts became an integral part of the industrial production of enantiomerically enriched pharmaceuticals. Among the catalysts, chiral mononuclear metal complexes feature most prominently. Still the great potential of chiral multinuclear catalysts remains mostly unexplored. The lecture will describe the results of our own research in binuclear Lewis acid Ti(IV) based catalysis of asymmetric cyanation and allylation of aldehydes and ring openings of meso-epoxides. Much greater catalytic activity of binuclear catalysts, as related to mononuclear analogs, was found, as the catalyzed reactions produced final compounds with ee greater than 90%. At the same time an unexpected feature of the binuclear system was its great propensity to hold strongly the intermediates of the reactions in the coordination sphere of the two Ti ions. As a result, the rate limiting stage of the catalytic cycle becomes the dissociation of the intermediate from the coordination sphere of the two Ti-ions. Thus, greater catalytic capabilities of the binuclear complexes in the first stage of the processes, leading to the formation of the intermediates, become masked by the slowness of the next stage. The ways of designing novel chiral binuclear catalysts with improved performance will be described.

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Paul Knochel was born in 1955 in Strasbourg (France). He did his undergraduate studies at the University of Strasbourg (France) and his Ph.D at the ETH-Zürich with Prof. D. Seebach. He spent 4 years at the CNRS at the University Pierre and Marie Curie at Paris with Prof. J.-F.Normant and one year of post-doctoral studies at Princeton University in the laboratory of Prof. M. F. Semmelhack. In 1987, he accepted a position as Assistant Professor at the University of Michigan at Ann Arbor, Michigan. In 1991, he became Full Professor at this University and in 1992, he moved to the Philipps-University at Marburg as C4-Professor in Organic Chemistry. In 1999, he moved to the Chemistry Department of the Ludwig-Maximilians-University at Munich.

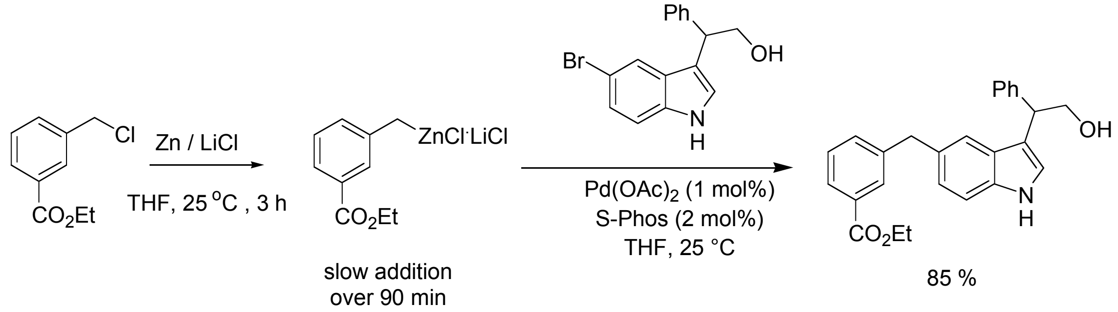
Our research interests are focussed on the development of new synthetic methods for organic and heterocyclic chemistry using organometallic catalysts and reagents, the development of new reagents for asymmetric catalysis. Especially, our research focussed on the preparation of polyfunctional zinc, magnesium and copper reagents. Recently, new Mg-, Al-, Fe-, La-, Mn-, and Zn-bases have been prepared. They are powerful reagents for the regioselective metalation of functionalized aromatics and heterocycles. Applications of these new methods to natural product or biologically active compounds syntheses are performed.

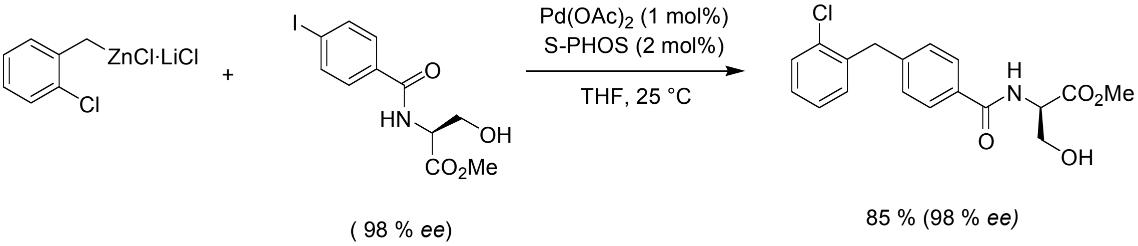
New Chemoselective and Regioselective Cross-Couplings with Functionalized Organometallics

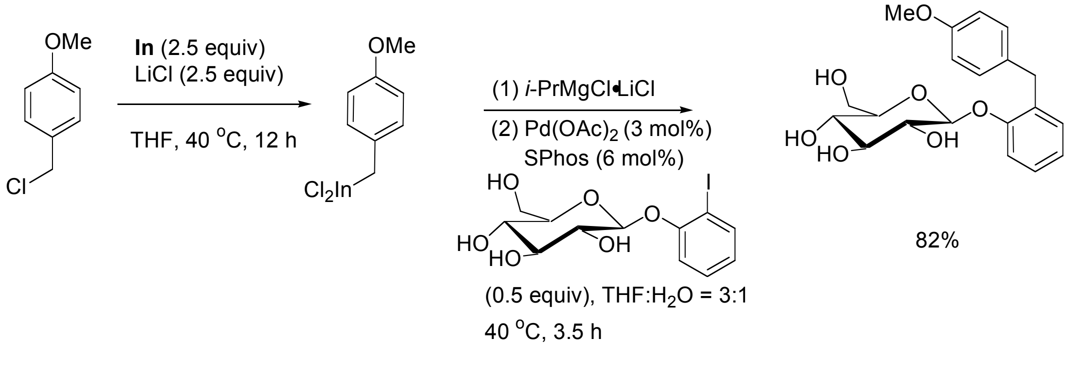
Prof. Paul Knochel

Ludwig Maximilians-University of Munich, Germany

In the presence of LiCl, various metals like Zn, Mg or In undergo a smooth insertion to various organic halides, providing polyfunctional organometallics. These highly functionalized organometallics will be used for the performance of highly regio and chemo-selective Negishi cross-coupling reactions. A new radical Pd(I)/Pd(III)-catalysis for the performance of Kumada reactions will also be presented. Applications for the synthesis of bioactive molecules and material precursors via new cross-coupling reactions will also be shown.







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Birth: August 24, 1946, Ibaraki, Osaka, Japan

Education:

1975 Sept	Doctor of Engineering	Kyoto University
1969-1972	Grad. School of Eng. (Master 1971)	Kyoto University
1965-1969	Bachelor of Eng.	Kyoto University

Professional Career:

1997-present	Professor, Kyoto University
1992-1998	Professor, Research Lab. Resources Utilization, Tokyo Inst. of Tech.
1988-1992	Executive Research Fellow, Group Leader, Sagami Chem. Research Ctr.
1983-1988	Senior Research Fellow, Group Leader, SCRC
1981-1983	Research Fellow, Group Leader, SCRC
1975-1976	Postdoctoral Research Fellow, Harvard University
1972-1981	Assistant Professor, Department of Industrial Chemistry, Kyoto University

Selected Recent Publications other than the topics to be presented:

1. *Palladium-Catalyzed Intramolecular Coupling of 2-[2-Pyrrolyl]silyl]aryl Triflates through 1,2-Silicon Migration.* Mochida, M.; Shimizu, M.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, *131* (24), 8350-8351.
2. *1,4-Bis(alkenyl)-2,5-dipieridinobenzenes: Minimal Fluorophores Exhibiting Highly Efficient Emission in the Solid State.* Shimizu, M.; Takeda, Y.; Highashi, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2009**, *48* (20), 3653-3656.
3. *Synthesis, Crystal Structure, and Photophysical Properties of (1*E,*3*E,*5*E*)-1,3,4,6-Tetraarylhexa-1,3,5-trienes: A New Class of Fluorophores Exhibiting Aggregation-Induced Emission.* Shimizu, M.; Tatsumi, H.; Mochida, K.; Shimono, K.; Hiyama, T. *Chem. Asian J.* **2009**, *4* (8), 1289-1297.
4. *Palladium-Catalyzed Annulation of vic-Bis(pinacolatoboryl)alkenes and –phenanthrenes with 2,2'-Dibromobiaryls: Facile Synthesis of Functionalized Phenanthrenes and Dibenzo[*g,p*]chrysenes.* Shimizu, M.; Nagao, I.; Tomioka, Y.; Hiyama, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 8096-8099.
5. *Modular Approach to Silicon-Bridged Biaryls: Palladium-Catalyzed Intramolecular Coupling of 2-(Arylsilyl)aryl Triflates.* Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 9760-9764.
6. *Solid State Structures and Photophysical Properties of (Trimethylsilyl)methyl-substituted Anthracenes and Pyrenes.* Shimizu, M.; Tatsumi, H.; Mochida, K.; Hiyama, T. *Chem. Commun.* **2008**, 2134-2136.
7. *A Novel Strategy for Two-Photon Holographic Recording: Stepwise Two-Photon Absorption of a-Quinquethiophene Followed by energy Transfer to an Aryl Azide.* Shimizu, M.; Schelper, M.; Mochida, K.; Hiyama, T.; Adachi, M.; Sasaki, Y.; Akiyama, S.; Maeda, S.; Kanbara, H.; Mori, Y.; Kurihara, T. *Adv. Mater.* **2007**, *19*, 1826-1829.
8. *Straightforward Synthesis of* CF_3*-Substituted Triarylethenes by Stereoselective Threefold Cross-Coupling Reactions.* Takeda, Y.; Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 8659-8661.
9. *(Z)-1,2,3,4-Tetraboryl-2-butene: A Reagent for Stereoselective One-pot Triple Aldehyde Addition.* Shimizu, M.; Shimono, K.; Hiyama, T. *Chem. Lett.* **2006**, *35*, 838-839.
10. *Modern Synthetic Methods for Fluorine-substituted Target Molecules.* Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 214-231.

Research Interests:

Novel Organometallic Reagents and Reactions for Selective Organic Synthesis, Organofluorine and Organosilicon Chemistry, Synthesis of Biologically Active Substances, Design and Synthesis of Novel Functionality Molecules and Materials

Awards:

1980	Young Chemist Award of the Chemical Society of Japan
2004	Academic Award of the Japan Liquid Crystal Society
2007	Academic Award of the Society of Synthetic Organic Chemistry, Japan
2008	Award of the Chemical Society of Japan

Invention of Transition Metal-Catalyzed Carbon–Carbon Bond Forming Reactions for Orgranic Synthesis

Tamejiro Hiyama
Department of Material Chemistry, Kyoto University

Four synthetic reactions will be presented that involve cleavage of a stable C–Si, C–C, or C–H bond and make new C–C bonds with the aid of transition metal catalysts. The first reaction employs organosilicon reagents that contain a hydroxymethylphenyl group for intramolecular activation. The reaction design turned out to be highly effective and selective to achieve silicon-based cross-coupling reaction with organic halides using *palladium or palladium/copper* catalysts. The key of success is attributed to the formation of pentacoordiate silicate species responsible for smooth transmetalation from silicon to palladium. The same organosilicon reagents are also shown to deliver organic groups on silicon in a conjugate manner to α,β-unsaturated carbonyl substrates smoothly at ambient temperatures with extremely high efficiency by the aid of *rhodium* catalysts. The third type of transformation involves *nickel(0)* catalysis that proceeds through reductive cleavage of C–CN bonds and insertion of unsaturated bonds like acetylenes, olefins, and allenes between the two organic moieties. The reaction was found to be remarkably accelerated by Lewis acid co-catalysts and to have cinnamonitrile, acetonitrile and propionitrile also undergo the reaction. Meanwhile, the similar *nickel* catalysts were found to cleave (hetero)aryl C–H bonds to allow inner acetylenes and styrene derivatives to insert inbetween in a *cis*-manner. Thus, by appropriate activation, C–Si, C–C, and C–H bonds that are stable under normal conditions are effectively cleaved and employed for novel C–C bond forming reactions. All the transformation proceeds with minimum loss of reactants, thus, contributing to future green chemistry.

Poster
Presentations

PALLADIUM CATALYZED AMINATION IN THE SYNTHESIS OF BISMACROCYCLIC AZACROWN ETHERS

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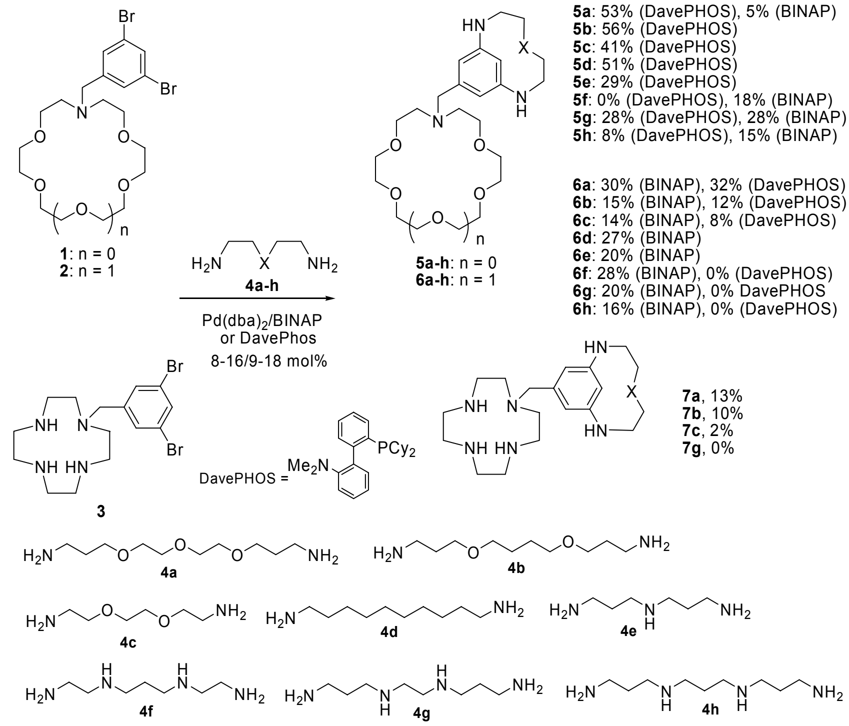
Pd-Catalyzed amination of dihaloarenes proved to be a reliable approach to various polyazamacrocycles. N-(3,5-dibromobenzyl)substituted azacrown ethers **1-3** were aminated with a number of di- and polyamines **4a-h** to give target bismacrocyclic compounds **5-7** in yields from moderate to high. In some cases the yields were even higher than that of corresponding macrocycles synthesized from 1,3-dibromobenzene. The yields were found to be dependent on the nature of polyamines and azacrown ethers. The best yields were provided by the derivative of 1-aza-15-crown-5 **1**, DavePHOS being the best ligand for the majority of cases. On contrary, the reactions with the derivative of 1-aza-18-crown-6 **2** preferred BINAP. Cyclen derivative **3** was found to be quite inert in this process.



The work was supported by the RFBR grants N 09-03-00735 and 08-03-00628.

METAL-MEDIATED REACTIONS IN THE SYNTHESIS OF [2.2]PARACYCLOPHANE DERIVATIVES WITH DIFFERENT TYPES OF CHIRALITY

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A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, Moscow, Russia

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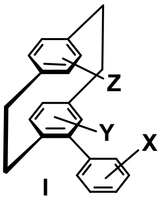
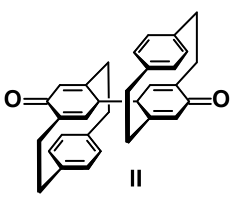
Working in the field of the design of the chiral ligands and auxiliaries based on [2.2]paracyclophane, we repeatedly turned our attention to the structures comprising two or more structural blocks with different functional groups. Thus, we elaborated efficient approaches to a number of novel types of paracyclophane derivatives containing aryl and paracyclophanyl fragments (**I**, **III**, **IV**, **VI**) or two paracyclophanyl fragments (**II**, **IV-VI**) either bonded together directly (**I-III**) or bridged by one, two or three carbon atoms (**IV-VI**). These structures are of the great interest for asymmetric catalysis because they possess different types of chirality (planar chirality combined with central or/and axial chirality).



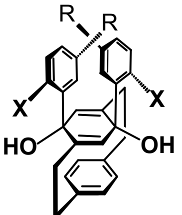
I

X, Y, Z = Alk or donor groups



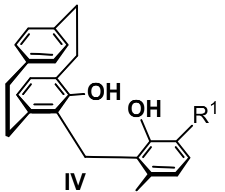
II

chiral- and *meso-*



III

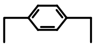
X= OMe, NMe$_2$

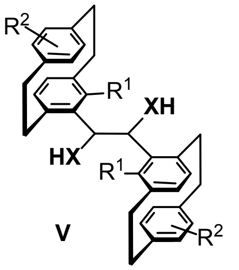


IV

R^1 = Me, R^2 = H

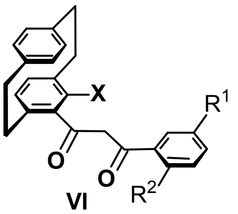
R^1 = *i*-Pr, R^2 = Me

R^1, R^2 = 



V

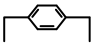
X= O or NR



VI

X= OH; R^1, R^2 = H

X= H; R^1, R^2 = H or

R^1, R^2 = 

Most of the elaborated approaches include metal-mediated reactions, namely:

I: Pd-catalyzed Suzuki cross-coupling reaction of the functionally substituted paracyclophanyl halides and *ortho*-substituted aryl boronic acids;[1a,b] Pd or Ni-catalyzed cross-coupling reaction of bromo-substituted paracyclophanes and arylmagnesium bromides;[1c]

II: Cu(II)-catalyzed oxidative coupling of 4-hydroxy[2.2]paracyclophane;

III: addition of *ortho*-substituted aryllithium reagents to paracyclophane-4,7-quinone;[2]

IV: condensation of magnesium phenolates and paracyclophane analogues of salicylic alcohol;*[3]

V: Zn/Cu- or TiCl$_4$/Zn-mediated pinacol coupling reactions of paracylophane derived imines and aldehydes respectively;[4]

VI: acylation of acetyl[2.2]paracyclophanes with esters in the presence of bases.*[5]

The compounds of types **I-VI** were obtained in enatiomericaly or diastereomerically pure forms and a number of them were tested as ligands and auxiliaries in enantioselective reactions.

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* In collaboration with Prof. Yu. N. Belokon’, INEOS RAS.

C-C COUPLING OF LITHIUMOXAZOLINYLFERROCENE AND TRIAZINES WITHOUT CATALYSIS BY METALS

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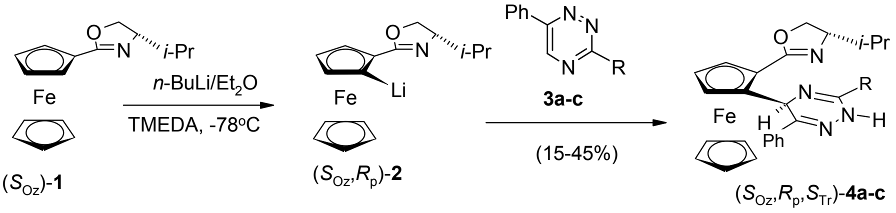
Planar chiral ferrocenyl-containing ligands have a wide application as catalysts of asymmetrical reactions. Therefore, a development of new obtaining methods of optical active ferrocenes is a foreground task at the present time.

Oxazolinylferrocenes **1** subject to the stereoselective lithiation forming the planar chiral derivatives. The approach of direct uncatalysed by metals coupling of lithiumoxazolinylferrocene **2** and 1,2,4-triazines (S_N^H) **3a-c** was suggested by us [1]. Thus, the stable σ^H-adducts **4a-c** of the reaction of nucleophilic substitution of hydrogen in triazines (S_N^H) have been synthesized (yield 15-45%, de 78-99%) (Scheme 1).

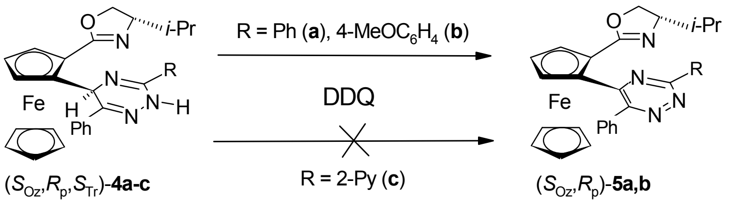


3,4: R = Ph (**a**), 4-MeOC$_6$H$_4$ (**b**), 2-Py (**c**)

Scheme 1

An aromatization of the mono substituted ferrocenyl-containing intermediates occurs smoothly using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidative reagent[2] [3]. The heteroaromatic S_N^H products are formed in these conditions.

Thereby, we have obtained planar chiral azaheterocyclic ferrocenes **5a,b** containing phenyl or 4-methoxyphenyl substituent in a position 3 of the triazine cycle (Scheme 2).



Scheme 2

It should be noted that the aromatization is not observed in the case of pyridyl-containing intermediate **4c**. As a result, a mixture of its destruction products is formed.

[1] M.V. Varaksin, I.A. Utepova, O.N. Chupakhin, V.A. Davankov, M.M. Ilyin, M.M. Ilyin (j.), V.L. Rusinov, P.A. Slepukhin, *Russ. Chem. Bull., Int. Ed.*, 2009, **6**, 1126

[2] O.N. Chupakhin, I.A. Utepova, I.S. Kovalev, V.L. Rusinov, and Z.A. Starikova, *Eur. J. Org. Chem.,* 2007, **5**, 857.

[3] I.A. Utepova, A.E. Lakhina, M.V. Varaksin, I.S. Kovalev, V.L. Rusinov, P.A. Slepukhin, M.I. Kodess, O.N. Chupakhin, *Russ. Chem. Bull., Int. Ed.*, 2008, **10**, 2116

Synthesis of Well-Defined Phenylene-Thiophene Oligomers using Zirconocene Complex

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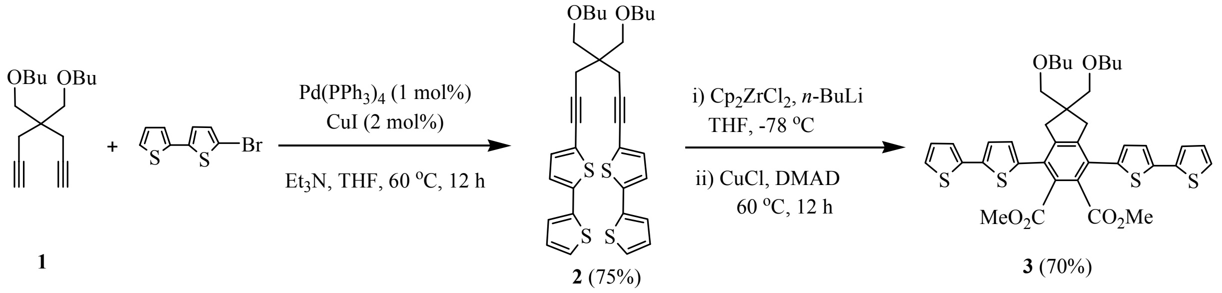
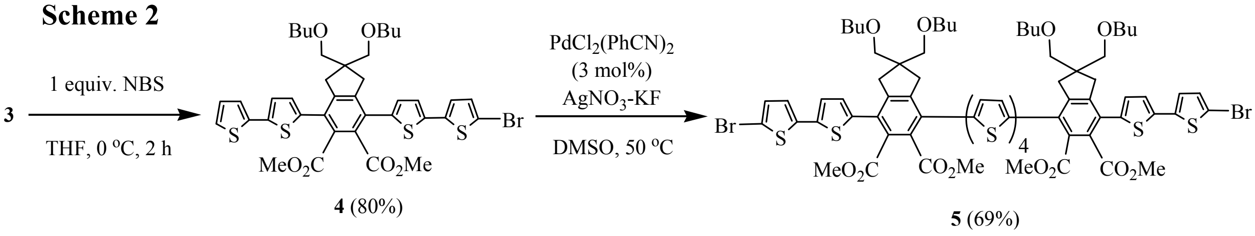
In recent years oligothiophenes have raised an increasing interest due to their application in electronic and optoelectronic devices. To accomplish high performance from such extended π-conjugated systems, the synthetic strategy for well-defined oligomers plays a significant role. As a synthetic methodology of π-conjugated compounds, a zirconocene-mediated cycloaddition reaction provides a unique route as our group developed so far.[1] Herein we would favor to report the synthesis of 1,4-bis(dithienyl)benzene derivatives and their dimers through C-H homocoupling.

Scheme 1 shows our approach for the synthesis of 1,4-bis(dithienyl)benzene. Butylated diyne **1** was subjected to Sonogashira coupling reaction with 2-bromo-5-(2′-thienyl)thiophene to afford bis(dithienyl)-substituted diyne **2** in good yield. Then, 1,4-bis(dithienyl)benzene **3** was obtained using zirconium-mediated cycloaddition of diyne **2** with dimethyl acetylenedicarboxylate (DMAD).

Scheme 1



Scheme 2



In the next step, monobromination of **3** was performed using 1 equiv of NBS in $CHCl_3$ and acetic acid. When bromide **4** was subjected to Pd-catalyzed homocoupling reaction,[2] thiophene oligomer **5** containing 8 thiophene and 2 benzene rings was obtained in a good yield. This dimer possesses two terminal C-Br bonds, which are also available for a variety of coupling reactions.

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2. Mori, A. *et al. J. Am. Chem. Soc.* **2006**, *128*, 10930-10933.

METAL COMPLEX CATALYSIS IN THE SYNTHESIS OF MACROCARBOCYCLES

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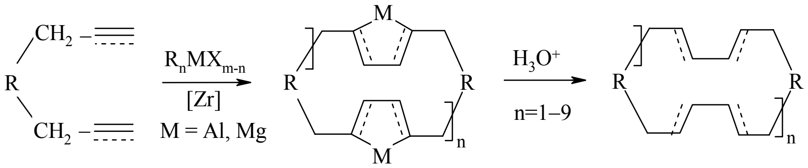
Most of the known methods for the synthesis of macrocarbocycles and their functional derivatives are multistep and require expensive or hard-to-reach reagents. These circumstances greatly reduce the practical value of the described in literature methods for the construction of macrocyclic compounds and appear to be a major deterrent factor in creating new materials.

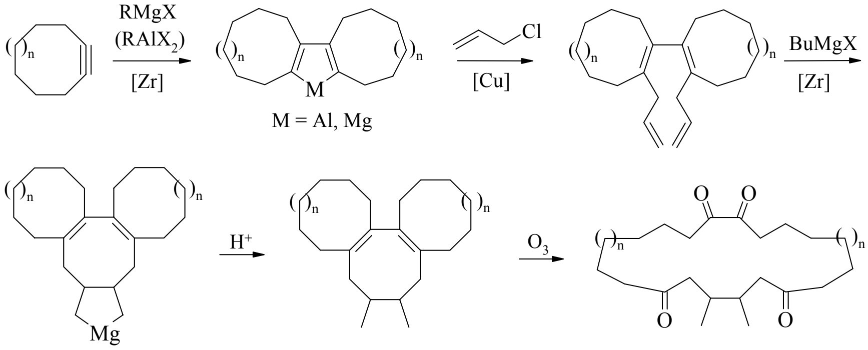
We have developed original approaches and «one pot» synthetic methods to obtain hard-to-reach macrocyclic compounds based on olefins, allenes, and acetylenes with the participation of highly active and selective metal complex catalysts.

The proposed methods are based on discovered by us the catalytic cyclometalation reactions of unsaturated compounds with alkyl and halogen alkyl Mg or Al derivatives.

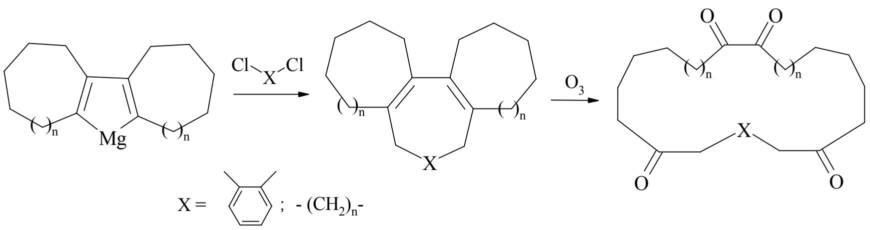
Using the intermolecular cyclometalation reaction of α,ω-diallenes, α,ω-diacetylenes, α,ω-diolefins, available organomagnesium and organoaluminum compounds (OMCs) in the presence of Ti and Zr complex catalysts novel organometallic macrocycles with the alternating magnesa- and aluminacyclopentane (cyclopentadiene) fragments as well as the alternating double bonds were synthesized. Hydrolysis of the obtained compounds led to the appropriate macrocarbocycles.



We have developed a methodology for the synthesis of hard-to-reach functionally substituted C_{20}−C_{28} macrocarbocycles from cyclic acetylenes involving RMgX, R_2Mg or $RAlX_2$, AlX_3 (where X = Cl, Br) in the presence of the catalytic amounts of Zr complexes. The symmetric tricyclic annulated OMCs obtained without preliminary isolation are involved successively in the cross-coupling reaction with allyl chloride, the cyclometalation reaction with Grignard reagents RMgX or $AlCl_3$, and then the oxidative cleavage giving rise to the target gigantic carbocyclic ketones in high yields (80−85%).



In continuation of research to design the effective methods for the synthesis of macrocarbocycles the new original approach to macroheterocycles of specified structure via the cross-coupling between tricyclic OMCs and hydrocarbon dihalogenides have been elaborated. The subsequent oxidative cleavage of the double bonds in the formed tricyclic dienes resulted in the target C_{20}−C_{28} polyketones.



Thus, we have demonstrated the possibility of one pot construction of unique gigantic multifunctional macrocarbocycles from simplest unsaturated compounds namely olefins, allenes, and acetylenes as well as available organoaluminum and organomagnesium reagents using the cyclometalation reaction catalyzed by transition metal based complexes.

These studies unclose completely new opportunities for macrocarbocycles being of interest as selective ionophores, the complexing agents for isolation and purification of rare and noble metals, potential prolongators of medicines, materials for molecular electronics as well as unique monomers for the synthesis of oligo-and polymeric macromolecules, which are promising in various fields of industry.

CONTROL OF THERMORESPONSIVE PROPERTY OF UREA END-FUNCTIONALIZED POLY(*N*-ISOPROPYLACRYLAMIDE) BASED ON SELF-ASSEMBLY

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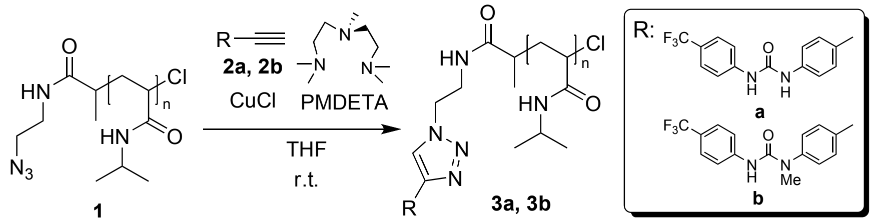
Poly(*N*-isopropylacrylamide) (PNIPAM), a major representative of the thermoresponsive polymer, exhibits a coil-to-globule transition in water at the specific temperature called the lower critical solution temperature (LCST) [1]. Since the LCST of PNIPAM is largely affected by the nature of the coil-to-globule transition accompanied by aggregation of the resulting globules [2], it was expected that the thermoresponsive property of PNIPAM would drastically vary due to the introduction of urea group, which is capable of self-assembly [3], into the polymer terminus. Herein we report a precise synthesis of novel urea end-functionalized PNIPAM and control of its thermoresponsive property based on self-assembly assisted by hydrogen bonding between the terminal urea groups.

Chart 1



Urea end-functionalized PNIPAM (**3a**) was synthesized by the copper(I) catalyzed azide-alkyne cycloaddition between azide end-functionalized PNIPAM (**1**) and newly synthesized diphenylurea derivative bearing a terminal alkyne group (**2a**). To investigate the effect of hydrogen bonding between urea groups on the cloud point of **3a**, we synthesized a PNIPAM bearing *N*-methylated urea group (**3b**) with inhibited hydrogen bonding ability in the same way (Chart 1). The cloud points of **3a** and **3b** were determined to be 29.5 and 34.4 °C, respectively, by using the turbidimetric analysis (Figure 1). This result indicated that the higher hydrogen bonding ability of terminal urea groups in **3a** certainly contributed to the decrease in the cloud point of **3a**. In the ^{1}H NMR spectrum of **3a** measured in D_2O at 25 °C, terminal aromatic groups showed broad signals. In contrast, similar aromatic protons showed sharp signals in the spectrum of **3b**. This result suggested that **3a** aggregates in water at a temperature below its cloud point based on the self-assembly of terminal urea group through hydrogen bonding. In fact, large particles were observed by dynamic light scattering and transmission electron microscopy measurements of aqueous solutions of **3a** at 25 °C.

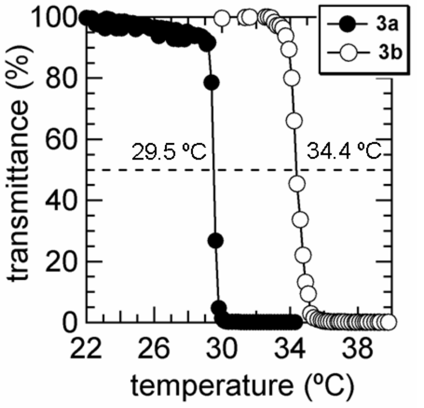


Figure 1. Transmittance (λ = 500 nm) vs temperature for aqueous solutions of **3a** and **3b** (2.0 mg mL^{-1}). Heating rate = 1.0 °C min^{-1}.

Consequently, it was revealed that the urea end-functionalized PNIPAM produced aggregates in water based on the hydrogen bonding of the terminal urea group, which caused the decrease in its cloud point. Thus, the present study realized for the first time the control of thermoresponsive property of PNIPAM based on self-assembly assisted by hydrogen bonding.

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Colorimetric detection of Volatile Organic Compounds (VOCs) Based on Self-Assembled Carbamate Substituted Polydiacetylene Microfibers

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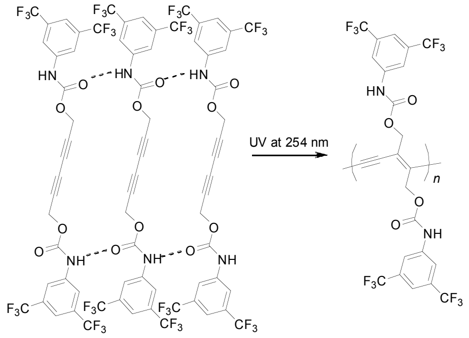
Polydiacetylenes (PDAs) are a unique group of polymers that consist of a highly conjugated backbone with modifiable pendants side groups. Apart from their important applications in conducting polymer chemistry, PDAs have been attracting much attention in the field of colorimetric detection recently, owing to their well-established ability to exhibit changes in color in response to external stimuli such as solvents, pH and temperature. PDAs that enable solvent detection simply by naked eye observation are ideal candidates for applications in volatile organic compounds (VOCs) detection, a crucial aspect of environmental monitoring since VOCs are harmful to human health and yet are present in our everyday lives. Another novel aspect of PDAs that distinguishes it from other polymers is its straightforward synthesis through solid-state photopolymerization, whereby monomer molecules are oriented orderly by means of hydrogen bonding prior to polymerization, giving rise to highly aligned polymerized domains in the product.

Here we report the fabrication of a new PDA exhibiting fast and selective vapochromic responses to a range of organic solvents, a unique property yet to be thoroughly investigated upon by other authors. The DA monomer was readily prepared from commercially available 3,5-bis(trifluoromethyl)phenyl isocyanate and 2,4-hexadiyne-1,6-diol.

Chart 1



Upon irradiating the crystallized monomer under 254nm UV light, polymerization occurred according to **Chart 1** and polymer conjugation length increased, thereby resulting in a darkening in color from white to purple to brown within only 5 minutes (**Fig. 1**). The resulting polymer exhibits positive vapochromic response to various organic solvents, since it showed a bathochromic shift with increasing solvent polarity i.e. a tendency to portray longer wavelength red chromic reflectance in polar solvents and on the contrary, shorter wavelength orange chromic reflectance in non-polar solvents (**Fig. 2**). Such an observation may be attributed to the release in strain within the methylene groups next to the DA backbone upon solvent adsorption onto the polymer.

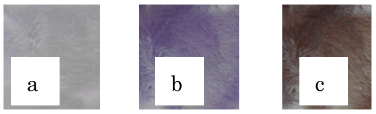


Fig. 1: Photograph of monomer crystals a) before UV irradiation; b) after UV irradiation at 254 nm for 10 s; c) after UV irradiation at 254 nm for 5 min. All of the above procedures were conducted at room temperature.

Fig. 2: Vapochromic response of polymer to various organic solvents

In conclusion, an effective carbamate-substituted PDA VOC sensor possessing an added advantage of stability towards the target solvents was synthesized. Moreover, modification of the substituent pendants in the polymer is a source of great potential for monomer design that can give rise to further variations in its vapochromic properties.

POLYAZAMACROCYCLES WITH PYRIMIDINE UNITS

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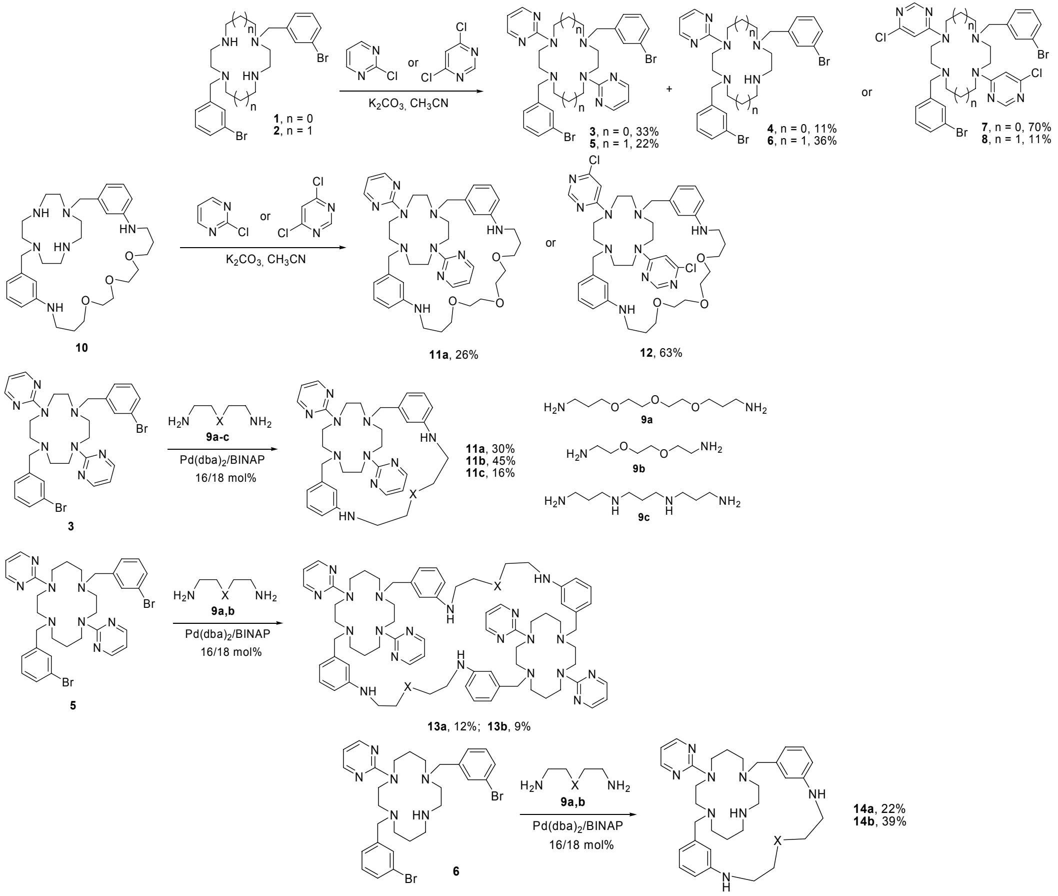
Cyclen and cyclam derivatives **1**, **2**, **10** were modified with 2-chloro- and 4,6-dichloropyrimidines to give 2- and 4-pyrimidinyl substituted tetraazamacrocycles **3**, **5**, **6**. Compounds **3**, **5** were introduced into the Pd-catalyzed amination reactions with polyamines **9a-c** to provide bis- and trismacrocycles **11**, **13**, **14**. The yields of the products strongly depend on the nature of cyclic and linear polyamines.



The work was supported by the RFBR grants N 09-03-00735 and 08-03-00628.

PD-CATALYZED HYDROPHOSPHORYLATION OF ALKYNES WITH HIGH SELECTIVITY

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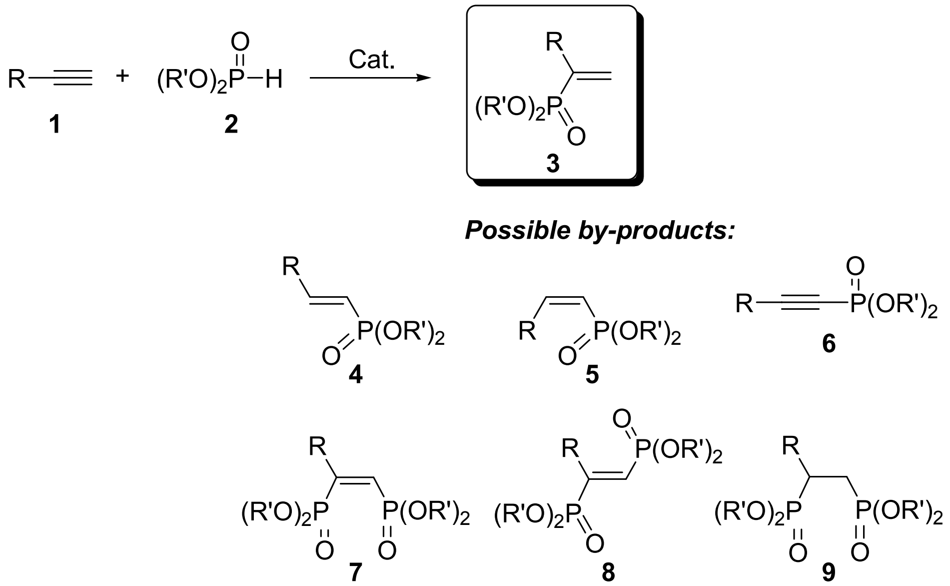
A novel catalytic system was developed to accomplish hydrophosphorylation of terminal and internal alkynes with high yields (65-96%) and excellent regioselectivity (>99/1). The key issue was to apply a low-ligated $Pd/2xPPh_3$ catalytic system in the presence of catalytic amounts of acid. The origins of the dramatic influence of acid on the activity and selectivity of the catalyst were revealed with mechanistic NMR study, and the nature of the processes involving Pd complexes was established. The developed catalytic system has been applied successfully to furnish formation of diverse alkenylphosphonates structures from readily available H-phosphonates and alkynes (Scheme 1).



Scheme 1. Alkynes hydrophosphorylation reaction towards formation of Markovnikov product **3** and possible by-products (**4 - 9**).

The study of catalytic reaction in various solvents and under solvent-free conditions will be presented and discussed.

Acknowledgement. The research was supported in part by the Russian Foundation for Basic Research (Project No. 07-03-00851), Program No 1 of Division of Chemistry and Material Sciences of RAS and Program No 20 of RAS.

Reference: V.P. Ananikov, L.L. Khemchyan, I.P. Beletskaya. *Synlett,* **2009.** DOI = 10.1055/s-0029-1217739

ADDITION OF CF3- AND C6F5-GROUPS TO C=N BOND USING SILICON REAGENTS

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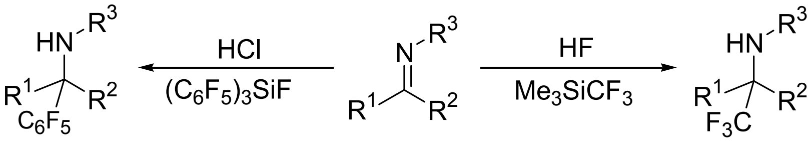
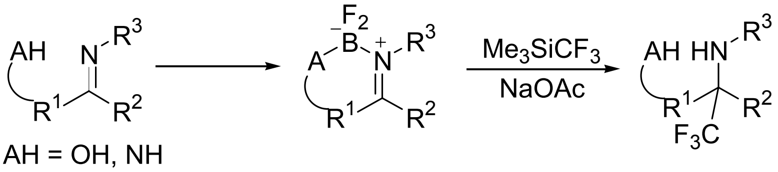
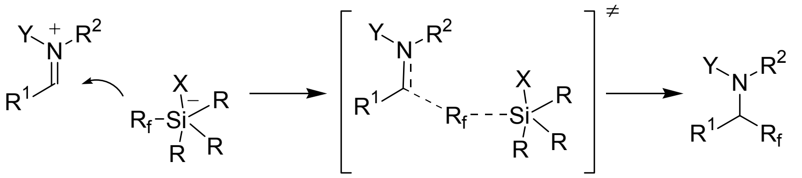
Use of fluorinated silanes for the addition of a fluorinated group to C=N bond constitutes an attractive way to pharmacophoric amines. However, these processes are hampered due to inherently low reactivity of imines and related compounds. We present a new methodology for performing such reactions employing CF_3- and C_6F_5-substituted silanes [1-5]. Our concept is based on the simultaneous use of acidic and basic reagents for the activation of substrate and fluorinated silane, respectively. For the activation of silanes a wide range of Lewis bases can be employed ranging from strongly basic fluoride and acetate ions to poorly nucleophilic chloride ions. The activation of C=N bond can be achieved by different methods. Unactivated imines react with $(C_6F_5)_3SiF$ [1] or Me_3SiCF_3 [2] in presence of HCl or HF respectively.



Imines, bearing adjacent OH or NH can be transformed trifluoromethylated using Me_3SiCF_3 activated by sodium acetate through the intermediacy of boron chelates [3].



It is believed that in these reactions the C-C bond forming event proceeds as transfer of fluorinated group from five-coordinate silicon complex to iminium electrophile.



This work was supported by the Russian Academy of Sciences (program # 18), Russian Foundation for Basic Research (project 08-03-00428), and the Russian Science Support Foundation.

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(b) Dilman, A. D.; Arkhipov, D. E.; Levin, V. V.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *J. Org. Chem.*, **2008**, *73*, 5643

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SYNTHESIS OF AZIDE- AND TRIAZOLE-CONTAINING COUMARIN-TYPE COMPOUNDS

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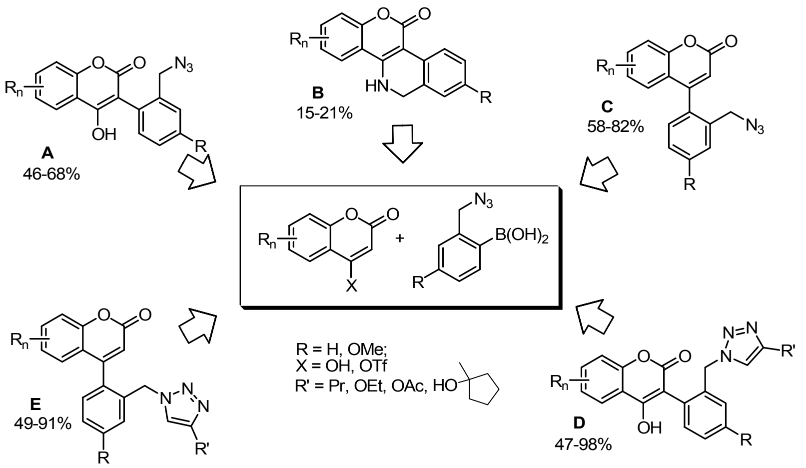
Several families of new iso- and neoflavonoid compounds derived from 4-hydroxycoumarins and 4-trifluoromethylsulfonyloxycoumarins were synthesized using 2-(azidomethyl)arylboronic acids. The key steps for the synthesis of **A-E** derivatives were Suzuki-Miyaura cross-coupling, reductive ligand coupling C-arylation and [3+2] dipolar cycloaddition (Scheme).[1]



Scheme

Synthesized flavonoid derivatives **A-E** are showed to be structurally similar to naturally occurring stilbenes - resveratrol and combretastatin A-4, binding to the colchicine site of tubulin and manifesting potent antimitotic and cardioprotecting activity.

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Acknowledgments

This work was supported by Russian Foundation for Basic Research (09-03-00647-a and 09-03-97038-r_povolzh’e_a).

SYNTHESIS OF METAL-COMPLEX CATALYSTS FOR POLYMERIZATION PROCESSES, BASED ON THE REACTIONS OF THE METAL-ORGANIC COMPOUNDS

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The fundamental investigations, performed at the A. V. Topchiev Institute of Petrochemical Synthesis RAS in the field of coordinative polymerization of olefins and dienes, lead to the creation of effective metal-complex catalytic systems. The presentation contains the results of investigation of synthesis, structure and activity of some of these system.

Di-lithiumorganic initiators.

According to the mechanism of electrode process the electroreduction of organic molecules can be considered as nucleophilic reaction. Thus it was shown that when determining polarographically the electron affinity in *meta*-diisopropenylbenzene (m-DIPB), *para*-diisopropenylbenzene (p-DIPB) and α-methylstyrene the attachment of electron to two isopropenyl groups in the case of m-DIPB takes place independent for every of groups, whereas in the case of p-DIPB the mutual influence of groups manifastes in the formation of two separated waves and in significant shift of potential of half-wave compared to the latter for α-methylstyrene. That is why the synthesis of di-lithium initiators was performed on the basis of m-DIPB and butyllithium. These compounds were tested as catalysts for receiving of triple co-polymers of olefins or dienes with styrene.

Oligodienyl complexes of transition metals.

Oligodienyl complexes of transition metals were synthesized on the basis of reaction of alkilation of salts of transtion metals (Ni, Co, Zr, Ti) and Nd by triisobutylaluminum in the presence of 1,2- and 1,3-dienes as well as on the basis of interaction of carbonyls of metals (Fe, Co, Mo, W, Cr) with allenes and acetylene.

On the basis of organic compounds of transition metals – oligodienyl complexes of Ni, Co, Zr, Ti, Nd – effective catalytic systems of new generation for oligomerization and polymerization of unsaturated hydrocarbons of different classes (olefins, 1,2- and 1,3-dienes) were developed. The composition and structure of metal-aluminum oligodienyl complexes formed, as well as their stability and activity in the oligomerization and polymerization were studied. In particularity it was shown that in the case of olefins these complexes in combination with electron acceptor compounds permit to obtain different type of oligomers – starting with dimers and up to higher α-olefins. In the case of dienes the catalysts lead to the polymerization.

The specific behavior of allen hydrocarbons in interaction with metal-organic compounds was established. It was shown that on the basis of interaction of chlorides of Ni, Co, and Fe with triisobutylaluminium in the presence of allenes the formation of metal complexes was observed. The complexes contain metal-carbon σ-π-bonds which activity and stability are intermadiate between σ and π-allyl bonds. It was found also that polymerization of allenes can be conducted in absent of electron acceptors.

The reactions of allene hydrocarbons with dicobaltoctacarbonyl and ferrum pentacarbonyl were studied as well.

It was shown that interaction of dimethylallene with dicobaltoctacarbonyl (DCOC) in pentane or octane leads to formation in atmosphere of carbon oxide acylcobaltorganic compound with Co-Co fragments. The same interaction in Ar -atmosphere results in formation of σ-π-alkenyl complex. It was found that such compounds are active as catalysts for polymerization of allene hydrocarbons and for hydroformylation of olefins. Stoichiometric decomposition of Fe-pentacarbonyl under the action of UV proceeds with CO extraction. The fotodissociation of this compound leads to formation of complex $Fe(CO)_4{*}C_3H_4$. By means of IR, UV, Moessbauer spectroscopy as well as chromatography the products of interaction of $Fe(CO)_4{*}C_3H_4$ with Al(i-

$C_4H_9)_3$ were studied. It was shown the formation of σ-π-alkenyl complex of Fe, which appeared to be active in polymerization of allene.

Titanium-magnesium nanocatalysts.

During some last years a grate attention was paid to synthesis of titanium-magnesium nanocatalysts *in situ* in the process of simultaneous decomposition of titanium- and magnesium-organic compounds.

The catalysts obtained were investigated by means of IR, ESR, X-Ray analysis. According to the data of electron transparent microscopy the catalyst consists from fine particles with the main dimension in the range of 15-35 nm, inclined to formation of fractal structures typical to nano-particles with such dimensions. It was established that the catalysts in question are highly effective in reactions of polymerization of olefins and 1,3-dienes.

Arentricarbonyl complexes.

It was shown that the adducts of interaction of arentricarbonyl complexes of Mo, Cr, W with alkines, preliminarily subjected to UV irradiation, are effective catalytic systems for polymerization of phenylacetylene and its derivatives.

The investigation is partly supported by RFBR (grants No 08-03-12064 and 09-03-00231).

NOVEL NICKEL-CATALYZED SYNTHESIS OF THIO- AND SELENOSUBSTITUTED DIENES WITH DEFINED GEOMETRY

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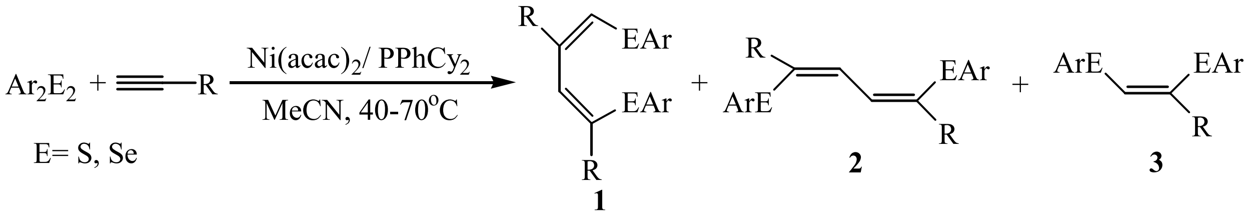
Formation of carbon-heteroatom and carbon-carbon bonds with defined stereochemistry is a challenging problem of modern organic chemistry [1-3].

Recently we have shown that palladium catalysts traditionally used in ArEH (E = S, Se) addition to alkynes leading to Markovnikov type vinyl chalcogenides can be successfully replaced by nickel complexes [4-6]. It was found that formation of nanostructure of the nickel catalyst particles was the key factor determining its high activity [5].

Use of nickel complexes in Ar_2E_2 (E = S, Se) addition to alkynes resulted in unexpected formation of functionalized dienes **1** and **2** instead of alkenes **3** obtained in the palladium catalyzed reaction [4, 7]. Thorough investigation of the reaction found led to the development of efficient protocol for selective preparation of functionalized dienes with excellent chemo- and stereoselectivity based on nickel-catalyzed addition of dichalcogenides to alkynes (scheme 1). The method developed was successfully used for preparative synthesis of dienes of type **1** [8].



Scheme 1. Nickel-catalyzed selective formation of chalcogenesubstituted dienes **1** and **2** upon interaction of Ar_2E_2 (E = S, Se) with alkynes.

The scope of the reaction and mechanistic investigations will be discussed in the presentation.

The work was supported by the Russian Foundation for Basic Research (Project No. 07-03-00851) and Research Grant MK-1085.2008.3.

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ON MECHANISM OF REACTIONS OF TRIALKYLALANES WITH ALKENES, CATALYZED WITH ZR PI-COMPLEXES

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Catalytic systems using early transition metal complexes have been developed for the hydro-, carbo- and cyclometallation reactions of unsaturated hydrocarbons by organomagnesium and organoaluminium compounds [1]. The process chemoselectivity significantly depends on the type of organoaluminium compounds (OACs), catalyst structure and reaction conditions. However, the reaction mechanisms are still questionable, since both the structure of the catalytically active centers and the mechanism of alkenes introduction into bimetallic systems are unclear.

The work is devoted to a study on mechanism of action of Zr π-complexes (L_2ZrCl_2: L= Cp, CpMe, $CpMe_5$, Ind, Flu) as catalysts in reactions of organoaluminium compounds (OACs) with alkenes, namely, in the processes of olefins hydro-, carbo- and cycloalumination. The effect of the OACs nature, Zr π-ligand environment, solvent type, temperature and reagents ratio on reaction chemoselectivity has been studied. In the case of $AlMe_3$, the hydro- and carboalumination products, and alkene dimers are formed. The catalytic reaction of $AlEt_3$ with the olefins yields aluminacyclopentanes altogether with the hydro- and carboalumination products, and the dimers. It was shown that the OAC nature and Zr π-complex structure exhibit the most effect on the reactions pathway. The reaction of alkenes with $AlMe_3$, which runs in chlorine-containing solvents (CH_2Cl_2) in the presence of Zr complexes with small π- ligands (Cp and Cp'), yields mainly dimers. The use of Zr complexes substituted with more bulky π- ligands (Cp*, Ind) and chlorine-containing solvents (CH_2Cl_2) increases the carboalumination products yield. The chlorinated solvent replacement with hydrocarbons in reaction with $AlEt_3$ substantially increases the yield of aluminacyclopentanes.

We found that reaction of terminal alkenes with $AlMe_3$ in the presence of either L_2ZrH_2 or L_2ZrHCl (L= Cp, Cp′) both under the catalytic and stoichiometric conditions results in the same products as in the case of L_2ZrCl_2. This fact implies participation of zirconcene hydrides as intermediates in the reaction of alkenes with AlR_3, catalyzed with L_2ZrCl_2.

The structure and reactivity of intermediates, which are formed in the systems AlR_3-L_2ZrCl_2-alkene, have been investigated by the means of dynamic NMR spectroscopy, encounter synthesis and kinetic studies; and the key complexes responsible for the hydro-, carbo- and cyclometallation pathways were determined.

The quantum-chemical calculations of geometric and energetic parameters of intermediates and transition states of the processes of interligand exchange, β-C-H-activation and alkene coordination were carried out.

On the basis of experimental and theoretical investigations, a generalized model of olefin hydro-, carbo- and cyclometallation, catalyzed with Zr π-complexes is suggested.

The authors thank the Foundation of the President of Russian Federation (Program for Support of Leading Scientific Schools, U.M. Dzhemilev, Grant NSh-2349.2008.3), the Russian Foundation of Basic Research (Grant No. 08-03-97010) for financial support.

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ALUMINUM CARBENOIDS IN THE TRANSFORMATION OF ALKYNES TO CYCLOPROPANE DERIVATIVES

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2 - N. D. Zelinskii Institute of Organic Chemistry of Russian Academy of Sciences, Moscow, Russia
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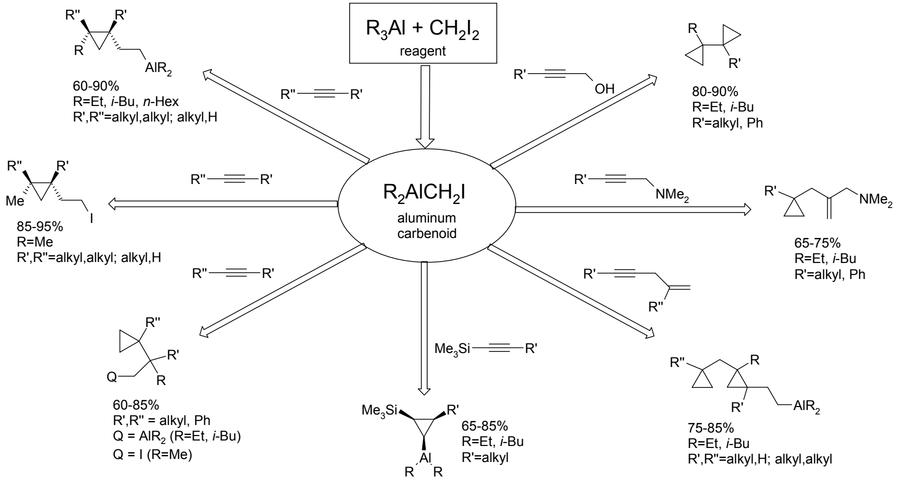
The presentation describes our research study on the reaction of alkynes with R_3Al-CH_2I_2 system (R=alkyl). We have found that aluminum carbenoids are efficient agents for the one-step transformation of mono- and disubstituted alkynes to aluminum- and iodo-containing di-, tri- and tetra-substituted cyclopropanes,**[1]** propargylic alcohols to 1,1′-disubstituted bis-cyclopropanes,**[2]** alkynyl(trimethyl)silanes to silicon-containing cyclopropylaluminums,**[3]** propargyl amines to cyclopropylmethyl-substituted allyl amines,**[4]** allyl alkynes to dicyclopropane derivatives.**[4]**



Reaction conditions: CH_2Cl_2, 20-23 °C

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4) Submitted for publication.

USE CHIRAL COMPLEXES OF THE TITAN(IV) AND VANADIUM(IV) IN ASYMMETRIC OXIDATION OF POLYFUNCTIONAL SULFIDES

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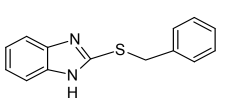
Interest to nitrogen containing chiral sulfoxides is caused by their high biological activity as antioxidants, antidepressants and inhibitors a gastric acid, and also application in modern systems of photoprogramming as DIR-components and antiveiling agents. Chiral sulfoxides are widely applied in asymmetric synthesis and synthesis of sulfides and unnsymmetric disulfides.

Sulfoxides with enantiomeric excess receive by oxidation of corresponding sulfides by modified catalytic systems in which apply catalysts on the basis of the titan(IV) and vanadium(IV) with Shiff's chiral bases.

In this work results of experiments of asymmetric oxidation 2-benzylthio-1H-benzoimidazole (I), 1-phenyl-5-methylthiotetrazole (II), 1-butyl-4-nitrobenzene (III) in corresponding sulfoxides with enantiomeric excess with use of complexes on the basis of the titan(IV) and vanadium(IV) are presented.



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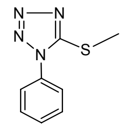

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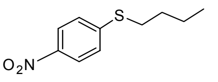
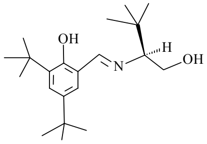


III

As ligands have been used (S)-(-)-2-(3,5-Di-*tert*-butylsalicylideneamino)-3,3-dimethil-1-butanol **(1)**, (*S,S*)-(+)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine **(2)**, synthesized by us 2-(3,5-di-*tert*-butyl butylsalicylideneamino)-3-p-nitrophenilpropandiol-1,3 **(3)** and 2-(butylsalicylideneamino)-3-p- nitrophenilpropandiol-1,3 **(4)**.



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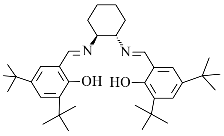

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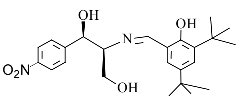

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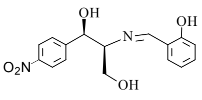

4

As a result of oxidation are received corresponding sulfoxides with a yield 75-92 % and enantiomeric excess 10.3-81.0 % *ee*. Influence of the nature of an oxidizer, a structure of ligands (*tert*-butyl groups in **3** and **4**), additions of N,N'-diisopropylethylamine in case of oxidation I is considered. According to UV-spectroscopy addition of N,N'-diisopropylethylamine in a reactionary mixture at oxidation I conducts to significant changes in an electronic structure of a substratum and as consequence, enantiomeric excess increases from 22 % up to 81 %.

As oxidizers have been used *tert*-butyl hydroperoxide, hydrogen peroxide, chlorine dioxide. Structures of the received compounds are proved by IR-, NMR-, mass-spectrometry and data of the element analysis. Enantiomeric excess determined by HPLC.

RECYCLABLE CATALYTIC SYSTEMS POLYMER SUPPORTED PD NANOPARTICLES IN THE C-C BOND FORMATION

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Two polymer supported palladium nanoparticles catalytic systems were investigated. The palladium nanoparticles stabilized in micelles formed by polystyrene-co-polyethyleneoxide and cetylpyridinium chloride as a surfactant were investigated as a catalyst in the following reactions: Heck reaction of 2-ethylhexyl acrylate with iodobenzene and p-bromoacetophenone, heterocyclisation of N-methylsulfonyl-o-iodoaniline with phenyl acetylene and methyl o-iodobenzoate with diphenyl acetylene leading to formation of substituted indole and isocumarine, respectively. The activity of the colloidal palladium catalytic system is comparable to the low-molecular weight palladium complexes whereas the stability of the colloidal palladium system is much higher. The reuse of the catalyst was demonstrated in the experiments with fresh starts as well as by thermomorphous separation of the catalyst from products.

Another catalytic system based on palladium supported on poly(N-vinylimidazole) or poly(N-vinylimidazole-*co*-N-vinylcaprolactam) was investigated in Mizoroki-Heck reaction. The high efficiency of the catalyst along with recycling ability was demonstrated.

The activity of the catalyst is as high as that observed for low molecular weight complexes whereas the stability is much higher. Reuse of the catalyst showed no loss of activity. These results promise rich perspectives of utilizing such systems in other catalytic reactions.

This work was supported by Russian Academy of Sciences (Program N 3 "Creation and investigation of macromolecules and macromolecular structures of new generations").

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2. I. P. Beletskaya, A. R. Khokhlov, E. A. Tarasenko, V. S. Tyurin. Palladium supported on poly(N-vinylimidazole) or co-poly(N-vinylimidazole-N-vinylcaprolactam) as a new recyclable catalyst for Mizoroki-Heck reaction. *J. Organometal. Chem.* **2007**, 692, 4402.

NEW BIS AND TRISMACROCYCLIC COMPOUNDS CONTAINING CYCLEN, CYCLAM AND NAPHTHALENE MOIETIES

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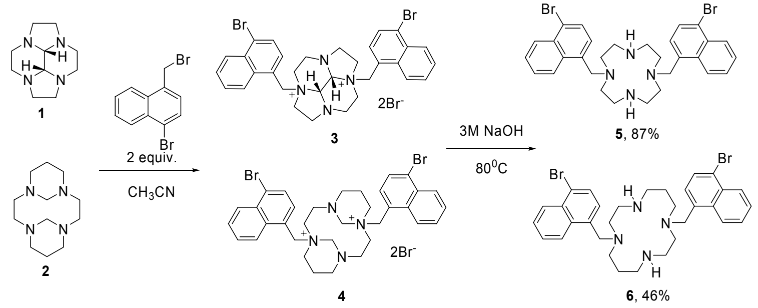
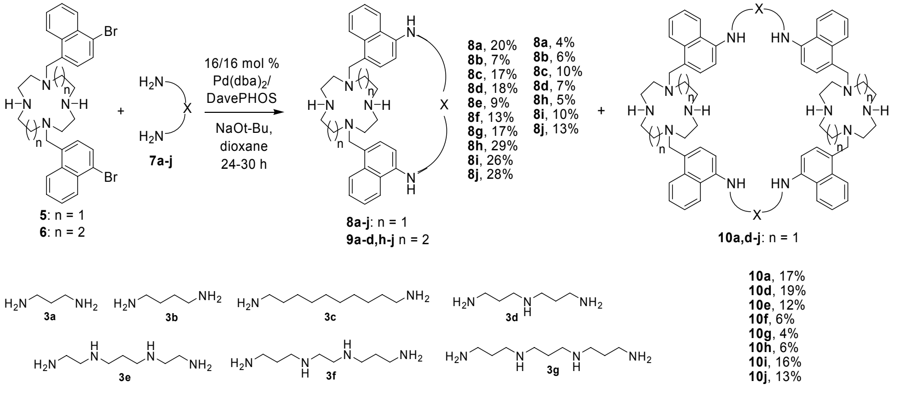
Trans-di(4-bromonaphthylmethyl) derivatives of cyclen and cyclam **5** and **6** were synthesized from protected cyclen and cyclam **1** and **2** (Scheme 1).



Scheme 1

Pd-catalyzed amination of compounds 5 and 6 with various linear di- and polyamines 7a-h led to the formation of bismacrocyclic compounds 8 and 9 in 7-29% and 4-13% yields, resp. (Scheme 2). Yields of the macrocycles depend on the nature of linear and cyclic polyamines, in the case of cyclen derivatives the formation of trismacrocycles 10 in yields up to 19% was observed.



Scheme 2.

The work was supported by the RFBR grants N 09-03-00735 and 08-03-00628.

Highly Selective Hydroquinone Synthesis from Benzene Using Porous Tungsten(VI) Oxide Photoelectrode under Visible Light

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Keywords : Hydroxylation of benzene, Tungsten(VI) oxide, Photoelectrochemistry

Hydroxylation of aromatics such as benzene is of particular interest in the chemical industry.[1,2] Although photocatalytic hydroxylation of benzene using titanium dioxide (TiO_2) powders has been studied, the yield and selectivity of the reaction products were low in almost all the cases, possibly due to the undesirable over-oxidation. The presence of oxygen, which is used as an electron acceptor in the most of reported TiO_2 photocatalytic systems, is suggested to induce radical chain reactions accelerating peroxidation of products.[3] In the present study, we report a highly selective production of hydroquinone (HQ) from benzene using a tungsten(VI) oxide (WO_3) photoanode coupled with a platinum counter electrode for hydrogen production. We found that HQ was produced with high current efficiency (> 90%) when the photoelectrochemical reaction was carried out in a deaerated water-acetonitrile (MeCN) mixture under visible-light irradiation.

A porous WO_3 photoelectrode was prepared by spreading a viscous slurry of WO_3 fine particles on a conducting glass (FTO), followed by calcination at 500 °C for 0.5 h. Reactions were performed in a two-compartment cell separated by an ion-exchange membrane (Nafion). An aqueous solution containing 0.5 mol-L^{-1} benzene and 0.1 mol-L^{-1} sodium sulfate was purged of air with argon. Then the photoelectrode was irradiated ($\lambda > 400$ nm) using a xenon lamp (300 W) with a cutoff filter. Current efficiency (CE) was calculated as: CE (%) = 100 × molar amount of product/molar amount of electrons passing through outer circuit. In photocatalytic reaction suspensions, platinum-loaded WO_3 powders were used.

Figure 1 shows the time course of production of phenol (PhOH) and HQ over the WO_3 photoelectrode in a water-MeCN (1:1 by volume) mixture. HQ was mainly produced with high current efficiency of ca. 90%, while negligibly small amounts of malleic acid, derived via cleavage of aromatic ring, were detected. Such a high current efficiency (90%) for HQ is unusual when ordinary sequential oxidation of benzene, in which four electrons are required to produce HQ from benzene via PhOH as an intermediate, is assumed. When the reaction was carried out in water, the current efficiency for HQ production became low (9%), while the current efficiency for PhOH production was almost same (5%) as that in a water-MeCN mixture (5%). These results suggest that MeCN participates to achieve to the highly efficient production of HQ from benzene. Results of photocatalytic reactions in suspensions also supported above-mentioned reaction mechanism.

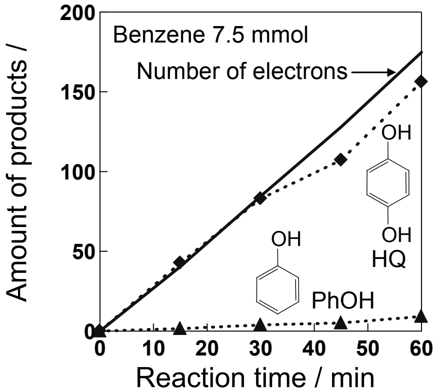

Fig.1. Time course of production of and HQ over WO

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PALLADIUM-CATALYZED ARYLATION AND AMINATION OF POLYCHLOROARENES

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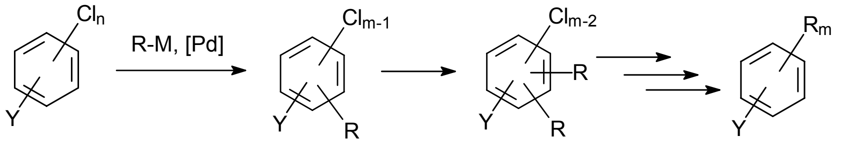
Polychloroarenes (PCA) are ecologically dangerous materials. Development of methods for the substitution of C-C and C-heteroatom for poorly reactive C-Cl bonds can allow transformation of PCA into practically useful aromatic compounds [1]. Catalytic cross-coupling of PCA has been scarcely studied so far.

We have demonstrated that highly-chlorinated PCA, *viz.*, hexachlorobenzene, do not react with arylboronic acids under conditions typical of bromo- and iodoarenes. For their successful processing special catalytic systems based on palladium source combined with sterically hindered electron-rich phosphines or imidazolium salts are required [2]. For example, di-, tri- and tetrachlorobenzenes afforded products of full substitution of all chlorine atoms in 80-100% yields in $Pd(OAc)_2$ – 2-dicyclohexylphosphino-2'-dimethylaminobiphenyl – K_3PO_4 – toluene system at 90 °C. Catalysts based on imidazolium salts and ligand-free systems were less efficient.



n = 2-6; m = n or n-1; RM = $ArB(OH)_2$, ArZnCl, PhC≡CZnCl, R^1R^2NH; Y = H, Cl, C(O)Me, OMe

Reaction of PCA with highly nucleophilic organozinc compounds proceed readily under the action of conventional $Pd(PPh_3)_4$ [2b].

We have found that cross-coupling of PCA with arylboronic acids can be achieved in supercritical carbon dioxide, with potassium carbonate serving as a cheap and convenient base.

This work was in part financed by the Program of the Presidium of Russian academy of sciences "Synthesis of chemical compounds and the development of novel materials", by Russian Science Support Foundation and INTAS (grant 04-82-7271).

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PALLADIUM CATALYSIS IN THE SYNTHESIS OF NEW POLYAZAMACROCYCLES WITH BIPHENYL, NAPHTHALENE AND BIPYRIDINE SPACERS

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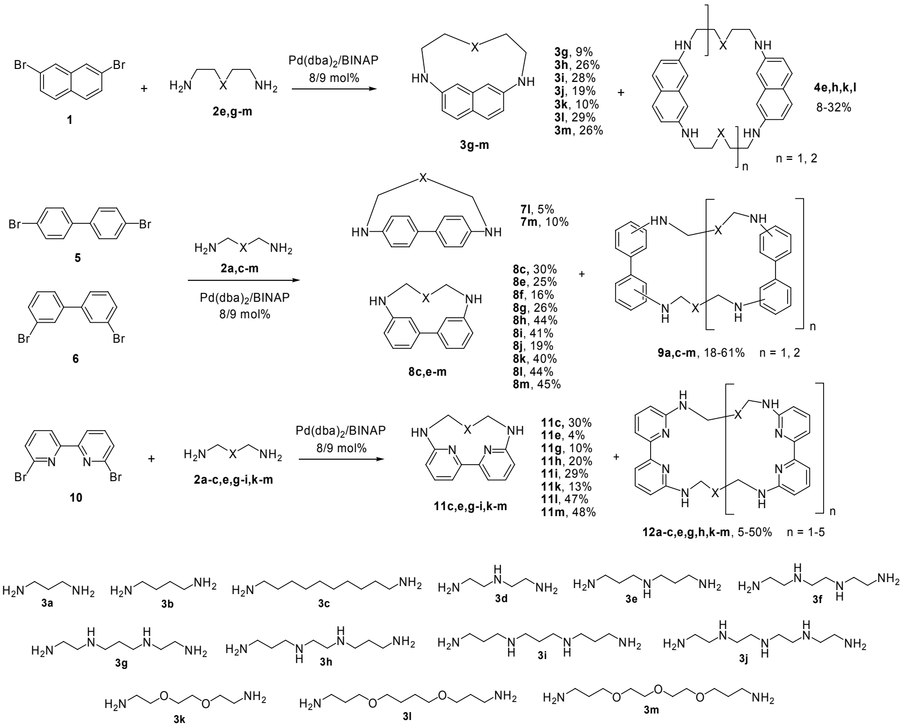
Pd-Catalyzed amination of 2,7-dibromonaphthalene **1**, 3,3'- and 4,4'-dibromobiphenyls **5**, **6**¸ and 6,6'-dibromo-2,2'-bipyridine **10** with a variety of di- and polyamines **2a-m** was studied. In the majority of cases macrocycles containing one polyamine and one arene fragments **3**, **8**, **11** were successfully synthesized, cyclic oligomers **4**, **9**, **12** were generally obtained as by-products.



The yields of target products were found to be strongly dependent on the nature of polyamines **2**, especially, on their length.

The work was supported by the RFBR grants N 09-03-00735 and 08-03-00628.

FLUOROALKYLATED 2-PYRONES AND 4-PYRONES IN THE REACTIONS WITH LITHIO KETONES AND OTHER C-NUCLEOPHILES

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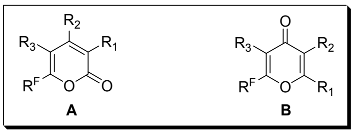
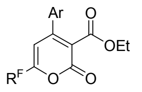
6-(Fluoroalkyl)-2*H*-pyran-2-ones **A** are valuable, poorly explored R^F-containing conjugated dienes and powerful electrophilic reagents for the synthesis of various heterocycles, particularly heterocyclic cage compounds with potential antiviral activity. We have recently discovered that treatment of 1-aryl-4,4,4-trifluorobutane-1,3-diones with PCl_5 and then sodium diethyl malonate afforded ethyl 4-aryl-6-(trifluoromethyl)-2-oxo-2*H*-pyran-3-carboxylates **1**. Carboxylates **1** can be rapidly decarbethoxylated to 6-(trifluoromethyl)-4-aryl-2*H*-pyran-2-ones **2** in high yields. Other fluoroalkylated diketones (R^F = CF_2H, CF_2CF_2H, C_2F_5) were also found to be sufficient for the synthesis of the corresponding 2-pyrones.

Fluoroalkylated 4*H*-pyran-4-ones **B**, cyclic conjugated enones, due to the presence of several reactive positions in their molecules towards nucleophilic attacks, arguably represent one of the most useful R^F-containing building blocks in organic synthesis. We described a convenient synthesis of novel reactive 4*H*-pyran-4-ones such as 6-trifluoromethylcomanic acid, its ethyl ester and amide.[2] It was described the regioselective reactions of **3** with phenylhydrazine under various conditions[3]and discovered that these reactions were selective based on the nature of the solvent.

We have found, that 6-CF_3-α-pyrones react vigorously with lithium enolates at the carbonyl group of the pyrone ring at low temperatures. Thus, treatment of pyrones **1,2** with lithioacetophenones, and then a strong acid led to the formation of pyranols **4**. Compounds **4** can be used as novel trifluoromethylated dienes in Diels-Alder reactions, and for the synthesis of functionalized aromatics.





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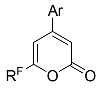

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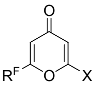
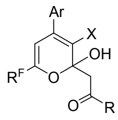


X = H, CO_2H, CO_2Et,
3 $CONH_2$



4 X = H, CO_2Et

In this presentation, we discuss the use of pyrones **1**,**2** and **3** in the reactions with α-lithio ketones and other C-nucleophiles for the synthesis of a variety of multi-substituted systems.

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SUZUKI CROSS-COUPLING REACTION AS THE KEY STEP IN THE SYNTHESIS OF PLANAR CHIRAL O,O-ARYL[2.2]PARACYCLOPHANE LIGANDS

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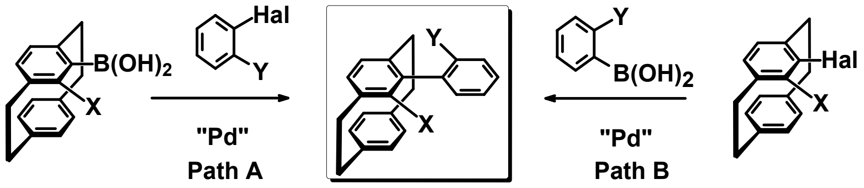
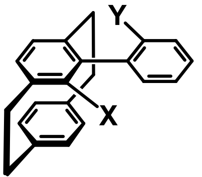
One of the conceptual approaches in the design of chiral ligands for asymmetric catalysis involves the construction of conformationally flexible ligands with chirally stable stereogenic part. Withing this approach we elaborated a novel class of [2.2]paracyclophane based bidentate ligands, in which flexible biphenyl unit is formed by one aromatic ring of the planar-chiral [2.2]paracyclophane and the *ortho*-substituted benzene ring. With the aim of formation of arylparacyclophanyl backbone the first Pd-catalysed Suzuki cross-coupling reaction in [2.2]paracyclophane series have been carried out.[1]

The elaboration of the synthetic approach was carried out using *O,O*-aryl[2.2]paracyclophane ligands of type **I** as model compounds. Among two possibilities, namely, cross-coupling of *ortho*-substituted [2.2]paracyclophanyl-boronic acids with *ortho*-substituted aryl halides (Path A) or cross-coupling of *ortho*-substituted [2.2]paracyclophanyl halides with *ortho*-substituted arylboronic acids (Path B), the last one was found to be more efficient.



I

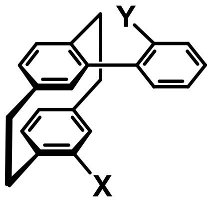
We synthesed new functionally substituted paracyclophanyl halides either in racemic or in enantiomerically pure form and successfully used them for the synthesis of a wide range of arylparacyclophanes with different types of substitution patterns (**1a-f, 1i, 2a-c, 3a**). Further transformations of these arylparacyclophanes lead to novel ligands **1g-l, 2d-e, 3e**.[2]



1

1a X = OMe Y = OMOM
1b X = OMOM Y = OMOM
1c X = OMOM Y = OMe
1d X = OCONEt$_2$ Y = OMe
1e X = OCONEt$_2$ Y = OMOM
1f X = OCONEt$_2$ Y = CHO

1g X = OH Y = OH
1h X = OMe Y = OH
1i X = OH Y = OMe
1j X = OH Y = OMOM
1k X = OCONEt$_2$ Y = OH
1l X = OH Y = CH$_2$OH



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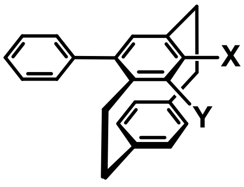

3

2a X = Br Y = OMe
2b X = *o*-MeOC$_6$H$_4$ Y = OMe
2c X = OH Y = OMOM
2d X = OH Y = OH
2e X = *o*-HOC$_6$H$_4$ Y = OH

3a X = OMe Y = H
3b X = OH Y = H
3c X = OCONEt$_2$ Y = H
3d X = OCONEt$_2$ Y = OH
3e X = OH Y = OH

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