ESOR
2015
KIEL

EUROPEAN SYMPOSIUM ON ORGANIC REACTIVITY

AUG 30 - SEPT 04, 2015
KIEL, GERMANY

CONFERENCE INFORMATION
BOOK OF ABSTRACTS

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IMPORTANT INFORMATION

Address of Venue:

Audimax lecture hall building
Olshausenstraße 40
24118 Kiel

Conference Office Phone:

+49 431 8804712 (Wiebke Wagner)
+49 171 9959351 (Dr. Torsten Winkler)

Conference language:

English, no simultaneous translation will be provided.

Internet Access:

will be provided via ***eduroam***. Guest accounts are available, see voucher in your badge.

WELCOME

On behalf of the organizing committee, I cordially invite you to attend the 15th European Symposium on Organic Reactivity (ESOR 2015). The conference will be held in Kiel (Germany) August 30 to September 04, 2015. The date coincides with the 350th birthday of the University of Kiel and our event will be part of the jubilee festivities.

The ESOR series is a string of biennial events that are hosted in different European cities. The conference series started in Paris in 1987 and it has been held every second year ever since: in Padova, Italy (1989), Göteborg, Sweden (1991), Newcastle, UK (1993), Santiago de Compostela, Spain (1995), Louvain la Neuve, Belgium (1997), Ulm, Germany (1999), Cavtat (Dubrovnik), Croatia (2001), Oslo, Norway (2003), Rome, Italy (2005), Faro, Portugal (2007), Haifa, Israel, (2009), Tartu, Estonia (2011), and Prague, Czech Republic (2013).

After the very successful symposium in Prague (2013) the upcoming event in Kiel will continue the tradition and highlight the most recent results in organic reactivity. The ESOR Symposia are dedicated to fundamental research in organic chemistry and related areas, emphasizing the understanding of reactions (e.g., mechanisms, energetics) as well as the structures of compounds and materials. Experimental as well as theoretical contributions are welcomed with a particular preference for multidisciplinary approaches.

The program will include plenary and invited lectures, oral presentations, poster presentations, and an exhibition. We wish to cover all important areas of physical-organic chemistry and its interactions with other sciences, e.g., mechanistic studies as a driving force in modern synthesis, physical-organic chemistry of complex systems, new experimental and theoretical methods in organic chemistry.

We are looking forward to seeing you in Kiel.

Warm regards and best wishes,

Rainer Herges
Chairman of the Local Organizing Commitee

OVERVIEW OF THE SCIENTIFIC PROGRAM

Time	Sunday August 30	Monday August 31	Tuesday September 1	Wednesday September 2	Thursday September 3	Friday September 4
09:00 →		Plenary P. Chen 09:00 - 09:40	Plenary G. Bertrand 09:00 - 09:40	Plenary H. Schwarz 09:00 - 09:40	Plenary S. Shaik 09:00 - 09:40	JPOC Award Plenary A. Braunschweig Miami 09:00 - 09:50
09:10						
09:20						
09:30						
09:40		Invited L. Echegoyen 09:40 - 10:10	Invited H. Mayr 09:40 - 10:10	Invited Y. Apeloig 09:40 - 10:10	Invited H. Zipse 09:40 - 10:10	
09:50						Invited R. Shenhar 09:50 - 10:20
10:00 →						
10:10		M. Klussmann 10:10 - 10:30	M. Canle López 10:10 - 10:30	M. Abe 10:10 - 10:30	R. Haver 10:10 - 10:30	
10:20						A. Stanger 10:20 - 10:40
10:30		coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	
10:40						coffee break 10:40 - 11:10
10:50						
11:00 →		Invited T. Linker 11:00 - 11:30	Invited A. Staubitz 11:00 - 11:30	Invited A. Berkessel 11:00 - 11:30	Invited S. Grimme 11:00 - 11:30	
11:10						E. Humeres 11:10 - 11:30
11:20						
11:30		Invited K. Lammertsma 11:30 - 12:00	Invited M. Sherburn 11:30 - 12:00	Invited H. Bettinger 11:30 - 12:00	Invited A. Krueger 11:30 - 12:00	E. Glebov 11:30 - 11:50
11:40						
11:50						M. Page 11:50 - 12:10
12:00 →		K. Nikitin 12:00 - 12:20	A. Dragan 12:00 - 12:20	G. Gescheidt 12:00 - 12:20	J. Kaleta 12:00 - 12:20	
12:10						closing remarks 12:10 - 12:30
12:20		B. Kovacevic 12:20 - 12:40	D. Hodgson 12:20 - 12:40	T. Müller 12:20 - 12:40	U. Siehl 12:20 - 12:40	
12:30						lunch break 12:30 - 14:00
12:40		lunch break 12:40 - 14:00	lunch break 12:40 - 14:00	poster award cerem. 12:40 - 13:00	lunch break 12:40 - 14:00	
12:50						
13:00 →	check-in at conference desk			lunch break 13:00 - 14:00		
13:10						
13:20						
13:30						
13:40						
13:50						
14:00 →		Plenary H. Anderson 14:00 - 14:40	Plenary P. R. Schreiner 14:00 - 14:40	excursion	J. Harper 14:00 - 14:20	
14:10						
14:20					P. Lainé 14:20 - 14:40	
14:30						
14:40		Invited J. Michl 14:40 - 15:10	Invited G. Bucher 14:40 - 15:10		R. Novikov 14:40 - 15:00	
14:50						
15:00 →					I. Williams 15:00 - 15:20	
15:10		S. Usui 15:10 - 15:30	E. Tretyakov 15:10 - 15:30			
15:20					B. Shainyan 15:20 - 15:40	
15:30		T. Slanina 15:30 - 15:50	A. O'Donoghue 15:30 - 15:50			
15:40					coffee break 15:40 - 16:30	
15:50		coffee break 15:50 - 16:20	coffee break 15:50 - 16:20			
16:00 →						
16:10	conference opening					
16:20		Invited G. Bodwell 16:20 - 16:50	Invited K. Koszinowski 16:20 - 16:50			
16:30	Opening Lecture: J.M. Lehn Strasbourg				Diels Planck Lecture B. Feringa Groningen 16:30 - 18:30 Concert	
16:40						
16:50		K. Nakata 16:50 - 17:10	I. Bilkis 16:50 - 17:10			
17:00 →						
17:10		G. Monaco 17:10 - 17:30	M. Lurdes Cristiano 17:10 - 17:30			
17:20						
17:30	welcome party	Q. Peng 17:30 - 17:50	M. Engeser 17:30 - 17:50			
17:40						
17:50						
18:00 →		poster session I 18:00 - 20:00	poster session II 18:00 - 20:00			
18:10						
18:20						
18:30					KINSIS reception	
18:40						
18:50						
19:00 →						
19:10						
19:20						
19:30				conference dinner until 22:00		
19:40						
19:50						

DETAILED SCHEDULE OF THE SCIENTIFIC PROGRAM

Sunday, August 30, 2015		
starting at 13:00	Check-In at Conference Desk	
16:15 - 16:30	Conference Opening	
16:30 - 17:30	Jean Marie Lehn Strasbourg	Opening Lecture: Perspectives in Chemistry: From Supramolecular Chemistry towards Adaptive Chemistry
17:30 - 20:00	Welcome Party	
Monday, August 31, 2015		
09:00 - 09:40	Peter Chen Zürich	Plenary Lecture: Catalytic Electrophilic Cyclopropanation without Diazo Compounds: De Novo Mechanistic Design and a Historical Twist
09:40 - 10:10	Luis Echegoyen El Paso	Invited Lecture: Regioselective Bis-Additions to Empty and Endohedral Clusterfullerenes: Tether or Cluster Control?
10:10 - 10:30	Martin Klussmann Mülheim a. d. Ruhr	Acid Catalyzed Radical Reactions Via Alkenyl Peroxides
10:30 - 11:00	coffee break	
11:00 - 11:30	Torsten Linker Potsdam	Invited Lecture: Mechanism of Acene Endoperoxide Formation and Cleavage
11:30 - 12:00	Koop Lammertsma Amsterdam	Invited Lecture: P-Chemistry - From P-Carbene to P4 to P-polymer to P-chirality
12:00 - 12:20	Kirill Nikitin Dublin	Phosphorus and Carbon: a Tetrahedral Connection
12:20 - 12:40	Borislav Kovacevic Zagreb	Design of Superbasic Organophosphorus Compounds
12:40 - 14:00	lunch break	
14:00 - 14:40	Harry L. Anderson Oxford	Plenary Lecture: Flow of Energy and Charge in Porphyrin Nanostructures
14:40 - 15:10	Josef Michl Boulder and Prague	Invited Lecture: Toward New Materials for Singlet Fission: Structural Design Rules
15:10 - 15:30	Satoshi Usui Niigata	Photodegradation of Decafluorobiphenyl Sensitized by Aromatic Hydrocarbon in Alcoholic Media
15:30 - 15:50	Tomáš Slanina Brno	Visible Light Photoactivated Metal-Free Carbon Monoxide-Releasing Molecules (photoCORM) Suitable for Bioapplications
15:50 - 16:20	coffee break	
16:20 - 16:50	Graham Bodwell St. Johns	Invited Lecture: The [n]Cyclophane Approach to Warped Nanographenes
16:50 - 17:10	Kazuhide Nakata Hosei	Computational Study of Substituent Effects on Gas-Phase Stabilities of Phenide Anions
17:10 - 17:30	Guglielmo Monaco Salerno	The intriguing class of *altan*-molecules
17:30 - 17:50	Qian Peng Oxford	Computational Ligand Design-guided Enantio- and Diastereoselective Cycloisomerization
18:00 - 20:00	poster session I	

Tuesday, September 01, 2015

09:00 - 09:40	Guy Bertrand San Diego	Plenary Lecture: Stable Carbenes and Related Species: Powerful Tools in Organic and Organometallic Chemistry
09:40 - 10:10	Herbert Mayr München	Invited Lecture: Polar and SET Reaction Pathways of Quinones
10:10 - 10:30	Moises Canle López A Coruña	Photofunctionalization of carbon surfaces with organic molecules
10:30 - 11:00	coffee break	
11:00 - 11:30	Anne Staubitz Kiel	Invited Lecture: Nucleophile Selective Cross-Coupling Reactions
11:30 - 12:00	Michael Sherburn Canberra	Invited Lecture: A Bigger Slice of the π
12:00 - 12:20	Andrei Dragan Glasgow	Metal-Free C-H Oxidation Using Malonoyl Peroxides: Mechanistic Insights
12:20 - 12:40	David Hodgson Durham	N,S-Bridging Thiophosphoramidates: Synthesis and Reactivity
12:40 - 14:00	lunch break	
14:00 - 14:40	Peter R. Schreiner Gießen	Plenary Lecture: Tunneling Control of Chemical Reactions
14:40 - 15:10	Götz Bucher Glasgow	Invited Lecture: Stable Phenalenyl Radicals Showing Reversible Redox Chemistry Under Air
15:10 - 15:30	Evgeny Tretyakov Novosibirsk	Triplet, Singlet and Nearly Degenerate Nitroxide Diradicals
15:30 - 15:50	Annmarie O'Donoghue' Durham	Nitron: From Bench Stable Carbene to Blatter-type Radical
15:50 - 16:20	coffee break	
16:20 - 16:50	Konrad Koszinowski Göttingen	Invited Lecture: Mechanistic Insights in Transition-Metal Catalyzed Cross-Coupling Reactions
16:50 - 17:10	Itzhak Bilkis Jerusalem	Electron Transfer and Water Penetration in Biological Systems: Unconventional Use of Nitroxides
17:10 - 17:30	Maria Lurdes Cristiano Faro	Tautomerism in Quinolone 3-esters Targeting the bc1 Complex of P. falciparum: Implications in Product Selectivity and Activity
17:30 - 17:50	Marianne Engeser Bonn	ESI mass spectrometric mechanistic studies with a charge-tagged proline-based organocatalyst
18:00 - 20:00	poster session II	

Wednesday, September 02, 2015

09:00 - 09:40	Helmut Schwarz Berlin	Plenary Lecture: Thermal Hydrogen-atom Transfer From Methane: A Mechanistic Exercise
09:40 - 10:10	Yitzhak Apeloig Haifa	Invited Lecture: Novel Silenyl Lithium Reagents and their Reactions
10:10 - 10:30	Manabu Abe Hiroshima	Time Resolved UV-vis and IR Spectroscopic Studies on A Singlet 1,2-Diazacyclopentane-3,5-diyl Diradical: Notable Nitrogen-Atom Effects on the Reactivity of the Singlet Diradical
10:30 - 11:00	coffee break	
11:00 - 11:30	Albrecht Berkessel Cologne	Invited Lecture: Carbene Catalysis and the Breslow Intermediate
11:30 - 12:00	Holger Bettinger Tübingen	Invited Lecture: The Boron-Nitrogen Analogues of ortho-Benzynes
12:00 - 12:20	Georg Gescheidt Graz	Conformational and Topological Dynamics of Radical Ions in Solution. Experiments and Simulations
12:20 - 12:40	Thomas Müller Oldenburg	Wagner-Meerwein-Type Rearrangements of Polysilanes - Subtle Trapping of Intermediates
12:40 - 13:00	poster award ceremony	
13:00 - 14:00	lunch break	
14:00 - 19:30	excursion (bus transfer from venue)	
20:00 - 23:00	conference dinner	

Thursday, September 03, 2015

09:00 - 09:40	Sason Shaik Jerusalem	Plenary Lecture: Does Carbon Break the Glass Ceiling of Triple Bonding?
09:40 - 10:10	Hendrik Zipse Munich	Invited Lecture: The Silylation of Alcohols
10:10 - 10:30	Renée Haver Oxford	Nested Nanorings: Molecular Russian Dolls
10:30 - 11:00	coffee break	
11:00 - 11:30	Stefan Grimme Bonn	Invited Lecture: Simple Quantum Chemistry for Complex Systems and Processes
11:30 - 12:00	Anke Krueger Würzburg	Invited Lecture: Tuning the reactivity of diamond surfaces
12:00 - 12:20	Jiří Kaleta Prague	Triptycene Based Arrays of Dipolar Molecular Rotors
12:20 - 12:40	Hans-Ullrich Siehl Ulm	Quantum Chemical Calculation of $J_{(Si,C)}$ Nuclear Spin-Spin Coupling Constants. A Tool for Investigation of Silicon Carbon Hyperconjugation and Hypercoordination in Carbocations
12:40 - 14:00	lunch break	

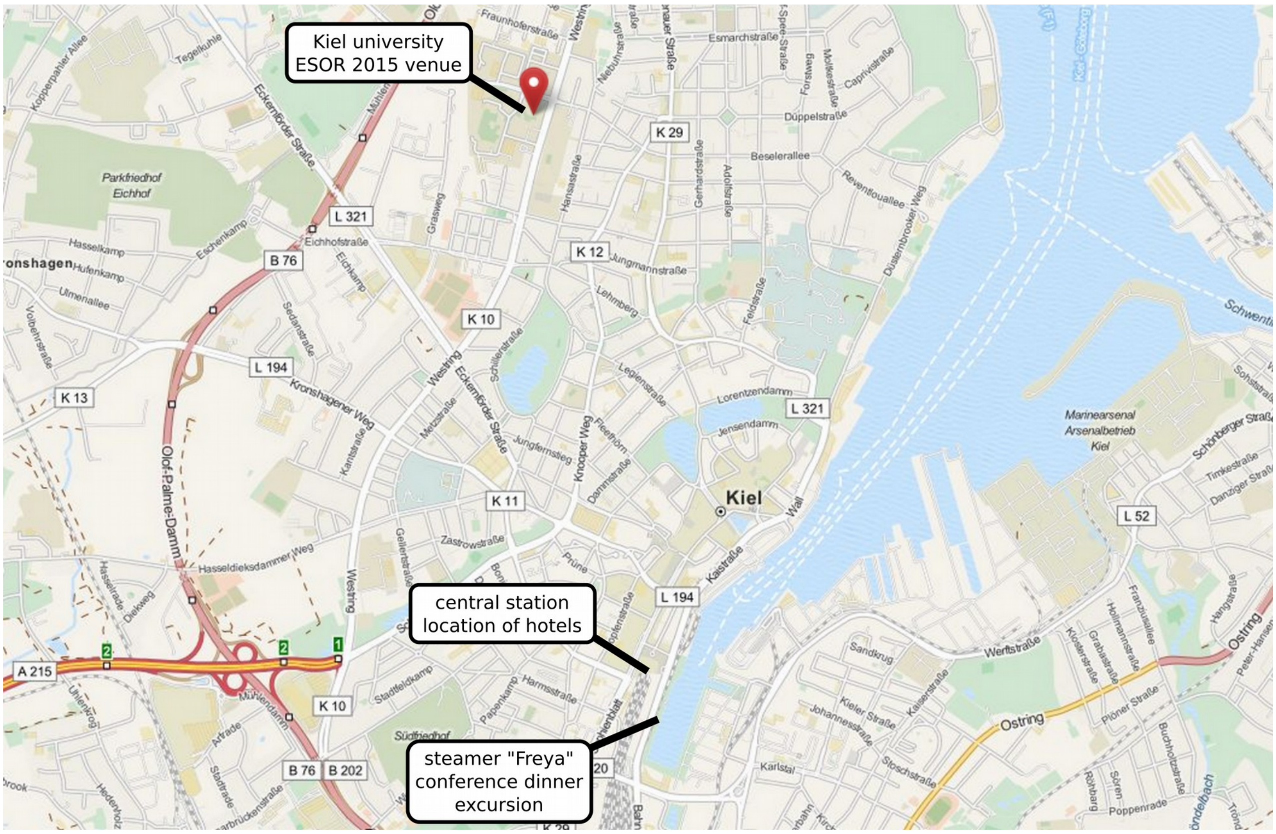
Thursday, September 03, 2015 (continued)

14:00 - 14:20	Jason Harper Sydney	Towards predictable application of N-heterocyclic carbenes in catalysis: Correlating structure, properties and catalytic efficacy
14:20 - 14:40	Philippe Lainé Paris	Mechanisms of Multi-Electron Transfers in N-Aryl Expanded Pyridiniums: Establishing their Unusual Versatile Electrophoric Activity
14:40 - 15:00	Roman A. Novikov Moscow	Donor-Acceptor Cyclopropanes as Sources of Gallium 1,2-Dipoles
15:00 - 15:20	Ian Williams Bath	Isotope Effect Calculations in the Supramolecular Age
15:20 - 15:40	Bagrat Shainyan Irkutsk	Conformational analysis of silaheterocyclohexanes versus their carbon analogues
15:40 - 16:30	coffee break	
16:30 - 18:30	B. Feringa Groningen	Diels Planck Lecture: The Art of Building Small from molecular switches to molecular motors
18:30 - 20:00	reception in honor of the laureates of the Diels Planck Lecture and the JPOC Award	

Friday, September 04, 2015

09:00 - 09:50	A. Braunschweig Miami	JPOC Award Ceremony: Supramolecular Polymers and the Subtleties of Molecular Recognition
09:50 - 10:20	Roy Shenhar Jerusalem	Invited Lecture: Inducing Structure in Polymers by Organometallic Surfactants: The Strength of Weak Interactions
10:20 - 10:40	Amnon Stanger Haifa	“Aroma” as a powerful tool for obtaining quantitative aromaticity and antiaromaticity information
10:40 - 11:10	coffee break	
11:10 - 11:30	Eduardo Humeres Florianopolis	Interconversion and Extrusion of the Sulfur Dioxide Reduction Intermediates Inserted on Graphene Oxide
11:30 - 11:50	Evgeni Glebov Novosibirsk	Photochromism of Spironaphthoxazines in Frozen Matrices
11:50 - 12:10	Michael Page Huddersfield	Micelle Formation and Catalysis in Liquid Ammonia
12:10 - 12:30	closing remarks	
12:30 - 14:00	lunch break	
14:00	departure	

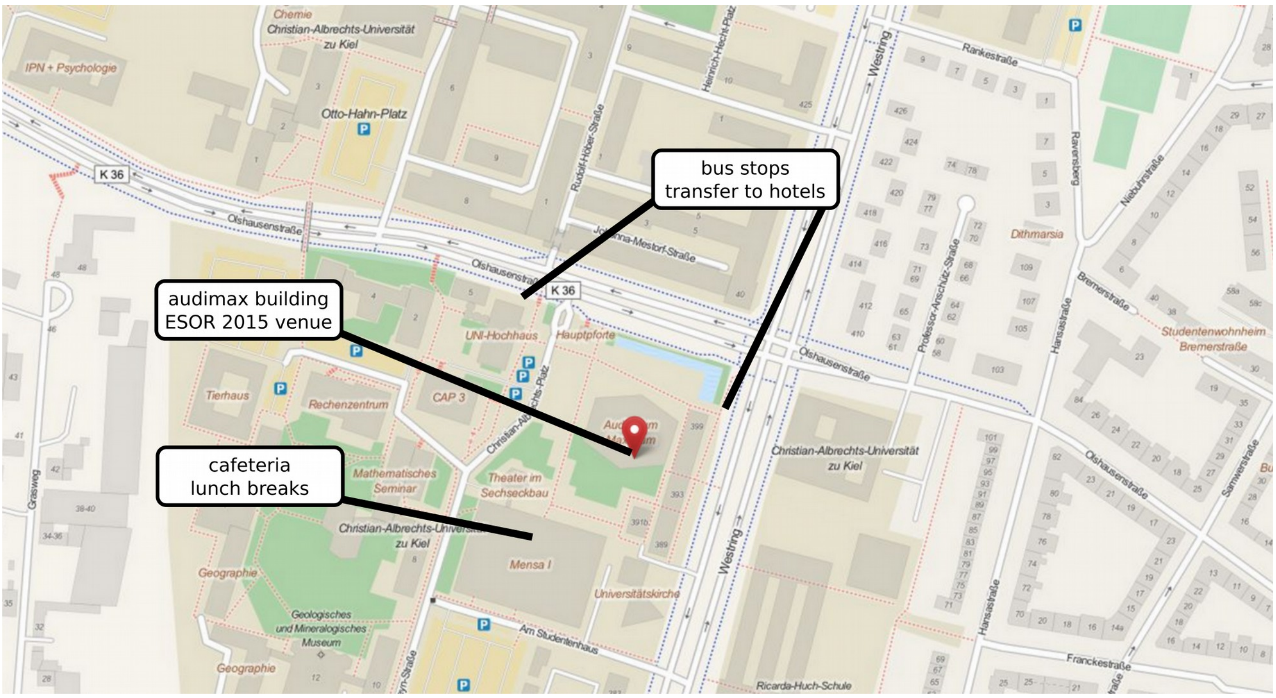
ORIENTATIONAL MAPS


Kiel university
ESOR 2015 venue

central station
location of hotels

steamer "Freya"
conference dinner
excursion

Kiel city general overview © openstreetmap.org, tiles courtesy of MapQuest


bus stops
transfer to hotels

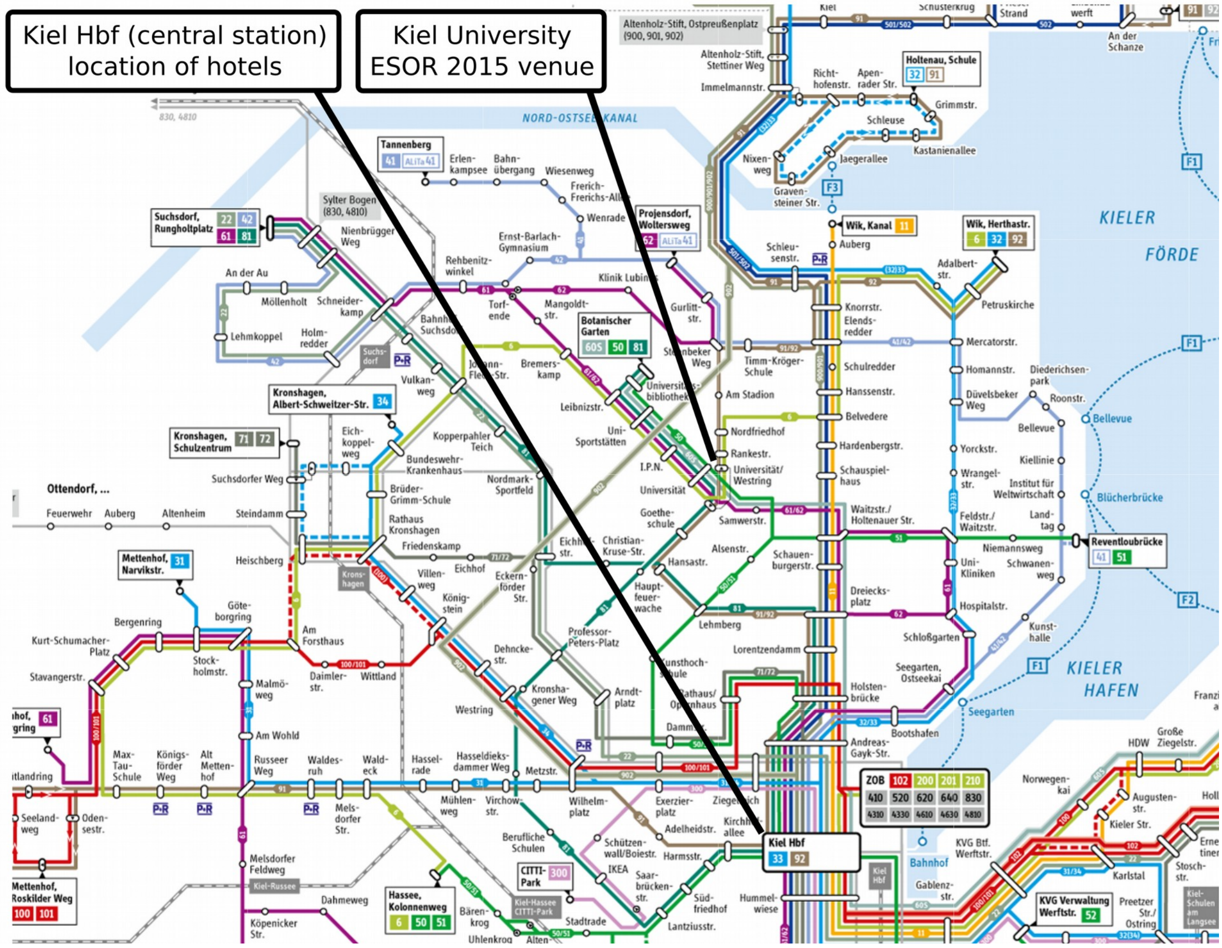
audimax building
ESOR 2015 venue

cafeteria
lunch breaks

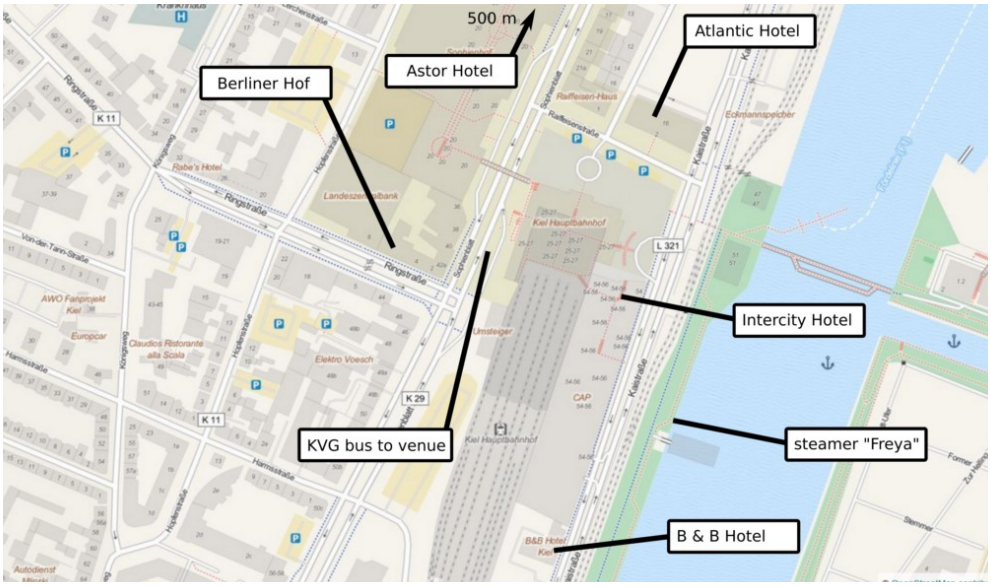
map of the CAU main campus and ESOR 2015 venue © openstreetmap.org, tiles courtesy of MapQuest

BUS NETWORK MAP

How to get from your hotel to the venue:
There is a frequent regular bus service between Kiel central station and the university. Buses leave approximately every 5 to 10 minutes, taking about 20 minutes to the destination. You can use any of the following bus lines: 60S (express service), 61, 62, 81, 91 or 92. Buses are operated by KVG.



Kiel city bus network map © KVG Kiel

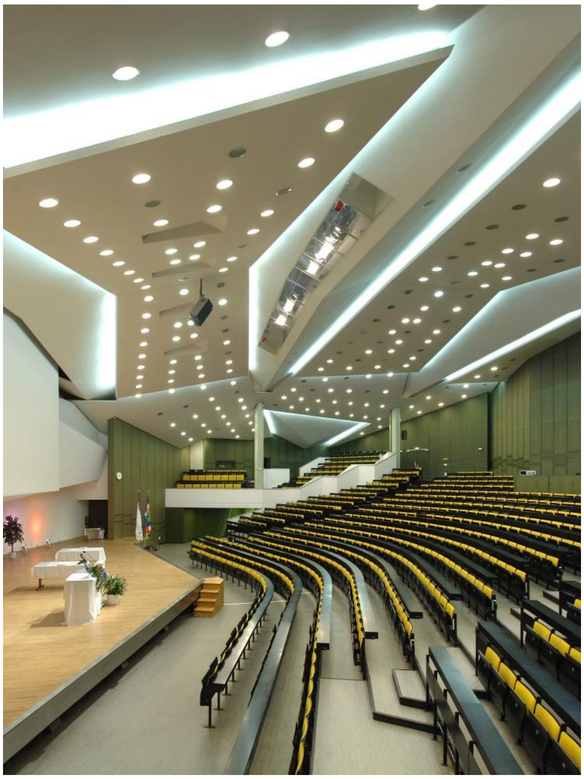


hotel location map © openstreetmap.org, tiles courtesy of MapQuest

VENUE

ESOR 2015 is held at the audimax lecture hall building of Kiel University. Most hotels are located near Kiel central station.


audimax lecture hall building


lecture hall


CAU campus


cafeteria

ORGANIZING COMMITTEE

LOCAL ORGANIZING COMMITTEE:

Chairman:
Prof. Dr. Rainer Herges
University of Kiel

Dr. Torsten Winkler
University of Kiel

Wiebke Wagner
University of Kiel

INTERNATIONAL STANDING COMMITTEE OF ESOR CONFERENCES:

Maria de Lurdes Cristiano
University of Algarve, Faro, Portugal

Mirjana Eckert-Maksic
Rudjer Boskovic Institute, Zagreb, Croatia

Florian Hollfelder
Department of Biochemistry, Cambridge, UK

Moises Canle Lopez
Universidade da Coruna, Spain

Michael I. Page
University of Huddersfield, UK

Jana Roithová
Charles University in Prague, Czech Republic

Alan E. Rowan
Rabboud University Nijmegen, The Netherlands

Hans-Ullrich Siehl
University of Ulm, Germany

Maurizio Speranza
Università degli Studi di Roma "La Sapienza", Italy

Amnon Stanger
Technion, Haifa, Israel

Einar Uggerud
University of Oslo, Norway

SPEAKERS

PLENARY SPEAKERS:

- Ben Feringa (Groningen)
- Adam Braunschweig (Miami)
- Jean-Marie Lehn (Strasbourg)
- Helmut Schwarz (Berlin)
- Peter Chen (Zürich)
- Peter R. Schreiner (Gießen)
- Guy Bertrand (San Diego)
- Sason Shaik (Jerusalem)
- Harry L. Anderson (Oxford)

INVITED SPEAKERS:

- Torsten Linker (Potsdam)
- Graham Bodwell (St. Johns)
- Josef Michl (Boulder and Prague)
- Koop Lammertsma (Amsterdam)
- Holger Bettinger (Tübingen)
- Konrad Koszinowski (Göttingen)
- Herbert Mayr (München)
- Hendrik Zipse (München)
- Mick Sherburn (Canberra)
- Yitzhak Apeloig (Haifa)
- Stefan Grimme (Bonn)
- Anne Staubitz (Bremen and Kiel)
- Albrecht Berkessel (Köln)
- Luis Echegoyen (El Paso)
- Anke Krueger (Würzburg)
- Roy Shenhar (Jerusalem)
- Götz Bucher (Glasgow)

AWARDS

The ESOR 2015 will include the delivery ceremonies of two renowned awards:

JPOC AWARD FOR EARLY EXCELLENCE IN THE FIELD OF PHYSICAL ORGANIC CHEMISTRY

Laureate:
Adam Braunschweig (Miami)

DIELS PLANCK LECTURE OF KIEL NANO, SURFACE AND INTERFACE SCIENCE (KINSIS)

Laureate:
Ben Feringa (Groningen)

SOCIAL PROGRAM

CONFERENCE EXCURSION AND DINNER

The conference excursion will take you aboard the historic paddle steamer "Freya" which was built in 1905. We will go on a small cruise on the Kiel Fjord and enter Kiel Canal through Holtenau locks. Kiel Canal, which connects North Sea and Baltic Sea, is one of the busiest artificial waterways in the world. After approx. 5 hours we will return to the port of Kiel. After our return, the conference dinner will be held aboard "Freya", which will be moored near your accomodation.

paddle steamer “Freya”

Kiel Canal: Holtenau bridges and locks

Kiel Canal: Levensau bridges

paddle steamer “Freya” at night

heavy traffic on Kiel Canal

Kiel - Sailing City

ESOR
2015
KIEL

City, beach, ships…

Gigantic ferries to Scandinavia, cruise liners from all over the world, shopping malls, Baltic beaches and the cultural scene make the life worth living in the city centre of Kiel.
Kiel is part of Hamburg's bid to host the 2024 summer olympics. It would be the third time to have the olympic sailing events in Kiel (after 1936 and 1972).
Through its unique location at Kiel Firth, the capital of Schleswig-Holstein is on the waterfront like no other Baltic metropolis. Therefore it is called KIEL.SAILING CITY…

KIEL
SAILING CITY

O24K
Für Olympia
2024
in Kiel

ESOR
2015
KIEL

SPONSORS

The standing committee of ESOR conferences as well as the local organizing committee would like to thank the following corporations and organizations for their valuable contribution to ESOR 2015.

DFG Deutsche Forschungsgemeinschaft

Sahlmann Photochemical Solutions

Advion

Agilent Technologies

RIGHT UP THERE FOR 350 YEARS
CAU

Liebig-Vereinigung

GDCh
Gesellschaft Deutscher Chemiker

KIEL nano surface interface SCIENCE

SFB 677

TECHNICAL INSTRUCTIONS FOR PRESENTATIONS

ORAL PRESENTATIONS

A PC with common presentation software (Powerpoint 2013, LibreOffice 5, PDF reader, image viewer, VLC player) connected to a projector will be available in the lecture hall. If you intend to use the provided equipment, please bring your file(s) on a USB flash drive well before the start of your respective session.

Alternatively, you can connect your own computer to the projector. HDMI and VGA connectors are natively supported, and we will additionally provide a number of adapters (mini-HDMI, DisplayPort, mini-DisplayPort). Please test the connection well before the start of your respective session.

Our technical team will be able to assist you with the setup during the coffee and lunch breaks.

TIME SLOTS

Please keep the following time allocations for our scientific program in mind. The presentation times will be enforced by the chairpersons. Please allow time for a short discussion after your lecture.

- **plenary lectures:** 40 minutes (including discussion)
- **invited lectures:** 30 minutes (including discussion)
- **regular lectures:** 20 minuted (including discussion)

POSTER PRESENTATIONS AND POSTER AWARDS

Posters should be in **A0 format** (1189 x 841 mm) and in **portrait orientation**. The poster walls will be marked with the respective submission IDs. Authors are invited to mount their posters on the afternoon of the respective date of their assigned poster sessions. Authors are assigned to the poster sessions as follows:

- **poster session I** (Monday, Aug. 31): Authors' last names **A through L**
- **poster session II** (Tuesday, Sep. 01): Authors' last names **M through Z**

Authors are supposed to be present near their respective posters during their allotted poster sessions to allow for discussion with the community. Beverages and snacks will be provided during the poster sessions.

Please remove your posters after your assigned poster session. Any posters still mounted on the following morning will be removed and trashed by the organizers. Authors of poster session II are kindly asked not to mount their posters before the cleanup of poster session I (e.g. not before Tuesday at noon).

The ESOR committee will decide on the **poster awards** during the poster sessions. The awardees will be announced on Wednesday before lunch.


ESOR
2015
KIEL

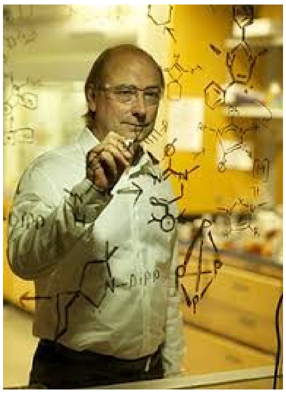
ABSTRACTS

ORAL CONTRIBUTIONS

PLENARY SPEAKERS

alphabetical order of surnames:

Harry L. Anderson (Oxford)



Guy Bertrand (San Diego)

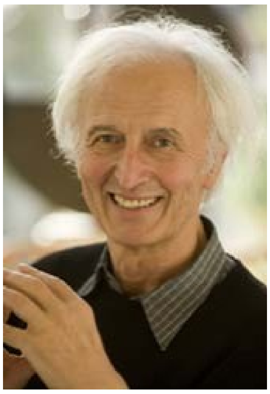
Adam Braunschweig (Miami)

Peter Chen (Zürich)

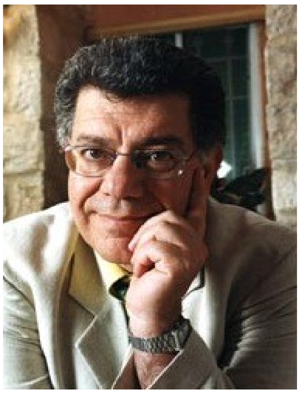
Ben Feringa (Groningen)

Jean-Marie Lehn (Strasbourg)

Peter R. Schreiner (Gießen)



Helmut Schwarz (Berlin)



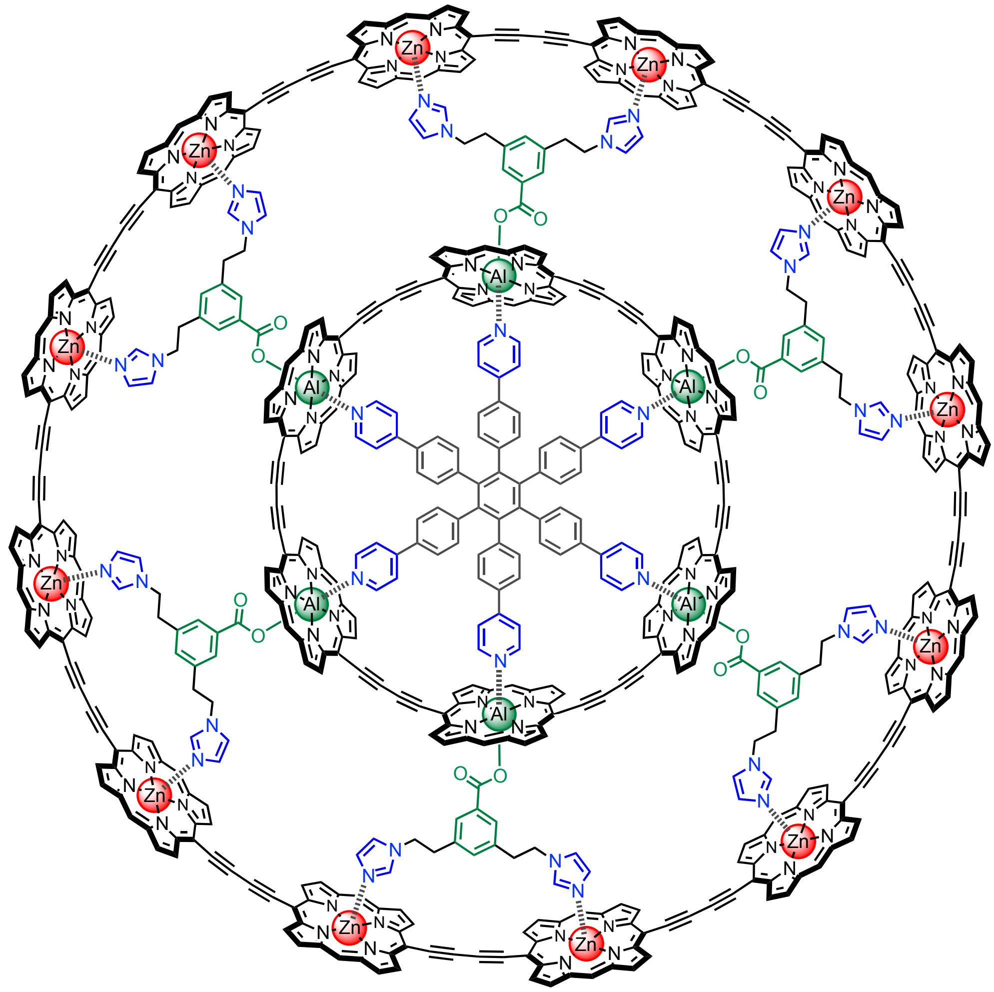
Sason Shaik (Jerusalem)

Flow of Energy and Charge in Porphyrin Nanostructures

Harry L. Anderson

Oxford University, Department of Chemistry, Oxford OX1 3TA, United Kingdom
(harry.anderson@chem.ox.ac.uk)

This presentation will summarize recent advances in the synthesis of macrocycles consisting of up to 50 covalently linked metalloporphyrin units,[1] and ring-in-ring assemblies such as that shown below.[2,3] Results from a variety of techniques will be presented to provide insights into the flow and delocalization of charge and electronic excitation in these synthetic nanostructures.



1. Kondratuk, D. V., et al. *Nature Chem.* **2015**, *7*, 317–322.
2. Neuhaus, P., et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 7344–7348.
3. *“Self-Assembly of Russian Doll Concentric Porphyrin Nanorings”*, Rousseaux, S. A. L.; Gong, J. Q.; Haver, R.; Odell, B.; Claridge, T. D. W.; Herz, L. M.; Anderson, H. L. *submitted.*

Stable Carbenes and Related Species: Powerful Tools in Organic and Organometallic Chemistry

Guy Bertrand

UCSD-CNRS Joint Research Chemistry Laboratory (UMI 3555), Department of Chemistry and
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Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. Spectacular results in this area have been achieved using cyclic diaminocarbenes, the so-called N-heterocyclic carbenes (NHCs), mainly because of their strong s-donor properties. Although it is possible to cursorily tune the structure of NHCs, any diversity is still far from matching their phosphorus-based counterparts, which is one of the great strengths of the latter. Beginning with our discovery in 1988 of a bottle-able (phosphino)(silyl)carbene, a variety of stable acyclic carbenes are known, but they give rise to fragile metal complexes. During the recent years, we have discovered new types of stable cyclic carbenes, as well as related carbon-based and boron-based ligands, which feature even stronger σ-donor properties than NHCs. The synthesis, electronic properties, coordination behavior, and catalytic activity of complexes bearing our ligands will be presented, and comparisons with their NHC cousins will be discussed.

We and others have shown that singlet carbenes with enhanced electrophilic properties, such cyclic (alkyl)(amino)carbenes (CAACs),[1] allow for the stabilization of organic radicals and metals in a formal zero oxidation state.[2] Bis(CAAC)M complexes in which the metal is gold, copper, cobalt, iron, nickel, manganese and zinc have been isolated. Depending on the metal, the majority of spin density can reside either on the metal or on the carbene carbons and the nitrogen atoms of the CAAC ligand.

We also found that CAACs allow for the isolation of catalytically active complexes, which were supposed to be only transient intermediates. Among them, bis(copper) complexes involved in the very popular CuAAC reaction (Click Chemistry) will be discussed.[3]

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Supramolecular Polymers and the Subtleties of Molecular Recognition

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Developing synthetic materials that emulate the architectural and functional sophistication of biomaterials involves creating supramolecular systems where multiple noncovalent interactions operate in concert. To this end, we have developed a system composed of an electron rich dikettopyrrolopyrrole (DPP) donor and an electron poor perylene bisdiimide (PDI) acceptor that aggregate into homochiral superstructures as a result of cooperative assembly driven by orthogonal H-bonding and π•••π interactions, and the resulting superstructures undergo photoinduced charge separation (**Figure**).[1-3] The question arises as to whether we can redesign the individual components to finely tune assembly, structure, and function of these superstructures. In this lecture, we report a systematic study on the homo- and hetero-aggregation of a series of mDPPs and PDIs to determine quantitatively how structure affects ΔG, ΔH, and ΔS by fitting spectroscopic changes in variable-temperature UV-Vis titrations to isodesmic or cooperative binding models. These efforts reveal that changes in the molecular components often result in unanticipated binding effects, and that attempts to design rationally even the simplest supramolecular assembly can overlook the subtle interrelationships between structure, bond-strength, and solvation that contribute to architecture and stability.

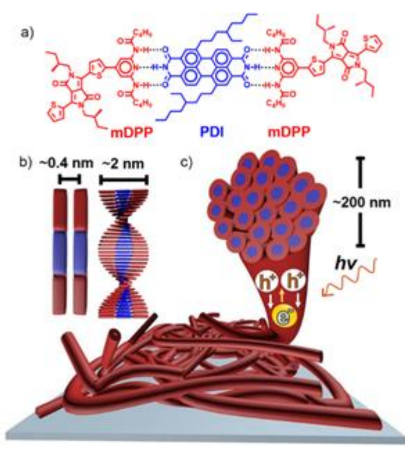

Figure. PDI and mDPP assemble as a result of complementary a) H-bonding, and b) π-stacking along an orthogonal axis drives the formation of homochiral superstructures that c) undergo photoinduced charge separation.

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Catalytic Electrophilic Cyclopropanation without Diazo Compounds: De Novo Mechanistic Design and a Historical Twist

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We report mechanistic studies aimed at a catalytic, electrophilic cyclopropanation of unactivated olefins without diazo compounds, especially without diazomethane. The reaction would replace the Simmons-Smith cyclopropanation, which is super-stoichiometric in metal. Mass spectrometric experiments on electrosprayed organometallic complexes lays the groundwork for computational studies, using DFT methods, which then proceed to development of synthetic methodology under realistic solution-phase conditions. The new reactions designed and discovered in this work provide a further basis for mechanistic studies; we show an iterative cycle of discovery, investigation, and improvement of catalytic cycles.

The Art of Building Small

from molecular switches to molecular motors

Ben L. Feringa

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In our body a fascinating collection of ingenious catalysts, molecular motors and machines make it possible that our cells divide, that we can use our muscles and that the consumption of ATP can be used to generate force and mobility. Dynamic self-assembly, integrated catalytic cycles, molecular information storage and retrieval and triggering and signal transduction are among the challenges ahead in the design of complex artificial molecular systems. Chemical systems ultimately require control over structure, organization and function of multi-component molecular assemblies at different hierarchical levels. Major challenges are the design of kinetic driven processes and control over translational and rotary motion.

In this presentation efforts to develop synthetic systems, in which several structures and functions are integrated, will be discussed. Focus is on control of the dynamics of complex molecular systems and the use of chemical reactivity to control triggering and assembly processes and vice versa. We design molecular systems such as switches and motors in which molecular dynamics is coupled to specific functions.

Responsive behaviour will be illustrated in molecular systems for information storage, responsive self-assembly and membrane transport .The design, synthesis and functioning of rotary molecular motors will be presented. In particular the use of rotary motors as multistage switches, acceleration of rotary motors, transmission and control of catalytic function is described. Finally autonomous motion and assembly of motors on surfaces is illustrated.

Perspectives in Chemistry:
From Supramolecular Chemistry towards Adaptive Chemistry

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Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. It takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

CDC generates networks of dynamically interconverting constituents, *constitutional dynamic networks*, presenting *agonistic* and *antagonistic* relationships between their constituents, that may respond to perturbations by physical stimuli or to chemical effectors.

The implementation of these concepts points to the emergence of *adaptive* and *evolutive chemistry,* towards *systems of increasing complexity.*

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Tunneling Control of Chemical Reactions[1]

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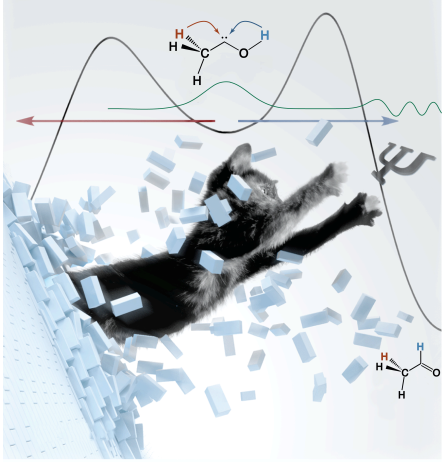

Chemical reactivity is traditionally understood[2] in terms of kinetic versus thermodynamic control,[3] wherein the driving force is the lowest activation barrier among the possible reaction paths or the lowest free energy of the final products, respectively. Here we expose quantum mechanical tunneling as a third driving force that can overwrite traditional kinetic control and govern reactivity based on nonclassical penetration of the potential energy barriers connecting the reactants and products. These findings are exemplified with the first experimental isolation and full spectroscopic and theoretical characterization of the elusive hydroxycarbenes (R–C–OH)[4] that undergo facile [1,2]hydrogen tunneling to the corresponding aldehydes under barriers of nearly 30.0 kcal mol^{-1} with half-lives of around 1–2 h even at 10 K, despite of the presence of paths with substantially lower barriers. We will demonstrate that this is a general phenomenon,[5] as exemplified by other OH-tunneling examples such as the rotational isomerization of a variety of carboxylic acids[6] including *domino tunneling*.[7] Such tunneling processes do not merely represent corrections to the reaction rate, they *are* the reaction rate, i.e., the completely *control* the reaction outome.[1]

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Thermal Hydrogen-atom Transfer From Methane: A Mechanistic Exercise

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Hydrogen-atom transfer (HAT) constitutes a key process in a broad range of chemical transformations as it covers heterogeneous, homogeneous, and enzymatic reactions. While open-shell metal oxo species $[MO]^{\bullet}$ are no longer regarded as being involved in the heterogeneously catalyzed oxidative coupling of methane ($2CH_4 + \langle O \rangle \rightarrow C_2H_6 + H_2O$), these reagents are rather versatile in bringing about (gas-phase) hydrogen-atom transfer, even from methane at ambient conditions. In this lecture, various mechanistic scenarios will be presented, and it will be demonstrated how these are affected by the composition of the metal-oxide cluster ions. Examples will be discussed, how 'doping' the clusters permits the control of the charge and spin situation at the active site and, thus, the course of the reaction. Also, the interplay between supposedly inert support material and the active site – the so-called 'aristocratic atoms' – of the gas-phase catalyst will be addressed. Finally, gas-phase HAT from methane will be analyzed in the broader context of thermal activation of inert C–H bonds by metal-oxo species and it will be shown that the investigation of 'doped' metal oxide clusters as mimics for catalytic processes is about to enter into widely uncharted territory of chemistry, a field in which "each atom counts".

Does Carbon Break the Glass Ceiling of Triple Bonding?

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Abstract

My talk will try to answer the title question, by focusing on C_2 and its isoelectronic molecules, based on published results [1] as well as some new ones.[2]

Acknowledgments: I acknowledge collaborations of the coworkers mentioned in references [1] and [2].

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ABSTRACTS

ORAL CONTRIBUTIONS

INVITED SPEAKERS

alphabetical order of surnames:

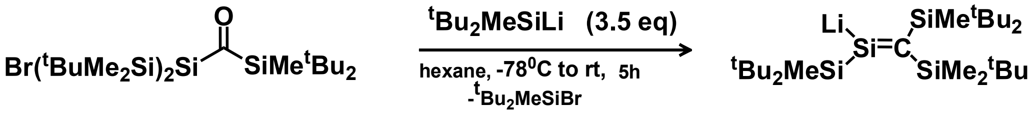
- Yitzhak Apeloig (Haifa)
- Albrecht Berkessel (Köln)
- Holger Bettinger (Tübingen)
- Graham Bodwell (St. Johns)
- Götz Bucher (Glasgow)
- Luis Echegoyen (El Paso)
- Stefan Grimme (Bonn)
- Konrad Koszinowski (Göttingen)
- Anke Krueger (Würzburg)
- Koop Lammertsma (Amsterdam)
- Torsten Linker (Potsdam)
- Herbert Mayr (München)
- Josef Michl (Boulder and Prague)
- Roy Shenhar (Jerusalem)
- Mick Sherburn (Canberra)
- Anne Staubitz (Bremen and Kiel)
- Hendrik Zipse (München)

Novel Silenyl Lithium Reagents and their Reactions

Yitzhak Apeloig, Daniel Pinchuk, Lieby Zborovsky and Dmitry Bravo-Zhivotovskii

Schulich Faculty of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

In this lecture we discuss the synthesis (eq. 1), characterization and reactions of a novel group of metallosilanes, silenyl lithium compounds. We were able to isolate, characterize and determine using X-ray spectroscopy the structures of both the tight ion-pair and the free anion of the same silenyl lithium (eq. 2) allowing to compare their spectroscopic and other properties. To the best of our knowledge this is an unprecedented example. Their reactions with various reagents, as well as their oxidation to the corresponding silenyl radical (also observed for the first time) and comparison with the analogous vinyl sytems will be discussed.



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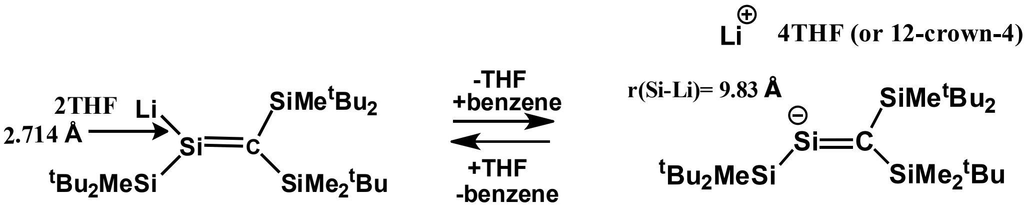

(2)

X-ray
red crystals

X-Ray
blue crystals

Carbene Catalysis and the Breslow Intermediate

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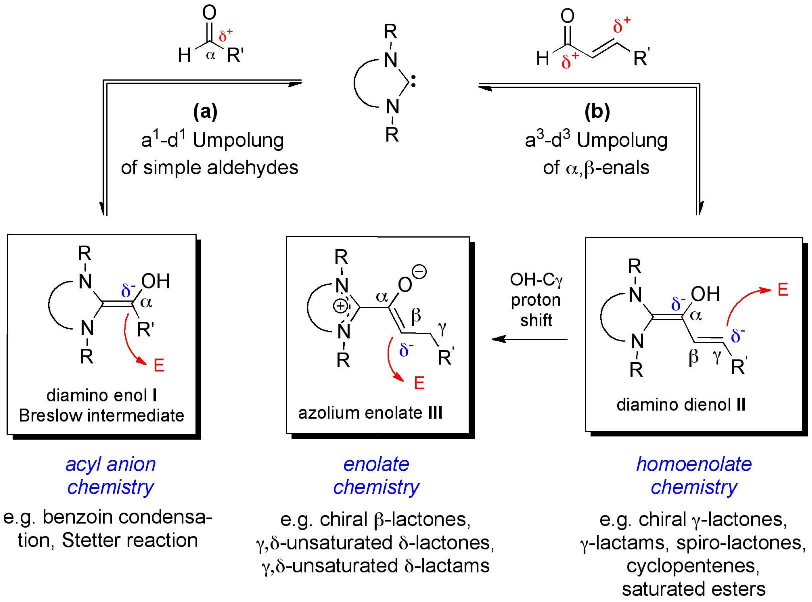
Both in B_1-enzymes and in organocatalytic Umpolung, catalysis by N-heterocyclic carbenes hinges on the formation of the so-called Breslow-intermediates [(di)amino enols] **I** (Scheme, reaction a), in which the innate polarity of e.g. an aldehyde substrate is inverted from electrophilic to nucleophilic. In the related a^3-d^3 Umpolung ("conjugate Umpolung"; Scheme, reaction b), the diamino dienol **II**, a homoenolate equivalent, is assumed to be pivotal. OH-C■ proton shift in the diamino dienol **II** leads to the azolium enolate **III**, an enolate equivalent. The lecture will report the generation and characterization, by NMR and X-ray crystal structures, of intermediates **I-III** and their transformations which support the reactivity patterns shown in the Scheme.



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The Boron-Nitrogen Analogues of *ortho*-Benzynes

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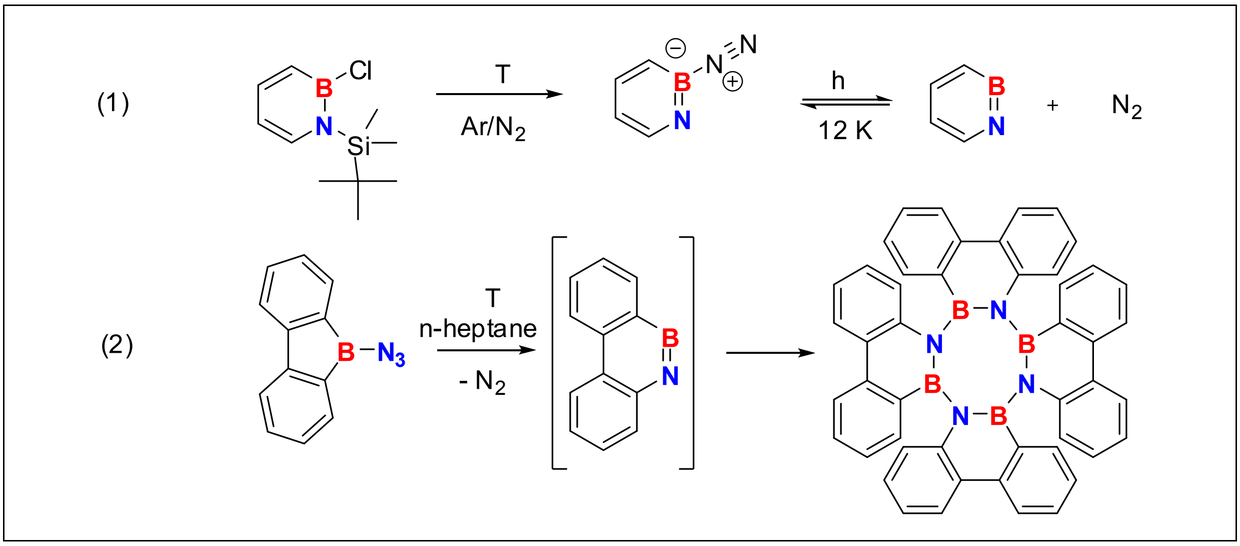
The isoelectronic nature of CC and BN units was extended to reactive intermediates: borylnitrenes R_2BN are isoelectronic to vinylidenes R_2CC.[1] Here the BN analogues of *ortho*-benzyne, 1,2-azaborines, are introduced. They can be generated either under flash vacuum pyrolysis conditions and studied by matrix isolation (reaction 1) or by solution phase thermolysis (reaction 2) of suitable precursors.[2]



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The [*n*]Cyclophane Approach to Warped Nanographenes

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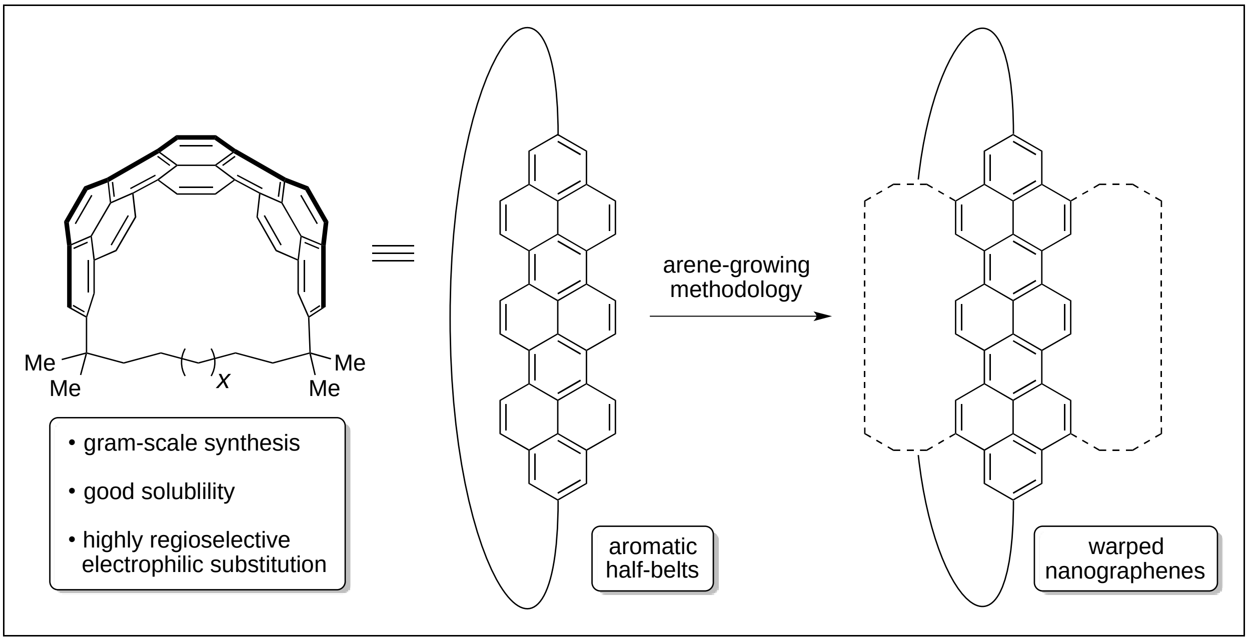
The synthesis of a series of 1,1,*n*,*n*-tetramethyl[n](2,11)teropyrenophanes was originally achieved on the milligram scale,[1,2] but can now be accomplished on the gram scale using a heavily modified synthetic pathway. The availability of useful amounts of the teropyrenophanes has not only enabled the study of the chemistry of the teropyrene system and how it changes with increasing distortion of the aromatic system, but also opened the door to work aimed at exploiting various arene-growing methodologies (*e.g.* Scholl reaction, Scott's Diels-Alder reaction, Itami's arylation chemistry) for the synthesis of cyclophanes containing much larger polynuclear aromatic systems than teropyrene, *i.e*. nanographenophanes.



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Stable Phenalenyl Radicals Showing Reversible Redox Chemistry Under Air

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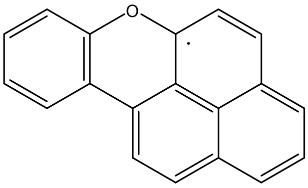
Stable free radicals based on the phenalenyl moiety for some time have been a chromophore of choice, if an organic framework capable of existing in different redox states was required, with nearly invariant bond orders.[1,2] For stability towards dimerization, however, phenalenyl radicals normally would require steric protection, hindering spin-spin communication. In this contribution, we present new data on a series of phenalenyl-based free radicals such as **1**-**3**, which are stabilized electronically via a ring oxygen atom, and do not require steric protection.[3] We will outline the synthesis, characterization, and properties of **1**-**3**, and present data that indicate that these radicals show unusual stability, both thermal, and towards oxygen.



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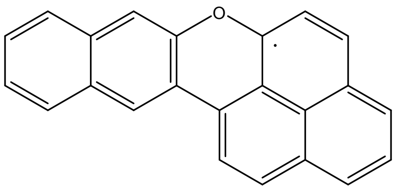

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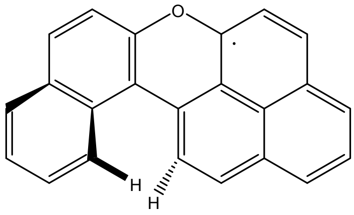

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Regioselective *Bis*-Additions to Empty and Endohedral Clusterfullerenes: Tether or Cluster Control?

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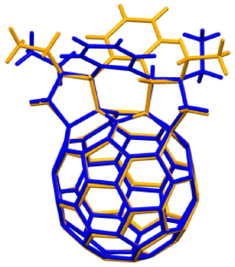

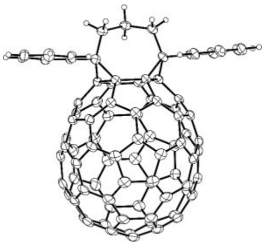

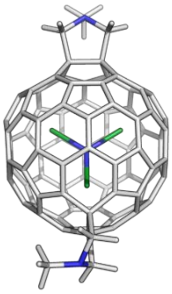

Several strategies have been utilized to control the regiochemistry of multiple additions on fullerene cages, most notable being the tether-directed-remote functionalization method, originally introduced by Diederich et al. In this method, two reactive centers, separated by a rationally designed tether (preferably rigid and with the appropriate length to guide the *bis*-addition regioselectively) are attached to the fullerene cages, see structures at the left. This strategy works well with C_{60} and to some degree with C_{70}, but surprisingly it fails completely when applied to endohedral clusterfullerenes, such as $Sc_3N@C_{80}$. In these cases only one reactive center leads to a fullerene adduct while the other remains unattached. These observations are interesting because independent *bis*-adducts (non-tethered) are easily formed without difficulty, see structure at the right. More interestingly, the number of *bis*-adduct regioisomers that form is very limited, indicating that the cluster inside must play an important role in directing the exohedral additions. These results will be presented and discussed in detail.

Simple Quantum Chemistry for Complex Systems and Processes

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Two topics from our recent theoretical research will be presented:
1. Computation of electron-impact mass spectra (EI-MS) based on a combination of fast quantum chemical methods, molecular dynamics, and stochastic preparation of 'hot' primary ions. The approach considers basic elementary processes with minor empiricism, employs realistic potential energy surfaces computed 'on-the-fly', is 'black-box' and provides decent spectra accompanied by detailed information of corresponding decomposition and reaction mechanisms. For the first time it enables the routine calculation of chemically important mass spectrometric data[1].
2. Automatic generation of a general inter- and intramolecular force-field from dispersion corrected DFT. The method (termed QMDFF) can be applied without specific fitting to any molecular system (including metal complexes), allows smooth dissociation of a molecule into atoms or fragments, and yields consistent intra- and intermolecular forcespproaching DFT quality [2]. It has recently made "reactive" which will be discussed briefly [3].

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Mechanistic Insights in Transition-Metal Catalyzed Cross-Coupling Reactions

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Transition-metal catalyzed cross-coupling reactions have revolutionized organic synthesis. Although palladium still is the most commonly applied catalyst, the use of earth-abundant 3d metals is highly advantageous for economic reasons. Currently, the rational development of 3d-metal catalyzed cross-coupling reactions is severely hampered by a lack of mechanistic understanding, however. To change this situation and to obtain insight into these reactions at the molecular level, we analyze reaction mixtures by electrospray-ionization mass spectrometry. Thus, we have been able to identify a series of elusive catalytic intermediates in iron-, cobalt, and copper-mediated cross-coupling reactions (Figure 1).[1,2] Gas-phase experiments on the mass-selected intermediates moreover reveal their microscopic reactivity and permit the direct observation of important elementary steps of the catalytic cycles.[1,2]

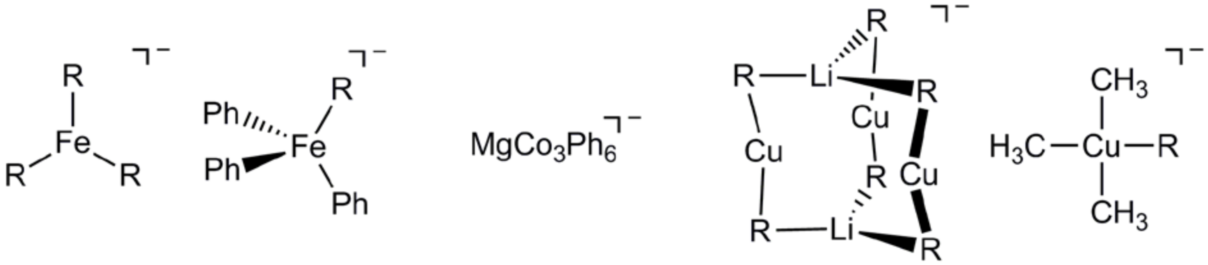

Figure 1. *Selected intermediates of 3d-metal-mediated cross-coupling reactions detected by ESI mass spectrometry.*

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Tuning the reactivity of diamond surfaces

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The reactivity of diamond surfaces, on bulk and nanoparticles alike, strongly depends on the actual surface termination and the arrangement of surface atoms. Whereas hydrogen terminated diamond is only accessible via rather harsh reaction conditions such as photochemical alkylation the reactivity of diamond with oxygen termination or a reconstructed surface is significantly increased. Reconstruction of the diamond surface e.g. by thermal annealing or electron irradiation leads to the removal of surface groups and the formation of graphene-like, curved structures made of sp^2 carbon.[1]

Here, we discuss the structure and chemistry of such surfaces and their reactivity in C-C bond forming reactions.[2,3] Reactions like arylation using diazonium salts, Diels-Alder, Bingel-Hirsch and Prato reaction on the fullerene-like surface structures can be successfully applied for the controlled surface modification of nanodiamond and the grafting of complex functional moieties.[4] This leads to functional nanodiamond materials that can be applied in many areas such as drug delivery, functional coatings, quantum engineering, labelling and sensing.

[1] T. Petit, J.-C. Arnault, H. A. Girard, M. Sennour, P. Bergonzo, *Phys. Rev. B* **2011**, *84*, 233407; A. Krueger, D. Lang, *Adv. Funct. Mater.* **2012**, *22*, 890.

[2] T. Meinhardt, D. Lang, H. Dill, A. Krueger, *Adv. Funct. Mater.* **2011**, *21*, 494; G. Jarre, Y. Liang, P. Betz, D. Lang, A. Krueger, *Chem. Comm*. **2011**, *47*, 544; Y. Liang, T. Meinhardt, G. Jarre, P. Vrdoljak, A. Schöll, F. Reinert, A. Krueger, *J. Colloid Interface Sci*. **2011**, *354*, 23; P. Betz, A. Krueger, *Chem. Phys. Chem.* **2012**, *13*, 2578; D. Lang, A. Krueger, *Diamond Relat. Mater* **2011**, *20*, 101.

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P-Chemistry – From P-Carbene to P4 to P-polymer to P-chirality

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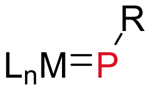
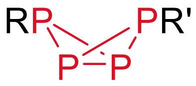
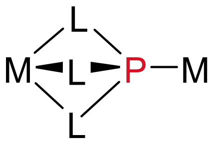
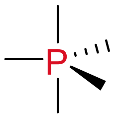
P-reagents, P-cages, reactions with white phosphorus, and P-dynamics will be highlighted.









Low-valent phosphorus reagents akin to carbenes have become readily accessible, are even bottleable and enable the synthesis of strained polycyclic systems that can both be stable and dynamic. In the context of FLPs with their Lewis acid/base sites that enable the activation of small molecules, the functionalization of white phosphorus will be presented. Scorpion-like systems with a phosphorus apex open new avenues in coordination chemistry, such as the one dimensional polymers. Finally, the dynamics of pentacoordinate systems will be discussed as stereomutations play often a determining role in enantioselective syntheses.

Mechanism of Acene Endoperoxide Formation and Cleavage

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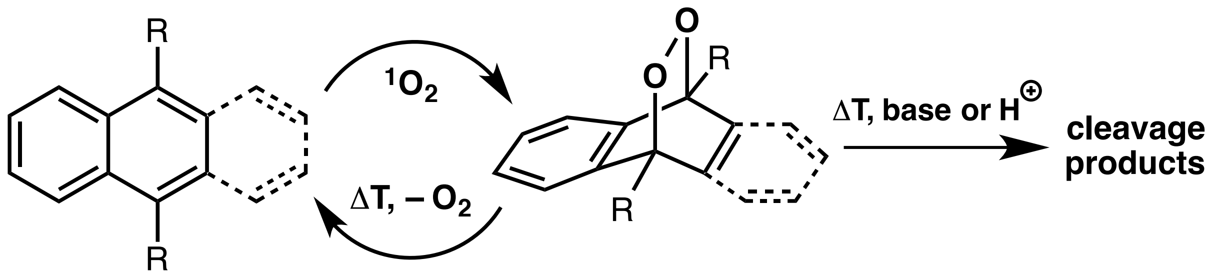
Acenes **1** react with singlet oxygen ($^1O_2$) to endoperoxides **2** under mild conditions.[1] Various mechanisms have been proposed for this oxidation.[2] Depending on substituents R, the reaction is completely reversible or leads to cleavage products. We applied the first reaction pathway for the patterning of surfaces[3] and for molecular rotors with R = Ar.[4] For R = alkynyl the back-reaction is very fast, which is interesting for applications in material sciences.[5] More recently, we found a stabilization of endoperoxides **2** by π-stacking in a sandwich complex.[6] We investigated their cleavage under thermal, basic and acidic conditions and propose various reaction pathways. The invited lecture will discuss the mechanisms of the reactions, which proceed via radicals, carbenium ions, or anionic intermediates.



(anthracene, naphthalene) **1** R = Ar, Alkynyl **2** R = H, Alkyl, OR

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Polar and SET Reaction Pathways of Quinones

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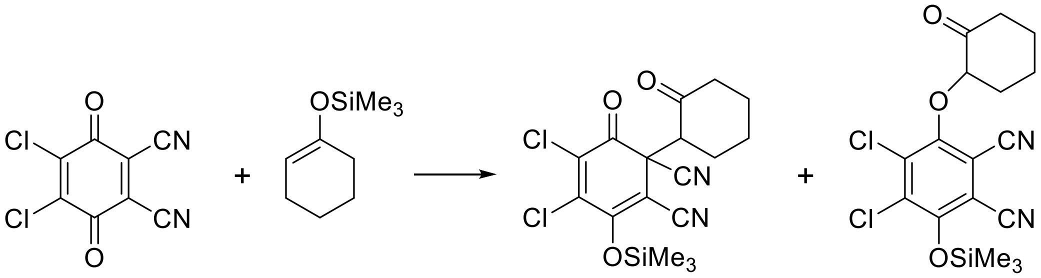
2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) is one of the most important oxidizing reagents in organic chemistry. Its reactions with silylated enol ethers were reported to yield products arising from C- as well as from O-attack as illustrated in Scheme 1.[1] Though both products were suggested to be formed via a radical ion pair, the possibility of a nucleophilic attack of the silyl enol ether on DDQ to form the product of C-attack was explicitly mentioned as an alternative.[1]



Scheme 1. Reaction of DDQ with 1-trimethylsiloxycyclohexene[1,2]

Bhattacharya's observation[1] prompted us to analyze the reactions of DDQ and other quinones with π-nucleophiles, amines, and hydride donors,[2-4] using our linear free energy relationship (1),[5] where electrophiles are characterized by one parameter (E) and nucleophiles are characterized by the solvent-dependent nucleophilicity parameter N and the susceptibility parameter s_N.

$$\lg k_{20°C} = s_N(E + N) \qquad (1)$$

By assigning electrophilicity parameters E to the different ring positions of a variety of quinones and correlation with the Gibbs free energies of SET processes, an ordering system for quinone reactivities has been established.[2-4]

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Toward New Materials for Singlet Fission: Structural Design Rules

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Singlet fission generates two triplet excitations from one singlet excitation in a dimer, aggregate, or solid, and promises to increase the efficiency of inexpensive single-junction solar cells. In the best case, using a layer of a singlet fission sensitizer and a layer of an ordinary sensitizer but applying no current matching requirement, it would increase the theoretical efficiency from the Shockley-Queisser limit of 1/3 to nearly 1/2. Unfortunately, the number of materials known to perform singlet fission efficiently is tiny and most are related to the notoriously air-sensitive hydrocarbons, tetracene and pentacene. In order to meet the numerous conditions that will be imposed on a practical singlet fission material, we consider it important to formulate structural design rules for materials that perform singlet fission efficiently. We shall outline how this can be accomplished using simple quantum chemical models. We proceed in two steps: (i) choice of chromophores, where we present promising structures of a new type related to indigo, and (ii) choice of the spatial relation between chromophores, where we present the results of an exhaustive optimization of the six-dimensional spatial relation of two ethylene molecules.
rences.

Inducing Structure in Polymers by Organometallic Surfactants: The Strength of Weak Interactions

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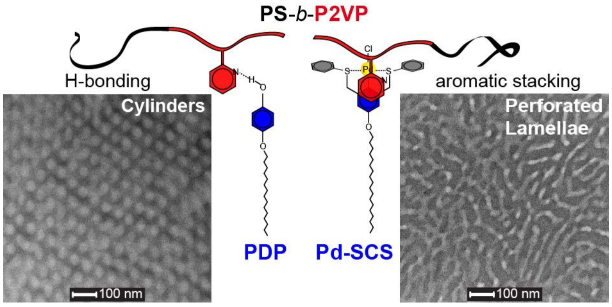
Employing non-covalent interactions opens many opportunities for structuring polymers on the molecular level and at the nanoscale. Specifically, designing surfactants to interact with functional groups in polymers leads to periodic structures due to the inherent phase separation properties of the surfactant.

The presentation will describe the utilization of palladium-pincer-based surfactants for the creation of hierarchical structures with homopolymers[1,2] and block copolymers.[3,4] It will be shown that employing weak supramolecular interactions between the surfactant and the polymer opens new opportunities for kinetically controlled polymer structuring. Lastly, the preparation of anisotropically ordered nanocomposites will be demonstrated.



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A Bigger Slice of the π

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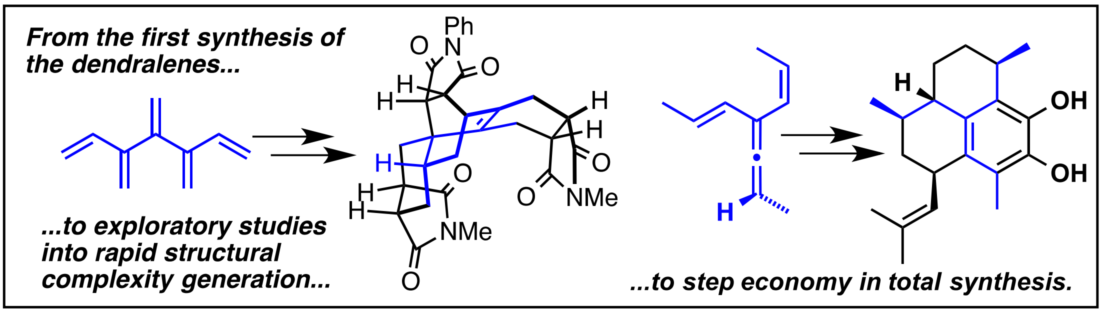
Canberra, ACT 2601, Australia

The two simplest branched acyclic structures comprising only conjugated C=C units, namely [3]dendralene (3-methylene-1,4-pentadiene) and [4]dendralene (3,4-dimethylene-1,5-hexadiene), were first reported in 1955 and 1962, respectively. No higher members of the series were described in the literature until 2000. This presentation will describe the modern phase of dendralene (and related *π*-bond rich hydrocarbon) chemistry. The outcomes of exploratory investigations into rapid structural generation involving dendralenes will be presented, along with methods to control chemoselectivity, regioselectivity and stereoselectivity, and applications of *π*-bond rich branched hydrocarbons in very short total synthesis.



From the first synthesis of the dendralenes...

...to exploratory studies into rapid structural complexity generation...

...to step economy in total synthesis.

This talk aims to convince you of three things: (a) that fundamental hydrocarbon chemistry still has significant potential for original discoveries; (b) that at least some of your assumptions about the instability of “polyenes” are wrong, and (c) that *π*-bond rich olefinic hydrocarbons are, at long last, coming of age.

Reviews: H. Hopf, M. S. Sherburn, *Angew. Chem., Int. Ed.*, **2012**, *51*, 2298-2338;
M. S. Sherburn, *Acc. Chem. Res.*, Article ASAP **DOI:** 10.1021/acs.accounts.5b00242

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Nucleophile Selective Cross-Coupling Reactions

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and Sebastian Beil[a]

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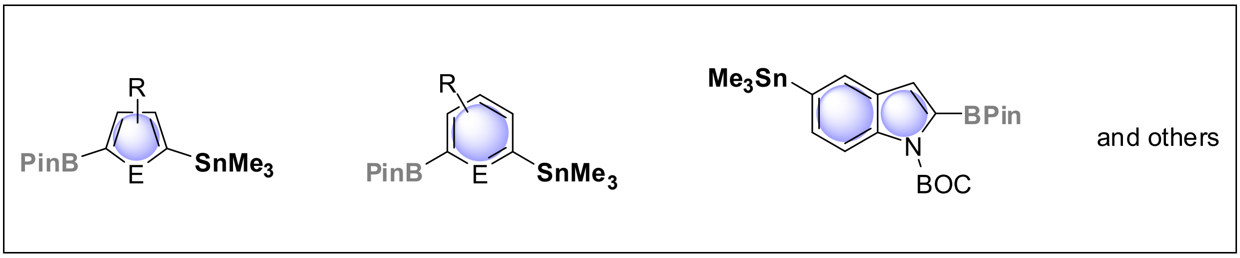
While electrophile selective cross-coupling reactions are an often-used, powerful tool in synthesis, the analogous nucleophile selective cross-coupling reactions have received very little attention, in particular for aromatic dinucleophiles.
One of the reasons for this striking lack of useful reactions is that there are very few reliable procedures for the synthesis of such aromatic dinucleophiles.
In this presentation, a new general route to (hetero-) aromatic dinucleophiles containing a stannyl and a boronic acid ester will be presented.
First studies concerning the selective cross-coupling of such dinucleophiles will be disclosed[1] and their application in the synthesis of semiconducting polymers will be discussed.[2]



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The Silylation of Alcohols

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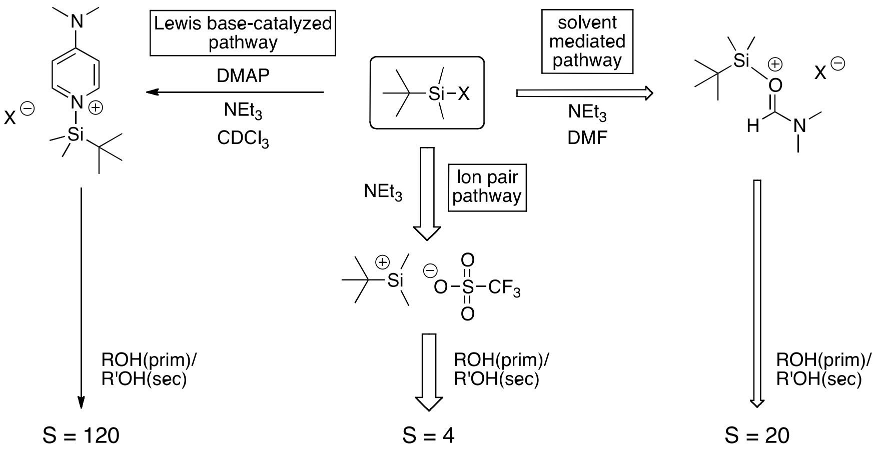
The selective silylation of alcohols represents one of the most powerful tools in the manipulation of polyfunctional molecules. The selectivity *S* can readily be quantified as the ratio of silylation rates of structurally similar primary and secondary alcohols.[1] Using selected reagents for transfer of the *tert*-butyldimethylsilyl (TBS) group we show that the underlying reaction mechanisms are highly variable, and include at least three different limiting scenarios. For the most reactive silyltriflate reagents the reaction rates show hardly any Lewis base catalysis and are characterized by low *S* values. Less reactive reagents such as silyl chlorides and cyanides react most readily in a Lewis basic solvent such as DMF, which is actively involved in promoting the reaction.[2] Much slower absolute reaction rates (and highest substrate selectivities *S*) are found for this latter group of reagents in apolar organic solvents. The reactions can then be promoted quite effectively be Lewis base catalysts.



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ABSTRACTS

ORAL CONTRIBUTIONS

REGULAR SPEAKERS

alphabetical order of surnames:

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- Itzhak Bilkis (Jerusalem)
- Moises Canle-López (A Coruña)
- Andrei Dragan (Glasgow)
- Marianne Engeser (Bonn)
- Georg Gescheidt (Graz)
- Evgeni Glebov (Novosibirsk)
- Jason Harper (Sydney)
- Renée Haver (Oxford)
- David Hodgson (Durham)
- Eduardo Humeres (Santa Catarina)
- Jiří Kaleta (Prague)
- Martin Klussmann (Mülheim)
- Borislav Kovacevic (Zagreb)
- Philippe Lainé (Paris)
- Maria Lurdes Cristiano (Faro)
- Guglielmo Monaco (Salerno)
- Thomas Müller (Oldenburg)
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- Kirill Nikitin (Dublin)
- Roman Novikov (Moscow)
- AnnMarie O'Donoghue (Durham)
- Michael Page (Huddersfield)
- Qian Peng (Oxford)
- Hans-Ullrich Siehl (Ulm)
- Bargrat Shainyan (Irkutsk)
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- Amnon Stanger (Haifa)
- Evgeny Tretyakov (Novosibirsk)
- Sstoshi Usui (Niigata)
- Ian Williams (Bath)

Time Resolved UV-vis and IR Spectroscopic Studies on A Singlet 1,2-Diazacyclopentane-3,5-diyl Diradical: Notable Nitrogen-Atom Effects on the Reactivity of the Singlet Diradical

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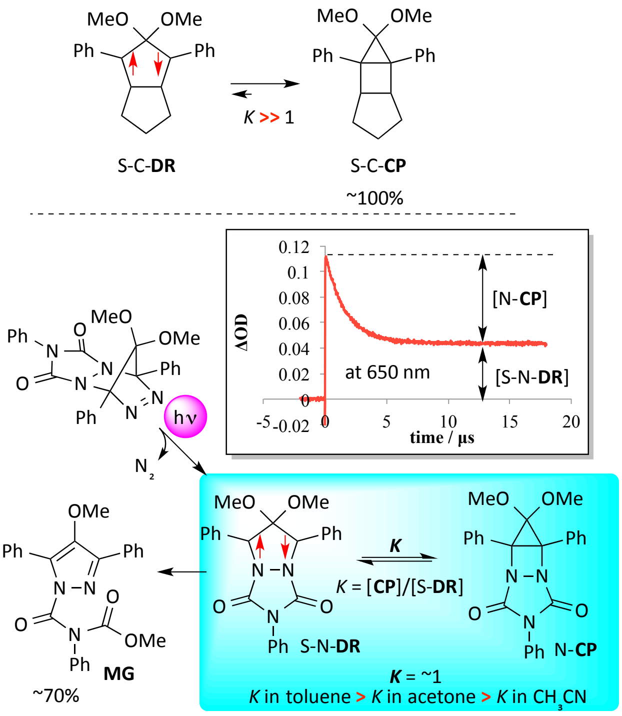
Bond cleavage and bond formation processes play a central role in chemistry. Localized singlet diradicals are key intermediates in the homolytic reactions. Last decade, the relatively long-lived singlet carbon-carbon diradicals S-C-**DR** (up to ~5 μs at 293 K, λ_{max} ~570-600 nm) were discovered by this laboratory by introducing the dialkoxy groups at C(2) position and the aryl groups at C(3) position in the cyclopentane-1,3-diyl skeleton, *Chem. Rev.* **2013**, *113* (9), 7011-7088. Our computational calculations revealed that the σ-bonded compound was calculated to be stable than the open-shell species by ca. 63 kJ mol^{-1}. More recently, a notable nitrogen atom effect was found by this laboratory to increase significantly the lifetime of a singlet 1,3-diyl **S-DR2a** (~10 ms at 293K in toluene; λ_{max} ~670 nm), *ACIE*, **2006**, *45*, 7828-7831. The major product isolated in ~70% after the denitrogenation was surprisingly not the ring-closed compound N-**CP** but the oxygen-migrated compound **MG**. In this study, the time-resolved absorption and infrared spectroscopic analyses at nanosecond time scale was performed in the photochemical denitrogenation of **AZ2** in detail, which revealed that N-**CP** was actually formed as a transient species that was equilibrated with the singlet diradical S-**DR2**.



this study

ELECTRON TRANSFER AND WATER PENETRATION IN BIOLOGICAL SYSTEMS: UNCONVENTIONAL USE OF NITROXIDES

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It is possible to induce electron transfer (ET) in many biological systems by introducing donor-acceptor pairs, i.e. metal ions [1], or by integrating systems into solid-state junctions [2]. We have recently proposed and validated a novel methodology. It takes advantage of a redox reaction between a nitroxyl radical and a metal Ru(III) center, both bound at selected specific positions within suitable biological systems [3]. The applicability of the method has been demonstrated by using bacteriorhodopsin (BR) and time-resolved EPR. Site-directed spin-labelled mutants of BR were prepared, and a spin-labelled analogue of BR retinal was synthesized and incorporated into the active site of the apoenzyme (BR_{art}). The Ru(II)-bipyridyl complex was also bound at a specific coordination site. ET was followed by monitoring the decrease in the intensity of nitroxyl EPR signal. It was shown that the rates of photo-stimulated ET were significantly lower for the buried retinal analogue in BR than for mutants in which the spin label was located at external sites. The crystal structure of BR was used to interpret the rates of ET observed. It was subsequently found that this methodology can be conveniently utilized to study water penetration to specific sites in the protein at which the nitroxide spin label is bound. We have used isotopic labelling water ($H_2{}^{17}O$) to demonstrate that it can penetrate to a buried spin-labelled site, and convert an EPR-silent oxoammonium cation to a nitroxide displaying a detectable EPR signal. This provides a novel and unique approach for measuring site-specific water penetration into biological systems.

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[3] T. Eliash, A. Barbon, M. Brustolon, M. Sheves, I. Bilkis, L. Weiner, Angew. Chem. Int. Ed. 2013, 52, 8689 –8692

Photofunctionalization of carbon surfaces with organic molecules

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We have devised a simple method to functionalize carbon surfaces with a variety of organic moieties, from small molecules to proteins or enzymes using UVC and/or Vis light. Irradiation of heterogeneous solutions of the solid in the presence of the organic molecules to be inserted leads to successful photoinsertion of the organic moiety onto the solid surface. The procedure has been tested with different carbonaceous materials: graphite, carbon nanotubes, graphene and their oxidized forms. The nature of the functionalized surface has been characterized through different techniques, such as total carbon analysis, ion chromatography, thermogravimetric analysis (TGA) coupled with FTIR, XPS and solid state ^{13}C-NMR, showing enough evidences to confirm the success of the photoinsertion. Relevant reactivity differences have been found when using oxidized and reduced surfaces.

Here, we will give some examples of the obtained results: kinetics, chemical and spectroscopic characterization, and a proposal of a suitable mechanism for the process.

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Metal-Free C–H Oxidation Using Malonoyl Peroxides: Mechanistic Insights

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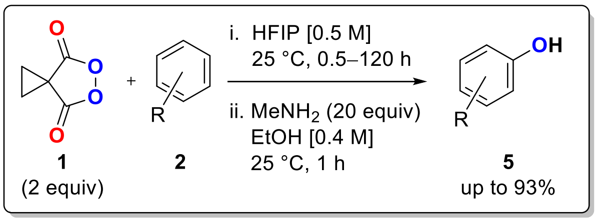
Increased molecular complexity at the expense of ubiquitous C–H bonds makes direct functionalization of C–H bonds a highly desirable transformation. Drawing inspiration from a recent report,[1] a simple and effective method for the direct oxidation of aromatic C–H bonds using malonoyl peroxide **1** will be presented, with emphasis on the mechanistic course of the reaction. Isotope labeling experiments, Hammett analysis, EPR studies and DFT calculations, along with reactivity patterns have all suggested that this metal-free oxidation of arenes proceeds *via* an ionic mechanism.[2]



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ESI mass spectrometric mechanistic studies with a charge-tagged proline-based organocatalyst

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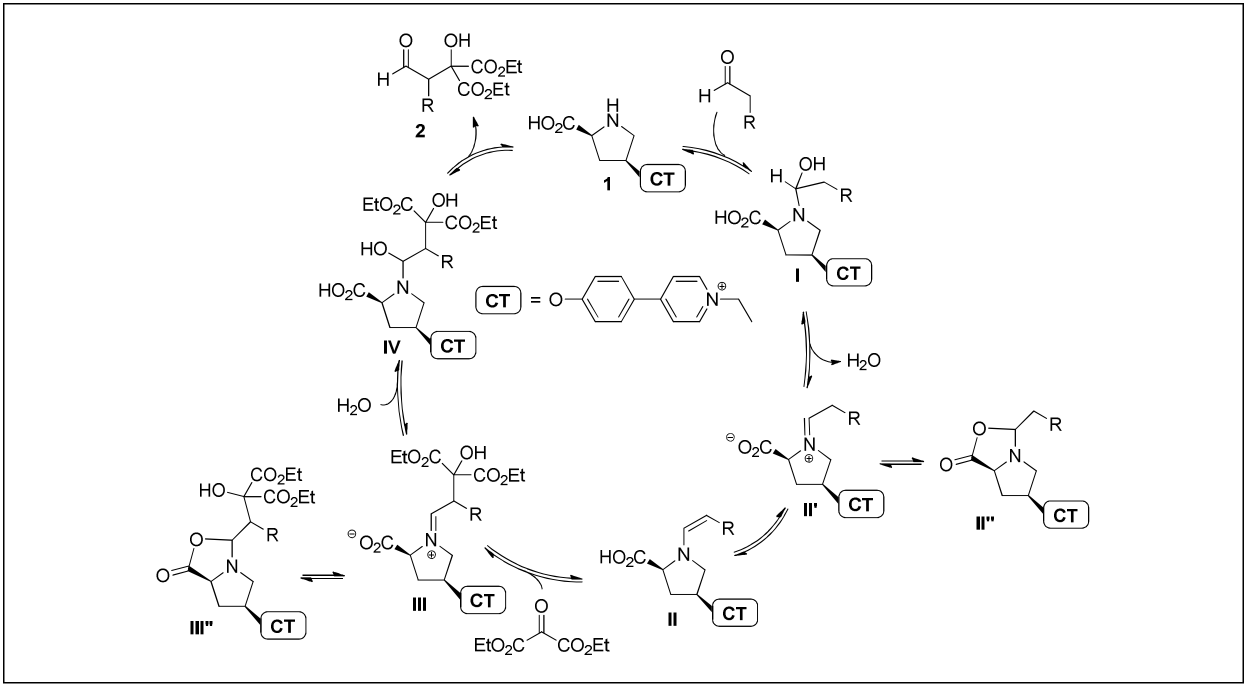
Proline-mediated enantioselective organocatalysis has become a major research topic in organic chemistry. The catalytic cycles typically are supposed to involve enamines or iminium ions as key intermediates. We have developed the synthesis of a charge-tagged L-proline-based organocatalyst **1** with the aim to elucidate mechanisms of organocatalyzed reactions by detecting reactive intermediates by ESI mass spectrometry.[1]

As an example, the markedly enhanced ESI response factor of catalyst **1** enabled us to detect two key intermediates as well as an off-cycle byproduct in the course of the asymmetric aldol reaction between aldehydes and diethyl ketomalonate. The species have been characterized by exact mass and CID MS/MS and their temporal evolution has been monitored.



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Conformational and Topological Dynamics of Radical Ions in Solution. Experiments and Simulations

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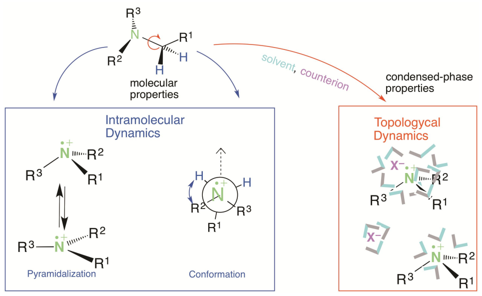
Dynamic interactions between reactive molecules and their environment, i.e. the solvent and (counter)ions are at the basis of many molecular conversions. In terms of reactive intermediates, radicals play a decisive role in a wide palette of contexts ranging from synthesis to biology.

In solution, these molecular interactions are dominated by diffusive processes generally occur at the nanosecond time scale. Experimentally, this dynamic time scale is ideally matched by EPR spectroscopy ranging from ca. 1 ns to 1 μs (at X band, ca. 9 GHz). Developments in the theory and analysis of configuration-space networks,[1] Markov state models[2] and QM/MM-approaches, together with the increasing power of computers allows now resolving dynamic phenomena at an EPR-compatible time scale even for open-shell systems that require a quantum-mechanical Hamiltonian.

Using EPR data and connecting them to molecular-dynamics simulations we started obtaining detailed insights into charge delocalization and solvent reorganization phenomena at the molecular scale (Fig).

Initial results on radical ion pairs will be presented. They indicate unusual views on ion-pairing phenomena.



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Photochromism of Spironaphthoxazines in Frozen Matrices

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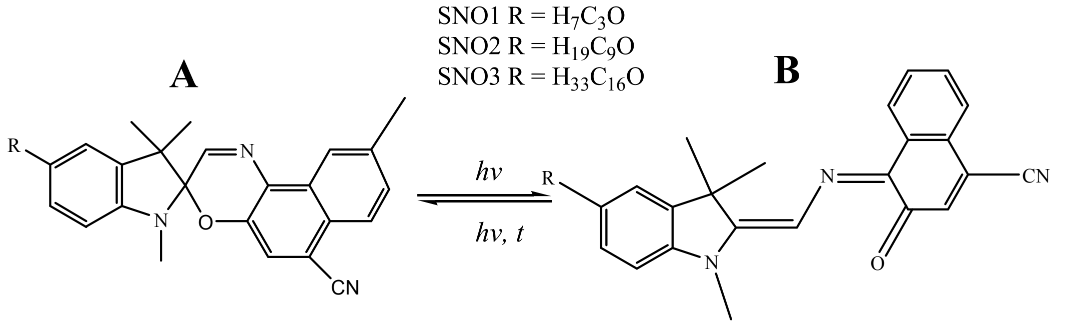
Spironaphthoxazines (SNO, Scheme 1) represent one of the most important classes of organic photochromic compounds. They demonstrate high molar absorptivity of coloured form and high fatigue resistance. Photochromic properties of spirooxazines are determined by the mutual transitions of a closed colorless spiro-form A and an open colored merocyanine form B (Scheme 1). In this work, photochromism of SNO in frozen matrices (77 K) was studied by means of stationary photolysis, ESR and quantum chemistry. Stabilization of high-reactive intermediates at low temperature opens a possibility in direct studying of the reaction mechanisms.

The quantum yield of A → B transition in ethanol matrix at 77 K was found to be high enough (0.01 – 0.02). For one of the SNO, the formation of a merocyanine radical was observed. The radicals were formed by an H atom transition from the solvent molecule to the light-excited B-form. The structure of radicals was confirmed by quantum chemical calculations. The formation of radicals represents a new channel of SNO photodegradation.



Scheme 1. Closed and open forms of SNO.

Towards predictable application of *N*-heterocyclic carbenes in catalysis: Correlating structure, properties and catalytic efficacy

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Ideally, the most appropriate *N*-heterocyclic carbene catalyst for a given process could be designed based on the relationship between the catalyst's (physicochemical) properties and that required for the reaction in question. The laborious screening currently required demonstrates this is yet to be realised. This presentation will focus on the potential to correlate catalyst structure to nucleophilicity and catalyst efficacy. The use of the acidity of the corresponding azolium salts as an indirect measure (the Brønsted relationship,[1] Equation 1) for a suite of *ca*. 70 systems (Figure 1) will be discussed, particularly in terms of control of nucleophilicity through variation of structure.[2] Preliminary studies of the determination of relative nucleophilicities through competition experiments (Equation 2) we have developed[3] and comparison to existing techniques will be highlighted.

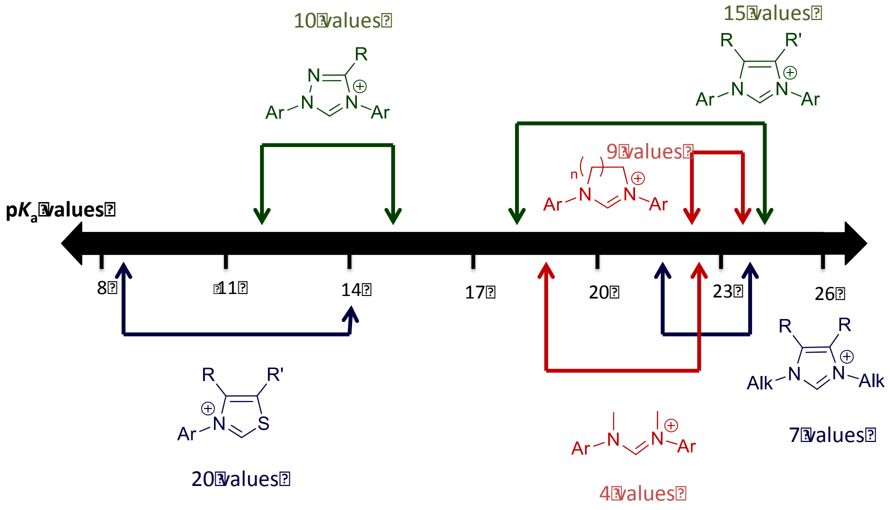

Figure 1. A pK_a scale, showing the range of acidities in DMSO covered by azolium (and related) salts.

$$\log(k) = \beta_{\mathrm{Nuc}} \mathrm{p}K_a + \log(C) \qquad (1)$$

$$\frac{\ln\left(\frac{x_1}{x_{1,\mathrm{t}=0}}\right)}{\ln\left(\frac{x_2}{x_{2,\mathrm{t}=0}}\right)} = \frac{k_1}{k_2} = f(x) \quad \Rightarrow \quad N_1 = N_2 + \frac{\log(f(x))}{S_N} \qquad (2)$$

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Nested Nanorings: Molecular Russian Dolls

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We have previously prepared and studied various oligomeric linear and cyclic nanostructures based on porphyrin building blocks. Strong electronic coupling between the individual porphyrins gives rise to efficient migration of charge and electronic excitation, mimicking natural photosynthetic systems.[1-3]

In this contribution, the synthesis and properties of nested Russian Doll assemblies such as that shown in Figure 1 will be presented.

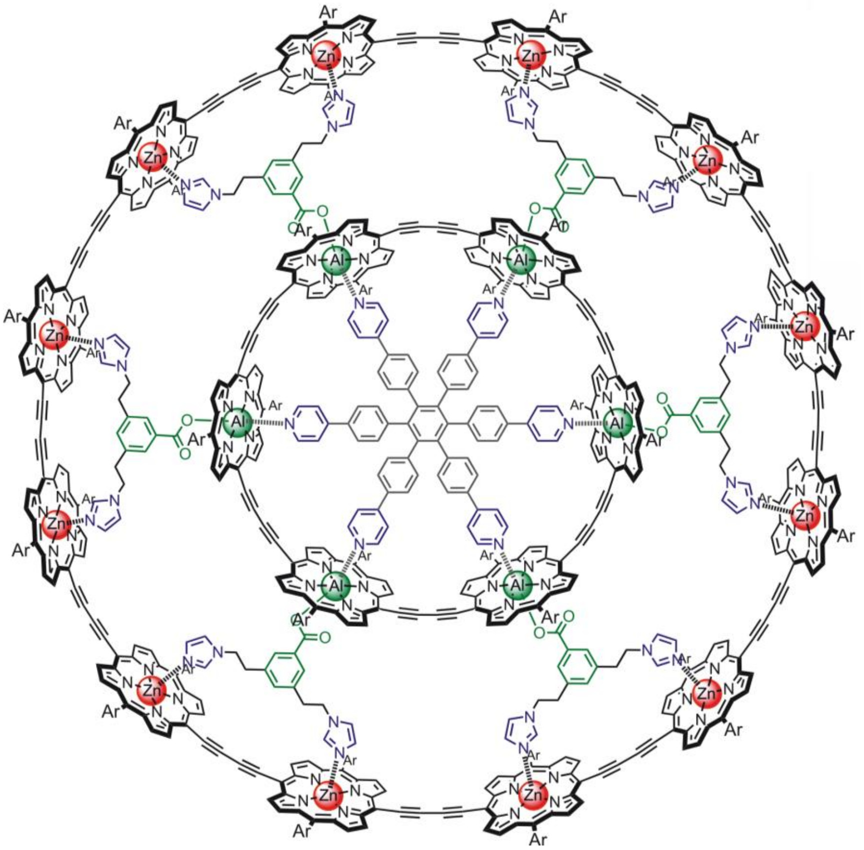

Figure 1: Russian Doll nested nanorings.

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N,S-Bridging Thiophosphoramidates: Synthesis and Reactivity

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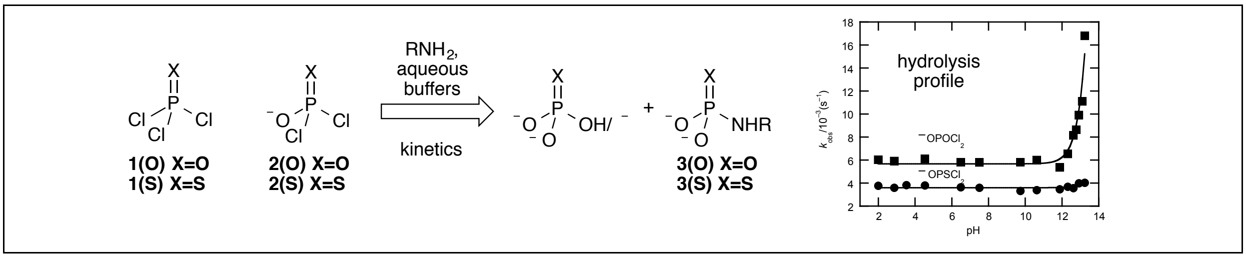
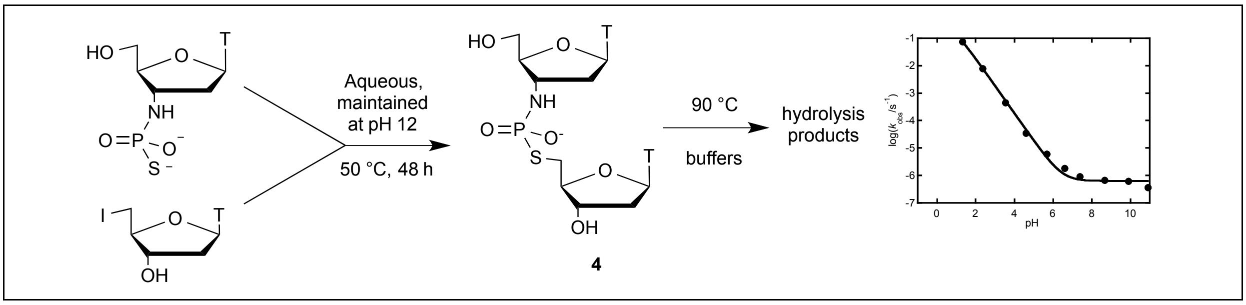
Phosphate analogues support mechanistic studies and biotechnologies such as nucleic acid ligation. We have prepared (thio)phosphoramidates **3** by reacting amines in aqueous media with $POCl_3$ **1(O)**, $PSCl_3$ **1(S)**, phosphodichloridate ion **2(O)** and thiophosphodichloridate ion **2(S)**.[1] Our kinetic and theoretical studies show that phosphodichloridate **1(O)** and thiophosphodichloridate **2(S)** ions discriminate significantly against hydroxide ion compared to water as a nucleophile.[2]



To explore the potential of thiophosphoramidate ions **3(S)** in ligations, we prepared dinuclotide analogue **4** through *S*-alkylation, and studied its stability towards hydrolysis. The pH-log k_{obs} profile of analogue **4** at 90 °C revealed a half-life of ~13 days between pH 7-10. Acid-promoted hydrolysis was evident at lower pHs.



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Interconversion and Extrusion of the Sulfur Dioxide Reduction Intermediates Inserted on Graphene Oxide

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The SO_2 reduction on carbons occurs through stable reactive intermediates chemically bound to the carbon matrix, as oxidized sulfur (1,3,2-dioxathiolane in equilibrium with 1,2-oxathietane 2-oxide) and non-oxidized sulfur (episulfide). The SO_2 reduction proceeds through a primary mechanism where upon the adsorption of SO_2 on a zigzag diradical hedge the carbon matrix, the oxidized intermediates decompose to produce an episulfide and a peroxide that decomposes to CO_2 in a further step. Graphene oxide sheets, obtained by oxidation of graphite microparticles by strong acids followed by thermal exfoliation, were treated with non-thermal plasma under a SO_2 atmosphere, at room temperature. The XPS spectrum showed that SO_2 was inserted only as oxidized intermediate at 168.7 eV in the S2p region. Short thermal shocks at 600 and 400 ^{o}C, under Ar atmosphere, produced reduced sulfur and carbon dioxide. Refluxing this material in CS_2 (b.p. 46 ^{o}C) resulted in sulfur elimination and interconversion of the intermediate into oxidized intermediate with no decarboxylation, as shown by the XPS spectrum and TGA analysis coupled to FTIR. Mechanisms for these reactions were postulated using the atom inventory method. These results support the hypothesis, based on theoretical calculations, that there are two major groups of reactions with different energetic demand in the sulfur dioxide reduction on carbons. The energy barrier for the interconversion between the sulfur dioxide reduction intermediates and sulfur extrusion from the matrix is much lower than the energy barrier for decarboxylation.

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Triptycene Based Arrays of Dipolar Molecular Rotors

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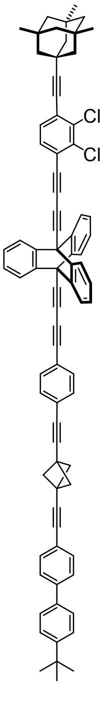
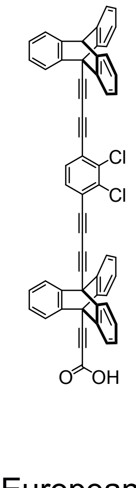
A new generation of rod-shaped molecules for controlled formation of well-organized two-dimensional arrays of dipolar rotors with expected ferroelectric properties was designed and synthesized. Two different approaches to such arrays were tested. (i) Formation of surface inclusions between molecular rotor guests and hexagonal tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP) host. The rotors contain a triptycene unit as an efficient stopper preventing complete insertion into the host channels. (ii) Formation of a Langmuir-Blodgett monolayer of molecular rotors on an aqueous subphase and its transfer to a solid substrate. These molecular rotors contain a carboxylate as an anchoring group. Their triptycene units interlock into a triangular network with the rotatable dipoles at lattice points.





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Acid Catalyzed Radical Reactions Via Alkenyl Peroxides

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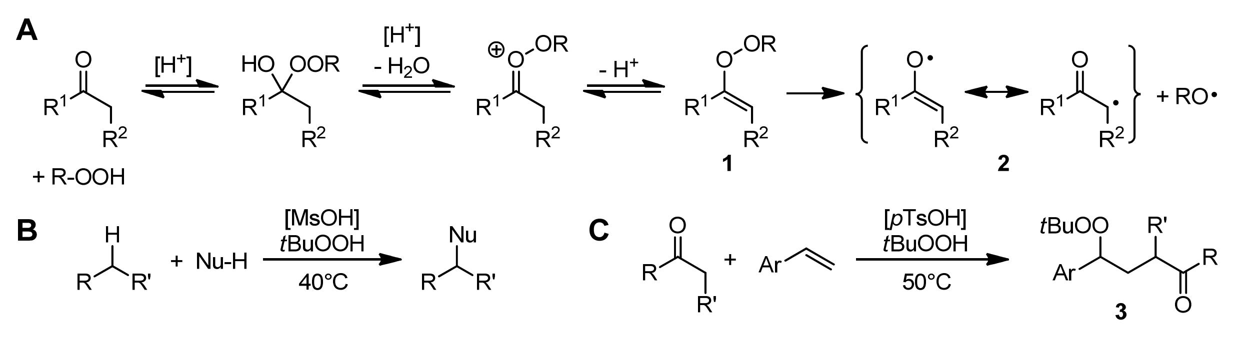
The combination of hydroperoxides, ketones and acid catalysis generates radicals. Mechanistic studies indicate that these reactions proceed via alkenyl peroxides **1**, formed in equilibrium by condensation, which decay by homolytic O-O bond cleavage into a stabilized ketone radical **2** and an oxyl radical (Scheme A).

Previously, alkenyl peroxide chemistry was essentially restricted to theoretical studies of atmospheric chemistry. From mechanistic studies, we realized that they can easily be formed in solution, which also allows to utilize them for various synthetic purposes.[1] For example, the radicals can mediate oxidative C-H functionalization reactions (Scheme B)[2] and they can be used to functionalize olefins (Scheme C).[1] The resulting γ-peroxyketones **3** are valuable products that can be converted to homoaldol products, 1,4-diketones or heterocycles.

An overview of alkenyl peroxide chemistry in solution will be given, including mechanistic studies and how they enable synthetic applications.



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Design of Superbasic Organophosphorus Compounds

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Phosphazene bases are extremely strong uncharged bases, built on a unit where a nitrogen basic center is double bonded to pentavalent phosphorus. One of the the most basic representatives, *t*Bu-P4, with an acetonitrile pK_a of the conjugate acid of 42.7, was synthesized and characterized by R. Schwesinger.[1] On the other side, Alder discovered the phenomenon of proton sponges in 1968, noticing the unexpectedly high basicity of 1,8-bis(dimethylamino) naphthalene (DMAN).[2] Such strong nonionic organic bases possess two basic nitrogen centers able to act as a chelate ligand for a proton which commonly is ligated in an asymmetric hydrogen bond N−H•••N. In this work we show that Schwesinger's phosphazene base concept and Alder's concept of proton chelation can be combined in a design of highly basic nonionic superbases. Some of them are synthesized and their basicities are theoretically rationalized.[3,4] Moreover, newly designed substituents that enable a construction of proton sponges with acetonitrile basicity several orders of magnitude more basic than *t*Bu-P4 are proposed. Finally, some organophosphorus compound where intramolecular hydrogen bonds play a crucial role in their superbasic properties will be presented too.[5]

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Mechanisms of Multi-Electron Transfers in *N*-Aryl Expanded Pyridiniums: Establishing their Unusual Versatile Electrophoric Activity

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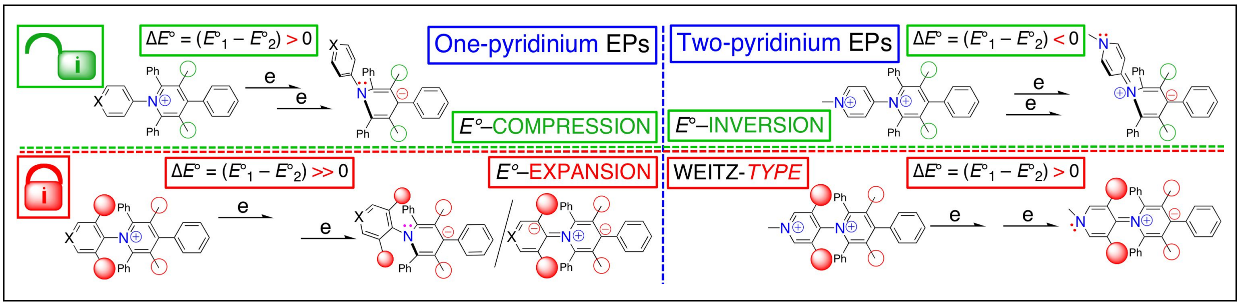
The study of a series of pyridinium-based electrophores, namely *N*-aryl expanded pyridiniums (EPs),[1a] is presented with the aim of elucidating multifaceted mechanisms underpinning the complex electrophoric activity of these fluxional EP systems.[1b] By kinetic mapping of the first two heterogeneous electron transfers (ETs) of electrophores and computational mapping, at the DFT level, of their electronic and geometrical features in various redox states, it is established that, depending on whether EPs are made of one or two "head-to-tail"-connected pyridinium rings, the nature of the redox-triggered distortions (when allowed) is different, namely, *N*-pyramidalization due to hybridization change in the former case *versus* saddle-shaped distortion originating from conflicting intramolecular interactions in the latter case. When skeletal relaxations are sterically hampered, zwitterionic states and electron delocalization with quinoidal features are promoted as alternative relaxation modes. It follows that "potential compression" is changed to "potential expansion" (*i.e*. a further separation of redox potentials) in single-pyridinium EPs whereas "potential inversion" (*i.e.* single-step two-electron transfer) is changed to stepwise ETs of the Weitz type, for two-pyridinium EPs. Overall, this study establishes EPs as a unique class of electrophores.[2]



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Tautomerism in Quinolone 3-esters Targeting the *bc1* Complex of *P. falciparum*: Implications in Product Selectivity and Activity

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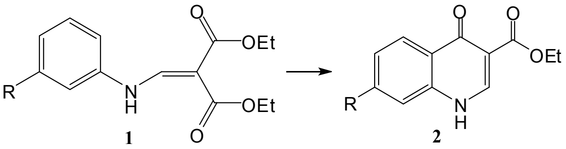
Considering the growing spread of resistance, development of new antimalarial drugs directed to new therapeutic targets remains a priority.[1] The approval of Malarone® for the treatment and prevention of multidrug resistant malaria validated the *P. falciparum* *bc1* protein complex as target for developing antimalarials. Inhibition of the *bc1* complex leads to a drop of mitochondrial function, resulting in collapse of the trans-membrane electrochemical potential and, ultimately, in parasite death.

Selected quinolone 3-esters (**2**) were proposed as inhibitors targeting the Qo site of the *bc1* complex and expressed activity at low concentrations. However, due to chemical and pharmacological liabilities, this chemotype requires optimization.[2,3]



Quinolones **2** may be prepared from an α,β-unsaturated derivative of aniline **1** by the Gould-Jacobs thermal cyclization. Alternatively, the cyclization may be mediated by phosphoryl chloride.[4] However, the possibility of quinolone/hydroxyquinoline tautomerism was found to limit the scope and selectivity and may also impact in antimalarial activity. Unexpected new products arose from the cyclization step,[3] raising structural and mechanistic issues. Results or our studies will be discussed.

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The intriguing class of *altan*-molecules

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As a result of a theoretical investigation on additive patterns in polycyclic systems,[1] we have introduced the *altan*-molecules, which are formed from parent totally fused neutral polycyclics upon substitution of outgoing C H bonds with C C bonds pointing towards alternant carbon atoms only of an outer annulene. The latter turns out to be a [4*n*]annulene, and is expected to host a paratropic current.[1b] The computational investigation of the altanisation process has led to the design of a paramagnetic closed-shell molecule ([12,5]coronene, or equivalently *altan*-[12]annulene)[2], and of aromatic anionic bowl-shaped molecules, e.g. altan-corannulene hexaanion.[3] The latter molecule, with three concentric loops of alternating tropicities which reverse changing the charge, actually forms half a cage of many C_{80} endohedral fullerenes, and could be a reasonable synthetic target. The altanisation design has been recently challenged as it has been shown to lead to a diatropic outer loop not only in *altan*-kekulene[1b], but also in *altan*-[10,5]-coronene.[4] We have recently unraveled this anomalous behaviour of the altanisation process, and we have found that several *altan*-molecules could be well added to the gamut of molecules, which are nowadays under intense experimental and theoretical scrutiny for the development of organic semiconductor devices.[6.]

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Wagner-Meerwein-Type Rearrangements of Polysilanes - Subtle Trapping of Intermediates

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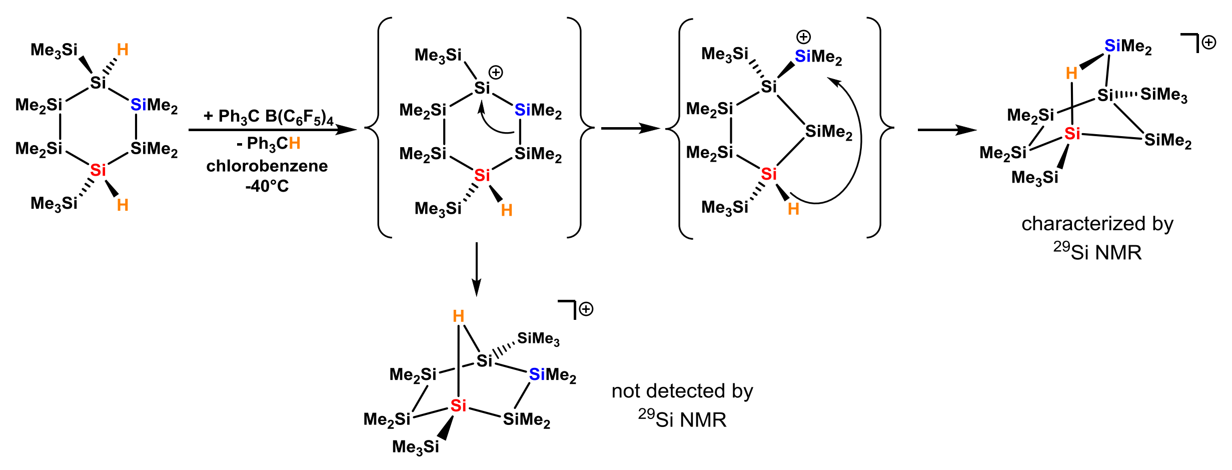
Linear and cyclic, permethylated polysilanes[1,2] transform in a Lewis acid catalyzed Wagner-Meerwein analogue rearrangement into branched isomers. Our experimental investigations on Lewis acid catalyzed rearrangements of polysilanes give astonishing insights into silyl cation chemistry. We use hydrogen-substituted polysilanes to define the position of the initial positively charged atom via a Bartlett-Condon-Schneider hydride transfer reaction. The rearrangement reaction of the formed cation is followed by ^{29}Si NMR spectroscopy. Cationic intermediates of these skeletal rearrangements are stabilized and trapped by the formation of Si-H-Si bridges (see Scheme 1 for an example). This structural motif[3] is easily detected by its characteristic NMR parameter. Based on the results of our stable silicon cation study we are able to provide important insights into the skeletal rearrangement reactions of polysilanes



Scheme 1. Cationic intermediates in the ring contraction reaction of cyclohexasilanes.

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Computational Study of Substituent Effects on Gas-Phase Stabilities of Phenide Anions

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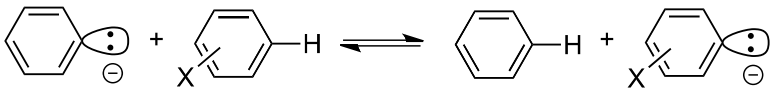
Stabilities of anions of aromatic compounds are governed by three kinds of electronic effects, and an extended Yukawa-Tsuno equation (1) was recently proposed to describe the substituent effects.[1]

$$-\Delta E_X = \rho(\sigma^0 + r^-\Delta\bar{\sigma}_R^- + s\Delta\bar{\sigma}_S) \qquad (1)$$

In order to establish the generality of Eq. 1 and reveal the physical meanings of resultant constants (the r^- and s values), more extensive analyses on various anionic species are desirable. Here, we extended the research to phenide anions. The relative stabilities of ring-substituted phenide anions were determined as energy differences (ΔE_X) of proton transfer reactions (2).



(2)

Energies of respective species were calculated by DFT method. Obtained substituent effects were analyzed by Eq. 1 to give an extended Yukawa-Tsuno plot as shown in Fig. 1. The r^- value of 0.0 and the s value of 1.1 were obtained, showing the absence of the through-resonance and the significance of the saturation effect, respectively. This can be interpreted by the structure of phenide anion in which the anionic p-orbital is attached directly to the *ipso* position of the benzene ring but is orthogonal to the benzene π-electron system. The independent relation between the r^- and s values in various carbanions revealed that two kinds of electronic effects quantified by the r^- and s values are independent with each other showing adequacy of Eq. 1.

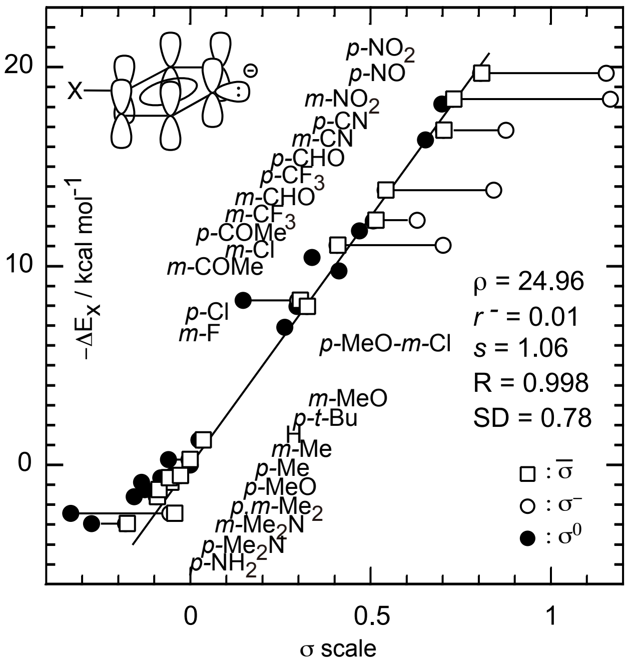


Fig. 1. Extended (Y-T) plots of $-\Delta E_X$ of phenide anions.

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Phosphorus and Carbon: a Tetrahedral Connection

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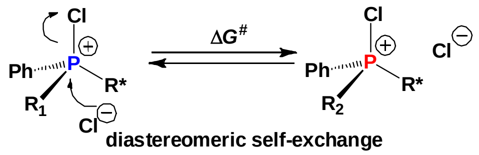
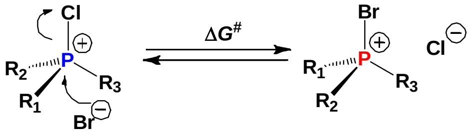
The solution dynamics of tetrahedral halophosphonium salts (XPS) were studied by variable temperature ^{31}P NMR in both diastereomeric series (a) and the cross-exchange series (b) which showed that this is a rapid reaction controlled sterically**:**

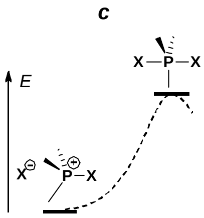


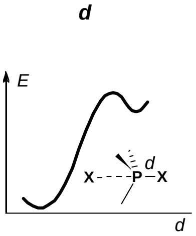
diastereomeric self-exchange

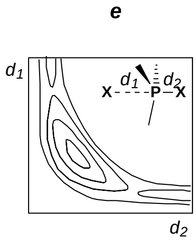


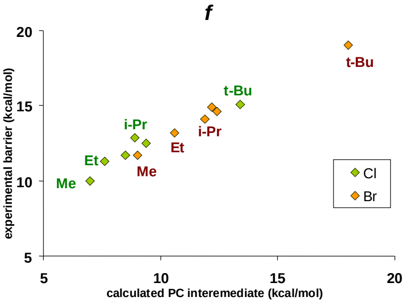
pseudo-degenerate cross-exchange

We have identified possible computational approaches to estimate the energy barriers to Walden-type epimerisation of XPS: single point method (c); single constrained method (d); and the three-dimensional PES approach (e). The computations were extended to the experimental systems and a good correlation (f) of calculated and experimentally determined reaction barriers was observed.[1]

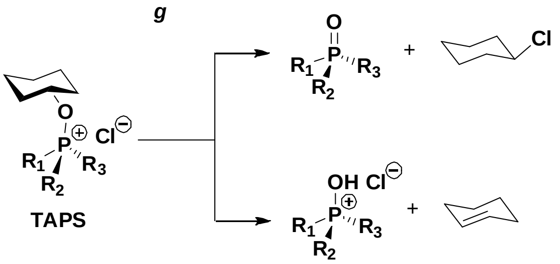


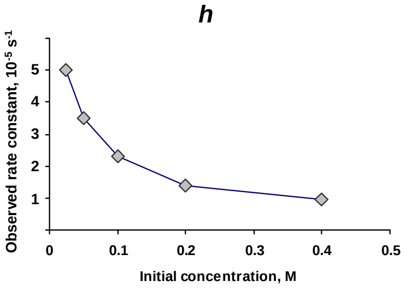






Formation[2] and thermal collapse of tetrahedral alkoxyphosphonium salts (TAPS, g) demonstrate unexpected effects of acids, bases and overall negative kinetic order (h). This is consistent with the presence of HCl_2 anions in the structure of TAPS.





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Donor-Acceptor Cyclopropanes as Sources of Gallium 1,2-Dipoles

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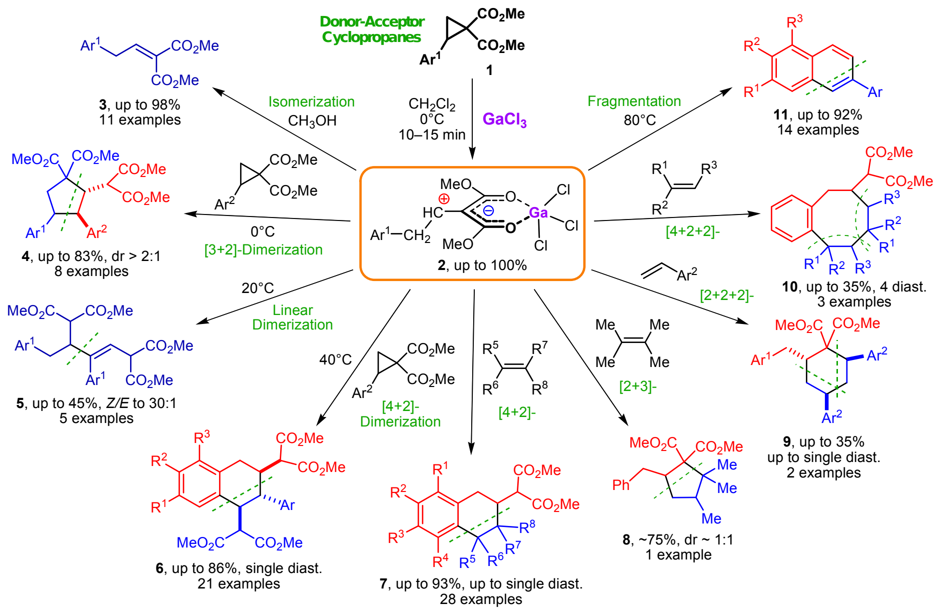
A new type of reactivity of donor-acceptor cyclopropanes has been discovered. On treatment with anhydrous $GaCl_3$, they react as sources of even-numbered 1,2- and formal 1,4-dipoles instead of the classical odd-numbered 1,3-dipoles due to migration of positive charge from the benzyl center. This type of reactivity has been excellent demonstrated for number of new reactions, *viz.*, isomerization, homo- and cross-dimerization, cycloaddition and annulation, with alkenes and second donor-acceptor cyclopropanes. Using this reactivity type it can be very easily and effective constructed different polysubstituted carbocyclic compounds, such as cyclopentanes, tetralines, naphthalenes, et al. The mechanisms of the discovered reactions involving the formation of a comparatively stable 1,2-ylide intermediate have been studied.



We are grateful to the Russian Scientific Fund (Grant 14-13-01054) for support of this research.

Selected Publications: *Organometallics*, **2012**, *31*, 8627–8638; *Angew. Chem. Int. Ed.*, **2014**, *53*, 3187–3191; *Mendeleev Commun.*, **2015**, *1*, 1–10; et al.

Nitron: From Bench Stable Carbene to Blatter-type Radical

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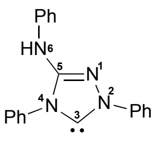
In 2012, Färber *et al* showed that the analytical reagent Nitron exhibits some reactivity consistent with NHC-type tautomer **1** rather than the conventional representation as Lewis structure **2**.[1] We now report C(3)-H deuterium exchange studies of Nitron, and compare these with our results for a large series of 1,2,4-triazolium ions **3**.[2]

During these studies, we noted that stock solutions of Nitron in CD_3CN changed colour over 1 day at room temperature. Black crystals were observed to form upon concentration of the aged solution, which, after isolation and purification, proved to be stable in air and at room temperature for months. X-Ray crystallographic analysis identified product **4**, which is similar to the stable Blatter-type 1,2,4-benzotriazinyl radicals **5** first described in 1968[3] as 'beautiful black needles'. EPR analysis supports the radical nature of **4**, which is the first example with a C(3')-amido substituent to our knowledge. Literature examples of stable Blatter organic radicals **5** have been mostly restricted to R_3 = alkyl, aryl or alkenyl. To explore the versatility of this route towards functionalized stable organic radicals, a range of Nitron derivatives was prepared and analysed. Our synthetic results and mechanistic proposals for radical formation will be presented.



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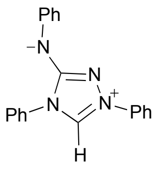

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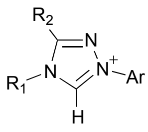

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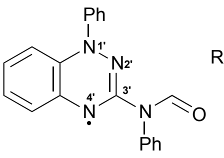

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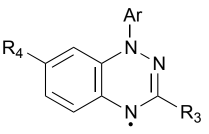

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Micelle Formation and Catalysis in Liquid Ammonia

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Perfluorinated long chain alkyl amides aggregate in liquid ammonia with increasing concentration which reflects micelle-type formation based on changes in ^{19}F NMR chemical shifts. The critical micelle concentrations (cmc) decrease with increasing chain length and give Kleven parameters A = 0.18 and B = 0.19. The micelles catalyse the ammonolysis of esters in liquid ammonia. The corresponding perfluorinated long chain alkyl carboxylates form ion-pairs in liquid ammonia but the equilibrium dissociation constants indicate favourable interactions between the chains in addition to the electrostatic forces. These perfluorinated carboxylates form micelles in aqueous solution and their cmc's generate a Kleven B-value = 0.52 compared with 0.30 for the analogous alkyl carboxylates. The differences in hydrophobicity of CH_2 and CF_2 units in water and liquid ammonia are discussed, as is the possible relevance to life forms in liquid ammonia. The solvolysis of triglycerides in liquid ammonia occurs by a stepwise conversion of the triester to diester to monoester to glycerol with one equivalent of carboxylic acid amide produced at each stage. Immobilised lipase B (CALB) is catalytically active in liquid ammonia and shows selectivity against triglycerides.

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Computational Ligand Design-guided Enantio- and Diastereoselective Cycloisomerization

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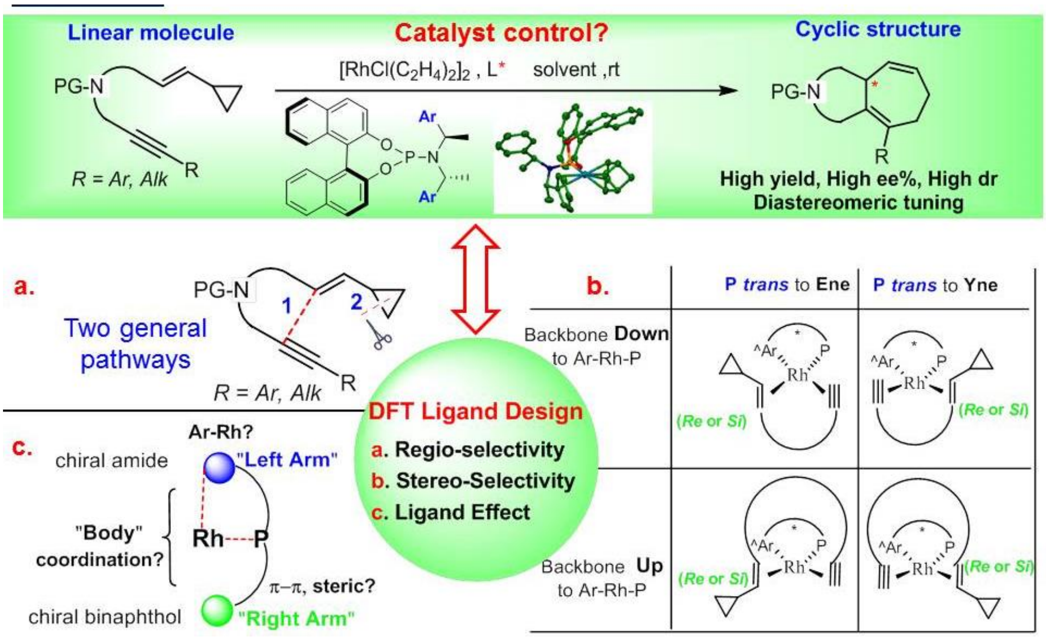
Demand for higher efficiency, economy, and selectivity in the synthesis of novel molecular scaffolds drives organic chemistry. Cycloisomerizations represent ideal methods for the formation of cyclic organic molecules, as they can fulfil all of these criteria. Computational understanding the reaction mechanism of catalyst-control can provide potential ideas to rationalize and guide in the organic synthesis. In collaboration with experimental group (Prof. Edward Anderson in Oxford), we finally realized highly enantio- and diastereoselective catalysed cycloisomerizations of ynamides using new designed chiral phosphoramidite ligands.



Detail mechanism study of Rh-catalyzed cycloaddition has performed to interpret the key factor of reaction selectivity by DFT calculation [1] with solvent correction. Quite noteworthy are the mechanism could be different for the Rh catalysed intermolecular and intramolecular cycloadditions [2]. The results provide a crucial idea for designing new chiral ligands which were tested and proved by our collaborators. These studies set the stage for the development of further computationally-guided enantio- and diastereoselective catalyst systems.

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Conformational analysis of silaheterocyclohexanes versus their carbon analogues

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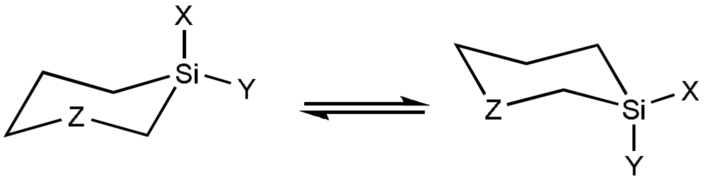
Conformational analysis of 3-silathianes,[1] 3-silapiperidines,[2] 3-silatetrahydropyran[3] in gas phase and solution by LT NMR, FTIR spectroscopy, gas phase electron diffraction showed principal differences in the conformational behavior of silaheterocyclohexanes as compared to their carbon analogues, as partly summarized in.[4] Energetically, the main differences are much lower conformational energies (*A*) of the substituents at silicon resulting in appearance or even predominance of the axial conformers and lower barriers to ring inversion with respect to cyclohexanes, thianes, piperidines, tetrahydropyranes. Structurally silaheterocyclohexanes are characterized by the longer Si–C vs. C–C bonds and less folding of the "Si-part" of the ring than of the "C-part" or "Z-part", which is responsible for the observed energetic differencies.



X, Y = H, Me, Ph, F, OR;
Z = N, O, S.

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Quantum Chemical Calculation of $J_{(Si,C)}$ Nuclear Spin-Spin Coupling Constants. A Tool for Investigation of Silicon Carbon Hyperconjugation and Hypercoordination in Carbocations

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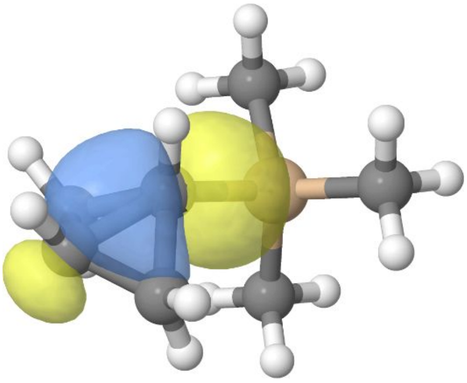
Nuclear spin-spin coupling arises through interaction of the nuclei with the spin or angular momentum of the intervening electrons in a magnetic field. Thus spin-spin coupling constants are dependent on the bonding, i.e. the electron density between the nuclei. [1,2]

$J_{(Si,C)}$-coupling constants in selected silyl-substituted carbocations[3] and structurally similar model compounds were calculated in order to explore the effect of delocalisation of electron density arising from hyperconjugation and hypercoordination on the magnitude of silicon-carbon spin-spin coupling constants.[4]

The variation of $J_{(Si,C)}$-spin-spin coupling constants can be correlated with structural parameters, such as Si-C-bond lengths, NBO-charges and localized molecular orbitals (NLMOs).



CCSD/cc-pVTZ calculated C^1C^3 NLMO of
endo-3-trimethylsilylbicyclobutonium cation

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Visible Light Photoactivated Metal-Free Carbon Monoxide-Releasing Molecules (photoCORM) Suitable for Bioapplications

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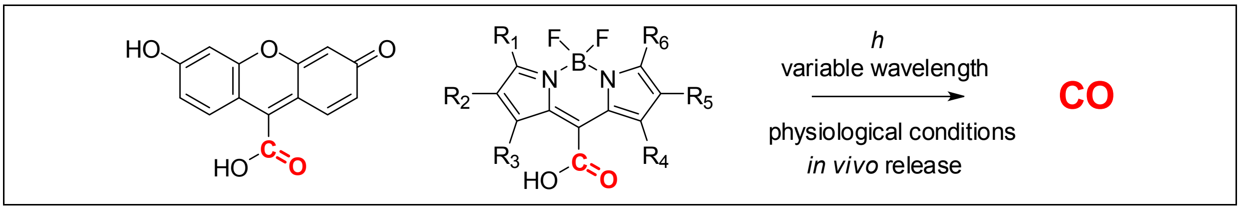
Carbon monoxide (CO) has been recognized as a signaling molecule with a broad spectrum of biological activities.[1] Anti-inflammatory, antiproliferative, and antiapoptotic effects of biogenic CO have been reported.[2] Various transition-metal-based CO releasing molecules (CORMs) have been introduced recently for biological applications. However, these molecules suffer from toxicity, low water solubility, extremely short half-lives and an uncontrolled CO release limiting thus their therapeutic potential. We have developed a family of metal-free photoactivatable CORMs based on the xanthene[3] and BODIPY structural motifs. Their absorption properties can easily be tuned by different substitution patterns. High chemical yields and a sufficient efficiency of the CO release, long biogenic half-lives and no toxicity make them suitable for biological and therapeutic purposes.



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“Aroma” as a powerful tool for obtaining quantitative aromaticity and antiaromaticity information.

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NICS-scan, the -only model and NICS-XY-scan are methods which provide quantitative information about aromatic and antiaromatic single-ring and multi-ring systems. These (and some other) methods are integrated in “Aroma” – a Python software.

The lecture will shortly describe the above-mentioned methods and the work with Aroma. Some applications will be presented as time permits.

Triplet, Singlet and Nearly Degenerate Nitroxide Diradicals

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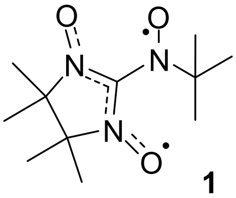
Being curious by the report on theoretical construction of hydrocarbon polyradicals published by W. Borden and E. Davidson in 1977, we explored the feasibility of preparing stable nitroxide diradicals with the low-lying triplet or singlet state, as well as a nearly degenerate state. We succeeded in isolating a triplet ground state nitroxide diradical **1** that is persistent at room temperature, possesses a singlet-triplet energy gap that is greater than the thermal energy at room temperature (J/k_B ~390K, $H = -2JS_{1/2}{\cdot}S_{1/2}$), and can be sublimed.[1] We prepared and studied another class of stable nitroxide diradicals (**2** as an example) with singlet ground state and low singlet-triplet energy splitting ($J/k_B = -7.4$K).[2] The diradical **3** with the diacetylene coupler was found to have singlet ground state with strong antiferromagnetic coupling and a high kinetic stability at ambient conditions ($J/k_B = -104$K).[3]



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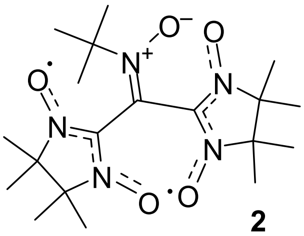

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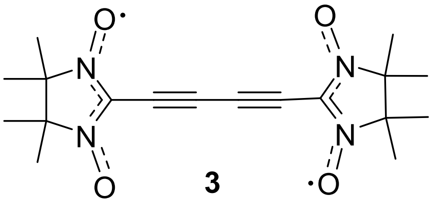

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Photodegradation of Decafluorobiphenyl Sensitized by Aromatic Hydrocarbon in Alcoholic Media

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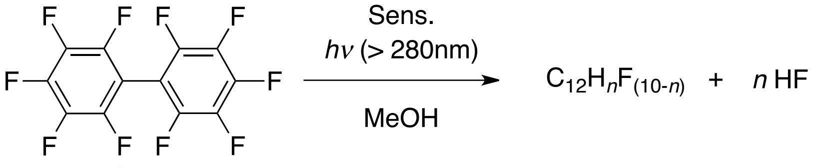
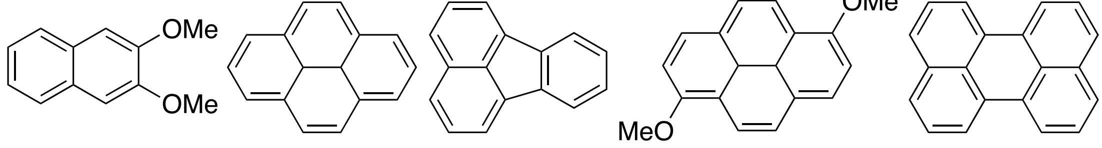
Photodegradation of decafluorobiphenyl ($C_{12}F_{10}$) in methanol was investigated by using aromatic hydrocarbon as sensitizer. When a methanol solution of $C_{12}F_{10}$ (1mM) was irradiated by Xe lamp with Pyrex filter ($\lambda > 280$ nm) in the presence of 2,3-dimethoxynaphthalene (2,3-DMN 1mM), substitution of fluorine by hydrogen underwent in accord with the formation of HF. The defluorination was preferentially proceeded at *o*- and *p*-positions, and successively at *m*-position. Pyrene (Py) also sensitized the defluorination, but peryrene (Pery) did not. The defluorination was also observed in the presence of 1,6-dimerhoxylpyrene (1,6-DMPy) or fluoranthene (Flu) with slower rate than in the case of 1,6-DMN or Py. Removal of O_2 from the solution exalted the defluorination rate without changing degradation products. The fluorescence of 2,3-DMN was effectively quenched by $C_{12}F_{10}$, but that of Py, Flu, or Pery was not. These results indicate that the reaction is sensitized by triplet excited state. The oxidation potentials of triplet excited state are -1.17 and -1.09 V for Py and Flu, respectively, and are more positive than the reduction potential of $C_{12}F_{10}$ (-1.39 V). The comparison of the redox potentials indicates that triplet energy transfer, rather than electron transfer from sensitizer to $C_{12}F_{10}$ is involved in the reaction.



$C_{12}F_{10}$



Sens.	2,3-DMN	Py	Flu	1,6-DMPy	Pery
E_T	2.60 eV	2.09 eV	2.29 eV	2.09 eV	1.52 eV
E_T^{ox}	-1.57 V	-1.17 V	-1.09 V	-1.81 V	-0.91 V

Isotope Effect Calculations in the Supramolecular Age

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Kinetic isotope effects (KIEs) are important experimental probes of mechanism for chemical reactions, the vast majority of which occur in condensed phases. Traditional methods for their calculation are molecular in nature, which is fine for gas-phase reactions but generally inadequate for systems in which coupling between a substrate and its environment is significant. However, atomic subsets of supramolecular systems, whose isotopically sensitive vibrational frequencies are explicitly considered, may be (surprisingly) small without significant error for KIEs provided that all their degrees of freedom are considered, but their Hessian elements must be evaluated within an adequately large environment whose electrostatic properties are accurately described.[1] KIEs should be evaluated as simple quotients of isotopic partition function ratios determined independently for the reactant state and the transition state averaged over thermally accessible configurations.[2]

Enzyme-catalyzed methyl transfer will be discussed in the light of experimental results for mutants of catechol-O-methyltransferase. Possible reasons for a discrepancy between calculation (so far) and experiment will be examined, including the role of the dielectric environment of the methyl group. EIE and KIE calculations for CH_3^+ *vs*. CD_3^+ and $^{14}CH_3^+$ within highly constrained cages comprising “axial” interactions (normal to the plane of the methyl moiety) and “equatorial” interactions (within the plane of the methyl moiety) will be discussed. Determination of isotope effects on the basis of a “cutoff” model which considers vibrational frequencies only for the 12 degrees of freedom of the methyl group (6 internal and 6 external) within the larger environment of aqueous solution, or a cage, or an enzyme active site, yields results that do not differ significantly from those obtained from “full-size” Hessians involving much larger numbers of atoms.

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Effect of UV/Ozone on the structural and thermal properties of hydroxypropyl methyl cellulose

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Abstract:

The effect of ultraviolet/ ozone treatments for different times on the characteristics of hydroxypropyl methyl cellulose (HPMC) films with respect to its thermal stability and structural changes was evaluated to be used as bioequivalent materials according to their importance broad practical and medical applications. The beneficial effects of this treatment on the crystallinity and amorphousity regions were followed by X-ray diffraction technique. Also, the change in the crystal size was calculated. Thermal analysis (differential scanning calorimetry and thermal gravimetric analysis) show variation in the glass transition temperature, shape and area of the thermal peaks. These changes are attributed to the different degrees of crystallinity after exposing the treated samples to UV/Ozone for 1, 2, 3 and 4 hours. This meant a change in the amorphousity of the treated HPMC samples, the oxidation of its chemical linkages on its surface and its bulk, and the formation of free radical species as well as bond formation.

Keywords: Hydroxypropyl methyl Cellulose, UV/Ozone, DSC, TGA, XRD

A Novel Approach for the Synthesis of Functionalised Carbazoles

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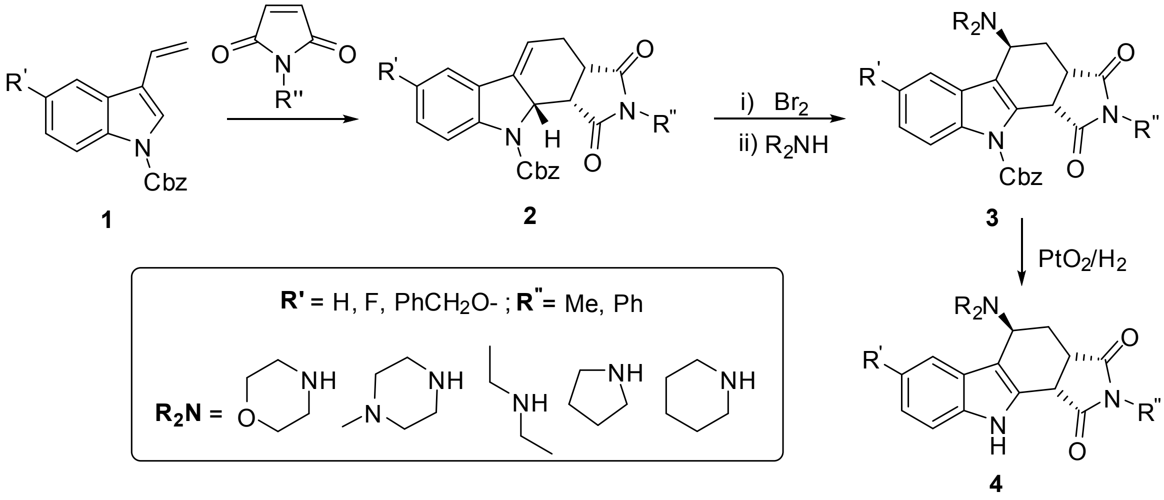
Carbazoles are privileged scaffolds found in many synthetic and naturally occurring biologically active compounds.(1,2) Thus our work has focussed on the development of new synthetic approaches to the carbazole ring system, which allow the stereo-controlled introduction of functional groups, as a route to new biologically active molecules.(3) Herein we disclose our recent investigations into a one-pot, bromination / substitution reaction sequence, allowing the diastereoselective introduction of amino groups into partially unsaturated carbazoles. Our approach starts with the formation of an appropriate Cbz protected Diels-Alder cycloadduct **2**, which is functionalised through bromination of the alkene followed by *in situ* trapping with a nucleophilic amine to give compound **3** and finally *N*-deprotection to give a focussed library of biologically active tetrahydropyrrolo[3,4-*a*]carbazole-1,3(2*H*,3a*H*)-diones **4** (Scheme 1).



Scheme 1: D-A, bromination/substitution approach to functionalised carbazoles

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Transfer Hydrogenation as a Redox Process in Open-shell Nucleotides and Peptides

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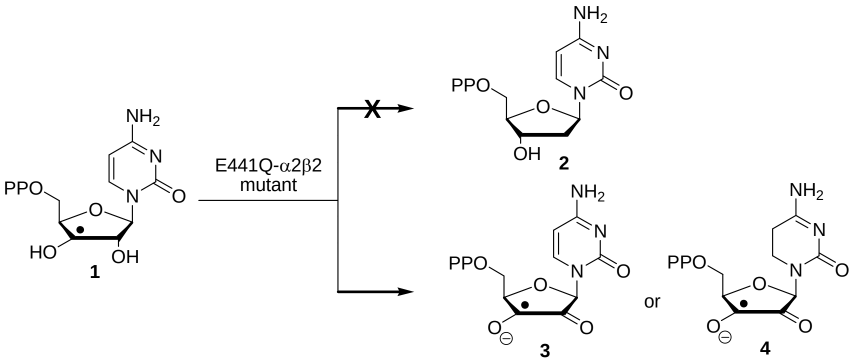
C-Centered (desoxy)ribosyl radicals play an important role in the strand cleavage of the nucleotide backbone, and also occur as transient intermediates in a number of enzyme-mediated reactions. One of the best studied radical enzymes is ribonucleotide reductase (RNR), whose E441-$\alpha 2\beta 2$ mutant in *E. coli* has recently been shown to generate the unusually stable semidione radical **3** when using cytosine diphosphate **1** as substrate.[1] We explore here the possibility of using the individual nucleotide bases as intramolecular oxidants through a formal dihydrogen transfer pathway. The potential of a large number of sugar- and peptide-derived radicals to act as H_2 donors in transfer hydrogenation reactions has been quantified through the calculation of hydrogenation enthalpies of the respective oxidized products.[2] The calculated values show, that many sugar fragment radicals can reduce pyrimidine nucleobases in a strongly exothermic fashion due to the formation of captodatively stabilized radicals.



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Anti tumoral Activityof Hydrazyl pyrrolidine 2, 5 dione and 2-Thioxo Imidazolidine 4-one

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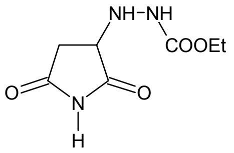
Abstract

Compounds containing the thiohydantoin structural motif have been identified to display a wide range of biological activities. For example, many of them exhibit anticonvulsant, antimicrobial and potential antitumor activities.[1] In this context, we have investigated *in vitro* potential anti tumoral activitiy of hydrazyl pyrrolidine 2, 5 dione **1** and 2-thioxo imidazolidine 4-one **2** previously synthesized by us.[2-3]

Compounds **1** and **2** were evaluated at 370 μg/mL on proliferation (Human Laryngeal Carcinoma cells) **HEp 2** cells. The malondialdehyde (MDA) was used as indicator to evaluate the lipid peroxidation of cells.



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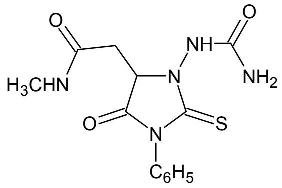

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New Approach Synthetic of 4-Thiazolidinones Scaffold. Evaluation of Antimicrobial Activity

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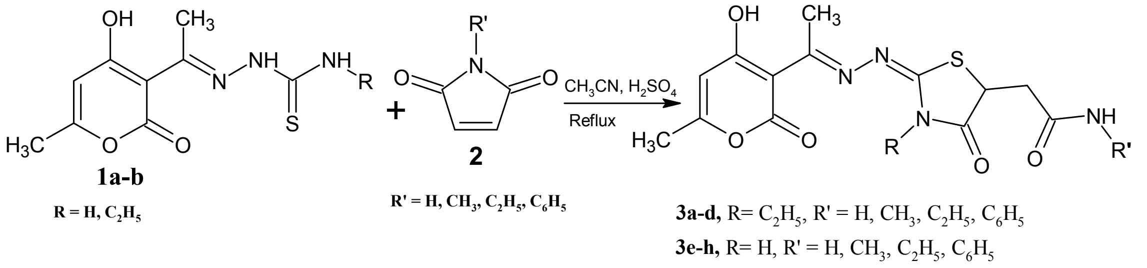
Abstract

In recent years, 4-thiazolidinones and their derivatives have become among the most extensively investigated compounds. They constitute an important group of heterocyclic compounds, displaying a broad spectrum of biological activity. [1-2] The diversity in the biological response of these molecules has attracted interest of chemists.

In this work, we report a new synthetic approach for the formation of 4-thiazolidinone compounds **3**a-h i, [3] from reaction of the thiosemicarbazones **1**a-b and maleimide derivatives **2**a-h described in Scheme 1.



Scheme 1. Synthetic pathway to generate 4-thiazolidinone structures **3**a-h.

The 4-thiazolidinones **3**a-h were evaluated for their *in vitro* antimicrobial properties against Gram positive, Gram negative and antifungal bacteria.

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Chemical reactivity of biothiols and sulfite on Michael acceptors modulated by a zwitterionic micellar solution.

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The zwitterionic micelles, similar to cationic micelles, are able to catalyze bimolecular reactions containing an anionic reactant.[1] Taking advantage of the latter and of our interest in the development of chemical sensors based on Michael addition reactions,[2] in the present work we studied the reaction of the Michael acceptors: N,N-dimethyl-4-((E)-2-(3-methyl-4-nitroisoxazol-5-yl)vinyl)benzenamine (**1**) and 5-(4-methoxystyryl)-4-nitroisoxazole (**2**), with sulfite (SO_3^{2-}) or the biothiols -glutathione (GSH) and cysteine (Cys)- in the presence of the micellized sulfobetaine surfactant (SB3-14). The addition reactions were studied by kinetic methods using absorption and fluorescence spectroscopy, ^{1}H-NMR and electrospray ionization mass spectrometry (ESI-MS) experiments.

Results show that the reaction of GSH and Cys with **1** or **2** is inhibited by the presence of the zwitterionic micelle SB3-14. However; the reaction between sulfite and the probes is accelerated by SB3-14 (near 2-fold larger than the second-order rate constant in water). Thus, on the basis of these results, it is suggested that the use of sulfobetaine surfactant can be considered as a strategy for eliminating typical interferences associated with the detection of sulfite *via* its addition reaction to alkenes.

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Determining the Rate of Hydrolysis of 2-Methoxyethoxymethyl Chloride as a Route to De-risking the use of a Mutagenic Reagent

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The 2-methoxyethoxymethyl (MEM) protecting group is a well known, acid labile protecting group for phenols and alcohols.[1]

A process for the production of an API undergoing development within our organization used a MEM protecting group during its synthesis. The 2-methoxyethoxymethyl chloride (MEM-Cl) used in the introduction of the MEM protecting group is a potentially mutagenic impurity (PMI) and as such required an assessment to be made of the potential level that could be present in the drug product. As the MEM-Cl was expected to be hydrolytically labile in the subsequent processing we desired to make a chemical purge based argument for its control in the isolated API. However, little could be found in the literature as to the rate of hydrolysis of MEM-Cl. A second order rate constant of 1×10^{-2} $M^{-1}s^{-1}$ in DMF containing low levels of water was found.[2] The authors were not explicit as to the water content of the system or the reaction temperature, although the reaction was clearly fast. We therefore set out to estimate the rate of hydrolysis of MEM-Cl.

Initial studies using ^{1}H NMR in DMF water mixtures were followed by solvolysis studies in acetone water mixtures using *in-situ* FTIR spectroscopy to monitor the hydrolysis of MEM-Cl. The Grunwald-Winstein[3] relationship was used to provide an estimate of the rate constant in pure water.

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Hydrogen-Bonding Effects on the Rotational Barrier of Triazenes: Experimental and Theoretical Study

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Electron delocalization in conjugated π moieties has long been recognized as a key structural feature. As shown next for a diazoamino (triazeno) group, i.e., [$–N^{(1)}=N^{(2)}–N^{(3)}<$ ↔ $–N^{-}–N=N^{+}<$], delocalization of N lone pair over the π system leads to a decrease and an increase, respectively, in $N^{(1)}=N^{(2)}$ and $N^{(2)}–N^{(3)}$ bond orders, which greatly influences corresponding bond rotational barriers and ultimately, geometrical isomerization.

Previous mechanistic studies from our laboratory on *cis*-to-*trans* isomerization of disubstituted and trisubstituted triazenes, have shown rotation around NN bonds to be, not surprisingly, very sensitive to the chemical environment. The energy barrier for rotation around the $N^{(1)}=N^{(2)}$ bond in trisubstituted *cis*-triazenes, for instance, is found to decrease with increasing electron-withdrawing character of $N^{(1)}$, increasing electron-donating character of $N^{(3)}$, and increasing solvent polarity, consistent with an increased contribution of the dipolar structure to the resonance hybrid for the ground state. Hydrogen-bonding solvents, however, seem to raise the rotational energy barrier, which is thought to result from diminished electron delocalization by (preferential) H-donor solvent–$N^{(3)}$ lone pair interactions.

In this contribution, the results of DFT calculations and of kinetic studies in binary solvent mixtures to elucidate the role of H-donor solvents on *cis*-phenyltriazenes rotational energy barriers are presented and discussed.

Stability of Anthracene Endoperoxides and their Cleavage Products

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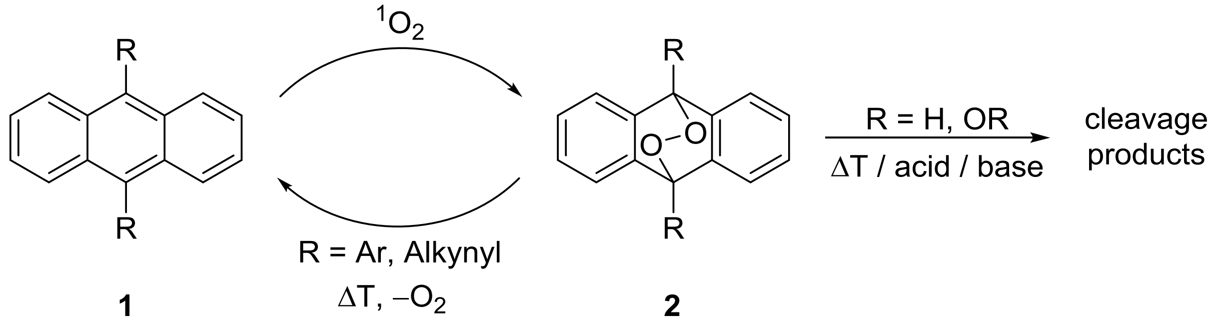
Anthracenes **1** can react reversibly with singlet oxygen ($^1O_2$) to endoperoxides **2**.[1] While phenyl- and alkynyl substituted acenes thermolyse cleanly to the parental species under release of oxygen,[2] non- and *O*-substituted anthracenes give a broad range of cleavage products.[3] The influence of acids and bases on the other hand is still not clarified.

Thus, we studied the behavior of these endoperoxides **2** (R = H, OR) under acidic and basic conditions. We investigated the occurring products as well as the mechanistic pathways. Since endoperoxides and other reactive oxygen species (ROS) are of current interest for medical applications like in the photodynamic therapy (PDT),[4] we set our focus on the characterization of short-lived intermediates such as hydroperoxidic species.



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Influence of side chains, stereo center & solvents on cyclic constrained tetrapeptides

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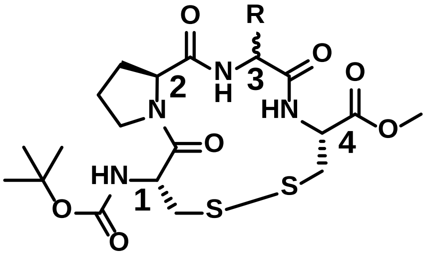
Detailed knowledge about conformations and dynamics of peptides and proteins is not only essential for a better understanding of biological processes but also for the design of new peptides and peptidomimetics with potential biological applications. In order to elucidate effects – such us the peptide environment, side chains and stereo center – on the structure of peptides, comprehensive studies on a set of cyclic disulfide-bridged tetrapeptides were carried out in various solvents. Previously, the peptides of the general form cyclo(Boc-Cys-Pro-X-Cys-OMe) with X being various amino acids (Gly, D-/L-Leu, Aib, Phe) were studied.[1-4] This set of peptides has been extended by the peptides containing the amino acids D-/L-Ala, D-/L-Trp and D-/L-Val at the third position (see figure below; R indicates different side chains of the various amino acids at position three). All peptides feature a β turn structure. Focussing on the type of β turn and its stabilization by intramolecular hydrogen bonding, the peptides were investigated using VCD spectroscopy, temperature-dependent FTIR experiments, 1D and 2D NMR experiments as well as temperature-dependent ^{1}H NMR experiments. Furthermore, the crystal structure for some of the tetrapeptides could be obtained.



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Novel Allyl Boronates for the regioselective Synthesis of Homo Allylic Alcohols

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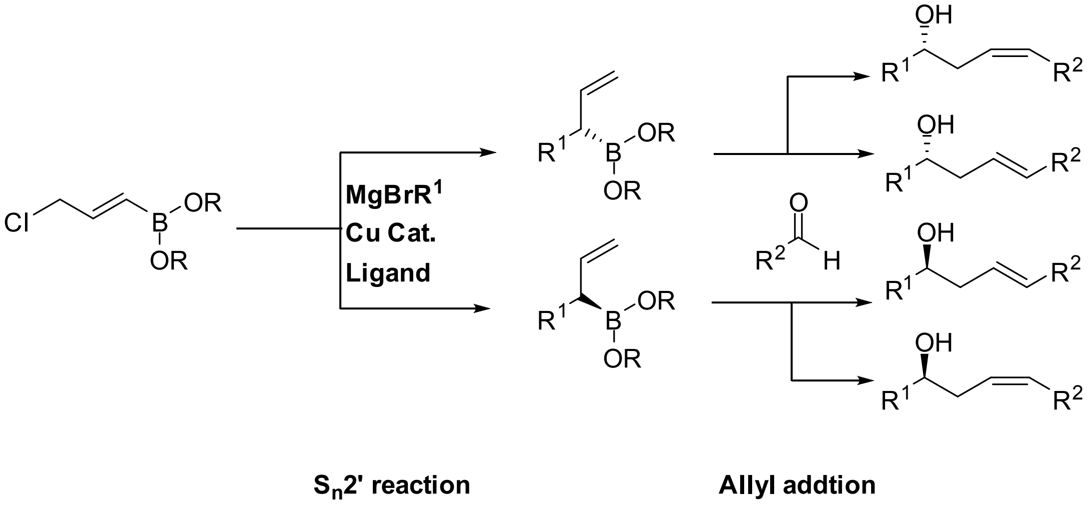
Allyl addition reactions of allyl boronates are a powerful tool to generate highly enantiomerically enriched compounds, which are of importance due to their character as building blocks for a huge variety of natural compounds.[1] However, conventional allyl addition reactions regularly lead to *E*-configured double bonds by using common allyl boronates.[2] Recently we have developed a novel protecting group for allyl boronates which allows the synthesis of *E*- and Z-configured homo allylic alcohols by using different isomers of the allyl boronate. All isomers of the corresponding homoallylic alcohol can be synthesized in good regio- and excellent enantioselectivities. Here we present the novel boronate protecting group and its application for selective S_n2' and allyl addition reactions to form *E*- and *Z*-configured homo allylic alcohols.[3]



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Theoretical and Experimental Study of CH/π Interactions in Phenyl-2-Pyridone Galactoside Supramolecular Complexes

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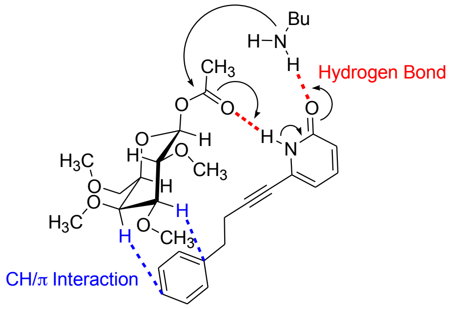
Carbohydrate−protein interactions are fundamental for cell communication, antigen−antibody recognition, etc.[1] It is well known that CH/π weak interactions play an important role for carbohydrate recognition.[2,3] There is a growing interest in designing artificial carbohydrate receptors.[4] The goal of the project is to study a chemical reaction model to demonstrate the participation of CH/π interactions in the recognition of monosaccharides. First, we have done geometry optimizations using the M062X level to find the most stable phenyl-2-pyridone galactoside supramolecular complexes. Then, the pyridones showing the best spatial arrangement with the saccharide were synthesized and evaluated in the aminolysis of *O*-acetyl-2,3,4,6-tetramethyl-*β*-D-galactoside with butylamine. The obtained results will be presented.



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The Reaction Paths of the Decomposition of Carbonates

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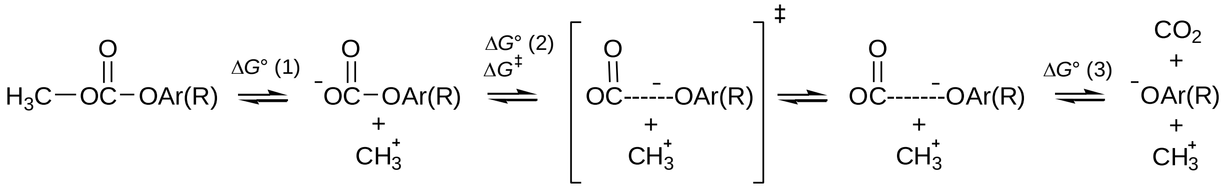
In continuation of our previous work on carbonates,[1] *ab initio* calculations at the MP2(full)/6-311+G(2d,p) level of theory have been employed to investigate the reaction paths for heterolysis of methyl aryl, methyl alkyl and methyl hydrogen carbonate esters that yields the methyl carbocation and the corresponding aryl/alkyl/hydrogen carbonate anion. The paths also include further decomposition of aryl, alkyl and hydrogen carbonate anions to free carbon dioxide and the corresponding phenoxide/alkoxide/hydroxide anion via heterolytic TS and a subsequent complex (Scheme 1). The calculations have been conducted in both gas phase and neutral solution (IEFPCM). Energy relations as well as geometry parameters and bond orders in optimized structures on the reaction paths strongly suggest that the negative hyperconjugation is a dominant electronic effect in the aryl, alkyl and hydrogen carbonate anions that stabilizes them toward a carbocation ($\Delta G°(1)$), but causes their further decomposition ($\Delta G^{\ddagger}$, $\Delta G°(2)$) as well. In addition, the energetics of model reactions of the aryl, alkyl and hydrogen carbonate anions with hydronium ion in PCM reveals that the negative hyperconjugation does not only decrease the basicity of the carboxylate oxygen atoms in these anions, but also increases the basicity of the aryloxy/alkoxy/hydroxyl oxygen which ultimately renders the decomposition of the Ar/R/H carbonate anion in acidic solution to carbon dioxide and phenol/alcohol/water dominant over forming the corresponding carbonic acid.



Scheme 1. Decomposition of methyl aryl/alkyl carbonates

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Engineering Exceptionally Strong Oxygen Superbases with 1,8-Diazanaphthalene di-*N*-oxides

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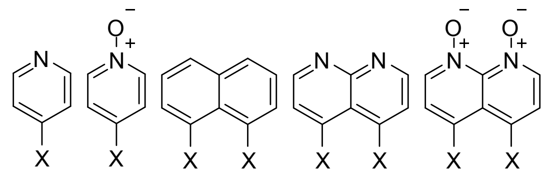
For more than four decades, the design and synthesis of neutral organic superbases have attracted much attention[1] because their unique characteristics allow deprotonation of a wide range of weak acids. Although usually weaker than their inorganic counterparts, uncharged organobases have become widely used standard reagents in organic synthesis.

DFT calculations revealed that naphthalenes bearing two 1,8-bis-substituted N–oxides provide extraordinary oxygen superbases, whose gas-phase and acetonitrile basicities surpass those of classical nitrogen proton sponges involving naphthalenes equally di-substituted with dimethylamino, guanidino, and phosphazeno groups. Such pronounced basicity is almost entirely a consequence of a large strain-induced destabilization in neutral bases, while only a small contribution is offered by the intramolecular [O–H·····O]– hydrogen bonding in conjugate acids.[2]



X					
-H	**1a**	**2a**	**3a**	**4a**	**5a**
-NMe_2	**1b**	**2b**	**3b**	**4b**	**5b**
-$N{=}C(NMe_2)_2$	**1c**	**2c**	**3c**	**4c**	**5c**
-$N{=}P(NMe_2)_3$	**1d**	**2d**	**3d**	**4d**	**5d**

Figure 1. Schematic representation of investigated bases

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Photoswitchable Contrast Agents for Magntic Resonance Imaging

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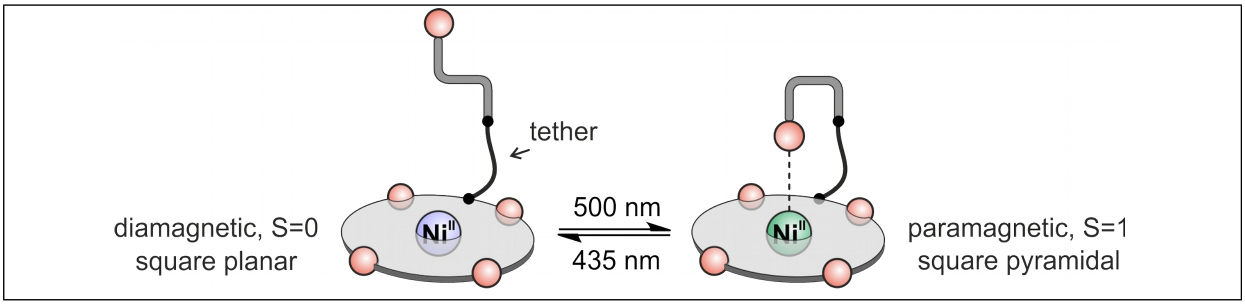
MRI is an important tool in diagnostic medicine for which contrast agents are frequently administered to enhance anatomical details. Once injected the contrast cannot be modified anymore. For catheter based operations, however, switchable contrast agents would be advantageous. We therefore designed, synthesized and investigated Ni-porphyrins that can be switched between the dia- and paramagnetic state, or in other words between MRI-active and MRI-silent state under ambient conditions by irradiation with light. Ni-porphyrins exist in two different spin states. Square planar complexes always give rise to the diamagnetic low-spin configuration. Axial coordination of one ligand leads to a square pyramidal geometry which has a high-spin configuration. This process was coined Coordination Induced Spin State Switch (CISSS). A photochromic azopyridine was covalently attached to the Ni-porphyrin [1,2]. The molecule is designed for exclusive coordination in *cis*-configuration. Switching is extremely efficient (between < 5 % to 95 %) with a half-life of the *cis*-configuration of 400 days at room temperature (DMSO). For in vivo applications the intramolecular LD-CISSS has to be performed in aqueous solution [4] and with wavelength in the biooptical window which are the current challenges.



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Synthesis and Study of Photoresponsible Amphiphiles Containing an Azobenzene Moiety

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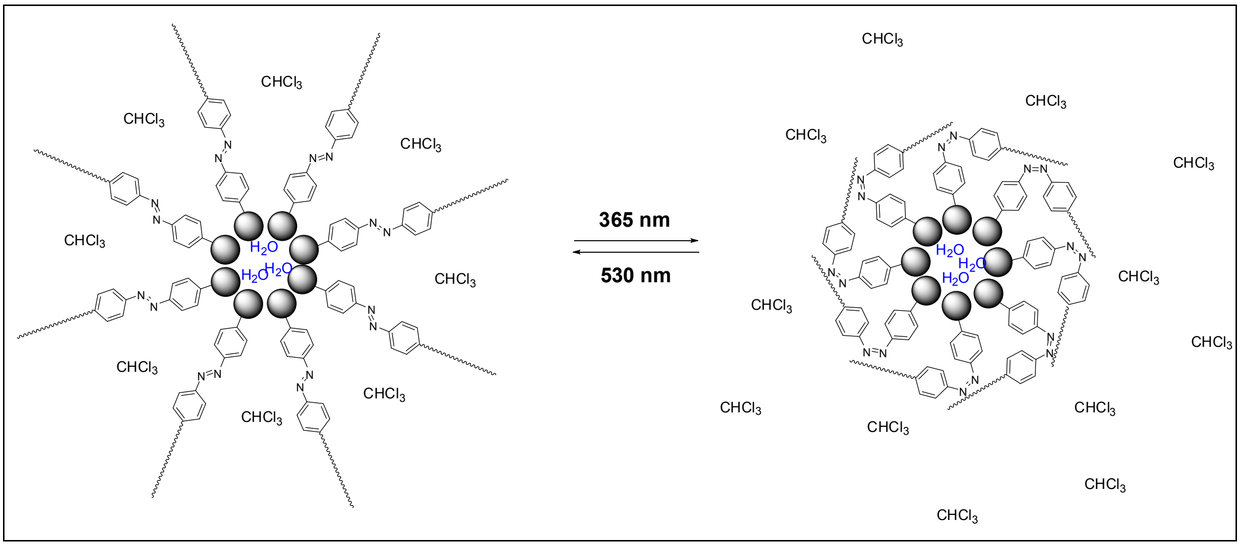
Recently, our group has examined the formation and physical behavior of reverse micelles in a ternary water/CTAB/chloroform system at room[1] and sub-zero temperatures.[2] The aim of this new study was to create photoresponsible reverse micelles from amphiphilic molecules that contain the azobenzene moiety and study their properties when the N=N group undergoes a photoinduced *E*/*Z* isomerization.

The physico-chemical properties of the synthesized amphiphiles and their ability to form reverse micelles in the all-*trans* configuration were investigated using NMR and UV-vis spectrometry, and the critical micelle concentration was determined. The *E*/*Z* photoisomerization and the corresponding reverse thermal isomerization at different temperatures, and its effect on the character of reverse micelles and encapsulated water will be discussed.



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Unraveling the Mechanism of the Zincke Reaction.

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In the last decade the design and synthesis of a new class of solvents, namely pyridinium based ionic-liquids, has became an important research area.[1] In this context, the Zincke reaction[2] provides an efficient and elegant approach for the preparation of new N-aryl or N-alkylpyridinium derivatives. Despite the broad utility of the Zincke reaction in organic synthesis, up to date this reaction has not been described from a theoretical view point.

Herein, we developed an in-depth computational study on the Zincke reaction, in order to elucidate its reaction mechanism. Thus, the transition structures (TSs) for the Zincke reaction between aniline and 1-(2,4-dinitrophenyl)pyridinium chloride has been studied by means of density functional theory (DFT) at the M06-2X/6-31+G(d,p) and SMD solvation models. The results obtained reveals that the reaction take place with the ring closing stage as the rate determining step. Nevertheless, calculations point out that the most favored path involves an intramolecular nucleophilic attack that proceeds via *6-exo-trig* TS, a result that challenges the electrocyclization mechanism previously proposed. Also, an alternative ring closing mechanism involving the formation of a glutaconic dialdehyde derivative has also been explored (Chart 1).

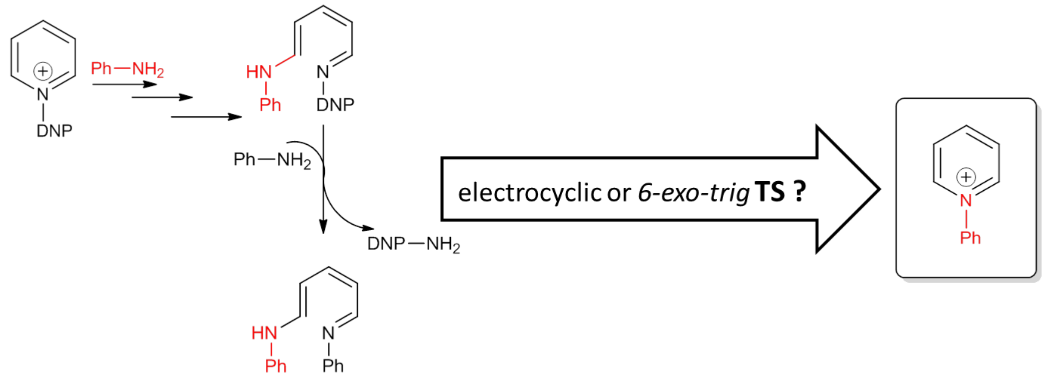

Chart 1

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Estimation of the intrinsic affinity between ionic liquids and Ibuprofen.

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The use of ionic liquids (ILs) as non-conventional media in chemical synthesis is receiving increasing attention because of their physical and chemical properties for task specific applications.[1]

On the other hand, it is well known that at constant temperature and pressure, chemical reactions are spontaneous in direction of decreasing Gibbs energy. This is also true for any process not necessarily associated with bond making/breaking processes.[2] In some cases we can deal with processes that involving the formation of different solute-solvent complexes.

In this study we present an estimation, in gas phase, of the intrinsic affinity of a series of ILs towards ibuprofen. The determination is made by evaluating the Gibbs free energy of formation of such complexes for a series of ILs, taking as reference the free energy of the isolated IL, because the free energy of the isolated Ibuprofen is a constant. We also include water as complexating agent in order to compare the H-bonding abilities of the different ILs with reference to water. It is expected by this procedure to set up a hydrogen bond acidity/basicity of the series of IL considered.

Acknowledgement:

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H-Tunneling in the Ground State Ketene Intermediate Derived Photochemically from *o*-Nitrobenzaldehyde

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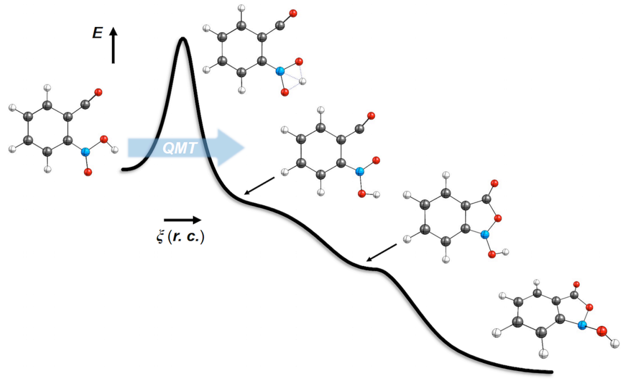
The prominent photochemical rearrangement[1] of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid has been thoroughly investigated in the past by means of ultrafast laser spectroscopy.[2-4] Mechanistic processes in solution have been followed on the femtosecond timescale, thereby confirming the existence of a ketene intermediate that had previously been inferred from matrix isolation studies.[5] After fast relaxation from its excited singlet state, *o*-nitrobenzaldehyde yields a hot ketene that undergoes vibrational cooling before rearranging to *o*-nitrosobenzoic acid. By employing the matrix isolation technique using Ne, Ar, Xe, Kr, and N_2 as host materials at temperatures as low as 3 K, we re-investigated the fate of the ground state ketene intermediate and found that H-tunneling dominates its reactivity in the lowest vibrational state, with half-lives τ of only a few minutes. Unexpectedly, the tunneling product is different from *o*-nitrosobenzoic acid formed in the photoprocess: Once prepared in the matrix by irradiation, the ketene spontaneously rearranges to 1-hydroxybenzo[*c*]isoxazol-3(1*H*)-one *via* a concerted mechanism that is initiated by H-tunneling. Semi-classical tunneling analyses employing the WENTZEL–KRAMERS–BRILLOUIN formalism in conjunction with density functional as well as *ab initio* quantum chemical computations supplement our experiments and provide a rationale for this unanticipated mechanism.



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Carboxylate-Assisted C-H Activation of Phenylpyridines: A Gas-Phase Study

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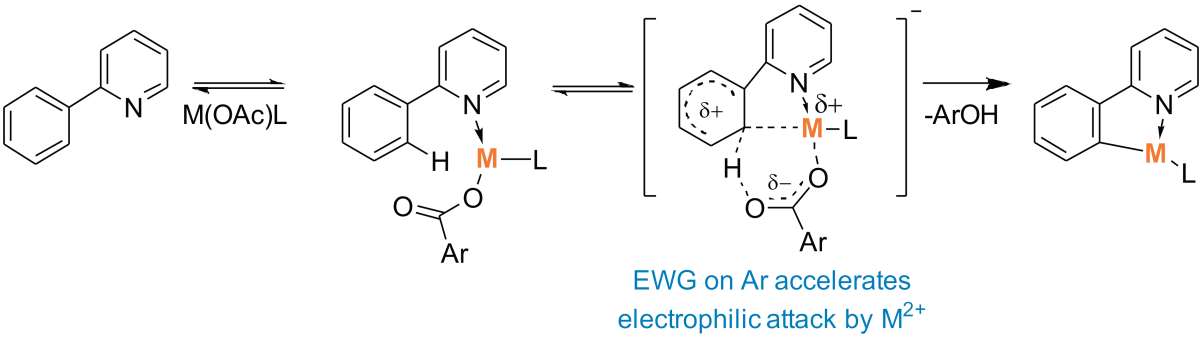
C-H bond activation is an important topic for modern organic synthesis. While selective C-H bond activation of pure hydrocarbons is still a challenge,[1,2] there are many approaches that allow the activation of C-H bonds in functionalized molecules. It has been shown that some C-H activation reactions can proceed much more efficiently, if a salt of a carboxylic acid is added to the reaction mixture, or if typical metal acetates are used as catalysts.[3]

In this work we applied mass spectrometry (MS), infrared multiphoton dissociation spectroscopy (IRMPD) and computational chemistry to study the model 2-phenylpyridine system with various metal carboxylates (Ru, Pd and Cu). MS revealed the formation of ions containing AcO^- ligands that lose acetic acid upon collision-induced dissociation (CID). We have also constructed Hammett plots that revealed that the use of stronger acids accelerates the C-H activation step.

Potential energy surfaces were calculated for C-H activation and for the loss of AcOH allowing the energy required for these processes to be determined. Infrared multiphoton dissociation (IRMPD) spectroscopy was combined with the computational studies to identify the structures of the observed ions.



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Reactions of 1-Acetoxy-1,3-Butadiene with Diazocarbonyls

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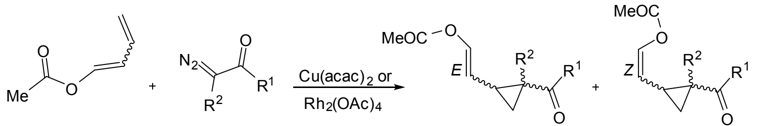
Carbene transfer to appropriate substrates is highly versatile tool for the construction of carbon frame-works with increased functional and structural complexity. The formal [2+1], [4+1], and [6+1] annulations of α,β,γ,δ-unsaturated carbonyl compounds have been widely applied in enantioselective construction of rings such as cyclopropane, oxirane, dihydrofurans, dioxoles, dihydrobenzoxepines, and other possible derivatives of them.[1-2] In this study, 1-acetoxy-1,3-butadiene was reacted with different diazocarbonyl compounds, in the presence of two catalysts. All the substituted cyclopropanes synthesized were obtained chemoselectively with respect of less hindered double bonds. Cyclopropanes from reaction of ethyl diazoacetate with 1-acetoxy-1,3-butadiene and an additional equivalent of ethyl diazoacetate yielded poly-functionalized cyclohexenes. Cyclopropanes from methyl (*E*)-2-diazo-4-phenylbut-3-enoate yielded poly-functionalyzed cycloheptadiene isomers by Cope-rearrangement.



(*E*)/(*Z*)-**6**

2a R^1 = OEt, R^2 = H
2b R^1 = OMe, R^2 = CO_2Me
2c R^1 = Me, R^2 = Ph
2d R^1 = OMe, R^2 = CH=CHPh

(*E*)-**7**

(*Z*)-**7**

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Photoswitching of Magnetic Bistable Strapped Nickel(II)porphyrins

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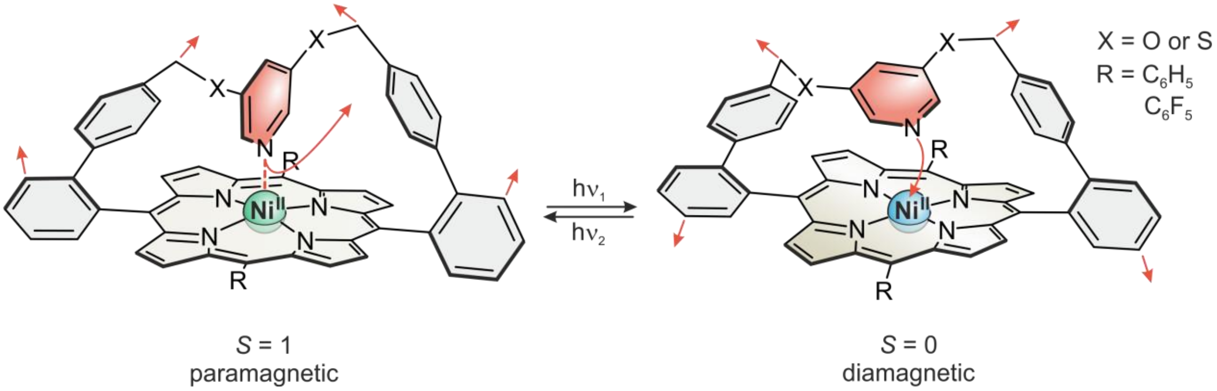
Hair Clip porphyrins combine the structural change and the ligand binding affinity of photoexcited Nickel(II)porphyrins into an intramolecular feedback.[1,2,3] This feedback allows a new highly efficient photoswitching mechanism of molecular magnetic properties without utilizing photochromic groups. The rigid bridge between two *meso*-substituents prevents the intramolecular coordination of the linked ligand in the ruffled conformation of the low spin state. After photoexcitation the bridge is stretched by the flattening of the porphyrin and forces the incorporated ligand close to the nickel ion. Subsequently axial coordination occurs due to increased ligand affinity of the high spin state and stabilizes the paramagnetic isomer permanently. By excitation with wavelengths of the paramagnetic bands the process should be reversible.



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Mechanistic Studies of the Building of B,B´,B´´-trichloro-N,N´,N´´-triphenylborazine

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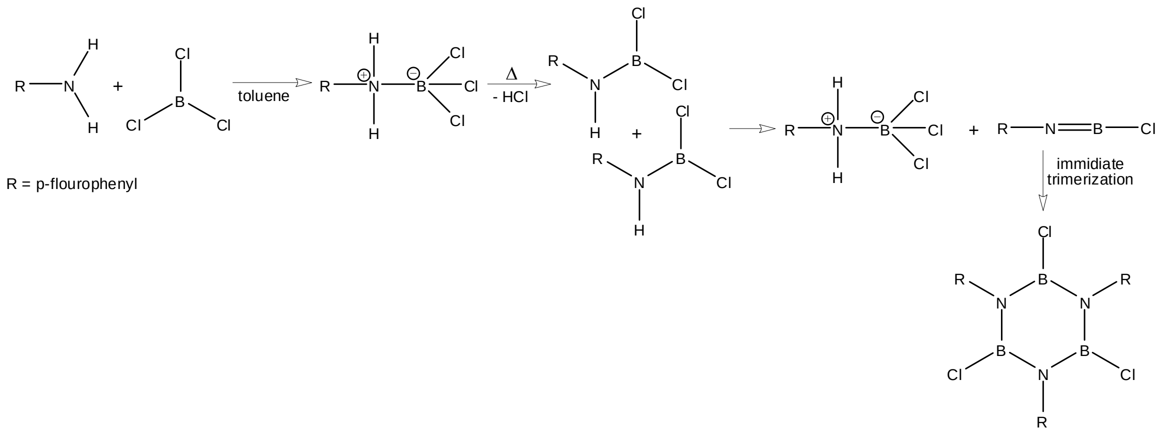
B,B´,B´´-tris(4-hydroxyphenyl)-N,N´,N´´-triphenylborazine, which was prepared from B,B´,B´´-trichloro-N,N´,N´´-triphenylborazine, can be used as a precursor for B,N and O doped carbon materials as shown by Chang *et al.*[1]. In general, these modified carbon materials are interesting because of their electronic properties and thus useful in many types of energy devices.[1]

B,B´,B´´-trichloro-N,N´,N´´-triphenylborazine was already synthesized and correctly characterized by Jones and Kinney in 1939[2], but the mechanism of its formation is not yet fully understood. Therefore, we investigated the reaction of p-fluoroaniline and borontrichloride by spectroscopic, elemental analysis, crystallographic, kinetical, and theoretical means. We suggest the following mechanistic pathway for formation of B,B´,B´´-trichloro-N,N´,N´´-triphenylborazine:



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Oxygen Bridged Diazocines: Synthesis & Optical Properties

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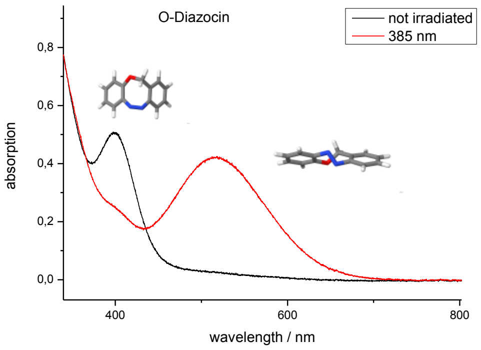
Diazocines exhibit excellent properties as photoswitches (SIEWERTSEN *et al.* in 2009).[1] However the synthesis of diazocines and the corresponding derivates proved to be difficult.[2] Using a novel approach we introduced an oxygen atom into the alkyl chain bridge. The synthesis can be achieved by a three step synthesis where the bridge between the phenyl rings is introduced by Williamson ether synthesis with high yields (> 90 %). Furthermore, the absorption band of the *trans* isomer is bathochromically shifted in comparison to the parent diazocine. Isomerization to the cis isomer is induced by irradiation with light (525 - 660 nm).



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A Computational Approach for the Discrimination of Agonists and Antagonists for Glutamate Receptors

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Ionotropic glutamate receptors (iGluR) are located at the membranes of neuronal cells and play key roles in synaptic plasticity. Proper function of the receptors is crucial for the central nervous system. Members of iGluR, become active via binding of glycine and glutamate to the subunits of the receptors. Thus, the binding sites of these subunits are important targets for pharmaceutical research. Regulation of receptor activity by introducing partial agonist-antagonist ligands to the glycine and glutamate sites became a promising strategy for the treatment of neuropsychiatric disorders, which are related with dysfunction of glutamate receptors.

An experimentally validated quantitative structure-activity relationship (QSAR) model would be enormously helpful for virtual screening of vast amount of molecules before synthesizing the ones with the highest expected activities. Intrinsic properties of molecules calculated by quantum chemical methods are one of the most common and effective approaches for QSAR modeling.

In this study, various quantum chemical descriptors are calculated to understand the link between chemical traits of molecules with their activities. These descriptors are further used to discriminate the partial agonism-antagonism nature of the ligands. The next step is to connect these molecular descriptors to their activities in order to design a robust QSAR model for ligands of NMDA and AMPA receptors. The results emerging from this study will be presented.

Towards Smart MRI Contrast Agents: Intramolecular LD-CISSS in Azoimidazole-functionalized Nickel(II)porphyrins

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Novel molecular spin switches based on intramolecular LD- CISSS (*light-driven coordination-induced spin state switch*)[1,2] are presented. The parent system consists of a Nickel(II)porphyrin covalently linked to an azopyridine ("record player" design). The *cis*- *trans*-photoisomerisation of the azo function allows the nickel(II) to be switched between a diamagnetic low spin state (*trans*) and a paramagnetic high spin state (*cis*) in solution at ambient temperature.[3,4] MRI (*magnetic resonance imaging*) investigations in DMSO reveal a great potential for applications as photoswitchable, functional contrast agents. As for medical applications, we work on the realization of the "record player" concept in aqueous solution which, among other modifications[5], requires optimized coordination of the photoswitchable ligand. In this regard, imidazole derivatives[6] were applied as imidazole is a much stronger donor ligand compared to pyridine. A geometrical and electronical tuning of the molecular design was performed aiming at optimal intramolecular coordination of imidazole as axial ligand. The most promising structures were synthesized and their switching properties will be reported.

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Quantum Chemical Calculation of $J_{(C,C)}$ Nuclear Spin-Spin Coupling Constants. A Tool for the Investigation of the Hypercoordination in bicyclic Carbocations

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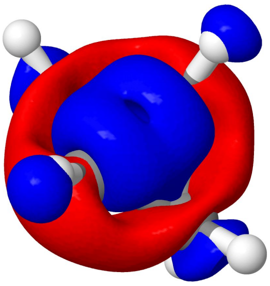
The structure of the bicyclobutonium ion $C_4H_7^+$ has been a controversially discussed topic of research for more than half a century.[1] Bicyclo[1.1.0]butane is a strained bicyclic hydrocarbon with a unique bridging bond between C^1 and C^3. This is reflected by the value of the $J_{(C1C3)}$ spin-spin coupling constant (SSCC) of J_{exp} = -15.5 Hz.

The bicyclobutonium cation undergoes a fast interconversion with isomeric cyclopropylmethyl cations even at very low temperatures (solid-state-NMR). The low energy dynamics interfere with an accurate experimental determination of NMR chemical shifts and nuclear spin-spin coupling constants (SSCC).
Quantum chemical calculations however allow an unequivocal calculation of NMR chemical shifts and SSCC for any calculated minimum structure.

Because of multiple pathways for spin-spin coupling in a bicyclo[1.1.0]butane framework the differentiation between couplings over one or two bonds is not possible. Coupling deformation density (CDD) is however a suitable tool for the visualisation of the changes in energy density of coupling nuclei. We demonstrate the application of CDD calculations to structures with a bicyclobutane framework. [2]



CCSD/cc-pVTZ//PERDEW/III-IGLO calculated C^1C^3 FC (Fermi Contribution) CDD (Coupling electron Deformation Density) for $J_{(C1,C3)}$ in bicyclobutane

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Synthesis of nano-chitosan irrigant with superior chelating ability and penetration

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Abstract:

Our first objective was to measure dentin penetrations for the unprecedented aqueous antibacterial nano-chitosan (NCS) solutions. The second objective was to compare and contrast such penetrations to those of chitosan (CS) itself, as well as sodium hypochlorite (NaOCl), chlorhexidine (CHX), and ethylenediamintetraacetic acid (EDTA), at the routinely used concentrations. Molar roots were split longitudinally by a rotary diamond saw. NCS was made by dissolving CS in acetic acid and adding tripolyphosphate (TPP), followed by a freeze-drying process. Dentin penetrations are estimated through measurements of sessile contact angles. Penetrations of probed irrigants were assessed as an inverse functions of their sessile contact angles. Accordingly, all NCS solutions showed smaller sessile angles compared to those of NaOCl, CS, and EDTA samples. Hence, NCS appeared as a superior irrigant for demonstrating a higher penetration than the latter three. It fell only behind CHX, yet, the superb chelating ability of NCS enabled it remove smear layer to a larger extend than all of our other irrigants including CHX. NCS could be considered as a new irrigant. Higher penetration was its main advantage over CS, and commercial NaOCl, and EDTA. This was witnessed with smaller sessile contact angle of NSC. Anticipated chelating effect of NCS could anchor more efficient removal of smear layer. This was another advantage of NCS over other irrigants including CHX. Other advantages of NCS included its reported biocompatibility, biodegradability and antibacterial effects. Commercialization of NCS was deemed in the near horizon.

Keywords: Nanochitosan, Chitosan, CHX, NaOCl, EDTA, Wettability, Dentin, Sessile contact angle

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Quantum chemical studies on the β-silicon effect in α-aryl-substituted ethyl and vinyl cations

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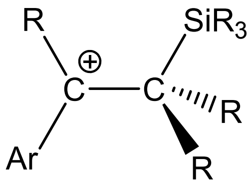
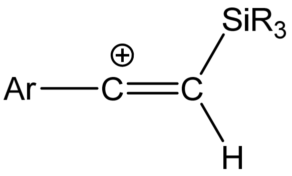
The geometries of several α-aryl-substituted ethyl and vinyl cations were optimised using 2nd order Møller-Plesset perturbation theory. NMR chemical shifts were calculated and compared to experimental values, and the electronic structure of the cations was investigated using natural bond orbital analysis methods. The effect of β-trialkylsilyl substitution was investigated. The influence of the common density fitting and local MP2 approximations on the accuracy of the calculated chemical shifts was evaluated, and the performance of several basis sets was compared. [1]





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Computational study of dynamic effects in the domino reactions.

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Non-transition state theory (TST) behavior could be detected as the results of the shape of the potential energy surface (PES) and the kinetic energy (KE) generated during the reaction.[1] Especially, energy disposition in reactive intermediates has been reported in a some of reactions.[1] A domino reaction is a multistage reaction in which activation sites successively appear. The KE that is produced from the change in the PES of the TS and intermediate is gained in the same way as energy disposition in reactive intermediates. In this study, the occurrence of energy disposition and the factor of this effect for some domino reactions (Fig.1) were analyzed using DFT calculations and Born-Oppenheimer molecular dynamics (BOMD) simulations.

BOMD simulations started at first transition state (TS1) generated products for a some systems. Energy disposition is happened in these systems. The poster presentation will be explained for factor of these effects.

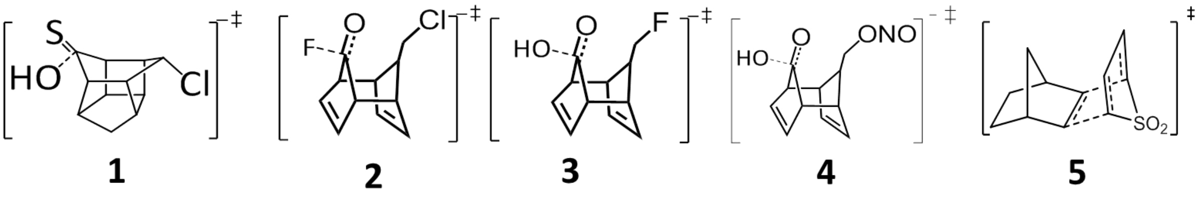

Figure 1. Investigated sysytem of some domino reactions.

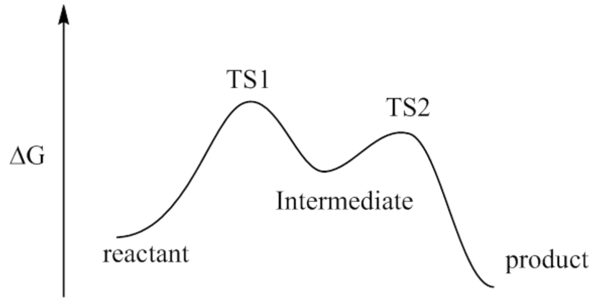

Figure 2. PES of domino reactions.

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On the Use of Urea as an Alternative for Phosgene in the Production of MDI

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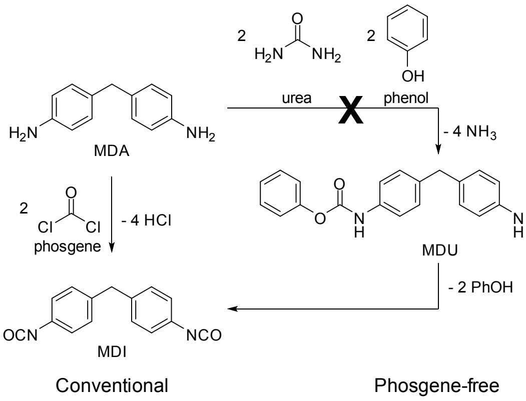
MDI (methylene diphenylene diisocyanate) is a large volume chemical and a key constituent of a variety of foams, elastomers, coatings, adhesives etc. It is conventionally produced by phosgenation of MDA, and although this route is efficient and atom-economic, there are some disadvantages associated with the use of phosgene: its toxicity requires the use of expensive specialized equipment and sophisticated operations to mitigate the associated risks.



Alternative routes to isocyanates nearly invariably make use of the thermolysis of carbamates. For the production of MDI the reaction has to be high-yielding and clean because options for purification are very limited. After comparing the likely economics of several routes, it was concluded that the urea-based route was most likely to be a viable future process to consider for the production of MDI.

Results show that a one-pot approach, where MDA, urea and phenol are made to react, is not suitable for a commercial process, because it is too slow, and needs too much phenol. The rate is not limited by ammonia mass transfer, but by the chemistry itself. The amount of phenol incorporation is initially low, simply because the phenol is not reactive enough, and because the ureas are too stable.

Several possible multi-step procedures were investigated, but these proved to be problematic as well, either because of the relative stability of ureas, or because of decomposition of the highly reactive isocyanic acid intermediate.

We will continue to look for alternative non-phosgene processes in the future.

Dynamics in Enzyme Catalysis– The Radical SAM Enzyme QueE

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Enzymes that react *via* a radical mechanism, catalysed by the cofactor *S*-adenosyl methionine (SAM), have attracted recent interest because of their involvement in chemical processes leading to products of potential use for anti-viral, anti-cancer and antibiotic treatments. While a general framework for the initial catalytic mechanism has been established over the past years[1] much less is known about the subsequent chemical rearrangements in most cases. A thorough knowledge of these mechanisms can lay the foundation for rational protein engineering, with the potential for opening up a wealth of novel biologically-accessible chemistry.

We have examined a number of key dynamic processes for the mechanism of 7-carboxy-7-deazaguanine (CDG) synthase (QueE), which catalyses the rearrangement of 6-carboxy-5,6,7,8-tetrahydropterin (CPH4) into CDG as a key step in queosine biosynthesis. This intermediate is a precursor to a number of interesting streptomycin antibiotics, and molecules with anti-viral and anti-cancer properties.[2]

In particular, the dynamic features - influencing reactivity and mechanism - of cofactor and substrate binding will be presented, with a precise look at the role of Mg^{2+} binding and coordination, which is known to be important for activity.[3] Results will be presented in the context of DFT calculations, molecular dynamics and QM/MM simulations, with an outlook to the future and scope for engineering the QueE reaction.

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IR spectral revealing of hydrogen bond between haloforms and tetraclorides at cryo temperatures. E-Cl_4 as proton acceptors.

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Andrej Vorotynsev, Anton Petukhov and Ilya Vorotynsev

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The consideration of the key factors in stabilizing of condensed state will lead us to control a wide range of important processes from obtaining high-purity gases to converting enzymes or proteins. But for this purpose it is necessary to understand the behavior of simple molecules in condensed phase. In the recent work this attempt has been made using IR spectroscopy, for EH_nX_m compounds, which were selected as models (E = C, Si, Ge; X = Cl, Br; n = 0, 1; m = 3, 4).

For all three ECl_4 molecules in the middle infrared region a few splitted bands were detected. Some of them disappear at film heating, and the amount of bands and their position notably change. A similar behavior of spectra can be explained by structural rearrangement of the molecules. We have assumed that the observed effect is tautomerizing of chlorine atoms, leading to the change of molecular symmetry and charge density. This hypothesis was confirmed by DFT calculations.

In the low temperatures spectra (30K) of mixture (1:1), containing Si- or Ge-tetrachloride and chloroform or bromoform, a new single band in CH stretching region has been detected. This one was assigned to CH bond stretching of CHX_3 molecule involved in the hydrogen bond. The band disappears after sample heating over 150 K, and appears again at cooling to initial temperature (30K). The observed band has an isotopic shift for deuterated haloforms. In case of CCl_4 the bonding between mixture components was not found. In the transition from $SiCl_4$ to $GeCl_4$ the manifestation of the hydrogen bond becomes more distinct.

The described hydrogen bonding is formed with the participation of mobile hydrogen atom of haloforms and displaced chlorine atoms of E-Cl_4 molecules. The increase of length and polarization of E-Cl bond in a series of C-, Si and Ge promotes tautomerism of Cl-atoms, as well as larger charge transfer from Cl- to H- atoms in the cluster. As a result, the enhancement of intermolecular bonding should be observed. This trend corresponds to the increase of the relative intensity for the stretching band of the hydrogen bond at the transition from silicon to germanium.

This work was supported by the RFFR, grant 14-08-00898-a.

Direct Alkylation of Gold Surface with Solutions of C_1 - C_4 *n*-Alkylstannanes

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We report methods for ambient solution coating of a gold surface with a self-limiting monolayer containing alkyl chains attached by one or more C-Au bonds, and no other elements. The alkyl transfer agents are organostannanes carrying short alkyls, methyl to n-butyl. This is a generalization of our previous finding that under ambient conditions solutions of alkylated stannanes carrying a leaving group deposit alkyl-containing monolayers on gold surface,[1] and is in accord with break-junction conductivity measurements on single molecules attached to gold through carbon by transfer from trimethylstannyl derivatives.[2]

Acknowledgment

The research leading to these results has received funding from the European Research Council under the European Community's Seventh Framework Programmme (FP7/2007-2013) / ERC grant agreement no. 227756, the grant agency of the Czech Republic (14-02337S) and the Academy of Sciences of the Czech Republic RVO: 61388963.

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Accurate pK_a Values of Organic Catalysts: Rationalizing Reactivity

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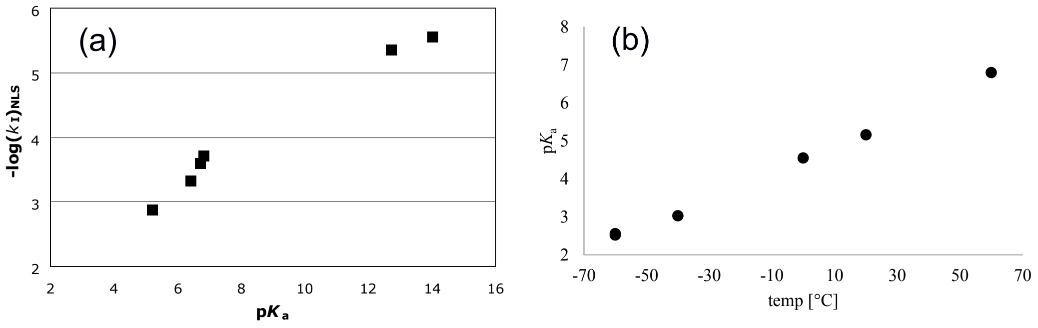
Most of modern synthetic chemistry relies on catalysts one way or another. The use of acids and bases as reaction promotors is probably the earliest form of catalysis. The core characteristic of acid-base strength, the pK_a value, is often useful for rationalizing the kinetic data for particular acid-base catalysts.

Recently we have been involved in measurements of different types of chiral Brønsted acid catalysts as well as various triarylphosphanes that together with electron-deficient boranes make up a *Frustrated Lewis Pair* (FLP) and are used as catalysts in hydrogenation reactions using molecular hydrogen.

The pK_a values of 17 chiral phosphoric acids as well as phosphoric and/or sulfonic imides with varying substitution and linker type were measured.[I,II] The results revealed for the first time correlation between the pK_a of these catalysts and the rate constant of Nazarov cycliazation reaction. For 8 phosphane bases it was shown that the temperature of reversible H_2 activation by the FLP is dependent on the pK_a of the base.[III]



(a) –log(k_I) *vs* pK_a of acid catalyst (b) pK_a of phoshane *vs* H_2 activation temperature

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Ionic liquids as solvents for organic reactions: the importance of microscopic interactions in predicting reaction outcome

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Ionic liquids are attractive alternatives to molecular solvents as they have negligible vapour pressure and low flammability, and variation of the ion combination used allows for 'tailor-made' physical and chemical properties.[1] Further, ionic liquids can affect organic reaction outcomes differently to molecular solvents.[2] Thus far, interactions between the ionic liquid components and specific sites on the reagents and transition state (such as charged centres, lone pairs and π systems) have been identified as affecting reaction outcome; a comprehensive understanding of these interactions is necessary to allow prediction of ionic liquid solvent effects.[2]

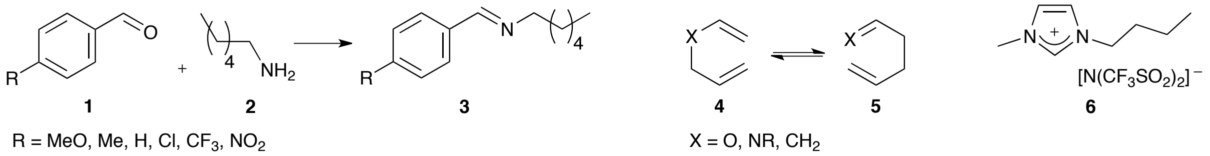

Figure 1: The condensation reaction studied (left), the pericyclic rearrangements of interest (middle), the ionic liquid [Bmim][$N(CF_3SO_2)_2$] (right).

In order to expand our understanding of ionic liquid solvent effects the representative condensation process between species **1** and **2** has been thoroughly investigated through a number of temperature-dependent kinetic studies to examine: 1) the effect of changing the nature of the cation[3] and anion[4] of the ionic liquid on the addition step; 2) the effect of varying the electronic character of the *para* substituent on the electrophile **1**, to determine whether our understanding of substituent effects in molecular solvents can be applied in ionic liquid media; and 3) the effect of the ionic liquid **6** on the elimination step. The effect of salt **6** on pericyclic processes, including the Claisen, Aza-Claisen and Cope rearrangements, is also being examined to provide insight into the importance of hydrogen bonding when an ionic liquid solvent is used. The overall aim of this work is to understand the microscopic origin of the changes in reaction rates and the products seen when using an ionic liquid, so that they can be rationally applied as solvents in organic synthesis.

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High Internal Olefins received from Renewable Sources

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There is increased interest in application of organic substances of vegetable origin as an alternative fuel and also for preparation of other useful products. First of all, it has been connected with renewability of this fuel resource and its ecological purity. In our work, unsaturated acids which are obtained from vegetable oils can increase the petrochemistry feedstock. So that, high internal olefins, such as heptadecene-8, are received by decarboxylation reaction of the high unsaturated acids. These obtained internal olefins are important feedstock in the synthesis of surface-active compounds, insecticides, and in the paper industry.

In the decarboxylation reaction, the various catalysts, such as oxides and nitrides of transition metals, palladium on coal, etc. have been used. In our investigations, series of catalysts, particularly, natural and synthetic aluminosilicates, nano-sized catalytic systems on the basis of Mg and Ti oxides has been tested for decarboxylation of organic acids received from vegetable oils. However, it is determined that, the best results obtained in the application of nano-sized MgO and TiO_2 catalysts. The structure of particles of nano-sized metal oxides has been studied on the atomic-force microscope C3MY-5 in semi-contact mode. It has been established that, an average size of particles of nano-sized magnesium oxide is in the range of 100 nm, and for titanium oxide – in the ranges of 20-25 nm.

Synthesis of high molecular olefins such as heptadecene-8 is mainly two steps process consisting hydrolysis and decarboxylation. As a feedstock, we have used different vegetable oil such as corn oil, canola oil, sunflower oil etc. First, unsaturated acids are obtained from vegetable oils by hydrolysis. Then, decarboxylation reaction of those unsaturated acids are carried out. Heptadecene-8 is obtained mainly from oleic and linoleic acid. The decarboxylation reaction is conducted in a continuous flow reactor, 250-400 ^{0}C temperature, 1 h^{-1} volume rate over nano-sized MgO and TiO_2 catalysts.

It is determined that, the best results are observed in 350^{0}C and volume rate 1.0 h^{-1}, in both cases of nano-sized magnesium oxide and titanium oxide. In these conditions, the conversions of oleic acid are 99.1 and 99.2 %, the acidic numbers of reaction product are decreased to 1.5 and 1.3 mg KOH/g, accordingly. The application of nano-sized catalysts – magnesium and titanium oxides allows to decrease the process temperature correspondingly.

The achieved decarboxylation product of oleic acid – heptadecene-8 has been identified by physical-chemical analysis method and had the following indicators: refraction index 1.4430; density 0.8021 g/ml, boiling temperature 173^{0}C (15 mm Hg).

As it was known, heptadecene-8 refers to industrially-important high internal olefins of C_{17} series and has applications in various areas of industry and agriculture. In this regard, synthesis of the similar internal olefins has certain practical and theoretical interest.

Self-Healing Polymers from Polybenzoxazines

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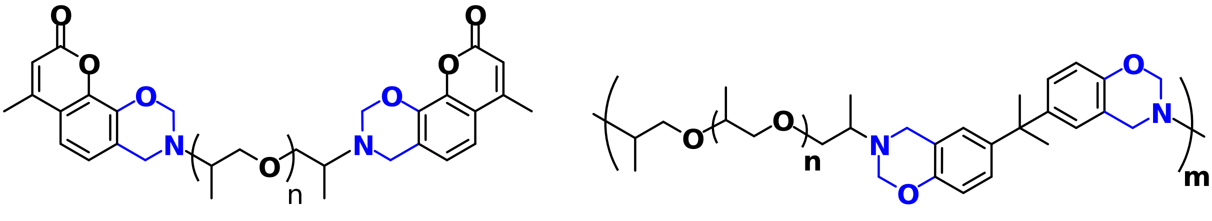
Self-healing strategy for poly(propylene oxide)s bearing benzoxazine units (PPO-Benz) through supramolecular attractions and poly(propylene oxide)s bearing coumarine-benzoxazine units (PPO-CouBenz)s based on light induced coumarine dimerization reactions is described. The coumarine groups present in the structure underwent efficient dimerization upon irradiation at λ>300 nm as confirmed by the UV-vis spectral investigations.[1] Moreover, addition of carboxylic acid containing benzoxazine into PPO-Benz films resulted in better healing by increasing the hydrogen bonding sites.[2]



(PPO-CouBenz)

(PPO-Benz)

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New Singlet Oxygen Donors Based on Naphthalenes

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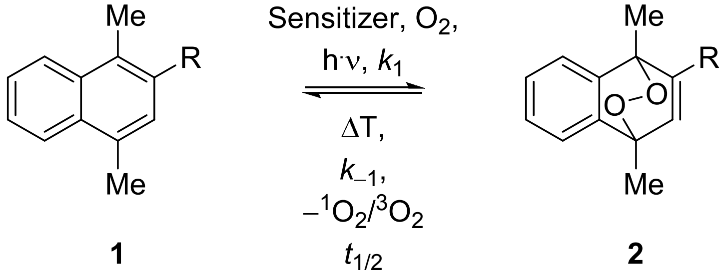
Singlet oxygen ($^1O_2$) is a very important oxidant in synthetic organic chemistry.[1] Furthermore, it plays the central role in the cure of cancer by means of photodynamic therapy (PDT).[2] However, the $^1O_2$ is generated by a photosensitized reaction, which causes side effects like light sensitivity of uninvolved tissue. Hence, endoperoxides **2** which are easily available by photooxygenation of naphthalenes **1** are an attractive alternative. These donors liberate $^1O_2$ under simple warming in the dark. First *in vitro* tests show encouraging results,[3] but these carriers suffer from short half-life times ($t_{½}$).[4] Here, we will report about the synthesis of new singlet oxygen donors **2** with enhanced stabilities.[5] We determined $t_{½}$, singlet oxygen yields, and thermodynamic as well as kinetic data. In combination with theoretical calculations we will propose different reaction pathways of the thermolysis with the release of $^1O_2$ and $^3O_2$.



1 **2**

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A thermally accessible triplet diradical state of a silyl substituted cyclobutadiene

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Ever since Kekulé first attempted the preparation of cyclobutadiene in 1872, this fascinating molecule presented a challenge to experimental and theoretical chemists. It was not until the mid-1970ies that cyclobutadiene derivatives could be synthesized and characterized. Herein, we report the observation by EPR spectroscopy of a thermally accessible triplet state of 1,2,3,4-tetrakis(trimethylsilyl)cyclobuta-1,3-diene (**1**). To our best knowledge, **this is the first example in which a triplet diradical state of a cyclobutadiene derivative was observed spectroscopically**. An EPR study of **1**, at 300K–395K, shows a typical spectrum for triplet diradicals with zero-field splitting (ZFS) $|D(\mathbf{2})|_{exp}=0.17 cm^{-1}$. From the temperature dependent EPR absorption area we derive a singlet-triplet energy gap, E_{ST}, of 14.2 $kcal \cdot mol^{-1}$. This value is supported by quantum chemical calculations of model **1** and **2** (in which the $SiMe_3$ substituents were replaced by SiH_3) at the CCSD(T)/def2-TZVPP//B3LYP/6-311+G(d,p) level, that gives $E_{ST}=12.4 kcal \cdot mol^{-1}$. To determine D theoretically, D values of other related delocalized organic diradicals were calculated at the B3LYP/TZVP level giving a linear experimental-theoretical correlation ($D_{exp}=1.565 \cdot D_{calc}$, $R^2=0.99$). Using this correlation we determine $|D(\mathbf{2})|_{calc}=0.167 cm^{-1}$, in excellent agreement with $|D(\mathbf{2})|_{exp}=0.17 cm^{-1}$. The mechanism of the retro-cycloaddition of **1** (*Scheme 1*) and the role of **2** in this process will be discussed.

Scheme 1

Reversible Spin-Switching of Fe^{III} Porphyrins

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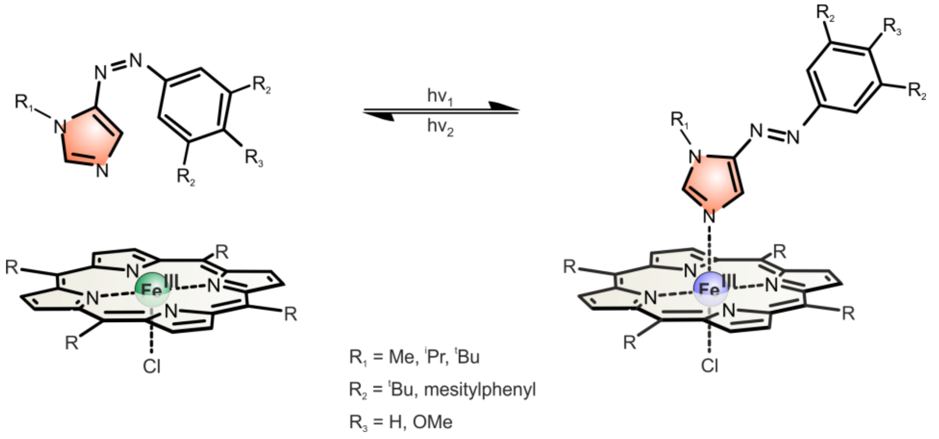
Magnetic resonance imaging (MRI) is an important technique for medical diagnosis and research. Common contrast agents are gadolinium complexes. A novel approach is to investigate photoswitchable MRI contrasts agents. Ni-porphyrins with covalently tethered azopyridine ligands are applied. The photochromic complexes switch between the diamagnetic low-spin-state (MRI silent) to the paramagnetic high-spin-state (MRI active) by irradiation with light of specific wavelengths. This process is known as light-driven coordination-induced spin-state switch (LD-CISSS).[1,2] Within this work the concept should be realized with Fe(III)-porphyrins which require different structures. Five-coordinated complexes have a spin of 5/2 (high-spin), whereas six-coordinated complexes tend to have a spin state of 1/2 (low-spin).[3] The spin-switching is realized by association and dissociation of 5-(phenylazo)imidazoles. These photodissociative ligands (PDL) are able to coordinate as the *trans*-isomer and dissociate upon irradiation as the *cis*-isomer.[4] The higher difference of the magnetic moment between the MRI active and the MRI silent state should improve the efficiency of the contrast switching.



R_1 = Me, ^{i}Pr, ^{t}Bu
R_2 = ^{t}Bu, mesitylphenyl
R_3 = H, OMe

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Reactions of Boriranes and Borirenes with Unsaturated Hydrocarbons: A Computational Study

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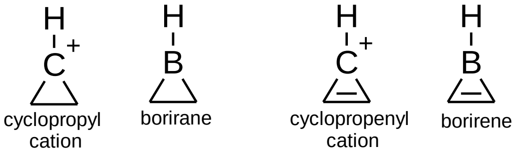
Boriranes and borirenes are the three-membered ring compounds containing one boron atom and are isoelectronic to the cyclopropyl and cyclopropenyl cations, respectively. They can be obtained for instance by the photorearrangement of boranes,[1] by the acetone or diphenylacetylene cycloaddition reaction with methyleneborane,[2] or by the borylene transfer to unsaturated hydrocarbons.[3,4]

To study their reactivity towards unsubstituted and substituted unsaturated hydrocarbons (ethyne or ethene), boriranes and borirenes with various electron donating and electron withdrawing substituents on boron atom (R = H, Me, Ph, NH_2, Cl, F) where chosen. All the individual species on the potential energy surface were computed at the CCSD(T)/def2-TZVP//M062X/6-311+G** level of theory.

The reaction of electron deficient boron atom and the π-system of the hydrocarbon can proceed according to two competitive mechanisms depending on the substitution of hydrocarbon. The reaction of borirane or borirene with unsubstituted hydrocarbon is the stepwise ring expansion. On the other hand, the reaction of boron heterocycle toward hydrocarbon with strongly electron withdrawing substituents can lead to borylene transfer to the hydrocarbon.



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Photorearrangement of 1-Furylpropenones-2 Into Fluorescent Products Under UV-Irradiation

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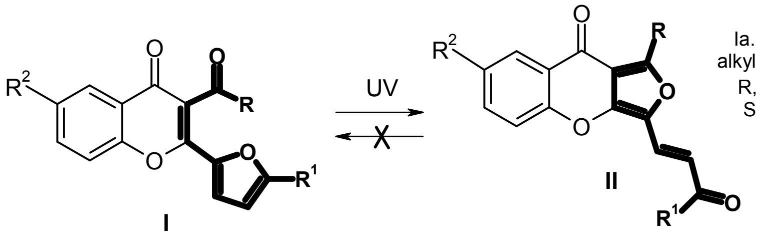
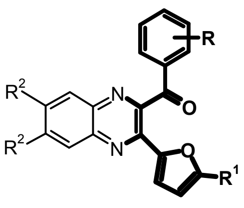
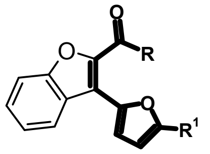
Earlier it has been shown that UV-irradiated acylchromones Ia that do not manifest fluorescence are irreversible rearrange to fluorescent furano[3,4-b]chromenones II. We have synthesized a wide range of benzopyranes Ia. Based on the latter, we have developed multilayered recording media for optical discs of the WORM type [1].



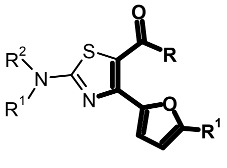
Ia. R = o-R-Ph,m-R-Ph, p-R-Ph, alkyl or aryl substituted heterocycles; R,R^1,= alkyl, aryl, hetaryl, NR^{3}R^4, SR^3, OR^3, CH$_2$SR^3, CH$_2$NR^{3}R^4, CH$_2$OR, Hal, NO$_2$, etc.



Ib. R,R^1,R^2, = H, Me, Hal



Ic. R,R^1,R^2= Alkyl, Br, Cl, Aryl, Hetaryl, NO$_2$,



Id. R = H, Me, Hal, Aryl, Hetaryl
R^1,R^2 = morpholine, pipyridine
R^3 = substituted Aryl or Hetaryl

This work is devoted to development of methods for synthesis and the study of the photochemical properties of their analogues Ib-c and the fluorescence of photoarrangement products IIb-c.

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A Molecular Assembler for Phosphate Condensation

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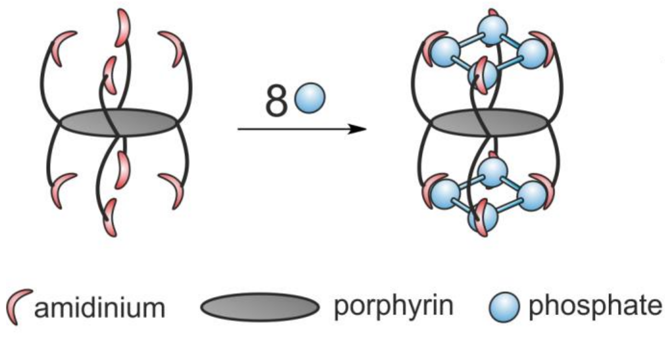
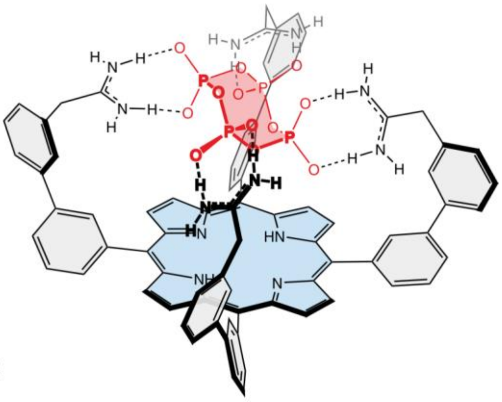
ATP-synthase is an enzyme that is able to condensate adenosine diphosphate and monophosphate to adenosine triphosphate which is a natural energy storage.[1] This work is focused on building an artificial assembler that is able to condensate monophosphate to oligophosphate in order to mimic ATP-synthase.

Based on quantum chemical calculations this receptor is designed to strongly bind cyclotetraphosphate. Due to the higher affinity of the tetramer compared to the monomer the condensation reaction inside the receptor is highly favored.

The assembler consists of a *meso*-substituted porphyrin as a scaffold and amidinium units as binding sites. This design fits in size and four-folded symmetry to the tetramer which after release hydrolyses to the stable linear triphosphate to overcome microscopic reversibility.





simplified structure, PBE/SVP

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The Solvolysis Mechanism of Secondary Tosylates in 50% TFE

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Whether simple secondary cation intermediates can be formed in polar but weakly nucleophilic solvents or not has been the subject of debate for a long time. No clear-cut conclusion has been reached despite a series of mechanistic studies with 2-propyl and 2-butyl substrate.[1,2]

In this work, 2-butyl, 2-pentyl and 2-octyl tosylates were studied; these all solvolyse at very similar rates ($k \sim 1$ ✐ 10^{-5} s^{-1}). Slow racemization of S-2-butyl tosylate (~1.8 ✐ 10^{-7} s^{-1}) is observed during solvolysis. This phenomenon is attributed mainly to a hydride transfer mechanism as S-2-pentyl and R-2-octyl tosylates do not show any significant racemization. Rearrangement of 2-pentyl tosylate to 3-pentyl tosylate and vice versa is observed during solvolysis and is attributed to 1,2-hydride transfer. Product analysis of 2-octyl tosylate showed only three products: the corresponding alkene, alcohol and trifluoroethyl ether. The alkene and alcohol are all stable under the reaction conditions excluding racemization occurring via the products. The stereochemistry of the 2-octanol product has been studied for the reaction of R-2-octyl tosylate by derivatizing the corresponding alcohol to 4-nitrobenzoate, and showed a large but not complete facial selectivity (8% R-2-octanol).

These results were consistent with a step-wise mechanism with an ‘open’ cation intermediate, which is being probed by applying ^{18}O isotope exchange methods.[4,5] These data will be reported along with a detailed mechanistic explanation of these reactions.

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Synthesis of One-Dimensional ZrB_2 by an Organic Reaction

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One-dimensional (1D) materials can increase mechanical properties along the long axis of the reinforcement for the composites because of the transfer of stress across the reinforcement-matrix interfaces parallel with the load. In this study, 1D hexagonal-prism-like ZrB_2 particles were synthesized by an organic reaction route using zirconium n-propoxide, boric acid, acetic acid and fructose. Fructose was acted as both a modifier and a carbon source for carbothermal reduction reaction. For comparison purposes, both nascent state gel and aged gel were used to clarify the aging-time-dependent mechanism for ZrB_2 synthesis. As a result, a single phase ZrB_2 could only be obtained from the aged gel with the optimum both fructose and acetic acid to zirconium n-propoxide molar ratios of 1.2 and 5, respectively, reduced at an optimum temperature of 1550 °C for 2h. Additionally, it revealed a perfect hexagonal-prism-like morphology for the ZrB_2 particles with a uniform size and shape distribution, and average particle size of *ca*. 0.8 μm in diameter of excircle of the hexagonal cross-section.

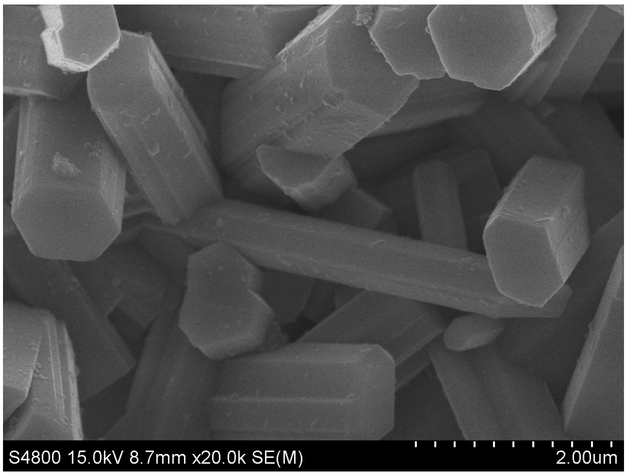

Fig. SEM image of ZrB_2 particles calcined at 1550 °C for 2 h using an aged gel.

Mechanistic study of fulvic acid assisted drug propranolol photodegradation in aqueous solution

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This study is devoted to the photochemistry of fulvic acid (FA) (Henan ChangSneng Corporation) and the effect of FA on photodegradation of propranolol (PR) (hydrochloride salt) (99%, Acros) in aqueous solution by laser flash and steady state photolysis methods. Flash excitation (355 nm) of FA solutions leads to instant appearance of wide absorption band with maximum at ≈ 620 nm. In oxygen-saturated solution we observed dramatic reduction of the intermediate lifetime, which allows us to suggest FA triplet state (^{3}FA) formation. Rate constant of ^{3}FA quenching by oxygen is equal to 7×10^8 $M^{-1}s^{-1}$. Kinetic curves of ^{3}FA decay in deoxygenated solution could be well fitted by the third-order kinetic law. ^{3}FA decay kinetics depends weakly on pH (2-10), but the amplitude of the transient absorption signal reaches the maximum value in the neutral (6-7) media and falls in alkaline and acidic solutions. This fact is most likely explained by the presence of acid-base equilibriums for the chromophores of FA, as well as by the quenching of excited singlet chromophore states with protons of medium, which affects the efficiency of intersystem crossing. Global processing of a set of kinetic curves in the range of 50-800 μs allowed us to determine the characteristic times of the FA triplet state decay: 4.3, 54 and 830 μs.
Pure PR was found to be stable under irradiation with UV-A but stationary photolysis (365 nm) of oxygenated FA and PR mixture led to photodegradation of amine drug. Flash excitation led to reduction of ^{3}FA yield, thus indicating of complexation of FA with PR and static quenching of ^{3}FA by PR via an electron transfer mechanism. Less than 1% of the total ^{3}FA participated in PR degradation, and the quantum yield of this process was 3.5×10^5. The triplet state yield ($\phi_T \approx 0.6\%$) and the T–T absorption coefficient ($\varepsilon_T^{620\ nm} = 5\times10^4\ M^{-1}\cdot cm^{-1}$) were estimated for the first time by modeling the yields of the FA triplet state in the presence of PR [1].
This work was supported by the Russian Foundation for Basic Research (projects 11-03-00268, 12-03-00482, 14-03-31003_mol_a).

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Thifluoromethylhydroxycarbene

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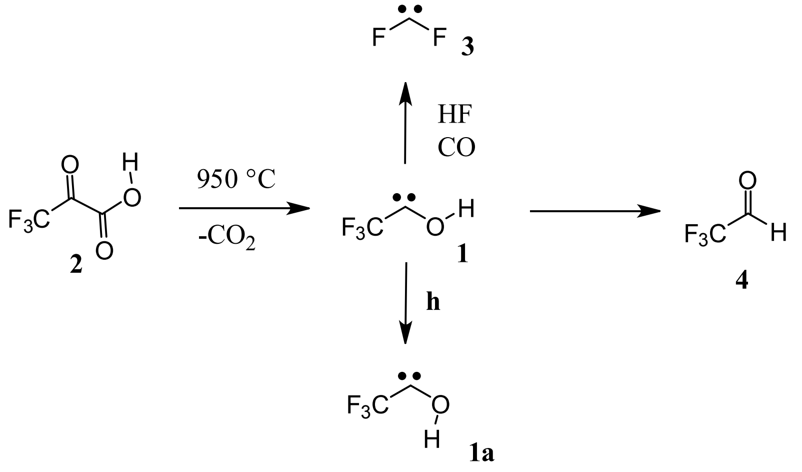
The thifluoromethylhydroxycarbene **1** was synthesized in the gas phase via high-vacuum flash pyrolysis of 3,3,3-trifluoro-2-oxopropanoic acid **2** at 950 °C and isolated in an argon matrix at 10 K. The **1** is a hitherto unobserved ? -acceptorsubstituted singlet carbene of the recently discovered hydroxycarbene family.[1-3] The pyrolysis products were characterized by IR and UV-vis spectroscopic methods. Under harsh pyrolysis conditions, the **1** undergoes rearrangements to difluorocarbene **3** with activation barrier of 24.88 kcal mol^{-1} calculated at the M062x/6-311++G(2d,2p) level of theory. Moreover, the matrix-isolated thifluoromethylhydroxycarbene **1** undergoes [1,2]H-tunneling through a barrier of approximately 34.4 kcal mol^{-1}, yielding 2,2,2-trifluoroacetaldehyde **4**. The half-life of **1** is 144 ± 11 h at 10 K. Interestingly, irradiation of **1** with visible light (λ=465 nm) for several minutes produces the cis- thifluoromethylhydroxycarbene **1a** in a clean reaction. The experimental IR spectra are in agreement with results from DFT calculations.



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Photochemistry of 1,3-Dithian-2-ylpyronin: A Mechanistic Study

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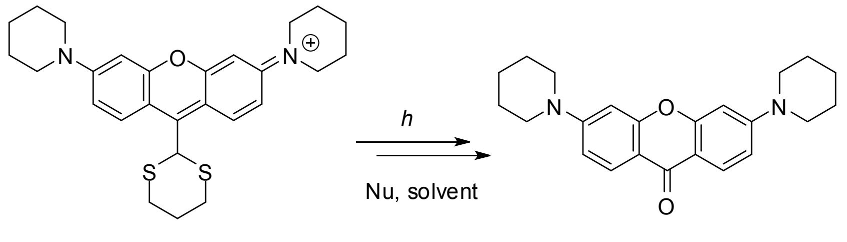
1,3-Dithianes can serve as a protecting group for carbonyl compounds. In our recent work, we have reported that a 1,3-dithian-2-ylpyronin analogue undergoes a C–C bond cleavage upon excitation with yellow light.[1] Unlike previously published photoinitiated deprotection protocols,[2] this transformation takes advantage of visible light absorption of a pyronin scaffold in the absence of photosenzitizers.

In this study, we present a detailed investigation of the possible pathways leading to both C–S and C–C bonds cleavage in the title derivative using laser flash photolysis, steady state photolysis, kinetic and quantum yield measurement studies. Elucidation of the structure of the reaction intermediates was accomplished by combination of advanced mass spectrometry techniques coupled with ion spectroscopy and is supported by quantum-chemical calculations.



ACKNOWLEDGEMENT:

This work was supported by the Grant Agency of the Czech Republic (13-25775S), the Czech Ministry of Education (LO1214) and (LM2011028) (P.K.), and European Social Fund and the state budget of the Czech Republic (CZ.1.07/2.3.00/30.0037) (P.Š.)

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Nucleofugality of Some Aryl and Alkyl Carbonates

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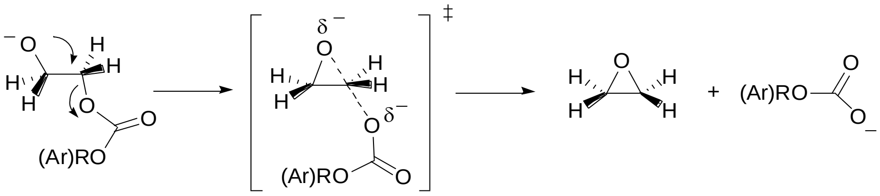
The leaving group abilities (nucleofugalities), defined by nucleofuge-specific parameters (N_f and s_f), were determined for some aryl and alkyl carbonates from solvolysis rate constants of X,Y-substituted benzhydryl carbonates in 80% aqueous ethanol by applying the previously established linear free energy relationship equation (1),[1] which had also been employed in determining nucleofugality of other types of leaving groups.[1,2] N_f values can be utilized for comparing heterolytic reactivities of diverse types of leaving groups in a wide range of reactivity. Furthermore, combining previously determined parameters in equation (1) for various electrofuges and nucleofuges, the duration of a particular solvolytic reaction can be estimated. Values of s_f parameter (which has a related meaning as the Hammett–Brown ρ^+ parameter) correlate well with corresponding solvolytic log *k* of benzhydryl carbonates, indicating that more reactive carbonate leaving groups (smaller values of s_f) yield earlier TS which is in agreement with Hammond postulate.

$$\log k\ (25\ °\mathrm{C}) = s_f\,(E_f + N_f) \qquad (1)$$

The applicability of DFT model reaction presented in Scheme 1 (M06-2X method) has been examined for determination of N_f parameters of carbonate leaving groups (including HCO_3^-). A very good correlation between experimental and calculated reactivities enables further extending the nucleofugality scale.



Scheme 1. DFT model reaction

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Synthesis of Fluorinated Tetrahydropyrans via Prins Cyclization of Aldehydes and Homoallylic Alcohols Using Electrochemical Oxidation

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Prins cyclization is one of the most reliable methods to synthesize tetrahydropyrans using aldehydes and homoallylic alcohols as the starting materials in the presence of an acid reagent to promote the reactions. Especially, it is important to introduce a fluorine atom in tetrahydropyrans, because a fluorine atom affects their properties and increases biological activities. So far, there have been a few papers, in which preparation of the fluorine containing tetrahydropyrans using the Prins cyclization are featured. Yoshida and co-workers reported that the intramolecular cyclization of ✓-stannyl ether using electrochemical oxidation afforded fluorinated tetrahydropyrans.[1] It is also reported the BF_3-OEt_2 [2] and the ionic liquid [3] such as Et_4NF-$5HF$ can be utilized in these reactions. However, these reports use the complicated starting material or expensive reagents.

Herein, we wish to report a simple and convenient synthesis of fluorinated tetrahydropyrans via Prins cyclizations of aldehydes and homoallylic alcohols using *in-cell* electrochemical oxidation in Bu_4NBF_4/CH_2Cl_2. The generation of electrochemically generated acids (EGAs) under the electrolysis condition was indicated.

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Understanding Structure and Reactivity of High-Spin Nitrenes

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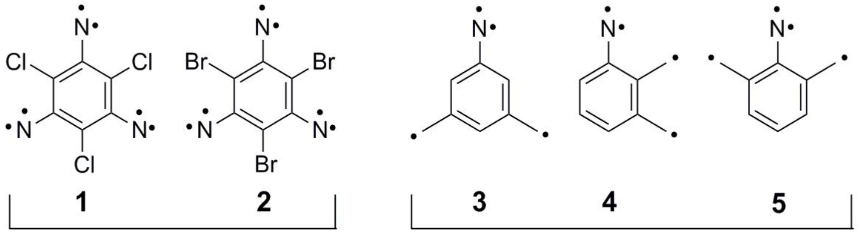
This work is focusing on observing high-spin nitrenes at cryogenic conditions, from surprisingly stable septet trinitrenes **1,2** to very reactive nitreno radicals **3,4,5**, the latter designed by combining both xylylene and phenylnitrene open-shell moieties on a spin-controlled fashion.

Herein, we report the trapping of a highly symmetrical trinitrene, 1,3,5-trichloro-2,4,6-trinitrenobenzene **1** as well as the similar tribromo derivate **2**. They show robust septet ground states and stability with no precedents on those kinds of compounds, it is actually the first UV spectrum reported for organic molecules with septet ground states. By means of the matrix isolation technique, septet trinitrene **1** was successfully isolated in inert gas matrices (Ne, Ar, Xe) at low temperatures (3-10K) allowing consequent spectroscopic characterization (IR and UV-Vis) with assessment of quantum chemical calculations. We have also succeeded in isolating trinitrene **1** in reactive hosts such as pure oxygen and water matrices in high yields. In case of water matrix experiments, trinitrene **1** was stable even at 170K, temperature where ice starts subliming; therefore, we propose water as novel host for studying reactions at unusual higher temperatures.

On the other hand, the isomeric nitreno radicals 2-, 4- and 5-nitreno-m-xylylene were generated by irradiation of the corresponding azido-diiodo precursors in cryogenic matrices and characterized by electron paramagnetic resonance spectroscopy. Moreover, interesting discussion is coming into play about spin ground state of the different isomers, **3, 4, 5** and their photo-stabilities in inert gases and p-H_2 matrices.



stable septet trinitrenes

reactive nitrene-xylylene tetraradicals

Reaction of Triplet Phenylnitrene with Molecular Oxygen

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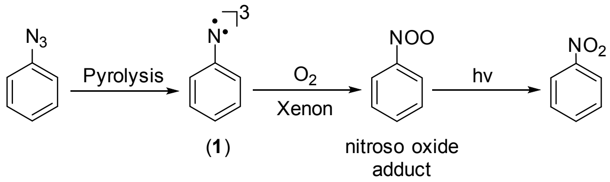
The reaction of triplet phenylnitrenes with oxygen has been investigated in many experimental and theoretical works for more than 40 years now.[1] However, the experimental works about this reaction in matrices at low temperatures do not involve the triplet phenylnitrene (1) but rather some derivative, like para-substituted (p-amino or p-nitro) phenylnitrene, in order to minimize the photochemical conversion to the cyclic ketenimine.[2]



In this work we present an approach using pyrolysis to produce the triplet nitrene, in order to study the reaction of 1 with oxygen at low temperatures. We formed 1 in sufficient yields that allowed us to study the reaction in $^{16}O_2$-doped argon and xenon matrices. We were able to isolate and characterize the nitroso oxide adduct of the thermal reaction and study the photochemical conversion to the nitrobenzene, which was identified by comparison with an authentic matrix isolated sample. The reaction was also carried out in $^{18}O_2$-doped matrix and the experimental shifts of the IR bands are in good agreement with the theoretical isotopic shifts predicted by the quantum chemical calculations.

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The cleavage of sugarnucleotides catalysed by metal ion complexes

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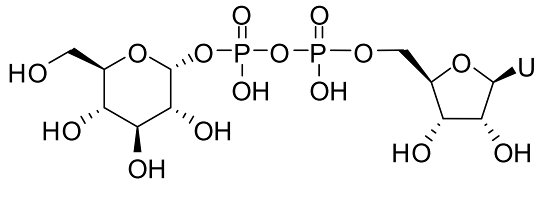
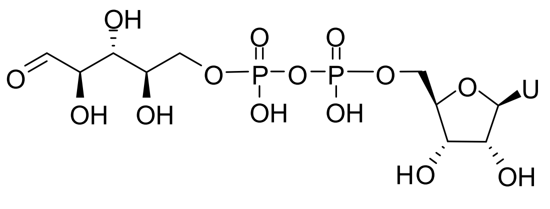
Sugar nucleotides act as sugar transfer agents in biological processes, where the diphosphate moiety acts as a good leaving group, which can be easily replaced by a nucleophile attacking on C1. In chemical research sugar nucleotides can be used as simple and easily detectable model compounds in studies of cleavage of carbohydrate phosphodiesters.

The chemical cleavage of a sugar nucleotide can take place *via* different routes depending on a structure. Glycosylic compounds such UDP-glucose react as glycosides or *via* intramolecular transesterification, provided that there is an adjacent *cis* –oriented HO –group available to serve as a nucleophile.[1] Reducing compounds such as UDP-ribose are cleaved through transesterification or *via* elimination of the diphosphate group.

In the present work the Cu^{2+}-BiPy and Cu^{2+}-TerPy promoted cleavage of various different types of sugar nucleotides were studied. Preliminary results suggest that the catalysis by Cu^{2+}-BiPy and Cu^{2+}-TerPy is different. While Cu^{2+}-TerPy enhance the cleavage by transesterification only, Cu^{2+}-BiPy may be able to provide the attacking nucleophile.



UDP-glucose; A glycosylic sugar nucleotide



UDP-ribose; A reductive sugar nucleotide

[1] The current knowledge of the reactions of sugar nucleotides has been recently reviewed in: Mikkola, S. *Curr. Org. Chem.* **2013**, *17*, 1525.

Insights on weak bonding from the current density

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The current density, describing the electron flow when molecules are set in a magnetic field, and determining the magnetizability and the chemical shift, has already received great attention for its use in defining molecular aromaticity.[1] As magnetizability and chemical shift have been routinely considered in investigations on bonding, the role of the current density is likely of importance even beyond the discussion on aromaticity.

Indeed, the topology of the current density can be used to asess the presence of hydrogen-bonded systems: just as in the density gradient field a bond critical point is observed, in the current density field a saddle is found.[2] The presence of the saddle allows quantifying the dimer-delocalized current, which well correlates with the binding energy.[3] In a similar manner, a saddle occurs in systems with the highly debated H-H interaction.[4] Quantification of the H-H stabilizing interaction has been obtained by integration of the current density. The 'steric' destabilization of the H-C-C-C-C-H moiety in phenanthrene is paralleled by a paratropic current within the bay, but should not be ascribed to the two close H atoms.[5]

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Computational Study of Substituent Effects on Gas-Phase Stabilities of N'-Phenylguanidinium Ions

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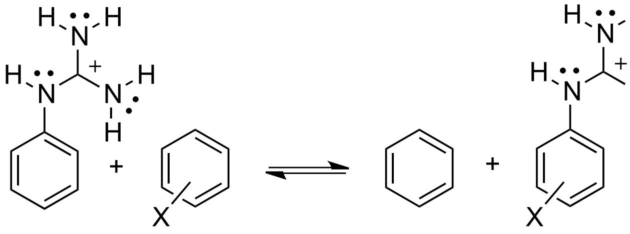
In the past two decades, ionic liquids (ILs) have attracted a lot of attention, and were proposed for a potential broad range of applications in various areas of natural and engineering sciences. Guanidinium ions constitute a new class of ionic liquids used for various applications. Since the six substituents connected to the nitrogen atoms of a guanidinium ion can tune the chemical properties of the ILs, investigations regarding to the substituent effects on the stabilities of the ions are expected to provide fundamental knowledge for developing ILs. Here, we report the substituent effect analyses of N'-phenylguanidinium ions using the Yukawa-Tsuno equation (1).[1]

$$-\Delta E_X = \rho(\sigma^0 + r^+ \Delta\bar{\sigma}_R^+) \qquad (1)$$

Resutant r^+ value reveals the degree of through-resonance between the cationic center and *para* –R groups.

The relative stabilities of ring-substituted N'-phenylguanidinium ions were determined as energy differences (ΔE_X) of the isodesmic reaction (2).



(2)

Energies of respective species were calculated at the B3LYP/6-311+G(2d,p) level of theory. The obtained substituent effects were analyzed by Eq. 1.

The r^+ value was –0.15 for planarly fixed N'-phenylguanidinium ions. A slightly larger r^+ value (–0.04) was found for fully optimized N'-phenylguanidinium ions in which the guanidinium moiety is orthogonal to the benzene ring. This increase was attributed to the through-resonance between cationic center and *para* –R groups which operates through a π–σ^* interaction between the benzene π-electron system and the guanidinium moiety. This mechanism was supported by NBO analyses. Detailed analyses regarding to the stabilities and the charge delocalization of the ion will be discussed.

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Computational Study of Substituent Effects on Gas-Phase Stabilities of N'-Phenylguanidinium Ions

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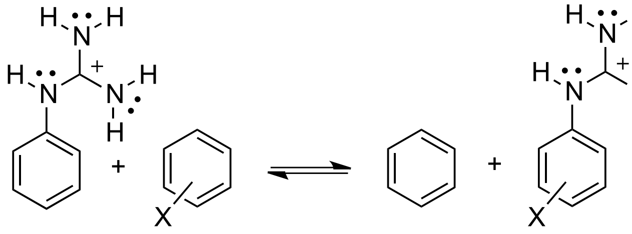
Resutant r^+ value reveals the degree of through-resonance between the cationic center and *para* –R groups.

The relative stabilities of ring-substituted N'-phenylguanidinium ions were determined as energy differences (ΔE_X) of the isodesmic reaction (2).



(2)

Energies of respective species were calculated at the B3LYP/6-311+G(2d,p) level of theory. The obtained substituent effects were analyzed by Eq. 1.

The r^+ value was –0.15 for planarly fixed N'-phenylguanidinium ions. A slightly larger r^+ value (–0.04) was found for fully optimized N'-phenylguanidinium ions in which the guanidinium moiety is orthogonal to the benzene ring. This increase was attributed to the through-resonance between cationic center and *para* –R groups which operates through a π–σ* interaction between the benzene π-electron system and the guanidinium moiety. This mechanism was supported by NBO analyses. Detailed analyses regarding to the stabilities and the charge delocalization of the ion will be discussed.

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Why the Synthesis of λ^5-Phosphinolines Occurs only in Microheterogeneous Medium?

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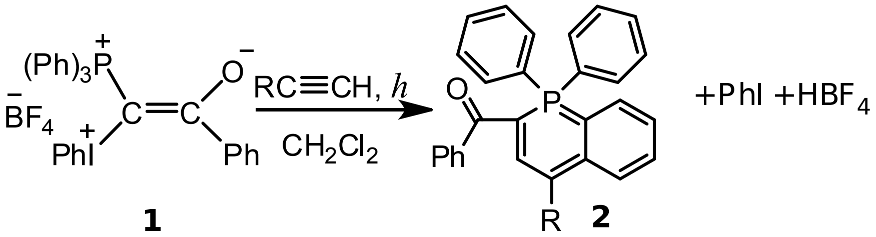
Recently, reaction of photoheterocyclization of mixed phosphonium–iodonium ylides (**1**) with acetylenes was opened up.[1] In this reaction novel exotic P-containing heterocycles, λ^5-phosphinolines (**2**), were synthesized with relatively high yields (30–80%, depending on **1** and acetylene structures) in a simple, one-pot and metal-free reaction under irradiation of the reagents mixture in CH_2Cl_2. (Scheme). The relatively high concentration of **1** ($\geq$ 0.01 M) is the necessary experimental condition for the synthesis of **2**. The solution of **1** in CH_2Cl_2 is microheterogeneous at these concentrations, with a mean size of an ylide particle being ~900 nm. The reaction has an induction time, starts on an ylide particle and then expands over the bulk solution.[2] The formation of **2** (neutral compound) occurs from cation **1** and is accompanied by elimination of H^+, which provides the autocatalytic character of the process.[3] The experimental kinetic study on the effect of added acid allows for the proposal that *nascent* H^+ catalyzes the reaction in the ylide–acetylene complex before exit from the nanoparticle to the bulk solution, where HBF_4, poorly dissociated in CH_2Cl_2, is formed. The mechanism of the photoheterocyclization will be discussed.



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SYNTHESIS AND CHARACTERISATION OF ORGANO-PHOSPHORUS COMPOUNDS *VIA* FREE RADICAL REACTIONS

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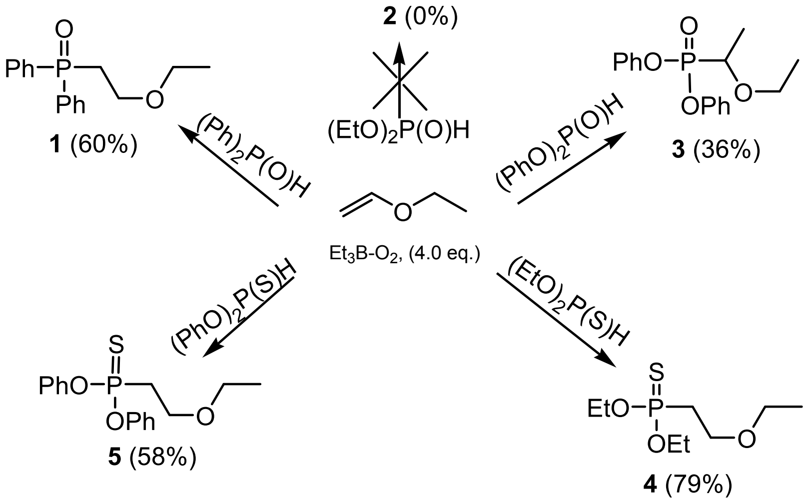
Under free-radical conditions, the P-H bonds of primary and secondary phosphine add across alkenes. Such reactions proceed with anti-Markovnikov regiochemistry(1). Under aerobic conditions triethylborane is oxidised by molecular oxygen, to form the corresponding peroxide, which undergoes homolysis at a wider temperature range than other typical organic peroxides.(2) The poster will examines the unexpected regioselectivity of addition products obtained from diphenyl phosphite, and enol alkenes under free radical reaction conditions, and compares them with those obtained from phosphonyl radicals derived from diphenylphosphine oxide, diphenyl thiophosphite and diethyl thiophosphite when treated at room temperature with enol alkenes under similar reaction conditions.



Scheme 1

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A QTAIM perspective of the Baldwin rules.

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Herein, we present an in-depth topological study within the quantum theory of atom in molecules (QTAIM)[1] in order to establish in a quantitative fashion, the stereoelectronic effects encompassed in the Baldwin rules[2]. We examined the stereoelectronic patterns involved in both *endo-trig* and *exo-trig* cyclizations. Calculations reveal that although the Bürgi–Dunitz angle[3] it is nearly achieved at the transition state of *endo-trig* cyclization, it becomes a highly disfavored process. As a matter of fact, the strain caused by the distortion of the double bond becomes apparent in this mechanism. In order to prove this hypothesis, the electron density reorganization at the π-bond in the bond-forming process is examined by using ~~a~~ reactivity indices profiles. Thus, bond ellipticity that provides a quantitative measurement of the anisotropy of the electron density at the π-bond successfully explains the observed reactivity patterns.

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Cross-coupling of Terephthalonitrile Dianion with Neutral Cyanoarenes: Mechanism and Synthetic Utilization

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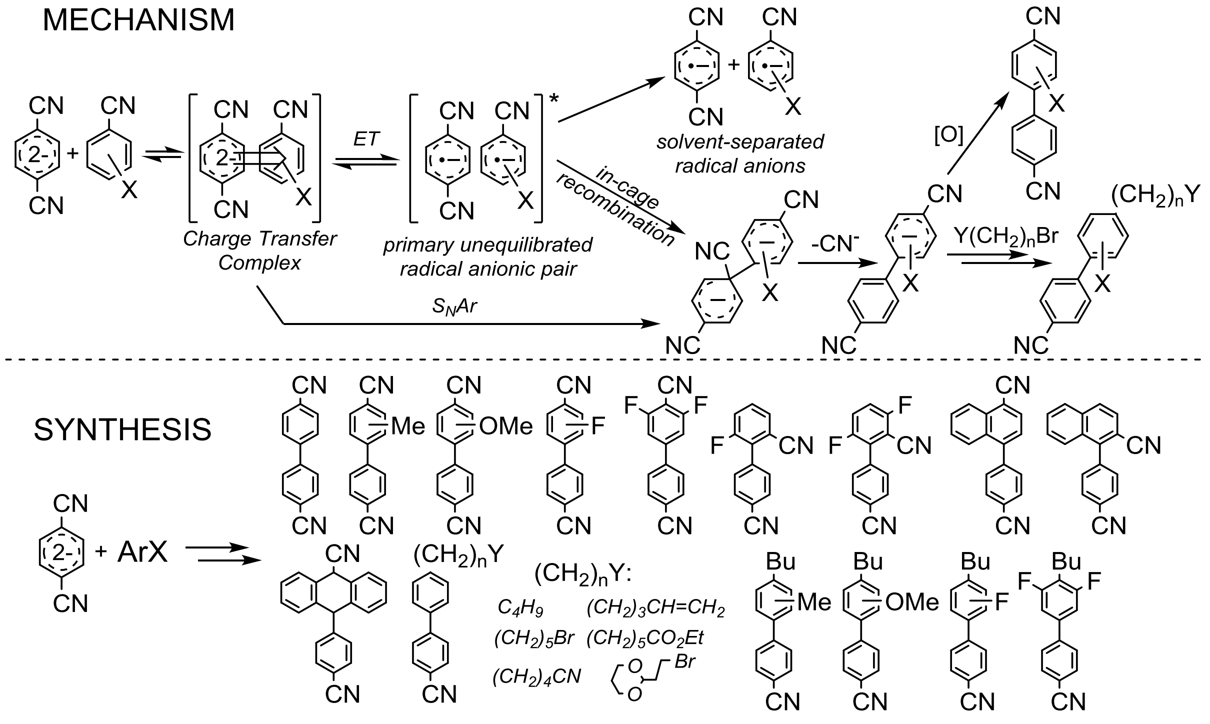
The cross-coupling of terephthalonitrile dianion with cyanoarenes[1], containing an extra substituent as well as a fused aromatic core is discussed. The reaction mechanism proposed includes as key intermediate CTC between dianion and cyanoarene, its further transformation into a long-living cyclohexadienyl anion through intracomplex ET or S_NAr followed by fast decyanation. The latter being treated with oxygen or alkyl halides (including ω-substituted), provides respectively dicyanobiaryls or alkylcyanobiaryls – valuable precursors of pharmaceuticals and new materials[2].



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Development of a contrast agent based on Fe^{III}-Recordplayer

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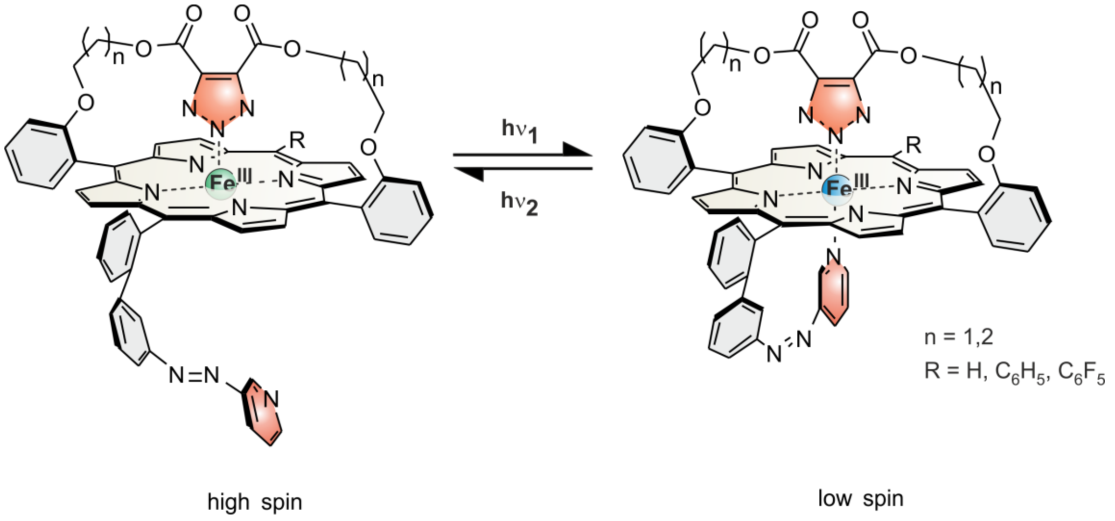
Magnetic resonance imaging (MRI) is an important technique for medical diagnosis and research. Common contrast agents are gadolinium complexes.

A novel approach is to investigate photoswitchable MRI contrasts agents. Ni-porphyrins with covalently tethered azopyridine ligands are applied. The photochromic complexes switch between the diamagnetic low-spin-state (MRI silent) to the paramagnetic high-spin-state (MRI active) by irradiation with light of specific wavelengths. This process is known as light-driven coordination-induced spin-state switch (LD-CISSS).[1,2]

Within this work the concept should be realized with Fe(III)-porphyrins which require different structures. Five-coordinated complexes have a spin of 5/2 (high spin), whereas six-coordinated complexes tend to have a spin state of 1/2 (low spin).[3] The square pyramidal geometry should be realized by a bridged porphyrin.

The higher difference of the magentic moment between the MRI active and the MRI silent state should improve the efficiency of the contrast switching.



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Kinetic study of the oxidation of pesticides: Paraquat

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It's known that actions and programs destined to the environmental protection of the ground against contamination (either the contamination proceeds of direct or diffuse sources) are been developing and coming in. Particularly, there is a special sensitivity with contamination caused by determined organic persistent substances, toxic and bioaccumulative, for which it's established that they can't achieve some limits because of their possible harmful action. Among these, there are included pesticides, of which, organic-chlorinated and organic-phosphate insecticides, carbamates, herbicides and fungicides are part, among other[1]. It's a general trend to offset these losses whit the addition of more pesticides, representing a serious threat to the environment[2].

The natural degradation of these compounds is the oxidation by the existing oxidants in the water, like: ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's reagent (H_2O_2/Fe) and peroxynitrite[3]. We have carried out a kinetic study focused on the oxidation of pesticide Paraquat by Fenton's reagent and peroxynitrite. Specifically, this work shows the dependence of the rate of oxidation with the oxidant and pesticide concentrations.

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The acetaldehyde and ammonia reaction mechanism: A computational study

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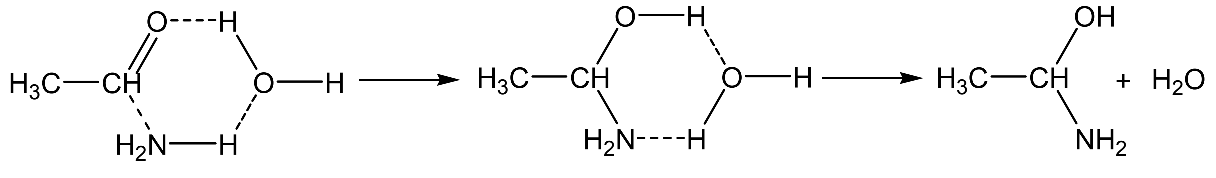
Reactions between carbonyl compounds and ammonia or ammonia derivatives are preferable for the preparation of valuable heterocyclic compounds. However, these processes, which are usually carried out in water solutions, are not very well understood in terms of reaction mechanisms. In this context, the objective of the present work was to study the kinetics and reaction mechanism of interaction between acetaldehyde and ammonia. The product of this condensation, 2,4,6-trimethyl-1,3,5-hexahydrotriazine trihydrate (acetaldehyde-ammonia trimer) [1], was isolated from the reaction mixture and analyzed by IR-spectroscopy with the melting point being also determined.

In the present work, the reaction between acetaldehyde and ammonia was simulated by quantum-chemical calculations at B3LYP/6-311++G** level. The comparison of the calculated and experimental geometrical parameters of acetaldehyde, ammonia and acetaldehyde-ammonia trimer molecules was performed to confirm the reliability of the chosen level of theory. The crucial role of water molecule as a proton transporter in the six-membered ring which was formed from acetaldehyde, ammonia and water molecules was discovered (Scheme).

Activation energies and transition states of the reaction were found for each stages of transformation.



Scheme

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DFT study of the amine diazotization reaction

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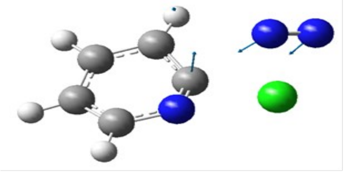
Diazonium salts of the aromatic and heterocyclic amines are of particular importance as the major building blocks of organic synthesis, and in recent years on their basis the latest methods of the surfaces modifying of the electrodes, nanoparticles, nanotubes, etc. In view of its importance, they have long been the subject of numerous quantum chemical studies [1]. However, it is surprising, in this case the structure was studied only isolated benzenediazonium cations, and quantitative data on their structure (except the results of X-Ray, IR and NMR in part) and the influence of the anion on the cationic part of the molecules and reactivity are absent.

We examine a broader series of the aromatic and heterocyclic amines, with focus on both geometrical parameters and the calculated binding energies. The calculations were carried out using CCSD(T) and DFT achieved within the GAUSSIAN'09 and Amsterdam Density Functional (ADF) packages. The formation energy of the complexes has been broken down using the extended transition state (ETS) scheme implemented in the ADF'2004 package. For the calculations in aqua solution, the model of the polarized continuum has been used. For reactants and products, the stationary character was confirmed by the absence of imaginary vibration frequencies, while the transition states were characterized by the presence of only one imaginary frequency. In addition, all transition states have been tested by the IRC method.

We investigated the reaction mechanism of the diazotization of aromatic and heterocyclic amines and its monosubstituted derivatives, with ClNO and TfONO. The thermodynamic parameters for the reactions have been calculated, the structures of the intermediate products and transition states have been defined, and profiles of free energies surfaces have been constructed.

It is shown that diazotization reaction of primary amines is thermodynamically possible due to large values of the salvation energy of the reaction ionic products.

Fig. Transition state of pyridine diazonium chloride reaction



It is clearly seen from ETS scheme [2] that in all the salts except chloride the contribution of the energy of the orbital interaction significantly more energy electrostatic interaction. Benzenediazonium chloride is very different from the other salts predominance of the electrostatic interaction. It is important to note that the calculated binding energy values are in a perfect linear relationship with the values of dissociation enthalpy of the same salts.

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Matrix Isolation and Solvation Studies of Diphenylmethyl radical

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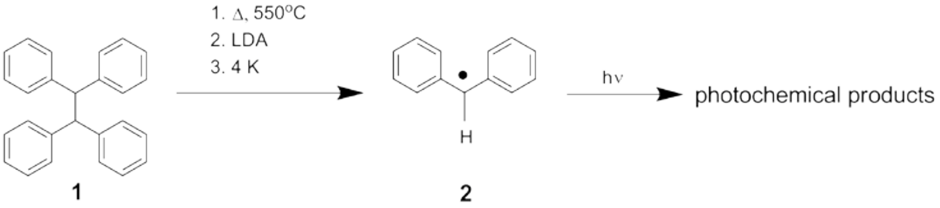
Reaction of radicals with water is one of the crucial steps in all the biological systems. Different type of interactions of the radicals with water and the subsequent species formed has been of great interest to the scientific world. The interactions and the species formed are extremely short-lived which makes it difficult to detect them spectroscopically. Hence the formation of the species is done at extremely low temperatures of 3K- 10K.

The diphenylmethyl radical **2** was successfully isolated in good yields in Low Density Amorphous Ice (LDA) matrix at 3K. Subsequent irradiation on using the Ultraviolet (UV) light leads to the generation of the benzhydryl cation. The species is stable enough to be detected spectroscopically. However an interesting photochemistry is observed after the formation of the benzhydryl cation which is the interconversion between the radical and the cation on subjecting it to lights of particular wavelengths. Further irradiation of the benzhydryl cation leads back to the formation of the precursor (1,1,2,2-tetraphenylethane) **1** itself.



We also performed Density Function Theory (DFT) calculations to confirm the formation of the diphenylmethyl radical and the benzhydryl cation.

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A change of reactivity with a change of regioselective solvation

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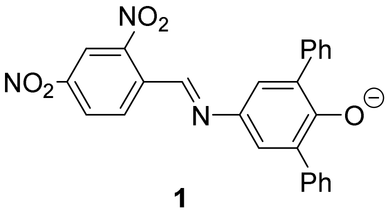
The solvatochromic behavior of iminophenolate **1** in aqueous alcoholic solutions offers an interesting example of an abrupt change of regioselective solvation in water-rich solutions.[1]



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This interesting behavior, deduced from a sharp inversion of its solvatochromic behavior, was investigated in the present communication by following the kinetics of methylation of **1** in aqueous alcoholic solutions.

Second-order rate constants k_2 at 25^{o}C for the reaction of **1** with dimethylsulfate in aqueous alcohols (1-propanol, ethanol and methanol) are given in the table below, for increasing water contents.

Table 1. $10^{3} \times k_2$ (M^{-1} s^{-1}) in aqueous alcohols with different water percentages (V/V)

Solvent	0%	20%	50%	70%	80%	90%
MeOH	16.3±0.8	17.9±0.9	26.0±1.4	59.0±3.0	6.4±0.4	4. 1±0.2
EtOH	15.0±0.7	16.2±0.8	24.9±1.2	55.5±2.9	57.0±2.8	3 .7±0.3
1-PrOH	14.5±0.4	15.9±0.8	24.7±1.3	54.0±2.7	55.2±2.9	3.5±0.2

Rate constants increased with the medium polarity, decreasing sharply in water-rich mixtures, in agreement with the suggestion of a change of the regioselective solvation of the phenolate group in these mixtures.[1]

These solvent effects were theoretically analyzed with a QM/MM approach, and compared with previously described effects on the reactivity of another solvatochromic phenolate, methylated by methyl iodide.[2]

Acknowledgments: Support by Fondecyt project # 1140212 and DICYT/USACH is gratefully acknowledged.

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Conformational behaviour of Ac-Ala-NHMe in different media

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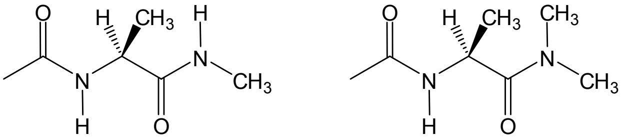
The conformational behaviour of individual amino acids has been widely studied in order to find the lowest energy conformers and to, possibly, understand the folding pathways of macromolecules built from these compounds.[1] As a closer approach of an amino acid in a peptide environment, compounds of general formula Ac-R-NHMe (R = amino acid) are also being studied,[2] but studies in solution are scarce. Recently, we have studied several amino acids and their derivatives as peptide models,[3] and also Ac-Gly-NHMe, in many different media. In the present work, in order to evaluate the side chain effect on the main chain geometry, we moved to Ac-Ala-NHMe (**1**) and its *N*-methyl derivative Ac-Ala-N(Me)$_2$ (**2**; Scheme 1). Data from their NMR spectra (spin-spin coupling constants), in several solvents, are in close agreement with the theoretical values (BHandH/EPR-III). A search of their main conformers for the isolated compounds was performed at B3LYP-D3/aug-cc-pVDZ theoretical level and in some solvents (IEF-PCM), which revealed that there are 12 main conformers for both **1** and **2.** The conformational preferences of similar systems have usually been assigned to the formation of intramolecular hydrogen bonds, while other effects, as steric hindrance and hyperconjugation, have been ignored. The later effects are ubiquitous and influence the geometry/energy even of simpler systems than dipeptide models.[4] Thus, several theoretical methods (QTAIM, ELF, NCI and DORI and also NBO) were employed to explain the conformer stabilities and are discussed in the interpretation of the experimental and theoretical results.



1 **2**

Scheme 1: Ac-Ala-NHMe (**1**) and Ac-Ala-N(Me)$_2$ (**2**) structure representations.

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FAPESP

Why Hypochlorous Acid Chlorinates Amines Rather than Hydroxylates Them

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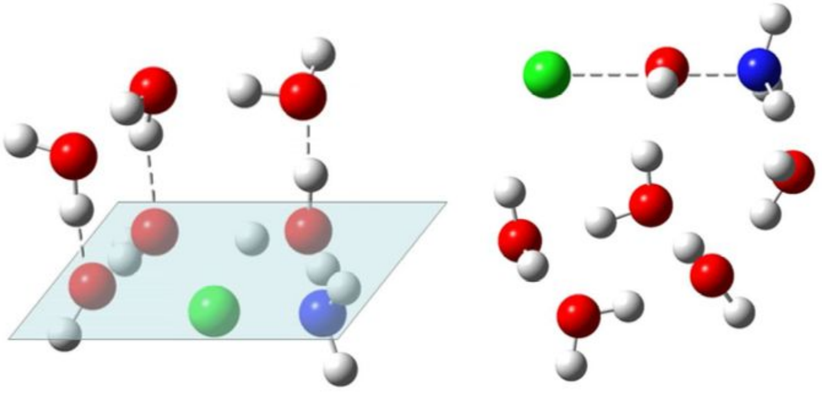
Reactions of hypochlorous acid (HOCl) with ammonia, (di)methylamine, and heterocyclic amines have been studied computationally in the gas phase and aqueous medium. Different oxidation pathways are possible in the gas phase, and only one is experimentally detected in aqueous solution. N-chlorination pathway is prohibitively expensive in the gas phase ($\Delta G^{\#}_{calc}$ > 250 kJ/mol), yet N-chloramines are readily detected in aqueous medium. N-hydroxylation is more feasible process in the gas phase, while in aqueous medium is much less preferred. We have found that the explicit solvent effects are crucial for determination of reaction mechanism in aqueous medium. Water molecules play important catalytic role in N-chlorination reaction, by facilitating the hydrogen-atom transfer between amines and HOCl. The planar structural motif, which includes HOCl, amine and two reactive water molecules, has been calculated as the most stable configuration for up to 9 explicit water molecules. In case of N-hydroxylation reaction, water molecules are not directly involved in the O-transfer process. The linear structural motif has been found as the most preferable configuration, in which all water molecules contribute in building the first hydration shell, and participate as reaction spectators only. Catalytic effect of explicit water molecules, observed for N-chlorination of amines, has not been calculated for N-hydroxylation process.



Transition state structures for N-chlorination (left) and N-hydroxylation (right) of NH_3 with HOCl. The rhomboid inserted illustrates molecular plane in which reactive waters reside.

A mechanistic study of bisphenols phototransformations in aqueous solutions

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Bisphenols (BPs) are widely used in production of polycarbonate plastics, epoxy resins, adhesives, coatings for drink packages and food cans. As a consequence BPs have been widely detected in the environment and food products.[1] However, many (e.g. well-known bisphenol A) of them refer to endocrine-disrupting chemicals (EDCs) and were reported to possess acute toxicity and estrogenic activity.[2] Conventional treatment techniques are not effective enough for the removal of majority of EDCs, while photochemical and photocatalytic processes have proved themselves as perspective methods for water purification and disinfection from these compounds. Besides the broad number of investigations devoted to decomposition of BPs using photochemical approaches, there is almost no information about mechanistic aspects regarding the photochemistry of BPs.

In this work aqueous photochemistry of three bisphenols (4,4'-hydroxyphenylmethane (BPF), 4,4'-hydroxyphenylethane (BPE) and 4,4-Bis(4-hydroxyphenyl)valeric acid (DPA)) was studied by means of stationary (XeBr excimer lamp, 282 nm) and laser flash photolysis (6 ns, Nd:YAG laser, 266 nm). Main attention was paid to determination of primary photochemical processes, nature, spectral and kinetic properties of excited states and primary intermediates, rate constants of their reactions. Also, final photoproducts and quantum yields of the photolysis were determined and on the basis of obtained data scheme of BPs photolysis was proposed.

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Reactions of *O*-(4-nitrophenyl) *S*-phenyl dithiocarbonate with Secondary Alicyclic Amines and Quinuclidines in Aqueous Ethanol.

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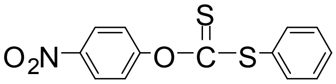
The kinetics and mechanisms of the aminolysis of diaryl dithiocarbonates has received little attention.[1,2,3] Some of these reactions have been shown to proceed through a concerted mechanism[1] and other by a stepwise mechanism with zwitterionic ($T^{\pm}$) and anionic (T^{-}) tetrahedral intermediates.[2,3]

In order to shed more light on the mechanisms of the aminolysis of diaryl dithiocarbonates, in this work we report a kinetic study of the reactions of *S*-phenyl *O*-(4-nitrophenyl) dithiocarbonate (**1**) with secondary alicyclic (SA) amines and quinuclidines, in 44 wt% aqueous ethanol.



1

The reactions of **1** with quinuclidines, piperidine and piperazine display linear plots of k_{obs} against [amine], nevertheless those for morpholine and formilpiperazine show upward curvature but at greater amine concentration are also linear.

The behavior found in the reactions of **1** with the SA amines is explained by a stepwise mechanism with formation of a $T^{\pm}$ intermediate and a thermodynamically favorable proton transfer from this intermediate to the amine to yield a T^{-} intermediate. With the slopes of linear plots for the reactions with the most basic SA amines and the slopes for the linear part for the plots with the less basic amines a linear Brønsted plot (log k_N *vs*. pK_a of the conjugate acids of the amines) with slope 0.26 was found.

On the other hand, in the reactions with quinuclidines, a linear Brønsted plot with slope 0.40, in accordance with concerted mechanism, was found.

For the reactions with morpholine and quinuclidine, HPLC analyses were performed showing the presence of 4-nitrophenoxide and benzenethiolate as final products.

ACKNOWLEDGEMENT: This work was supported by projects ICM-MINECON, RC-130006 - CILIS and FONDECYT of Chile (Project 1130044).

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Molecular Dynamics Study on the Vinyl-Type Rearrangement/Fragmentation/Cyclization Reaction of Vinyldiazonium Ion Derivatives: Dynamic Path Bifurcation

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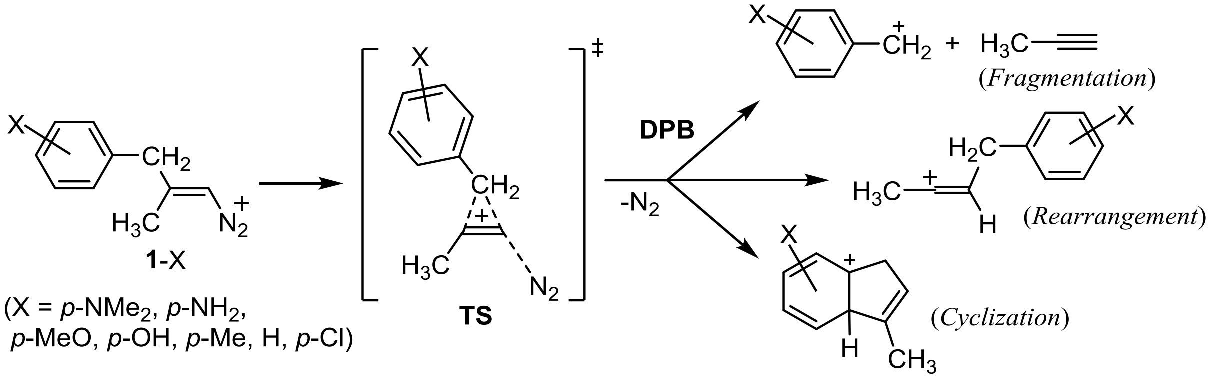
Dynamic path bifurcation (DPB) is one of the most interesting phenomena in the field of physical organic chemistry. We have reported theoretical and experimental studies of the Beckmann, Schmidt, E2/E1$_{cb}$, and S$_N$2/Addition reactions[1] as examples of DPB. In this work, DPB consisted of three kinds of reactions of vinyldiazonium ion derivatives (**1**-X) is reported: rearrangement, fragmentation, and cyclization (Scheme 1). Molecular orbital calculations at MP2/6-31G* revealed that the transition state (TS) descends to the fragmentation or rearrangement products depending on the electronic property of the substituent. On the other hand, ab-initio direct molecular dynamics (MD) simulations at the same level clearly showed that two or three reaction products are obtained from the single TS through DPB.



Scheme 1

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Single Electron Transfer with Carbonylmetallate Anions in the Reactions with 3-Halocyclohexen-2-ones

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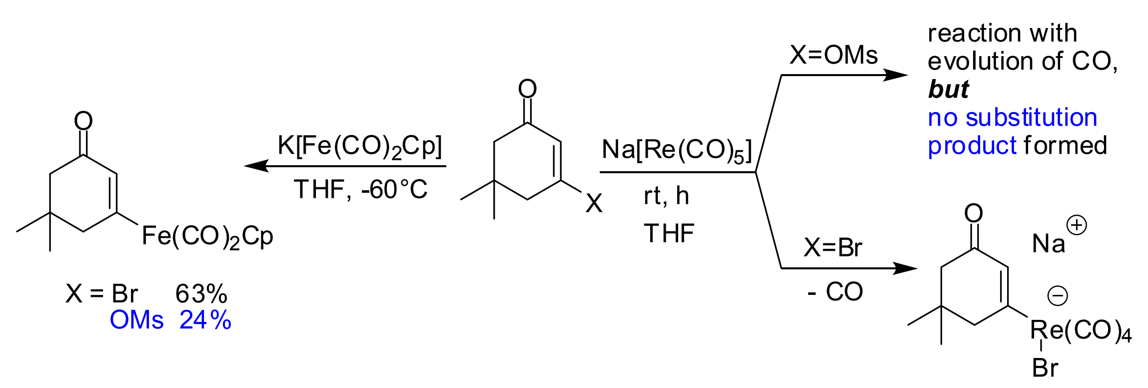
Single electron transfer (SET) as an initial stage is a fundamental and fruitful concept for many polar reactions. Chain radical-nucleophilic processes play an important role in nucleophilic aromatic substitution ($S_{RN}1$) as well as in various transformations of organotransition metal complexes. Metal carbonyl anions are good one-electron donors, but up to now there were no clear-cut examples of SET reactivity with these anions in vinylic or aromatic substitution reactions.

The 3-halocyclohexen-2-one system turned out to be unique in providing the possibility to observe the transition from polar addition-elimination reactivity to SET-mediated pathways in the reactions with carbonylmetallates. This mechanistic switch can be triggered by visible light or by steric hindrance introduced by 5,5-dimethyl substitution in cyclohexenone. In case of pentacarbonylrhenate anion SET initiates a radical-chain process leading to products of formal oxidative addition (Scheme). With iodide the reaction pathway is further shifted to halogenophilic process.

The use of mesylate as a leaving group is proposed as a test for "out-of-cage" radical mediated pathway. The alkenylsulfonate radical anions dissociate with the cleavage of S-O bond (instead of C-O), and this produces no substitution products in contrast to the corresponding iodides or bromides (Scheme).[1]



The financial support from Russian Scientific Fund (Grant 14-23-00186) is gratefully acknowledged.

Photoswitchable Protein Kinase Inhibitors for Novel Anticancer Applications

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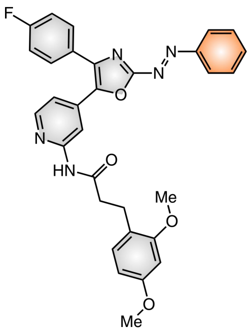
In the last couple of years kinase inhibitors have become one of the most emploited group of drug targets.[1] Today there are more than twenty different kinase inhibitors on the market used mostly against a variety of different cancer types. But most kinase inhibitors exhibited poor selectivity between kinases.[2] Our goal is to design, synthesize and characterize a reversible photoswitchable kinase inhibitor, which can be spatial and temporal controlled by light to minimize the risk of side effects or resistances. In addition such a photoswitchable inhibitor could be of great interest to inverstigate the mechanism of inhibition on a molecular level. Therefore we use a 4,5-diaryloxazol unit as core structure which already has been proven as a potential bulidung block for kinase inhibitors.[3] The 2-position of the oxazol can be used for the functionalization with a photoswitchable unit like azobenzene or diazocine derivates.



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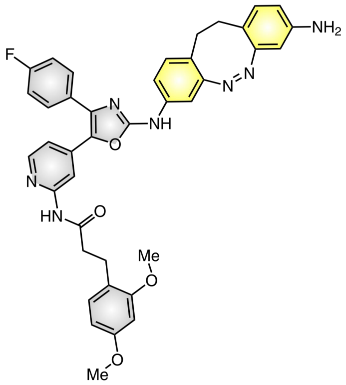

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Aggregation and Association of Grignard Reagents RMgCl and Their Turbo Variant RMgCl·LiCl

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Grignard reagents RMgCl are *the* prototypical organometallics and are heavily exploited in organic synthesis.[1] Knochel's discovery of the so-called turbo variant RMgCl·LiCl has led to a further boost in their application.[2] Despite the wide use of these compounds and their excellent reactivity, it is largely unclear how LiCl exerts its effect at the molecular level.[3] To obtain insight into the microscopic speciation of RMgCl and RMgCl·LiCl in ethereal solutions, we employed a combination of electrospray-ionization (ESI) mass spectrometry, electrical conductivity measurements, and NMR spectroscopy.[4,5] These studies indicate that the addition of LiCl to RMgCl results in the formation of ate complexes, which easily undergo heterolytic dissociation. While complexes containing a single Mg center predominate in solution, the concentration increase during the ESI process favors the generation of higher aggregates (Figure 1 for R = Bu).

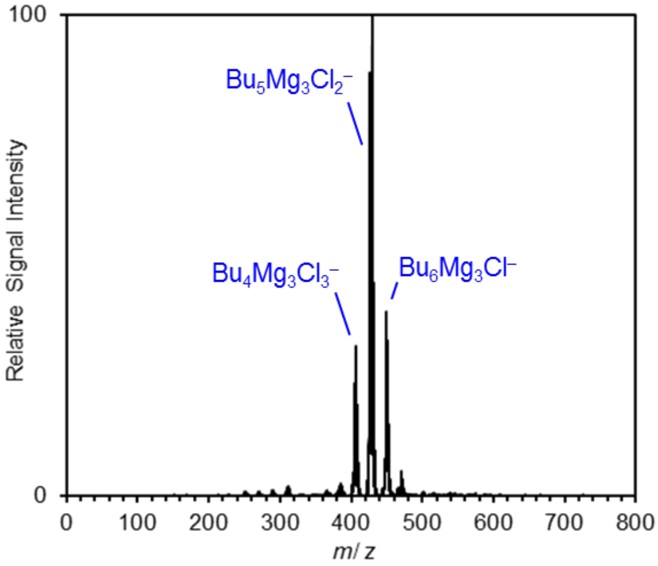

Figure 1. Negative-ion mode ESI mass spectrum of a solution of BuMgCl·LiCl in THF.

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Light-Driven-Coordination Induced Spin-State Switch: Rational Design of Photodissociable Ligands using Density Functional Theory Methods

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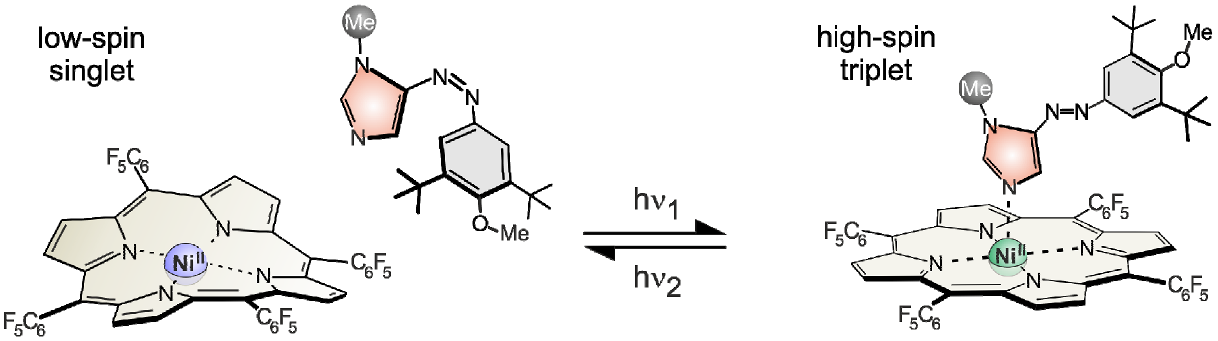
The coordination of axial ligands to porphyrins is of fundamental importance in many areas of chemistry, biology and materials science.[1] Azopyridine and azoimidazole derivatives which are isomerizing between the *cis* and *trans* configuration upon irradiation with UV and visible light were used to realize a Light-Driven-Coordination Induced Spin-State Switch (LD-CISSS) at Ni(II)-porphyrins.[2,3] Upon the association/ dissociation of axial ligands the Ni(II) center can be switched between the high-spin (HS) and the low-spin (LS) state. Whereas the *trans* isomer binds with the nitrogen domain the coordination of the bent *cis* isomer is sterically hindered. We performed density functional theory calculations to find a substitution pattern for the heterocyclic ligands with an optimum switching efficiency. A similar approach with the photochromic ligands covalently attached to the porphyrin has recently been published.[4,5]



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Advances towards the Synthesis of the First Triply Twisted ($L_k = 3$) Aromatic Möbius Annulene

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The credit of introducing the Möbius topology to chemistry goes to Heilbronner. As a consequence of his theoretical predictions, [1] the original Hückel rule is reversed for Möbius annulenes. Or more precisely, cyclic conjugated systems with L_k = odd (Möbius topology) are aromatic with 4*n* and antiaromatic with 4*n*+2 π-electrons. A number of theoretical articles followed, but not before 2003 a synthesis of the first aromatic Möbius molecule (L_k = 1) (one 180° twist) could be accomplished. [2] Spurred by this breakthrough the concept of Möbius topology has gained further attention. Meanwhile, a number of Möbius porphyrins were published by Latos-Grazynski [3] and Osuka [4]. Recently, we accomplished the synthesis of the first triply twisted (L_k = 3) Möbius Annulene. [5] Our current goal is the structural optimization of the system towards Möbius aromaticity.

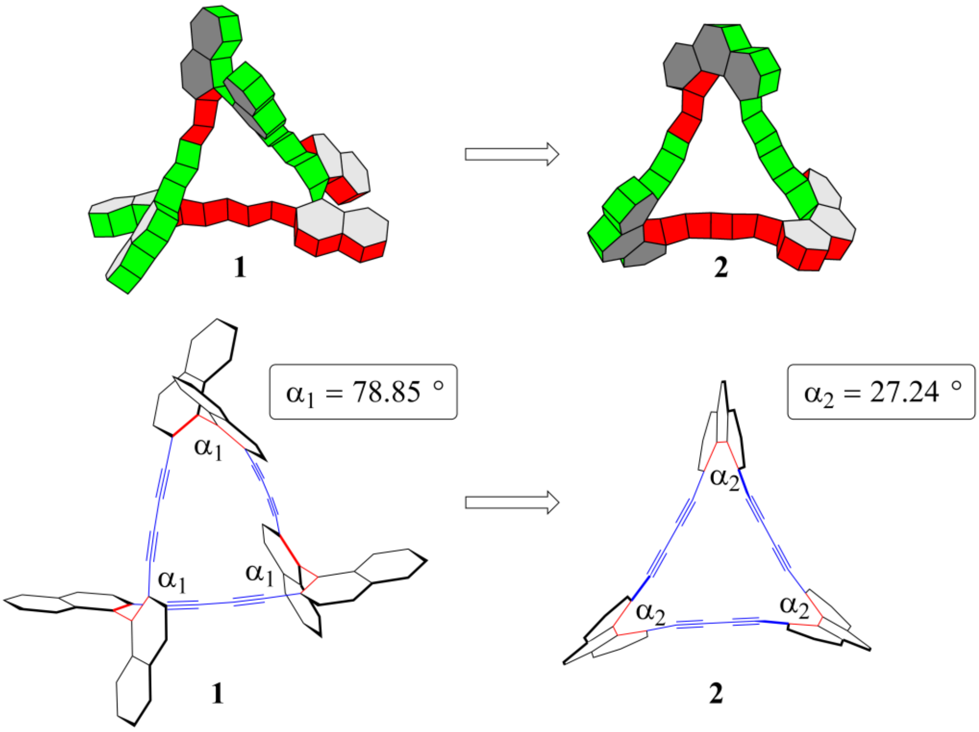

Figure 1: Approach to improve Möbius aromaticity. A decreasing dihedral angle in structure **2** should result in an enhanced π-π-overlap and give rise to a triply twisted aromatic system where the twist is smoothly distributed over the periphery of the [24]annulene.

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Protonated Hexaazamacrocycles as Selective K$^+$ Receptors.

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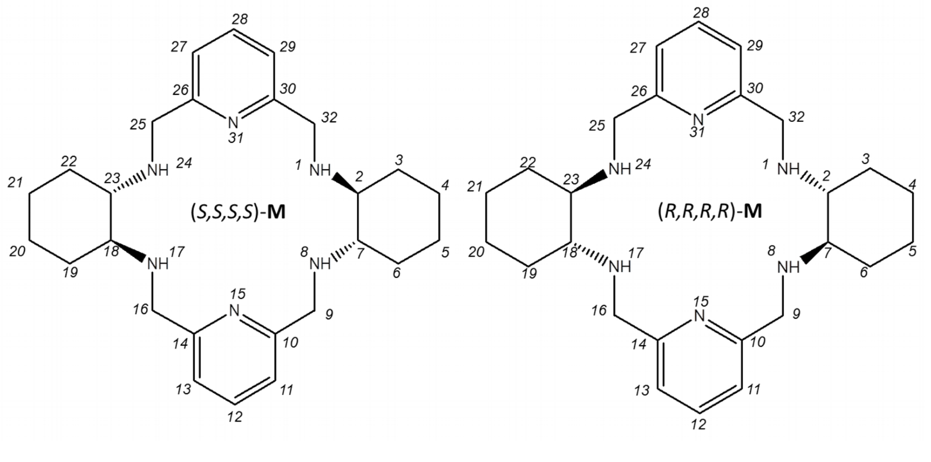
The ion pattern from ESI-MS of methanolic solutions of the chiral hexaazamacrocycle **M**, shown in the figure, is strongly dependent on the nature and the composition of the solvent employed. The protonated **M** macrocycle is able to detect K$^+$ ions present at ppb level in methanolic solutions, even when they contain 10^{-5} M of Na$^+$ ions. The high sensitivity and selectivity of [**M**•H]$^+$ for K$^+$ is ascribed to the favorable energy balance between the K$^+$ ion desolvation and its coordination to the [**M**•H]$^+$ macrocycle which allows the formation of the corresponding adduct before the Coulombic explosion of the ESI-MS nanodroplets. The extremely high sensitivity and selectivity of the [**M**•H]$^+$ ion for K$^+$ ions well compares with the performance of biotic K$^+$ channels.



Light-Driven Condensation of Vanadates

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In nature short-term energy storage in cells is achieved by the condensation of ADP and phosphate to ATP. The enzyme ATP synthase uses a proton gradient across a membrane to drive this endergonic reaction.

The condensation of monovanadate to divanadate can be used as a model system as its structure and electrostatic properties are similar to those of phosphate, while the activation barrier for the condensation reaction is lower compared to phosphate condensation.

By combination of a photoswitchable unit (such as azobenzene or diazocine) with a receptor for phosphates and vanadates (e. g. Zn-cyclene or Zn-triazacyclononane) a photoswitchable receptor is generated.

With Zn-benzylcyclene and azobis(Zn-benzylcyclene), the condensation of vanadate has been investigated by ^{51}V-NMR.[1,2,3]

Based on these results new azobenzene and diazocine-based receptors with benz-annulated Zn-cyclene or Zn-triazacyclononane are being developed. Annulation of azamacrocycles is supposed to prevent rotation which leads to undesired complex species. Utilization of diazocine leads to a molecular pincer[4] and, according to DFT calculations, is anticipated to break microscopic reversibility when two Zn-triazacyclononane rings are annulated.

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The structure of new electron-deficient amidines

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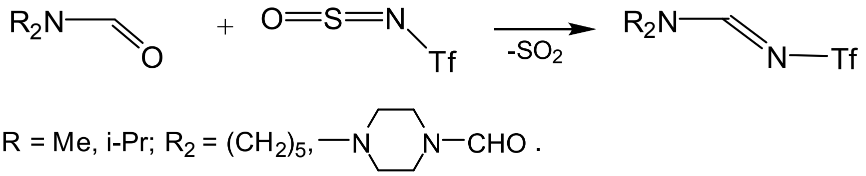
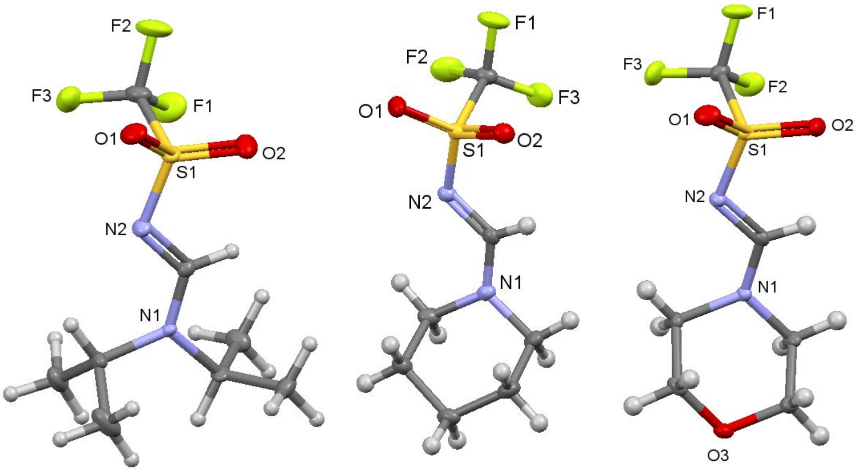
The spatial and electronic structure of new electron-deficient N-triflyl amidines $R_2N–CH=NTf$ ($Tf = SO_2CF_3$) will be presented. The compounds were prepared by a new method from N-formylated secondary amines and N-sulfinyltriflamide, as shown below.



While amidines $R_2N–CH=NR'$ are among the strongest neutral organic bases, the title compounds show very low basicity. The electron density on the amine nitrogen is low due to strong conjugation with the imino group, and the basicity of the imine nitrogen is drastically decrease by the strong electron withdrawing triflyl group. A very strong conjugation in the >N–CH=N fragment was proved by X-ray analysis: the formally double C=N bond in all of the synthesized compounds **2–4** is longer than the formally single N–C bond.



The C–N1 distance in **2–4** is 1.305-1.309 Å and the C=N2 distance is 1.328–1.325 Å, whereas in nonfluorinated amidines they are either close or the opposite relationship was observed.

Reactivity of Pyridinium N-Imines in 1,3-Cycloaddition with Alkynes: Combined Experimental and Theoretical Study

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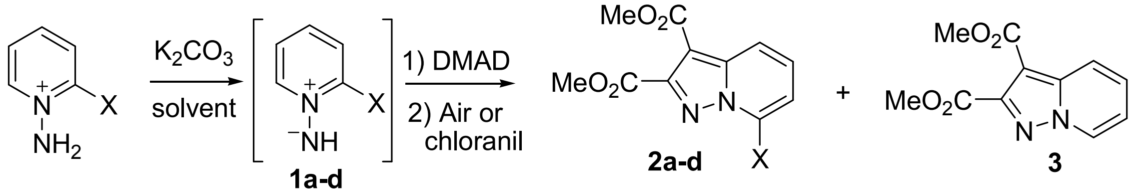
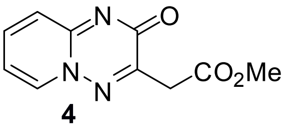
Pyrazolo[1,5-*a*]pyridine is an interesting structural motif for modern drug design. The main route to pyrazolo[1,5-*a*]pyridines is a 1,3-cycloaddition reaction of pyridinium N-imines with alkynes[1]. Recently, we reported on unusual cleavage of the C_{py}–C_{py} bond in the reaction of 2,2'-bipyridine N,N'-diimines with acetylenes[2]. In present work we have studied the reactivity of 2-substituted pyridinium N-imines with acetylenes.

Pyridinium N-imines **1a-d** were generated *in situ* from the corresponding N-aminopyridinium salts. Their reaction with DMAD yielded both 7-substituted and 7-unsubstituted pyrazolo[1,5-*a*]pyridines **2a-d** and **3**, respectively. The **2a-c**/**3** ratio significantly depends on solvent nature and decreases on solvent polarity growth.



X = Cl(**a**), Br(**b**), CN(**c**), OPh(**d**), NH_2(**e**)

In case of **1e** heterocyclic compound **4** was observed as a main product. When other acetylenes such as ethyl propiolate and methyl 3-phenylpropiolate were used, no pyrazolopyridines were formed. Possible mechanisms of these reactions are discussed on the basis of DFT calculations.



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Novel synthesis of chiral norbornene-based diphosphine oxides

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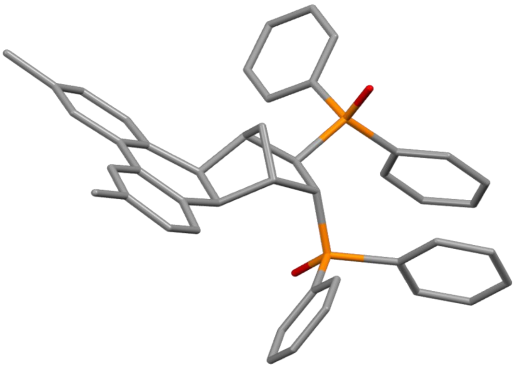
Chiral chelating diphosphines played a special role in early development of asymmetric catalysis. Optically active diphosphines are the best (pre)catalyst for chiral transition metal catalysts for a variety of asymmetric transformations.

The convenient approach to the synthesis of chiral ligands lies in high yielding modification of known, easily available and efficient ligands. Based on well-known C-stereogenic ligand Norphos structure we developed a series of transformation lead with high yields to new chiral ligand. Our modification of Norphos synthesis allow rapid obtaining of multigrams quantitative of ligands in extremely cost affordable manner. Although several Norphos type ligands are already known nevertheless the syntheses of all of them had been realized by application of own unique method.

Herein, we reporting a new reaction with Norphos oxide which may proceed likely according to *Catellani reaction mechanism*. Treated by aromatic halides in Heck reaction conditions, Norphos oxide was unexpectedly converted to tetracyclic and hexacyclic derivatives in high yield[1].



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1. Financial support in part were supported by Polish National Science Centre (grant 2012/05/B/ST5/00362)

Synthesis of bis-dibenzo[a.i]fluorenylidene

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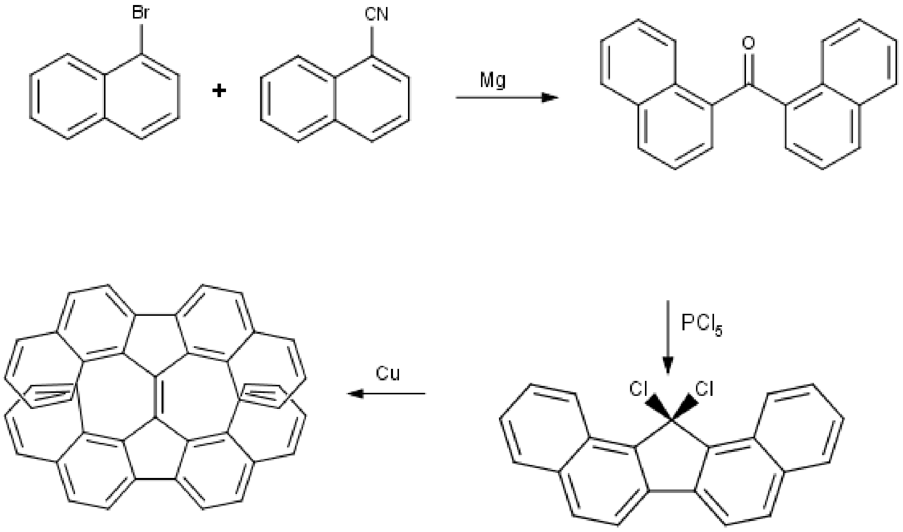
There have been made experimental and theoretical calculations which prove that some alkenes have highly strained carbon-carbon double bonds. Because of that the well-known planar double bond becomes twisted or bended. One of the reasons may be steric crowding such as in bis-dibenzo[a.i]fluorenylidene.[1] The strain has an important effect on the olefins reactivity and its acidic and basic properties.[2]



Scheme 1. The three step synthesis of bis-dibenzo[a.i]fluorenylidene.[3]

The McMurry reaction was also tested to synthesize the olefin of interest, but it has not yet succeeded. The method shown in scheme 1 has been succesful as far as the last step, where purifying is in progress.

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Ring Opening of Donor-Acceptor Cyclopropanes with Azide Ion. Experimental and Theoretical Study

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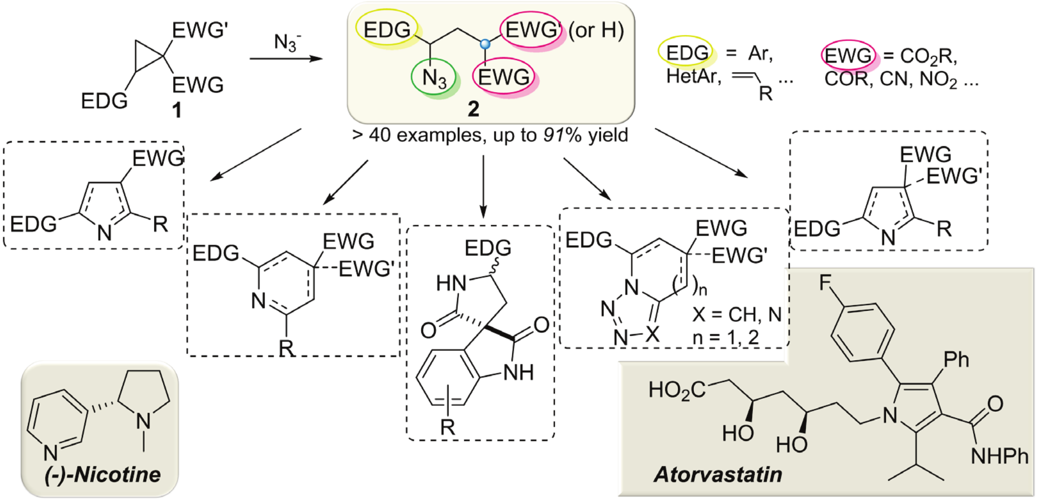
A general method for ring opening of various donor-acceptor cyclopropanes with the azide ion has been developed. The reaction provides a straightforward approach to a variety of polyfunctional azides in up to 91% yield. The high synthetic utility of these azides was demonstrated by the proposed multipath strategy of their transformations into a large variety of five-, six- and seven-membered azaheterocycles including complex polycyclic structures, natural products and medicines, such as (-)-nicotine and atorvastatin.[1]

Results of DFT calculations support the S_N2 mechanism of cyclopropane ring opening. Good qualitative correlation was found between the relative experimental reactivity of a series of cyclopropanes and the calculated energy barriers. The relative reactivity of cyclopropanes was explained invoking principle of non-perfect synchronization and "intrinsic energy barriers" as defined by the Marcus theory.



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Similarity Between Reaction Kinetics and Dissolution Equilibria in Water-Organic Binary Solutions

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Water-organic binary solvents are widely used in industrial and laboratory practices. Therefore, the impact of these complex reaction media on the reactivity of organic compounds is of great interest. In our recent studies we found that solvent effects in water-organic binary solutions could be governed by the same specific property of the reaction medium.[1,2]

In this work we compared two different phenomena, chemical reactions and dissolution equilibria, occurring in the same aqueous-organic binary solutions, for the first time within the framework of their linear-free-energy relationships through similarity analysis. Kinetic data for the pH-independent hydrolysis of (4-methoxyphenyl)-2,2-dichloroacetate and solubility data for naphthalene, and other substrates of low polarity, in aqueous binary mixtures of several different co-solvents were used. Linear similarity relationships were discovered for these data over the full range of the studied solvent compositions, pointing to a similar solvation mechanism that governs these fundamentally different phenomena.

To gain insight into the observed similarities, molecular dynamics (MD) simulations were carried out for naphthalene and a model ester in water-acetonitrile solutions. The results revealed considerable preferential solvation of these substrates by the co-solvent. It was found that the influence of binary solvents on reaction kinetics and dissolution processes is linearly related to mole fraction of co-solvent in solvation shells of substrates. This linearity indicated that a similar solvation mechanism governs such largely different phenomena as dissolution and reaction kinetics.

ACKNOWLEDGEMENTS

This research was financially supported by institutional research funding IUT (IUT20-15) of the Estonian Ministry of Education and Research and by Estonian Science Foundation (Grant No. 9268).

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Thermal *E-Z* Isomerization of Aromatic Azodioxides in Solid State

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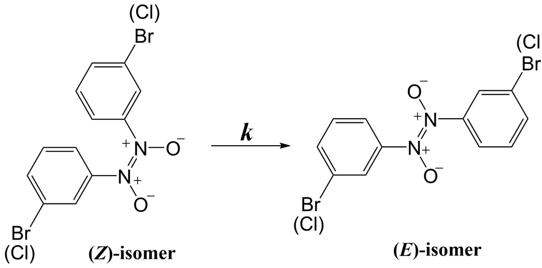
Most of the investigations of solid-state *E-Z* isomerizations have been focused on photoreactions. Thermal solid-state isomerizations of double bonds in organic molecules are very rare and not studied in details.

In our previous works we have developed the approach to the study of the solid-state reaction mechanisms by using the dimerizations and dissociations of the aromatic C-nitroso compounds as models.[1] The *E-Z* isomerizations of azodioxides in solution exclusively follow the pathway through the formation of the nitroso monomer intermediates. Direct "torsional" *E-Z* isomerization has not yet been observed.



Here we demonstrate that the azodioxide *Z-E* isomerization in solid state can occur without the formation of the free nitroso molecule. The reaction is studied by measuring the kinetics of isomerizations of 3-chloro- and 3-bromonitrosobenzene dimers. The mechanism is discussed on the basis of the measured activation parameters, DSC, and time-resolved XPRD. It is proposed that the two concurrent reactions, the azodioxide *E-Z* isomerization, and the dimerization of C-nitroso molecules, respectively, occur through the same type of the transition state.

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Refinement and New Avenues of Stereoselective Wittig Reactions

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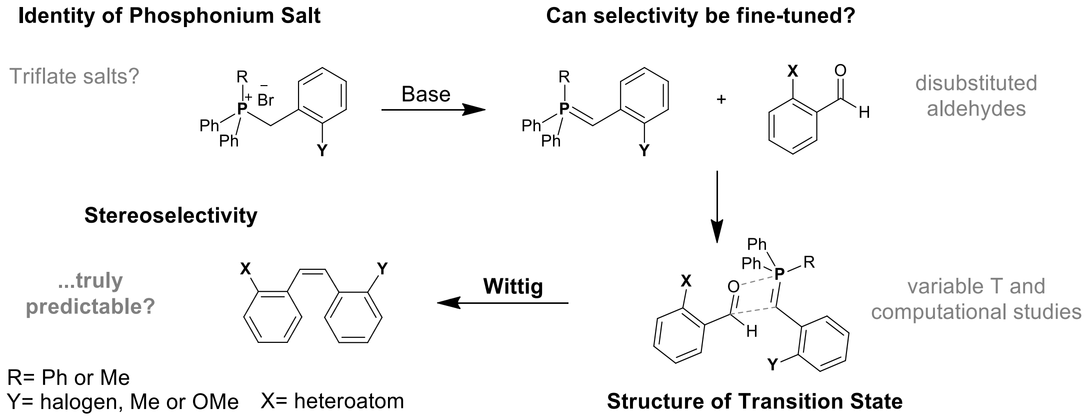
Since its discovery in 1953, there has been much dispute about the underlying mechanism of the Wittig reaction.[1] Recently, our group has reported an experimental effect, which all three major phosphonium ylide classes, *i.e.* non-stabilized, semi-stabilized and stabilized ylides, are subject to: in reactions involving aldehydes bearing a heteroatom substituent in the β-position there is a coherently raised selectivity for *cis*-oxaphosphetane and its derived products (*Z*-alkene and *erythro*-β-hydroxyphosphonium salt).[2] The effect operates with both alipathic and aromatic aldehydes, however, is shown not to operate in case of aldehydes lacking a heteroatom substituent.



The discovery of this common effect strongly suggests the operation of a common mechanism in all lithium salt-free Wittig reactions. Our results of this study are most easily explained by the [2+2] cycloaddition mechanism proposed by Vedejs and co-workers[3] as supplemented by Aggarwal, Harvey and co-workers.[4] The current study aims to explore the grounds for this effect and the mechanistic implications using a combination of computational and variable-temperature studies.

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Reaction kinetics in water-alcohol binary solutions are governed by hydrophobic solvation

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Current understanding of the solvent effects on reactivity in water-alcohol binary mixtures, despite the increasing use of these solvents in the laboratory and industry as relatively green reaction medium, are not yet fully understood.[1]

In this work, the solvation effects in these aqueous solutions were studied by applying kinetics of (4-methoxyphenyl)-2,2-dichloroacetate pH-independent hydrolysis measured in wide range of alcohol content using MeOH, EtOH and TFE as co-solvents. As expected, addition of alcohols to the reaction mixture substantially decreased hydrolysis of the ester. However, magnitude of these solvent effects was found linearly related with the hydrophobicity of co-solvents in the term of partition coefficient (Log P) and thus pointing to involvement of hydrophobic phenomenon in this case.

To gain insight into this phenomenon, molecular dynamics (MD) simulations were carried out to clarify the solvation of a model ester in water-alcohol solutions. The MD results demonstrated preferential solvation of the ester by co-solvent, which was greater in the case of more hydrophobic alcohols. Furthermore, radial distribution functions convincingly show that the hydrophobic ends of alcohol molecules in the solvation shell are oriented towards the ester molecule.

Most interestingly, linear relationship between the experimental data and the mole fractions of alcohols in the solvation shell of ester was found, despite the nonlinear dependences of kinetic data on the bulk solvent composition.

Thus, changes in the preferential solvation of ester appeared to be the primary driving force for changes in reaction rates. Undoubtedly, preferential solvation is a consequence of hydrophobic interactions occurring in these media.

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Study of Fluorescence Resonance Energy Transfer in Ruthenium Bipyridine Complexes Functionalized with Pyrene Dendrimers

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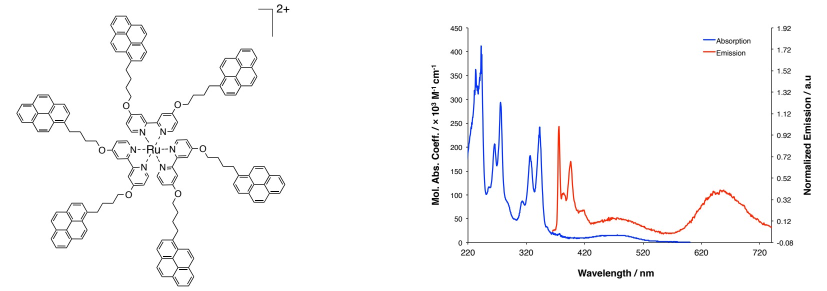
Dendrimers are well defined macromolecules and when photoactive units are incorporated at the periphery in the branches or at the core, the obtained constructs are able to harvest light mimicking the antenna effect of the process of photosynthesis.[1,2] Recently, dendrimers bearing a metal center at the core have been developed, giving them different properties such as absorption of low energy visible light and longer lifetime of fluorescence emission.[3] Moreover the emission and lifetime of the ruthenium-bipyridine complex become less sensitive to the presence of oxygen when surrounded by a dendritic shell.[4] The goal of our project is to synthesize and study the photophysical properties of dendrimers bearing pyrene moieties at the periphery and a ruthenium-bipyridine complex at the core. Pyrene moieties are known for their strong eximer emission and this emission band correspond to the absorption band of $[Ru(Bpy)_3]^{2+}$. In the designed constructs we have observed emission mainly from the $[Ru(Bpy)_3]^{2+}$ core indicating an efficient fluorescence resonance energy transfer (FRET) through a Förster mechanism from the pyrene moiety to the core. The obtained results will be presented.



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Regioselective Synthesis of Deuterated Pyrazolo[1,5-*a*]pyridine and 1,2,4-Triazolo[1,5-*a*]pyridine Derivatives

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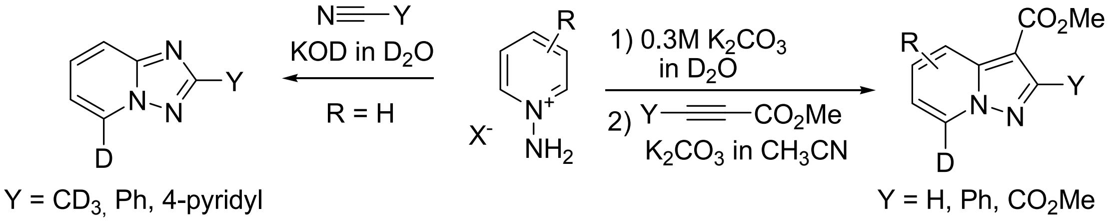
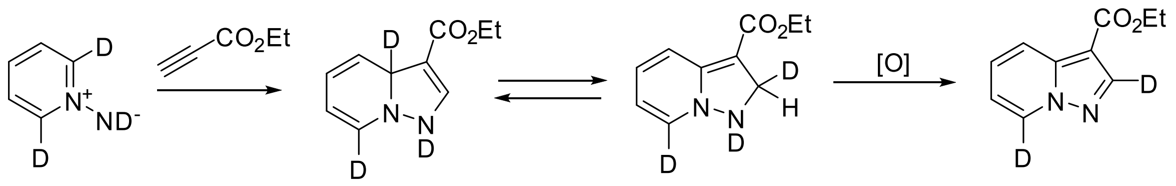
Pyrazolo- and 1,2,4-triazolo[1,5-*a*]pyridines are interesting scaffolds in modern drug design. Their deuterated derivatives are also of interest since deuterium-labeled compounds are widely used in chemical and biochemical studies.
Pyridinium cations readily undergo H/D-exchange at α-position of the ring in D_2O under basic conditions[1]. We have found that the interaction of N-aminopyridinium salts with acethylenes and nitriles in such conditions leads selectively to 7-deuteropyrazolo[1,5-*a*]pyridine and 7-deutero-1,2,4-triazolo[1,5-*a*]pyridine derivatives, respectively.



When ethyl propiolate is taken a significant amount of 2,7-dideuteroproduct is formed possibly via the following mechanism.



This mechanism is in agreement with DFT calculations.

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Experimental and Computational Study of Regioselective Ferrocenoylation of Pyrimidine Nucleobases

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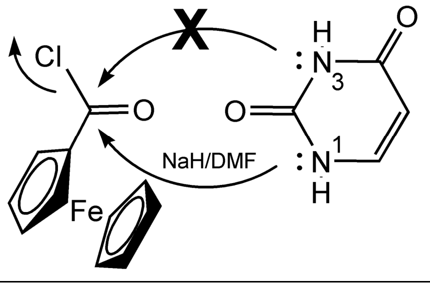
Uracil, thymine, and 5-fluorouracil (5-FU) have been ferrocenoylated selectively at N1-position. Deprotonated pyrimidine nucleobases, prepared by sodium hydride (NaH) in dimethylformamide (DMF), reacted with ferrocenoyl chloride (FcCOCl), or ferrocenoyl ethyl carbonate (FcCOOCOOEt), in DMF to obtain a single product. Regioselectivity of these reactions have been analyzed in details by NMR spectroscopy and quantum chemical calculations. ^{1}H and ^{19}F NMR spectra of reaction mixtures, and ^{13}C NMR and 2D NOESY spectra of products, confirm the formation of the N1-isomer only. The calculated energy barrier ($\Delta G^{\#}_{298}$; DFT methods) for acetylation at N3-position is significantly higher (> 40 kJ/mol), which suggests that the analogous reaction at N1-position is kinetically controlled. The nucleophilic addition of pyrimidine bases to the carbonyl group of FcCOCl proceeds by a concerted S_N2-like mechanism with the absence of the generally assumed tetrahedral intermediate.



Si···H···Si and H···Si···H interactions: structure and dynamics

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The silyl···hydride interactions of various kinds in transition-metal complexes are well known[1] but in certain cases the hydride can be linked to *two* silyl ligands simultaneously, as indicated by J(Si–H) spin-spin coupling constants and Mayer bond indices. For instance, the iron complexes $Cp(CO)Fe(SiMe_nCl_{3-n})_2H$ (Cp = cyclopentadienyl) exhibit a double Si···H···Si interaction, which can be interpreted as a disilylhydride ligand (R_3Si ˜ H ˜ SiR_3), while related complexes $Cp(CO)Fe(SiMe_nCl_{3-n})H(Me)$ are usual η^2-Si˜ H silane σ-complexes. The “dihydride” complexes $Cp(CO)Fe(SiMe_nCl_{3-n})H_2$ can be either usual dihydrogen complexes, e.g. $Cp(CO)Fe(SiMe_2Cl)(\eta^2\text{-}H_2)$, or have double H···Si···H interactions, e.g. $Cp(CO)Fe(H)_2(SiMe_3)$.[2] In the rhodium complexes $Cp(L)Rh(SiX_3)_2(H)$ and $Tp(L)Rh(SiX_3)_2(H)$ (Tp = trispyrazolylborate), the hydride ligand interacts at least with one of the silyls, and in many cases with both, but is located asymmetrically with regard to them.[3] This gives rise to a double-well potential of the hydrogen transfer, with a barrier $\Delta^{\ddagger}E$ varying from ~0.1 to 3 kcal/mol.

The Schrödinger equation was solved in three dimensions. The resulting vibrational wavefunction reveals various patterns of hydrogen dynamic behavior depending on the barrier.[4] If the barrier is small ($\Delta^{\ddagger}E<0.6$ kcal/mol), the hydrogen is *delocalized* between two silicons, but in the case of a larger barrier it is localized around the energy minima, and the hydrogen transfer occurs classically. Intermediate cases with two distinct minima and a substantial *tunneling* can also be found.

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Efficient Intramolecular Catalysis Involving Hydrogen Bonding

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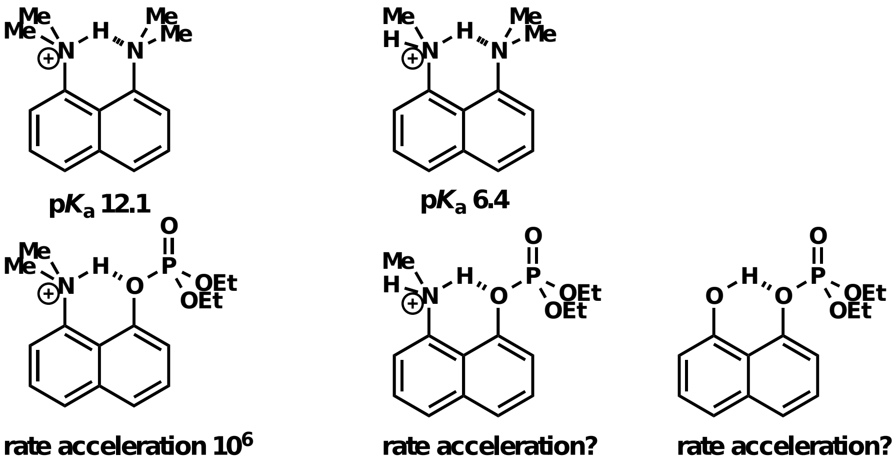
Proton sponges show unusually high p*K*as for their structure, but this property is very sensitive to the degree of methylation. If one methyl group is replaced by hydrogen, the pK_a drops by 6 units and becomes unremarkable for a protonated aniline.[1] This property can be assigned to an unusually strong hydrogen bonding or a destabilised conjugate base, with the latter being more plausible.[2] However, this structure is the basis of one of the few model compounds to show really efficient intramolecular general acid catalysis in water – such as a 10^6 fold increase in phosphate triester cleavage.[3] We have explored whether these remarkable kinetic properties are similarly sensitive to the methylation state of the ammonium site, or if catalytic activity is preserved as the methylation state is reduced. Similarly, we investigate whether the presence of a good hydrogen bond donor provides a significant catalytic advantage, even if proton transfer does not occur during the reaction.



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Mechanistic Study on the Photooxidaiton of Diphosphine

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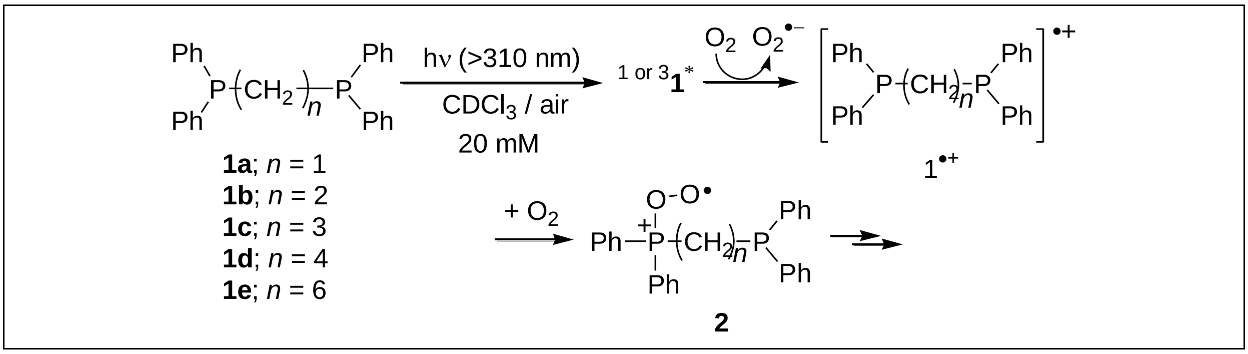
The treatment of phosphine Z_3P with an electron-deficient compound readily affords the radical cation $Z_3P^{\bullet+}$, which sometimes interacts with the parent Z_3P. To disclose how a neutral phosphine interacts with the phosphine radical cation, we examined the photooxidation of diphosphine, which has two phosphine moieties in a single molecule. Thus, the steady-state irradiation on the $CDCl_3$ solution of bis(diphenylphosphino)-alkane (**1**) in air resulted in the oxidation of both phosphine units in **1**. Highly likely, the initial step of this photooxidaiton is the generation of the radical cation $\mathbf{1}^{\bullet+}$, which is then trapped by O_2 to afford peroxidic radical cation **2**. We followed decrease in **1** by ^{31}P NMR spectroscopy to find the rate of the oxidation increases in the order of **1a** < **1b** < **1c** < **1d** ≈ **1e**.[1]

Meanwhile, we evaluated the rate constants for elemental steps in the photooxidation by laser flash photolysis – time resolved infrared spectroscopy (LFP-TRIR) and/or the Stern-Volmer technic using a sensitizer.

These kinetic data, along with the oxidation potentials of **1** obtained by the cyclic voltammetry (CV), allow us to discuss the mechanism of the photooxidation of **1** in details, which would give an idea about the interaction between $Z_3P^{\bullet+}$ and Z_3P.



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Photochemical Z/E Isomerization of Stable Silenes

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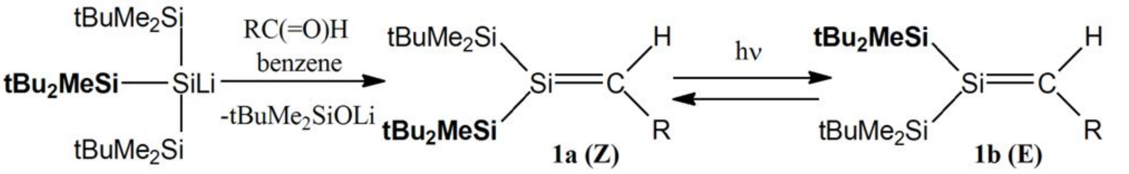
The photochemically promoted E⇌Z isomerization of alkenes is a very important class of reactions in chemical and biological processes and it has long been a subject of intense research. In contrast to alkenes, the chemistry of their silicon analogues, silenes ($R_2Si{=}CR_2$) and disilenes ($R_2Si{=}SiR_2$), is much less investigated.

In this work, we report the first stereospecific synthesis of two stable silenes (**1**) and study their photo-induced Z⇌E isomerization. **1** is obtained in a one-pot reaction of $(tBuMe_2Si)_2(tBu_2MeSi)SiLi$ with RC(=O)H in benzene at rt. Formation of **1** is stereospecific, giving the Z-isomer (**1a**) as the main product. Upon irradiation with a 250 nm UV lamp at rt, **1a** isomerizes to the E-isomer (**1b**), yielding at equilibrium a Z:E ratio of 51:49 for R=1-Ad and of 38:62 for R=Trip. The mechanism of the Z to E isomerization was computationally investigated by DFT theory, and will be discussed.



R=1-Ad; Trip = 2,4,6 - triisopropylphenyl

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ESOR 2015 - Aug 30 - Sept 04, 2015 - Kiel, Germany

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Time	Sunday August 30	Monday August 31	Tuesday September 1	Wednesday September 2	Thursday September 3	Friday September 4
09:00 →		Plenary P. Chen 09:00 - 09:40	Plenary G. Bertrand 09:00 - 09:40	Plenary H. Schwarz 09:00 - 09:40	Plenary S. Shaik 09:00 - 09:40	JPOC Award Plenary A. Braunschweig Miami 09:00 - 09:50
09:10						
09:20						
09:30						
09:40		Invited L. Echegoyen 09:40 - 10:10	Invited H. Mayr 09:40 - 10:10	Invited Y. Apeloig 09:40 - 10:10	Invited H. Zipse 09:40 - 10:10	
09:50						Invited R. Shenhar 09:50 - 10:20
10:00 →						
10:10		M. Klussmann 10:10 - 10:30	M. Canle López 10:10 - 10:30	M. Abe 10:10 - 10:30	R. Haver 10:10 - 10:30	
10:20						A. Stanger 10:20 - 10:40
10:30		coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	coffee break 10:30 - 11:00	
10:40						coffee break 10:40 - 11:10
10:50						
11:00 →		Invited T. Linker 11:00 - 11:30	Invited A. Staubitz 11:00 - 11:30	Invited A. Berkessel 11:00 - 11:30	Invited S. Grimme 11:00 - 11:30	
11:10						E. Humeres 11:10 - 11:30
11:20						
11:30		Invited K. Lammertsma 11:30 - 12:00	Invited M. Sherburn 11:30 - 12:00	Invited H. Bettinger 11:30 - 12:00	Invited A. Krueger 11:30 - 12:00	E. Glebov 11:30 - 11:50
11:40						
11:50						M. Page 11:50 - 12:10
12:00 →		K. Nikitin 12:00 - 12:20	A. Dragan 12:00 - 12:20	G. Gescheidt 12:00 - 12:20	J. Kaleta 12:00 - 12:20	
12:10						closing remarks 12:10 - 12:30
12:20		B. Kovacevic 12:20 - 12:40	D. Hodgson 12:20 - 12:40	T. Müller 12:20 - 12:40	U. Siehl 12:20 - 12:40	
12:30						lunch break 12:30 - 14:00
12:40		lunch break 12:40 - 14:00	lunch break 12:40 - 14:00	poster award cerem. 12:40 - 13:00	lunch break 12:40 - 14:00	
12:50						
13:00 →	check-in at conference desk			lunch break 13:00 - 14:00		
13:10						
13:20						
13:30						
13:40						
13:50						
14:00 →		Plenary H. Anderson 14:00 - 14:40	Plenary P. R. Schreiner 14:00 - 14:40	excursion	J. Harper 14:00 - 14:20	
14:10						
14:20					P. Lainé 14:20 - 14:40	
14:30						
14:40		Invited J. Michl 14:40 - 15:10	Invited G. Bucher 14:40 - 15:10		R. Novikov 14:40 - 15:00	
14:50						
15:00 →					I. Williams 15:00 - 15:20	
15:10		S. Usui 15:10 - 15:30	E. Tretyakov 15:10 - 15:30			
15:20					B. Shainyan 15:20 - 15:40	
15:30		T. Slanina 15:30 - 15:50	A. O'Donoghue 15:30 - 15:50			
15:40					coffee break 15:40 - 16:30	
15:50		coffee break 15:50 - 16:20	coffee break 15:50 - 16:20			
16:00 →						
16:10	conference opening					
16:20		Invited G. Bodwell 16:20 - 16:50	Invited K. Koszinowski 16:20 - 16:50			
16:30	Opening Lecture: J.M. Lehn Strasbourg				Diels Planck Lecture B. Feringa Groningen 16:30 - 18:30 Concert	
16:40						
16:50		K. Nakata 16:50 - 17:10	I. Bilkis 16:50 - 17:10			
17:00 →						
17:10		G. Monaco 17:10 - 17:30	M. Lurdes Cristiano 17:10 - 17:30			
17:20						
17:30	welcome party	Q. Peng 17:30 - 17:50	M. Engeser 17:30 - 17:50			
17:40						
17:50						
18:00 →		poster session I 18:00 - 20:00	poster session II 18:00 - 20:00			
18:10						
18:20						
18:30					KINSIS reception	
18:40						
18:50						
19:00 →						
19:10						
19:20						
19:30				conference dinner until 22:00		
19:40						
19:50						