

HRSMC SYMPOSIUM

PROGRAMME AND ABSTRACT BOOK

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WELCOME

On behalf of the Holland Research School of Molecular Chemistry, I am very pleased to welcome you to this 2011 HRSMC symposium. We extend a special welcome to Prof. dr. Gros, who has agreed to give a guest lecture, and to our guests from the Westfälische Wilhelms Universität Münster. Since 2001, the HRSMC has a successful cooperation with this university by exchanging guest lecturers and PhD students, and by the organization of joint courses and summer schools. Last but not least, we are of course very happy with our own HRSMC staff members and PhD students, who have accepted the invitation to give a seminar at this symposium.

The HRSMC organizes this annual symposium to inform its members and other scientists from universities and industry about its research activities and novel trends in chemical research. Following the suggestions of the Educational Committee and the PhD platform, we have adapted this year the format of the poster sessions, which are now organized theme-wise, as well as the voting procedure for the best posters.

The research topics of the HRSMC are collected in three themes: (1) 'Synthesis, Characterization, Reactivity and Properties of Molecules', (2) 'Photochemistry and (Laser) Spectroscopy' and (3) 'Theoretical Chemistry'. PhD students and HRSMC staff members covering the three themes have been invited to give a lecture on their research.

For the fourth time, the *Dick Stufkens Prijs* for the best PhD thesis that appeared under the auspices of the HRSMC will be awarded. The winner of this academic year is dr. Sergio Ioppolo. The prize will be awarded by Prof. dr. Jan Verhoeven from the University of Amsterdam and member of the External Advisory Committee of the HRSMC. After the award ceremony, dr Sergio Ioppolo will give a presentation of the work for which he has received the 2011 *Dick Stufkens Prijs*.

Finally, I would like to draw your special attention to the poster sessions where PhD students and Postdocs will present their research results and get to know those of others. This year we have an adapted procedure for collecting votes for the best poster. During the welcome ceremony the procedure will be explained. The lectures, poster sessions and the reception afterwards will provide a good opportunity to become acquainted with new members of the HRSMC and their research activities. Also on behalf of the Board of the HRSMC I wish you all a very festive and inspiring day!

Prof. dr. Wybren Jan Buma
(Scientific Director HRSMC)

PROGRAMME HRSMC SYMPOSIUM 2011

- 08:45 Coffee/ tea & registration
- 09:00 Opening by Scientific Director, Prof. dr. Wybren Jan Buma
- 09:10 Prof. dr. P. Gros, Professor of Biomacromolecular Crystallography at Utrecht University and winner of the NWO Spinoza Prize 2010
- Session 1: HRSMC theme 1 – Chair: Dr. Sylvestre Bonnet (UL)**
- 10:00 Dr. Eelco Ruijter (VU)
"New tricks for (smelly) old dogs: exploiting atypical reactivity of isocyanides"
- 10:30 Coffee/ tea & Postersession 1 (Theme 1, poster 1-13)
- 11:20 PhD lecture: Sipeng Zheng (UL, group of Prof. dr. Lies Bouwman)
"From molecules to materials: tuning the transition temperature and cooperativity of bapbpy-based mononuclear spin-crossover compounds"
- 11:40 PhD lecture: Pawel Dydio (UvA, group of Prof. dr. Joost Reek)
"Supramolecular control of selectivity in transition metal catalysis using ligand functionalized with Anion Binding Pockets"
- Session 2: HRSMC theme 2 – Chair: Dr. Alex Yanson (UL)**
- 12:00 Prof. dr. Fred Brouwer (UvA)
"Looking into materials with fluorescence microscopy"
- 12:30 – 13:45 Lunch at 13:00 starts the Postersession 2 (Theme 2, poster 22-37)
- 13:45 Postdoc lecture: Bhargava Ram Niraghatam (VU, group of Prof. dr. Maurice Janssen)
"A femtosecond mass-resolved microscope for chiral molecules"
- 14:05 PhD lecture: Peter Zijlstra (UL, group of Prof. dr. Edgar Groenen, Prof. dr. Michel Orrit and Prof. dr. Silvia Völker)
"Detection of single non-absorbin proteins using a gold nanorod"
- Session 3: HRSMC theme 3 – Chair: Dr. Bernd Ensing**
- 14:25 Dr. Francesco Buda (UL)
"Modeling key processes in photosynthesis"
- 14:55 Coffee/ tea & Postersession 3 (Theme 1, poster 14-21 Theme 3 poster 38-44)
- 15:40 Voting for best poster in theme 1, 2 and 3
- 15:45 PhD lecture: Kush Singhal (group of Prof. dr. Peter Bolhuis and Dr. Evert Jan Meijer)
" A molecular dynamics study of chaperone-protein binding"
- PhD Lecture WWU Münster – Chair: Dr. Chris Slotweg (VU)**
- 16:05 PhD Lecture WWU Münster: Steffi Roters (group of Prof. dr. Werner Uhl)
"Al-P heterocycles and their reactivity towards small molecules"
- Dick Stufkens Award Ceremony, chaired by Prof. dr. Jan Verhoeven (UvA)**
- 16:25 Award Ceremony followed by Lecture of Winner Dick Stufkens Prize: Dr. Sergio Ioppolo (UL)
"Surface formation routes of interstellar molecules"
- 16:55 Poster Prize and Closure by Prof. dr. Kees Elsevier (UvA)
- 17:00 Reception
- 18:00 End of symposium, Scientific staff meeting and Dinner staff

ABSTRACTS OF INVITED LECTURES

GUEST LECTURE 09:10 HOUR

INSIGHTS INTO THE MOLECULAR MECHANISMS OF THE COMPLEMENT SYSTEM

Piet Gros

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The complement system is an integral part of the innate immune defense in mammals. Complement is formed by ~30 large multi-domain plasma proteins and cell-surface receptors. This system enables to host to recognize, lyse and clear invading microbes and altered host cells from blood and interstitial fluids, while protecting healthy host tissue. Through structural studies we have revealed the molecular mechanisms responsible for the central amplification steps, the host protection by complement regulators and the initial events in formation of the membrane-attack complex (MAC). I will discuss the structural mechanisms, which involve large structural rearrangements due to an interplay of proteolysis and complex formation.

Key publications

- [1] B.J.C. Janssen *et al.*, *Nature* **2005**, 437, 505-511.
- [2] B.J.C. Janssen *et al.*, *Nature* **2006**, 444, 213-216.
- [3] F.J. Milder *et al.*, *Nature SMB* **2007**, 14, 224-228 .
- [4] M.A. Hadders *et al.*, *Science* **2007**, 317, 1552-1554.
- [5] S.H.M. Rooijackers, Wu *et al.*, *Nature Immunology* **2009** 10, 721-727.
- [6] J. Wu *et al.*, *Nature Immunology* **2009**, 10, 728-733.
- [7] F. Forneris *et al.*, *Science* **2010**, 330, 1816-1820.

Images and movies

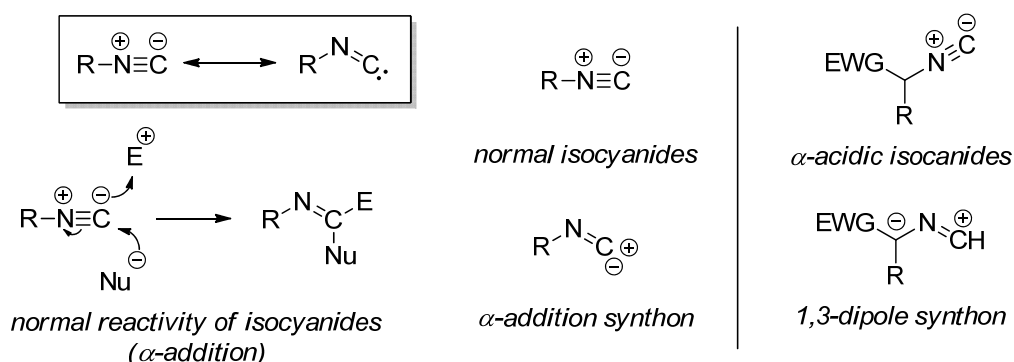
<http://www.crystal.chem.uu.nl/~gros/researchhighlights.htm>

NEW TRICKS FOR (SMELLY) OLD DOGS: EXPLOITING ATYPICAL REACTIVITY OF ISOCYANIDES

Eelco Ruijter

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More than a century and a half ago, Lieke discovered the first isocyanide, allyl isocyanide, in an attempt to synthesize allyl cyanide. The unpleasant smell of this class of compounds was undoubtedly one of the reasons that the discovery of the first isocyanide-based multicomponent reaction (IMCR) took until 1921, when Passerini reported the reaction of isocyanides with aldehydes and carboxylic acids. In this reaction and related IMCRs, the isocyanide terminal carbon atom reacts both as a nucleophile and an electrophile giving rise to the formation of an α -adduct (see Figure).



The introduction of an electron-withdrawing substituent adjacent to the isocyanide functionality leads to an increased α -acidity, resulting in a 1,3-dipolar reactivity. This feature has formed the basis for a new class of IMCRs based on the specific reactivity of α -acidic isocyanides.^[1]

As an additional useful property, isocyanides are isoelectronic with carbon monoxide. Considering the widespread application of palladium-catalyzed carbonylative cross-coupling reactions, the analogous reaction with isocyanides is severely underexploited and provides exciting opportunities.

This lecture will focus on recent contributions from our laboratories in novel (multicomponent) reactions of isocyanides based on the abovementioned reactivities.

References

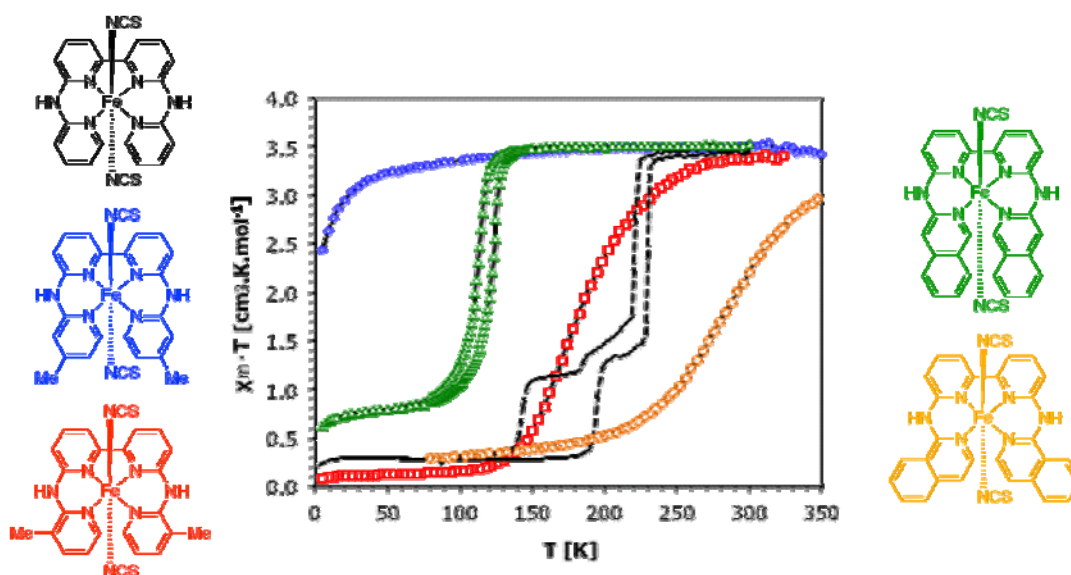
- [1] For recent contributions from our group, see: (a) N. Elders, E. Ruijter, F. J. J. de Kanter, M. B. Groen, R. V. A. Orru, *Chem. Eur. J.* **2008**, *14*, 4961. (b) N. Elders, E. Ruijter, F. J. J. De Kanter, E. Janssen, M. Lutz, A. L. Spek, R. V. A. Orru, *Chem. Eur. J.* **2009**, *15*, 6096 (c) R. Scheffelaar, M. Paravidino, A. Znabet, R. F. Schmitz, F. J. J. de Kanter, M. Lutz, A. L. Spek, C. Fonseca Guerra, F. M. Bickelhaupt, M. B. Groen, E. Ruijter, R. V. A. Orru, *J. Org. Chem.* **2010**, *75*, 1723.

FROM MOLECULES TO MATERIALS: TUNING THE TRANSITION TEMPERATURE AND COOPERATIVITY OF BAPBPY-BASED MONONUCLEAR SPIN-CROSSOVER COMPOUNDS

Sipeng Zheng, Zulema Arcís Castillo, Putro Vink, Maxime A. Siegler, Sylvestre Bonnet

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The design of molecular switches that can be utilized for information processing or data storage is an attractive goal in material science. Spin-crossover compounds, especially that based on iron(II), hold considerable potential in this field. In this study, the spin crossover of iron(II) complexes of the bisaminopyridinebipyridine (bapbpy) ligand has been investigated.^{1, 2} We show that 1) different isomers of the same mononuclear iron(II) complex give materials with different spin crossover properties, and 2) minor modifications of the bapbpy ligand allows for obtaining SCO near room temperature. We also provide a qualitative model to understand the link between the structure of bapbpy-based ligands and the SCO properties of their iron(II) compounds.



References

- [1] S. Bonnet; M. A. Siegler; J. S. Costa; G. Molnar; A. Bousseksou; A. L. Spek; P. Gamez; J. Reedijk, *Chem. Commun.* **2008**, 5619-5621.
- [2] Z. A. Castillo; S. Zheng; M. A. Siegler; O. Roubeau; S. Bedoui; S. Bonnet, *Chem. Eur. J.* **2011**, DOI: 10.1002/chem.201101301.

SESSION 1 PHD LECTURE 11:40 HOUR

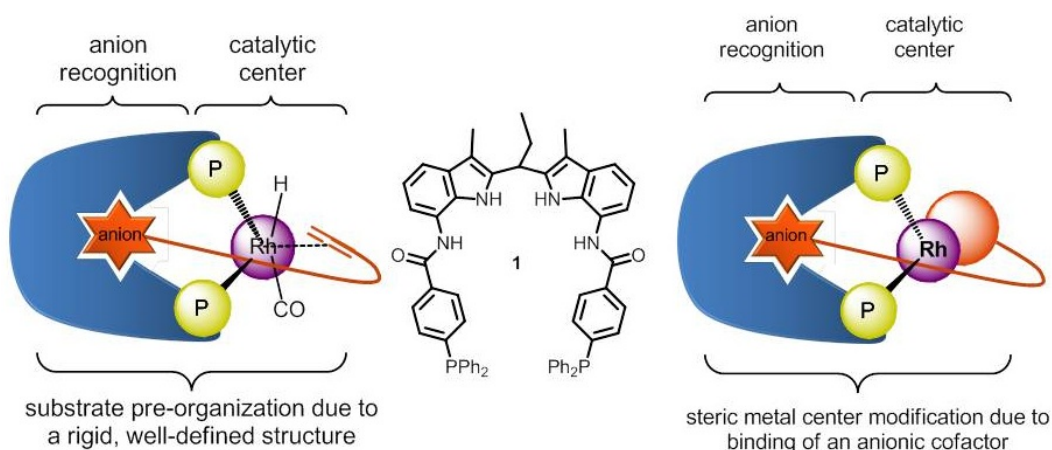
SUPRAMOLECULAR CONTROL OF SELECTIVITY IN TRANSITION METAL CATALYSIS USING LIGAND FUNCTIONALIZED WITH ANION BINDING POCKETS

Paweł Dydio and Joost N. H. Reek

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The selectivity displayed by a transition metal catalyst is one of the key elements in catalysis, and various tools to control this by ligand modification have been reported. Some selectivity issues are, however, difficult to solve using these traditional methods and therefore we have an interest in the development of supramolecular chemistry approaches, guided by the lessons that we can learn from Nature.[1]

Here we present DIMPhos (**1**), a new bidentate phosphorus ligand equipped with an integral anion recognition site.[2] The supramolecular interactions between the binding pocket of the Rh(**1**)-catalyst and alkenes containing anionic functionalities provide an excellent design-concept to achieve remote control of the regioselectivity in hydroformylation by the substrate pre-organisation (Figure, left). DFT calculations show that the substrate anchoring highly restricts movement of the reactive double bond, and hence favors one reaction pathway. This gives rise to the observed highly selective hydroformylation of a variety of terminally and internally unsaturated carboxylic and phosphonic acids.[3] This provides the first example of wide-ranging remote control of catalyst selectivity by secondary substrate-ligand interactions.



Further, the pocket of the Rh(**1**)-catalyst can be also used for the catalyst tuning by binding small cofactors - anions of chiral acids (Figure, right), allowing for remote modulation of the enantioselectivity of the catalyst. This strategy afforded excellent enantioselectivities (ee's up to 99%) for the hydrogenation of olefins, demonstrating its potential. Even when using a

mixture of 12 cofactors the selectivity was high, which indicates that catalysis is dominated by the best cofactor, allowing a deconvolution strategy for rapid identification of the best cofactor. Thus, catalyst optimization by non-covalent binding of simple cofactors expands the scope of new supramolecular approaches to the search of catalysts for challenging catalytic transformations.

In this contribution we discuss the mechanism and the substrate range of this multifunctional catalytic system for both the control of the selectivity by the substrate pre-organisation and the catalyst tuning by the cofactor binding.

References

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LOOKING INTO MATERIALS WITH FLUORESCENCE MICROSCOPY

Fred Brouwer, Joanna R. Siekierzycka, Tanzeela N. Raja, Chantal E. Carpentier

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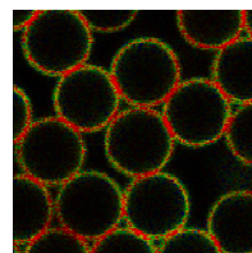
Fluorescence micro(spectro)scopy is intensively used in biology and medical sciences, but is still less popular in materials science.¹ I will present three applications in which molecular fluorescent probes provide local information on the structure and dynamics of materials via their various fluorescence properties such as intensity, excited state lifetime and spectrum.

The first example demonstrates how single molecule spectroscopy can be used to map out the glass transition in polymer films. Below T_g essentially all probe molecules are fluorescent. As the temperature is increased, more and more individual molecules appear to be switched off. The working principle of the method is based on excited state electron transfer. This type of process requires a thermodynamic driving force, but also enough free volume for it to occur on the short timescale of the excited state lifetime.²



A second area of application is film formation of latex emulsions. In this case, labelling of individual latex particles allows the direct observation of the spreading of polymer particles across the inter-particle boundaries in the last stage of coating formation.³

The third example is related to the force networks that control the dynamics (flow/arrest, depending on the density) of granular matter. We use fluorescence microscopy to observe the contact points between different particles of micrometer to millimeter sizes. Our ultimate goal will be to quantify the forces at the contact points.



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A FEMTOSECOND MASS-RESOLVED MICROSCOPE FOR CHIRAL MOLECULES

N. Bhargava Ram, C.S. Lehmann and M.H.M. Janssen

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Chiral molecules are a special class of molecules that come in two forms, a left and right handed form. Many amino acids, sugars and pharmaceutical drugs are chiral and it is observed that one enantiomer type dominates over the other in living systems (known as homochirality). Conventional analytical spectroscopic techniques that distinguish molecular chirality are often based on *circular dichroism* (CD), where the difference in linear absorption between left and right circularly polarized light is measured. This difference is typically of the order of 10^{-4} [1].

The angular distribution of electrons ejected from chiral molecules upon one-photon ionization using left and right circularly polarized light can produce a much stronger asymmetry. A forward – backward asymmetry of up to 0.2 was observed in one-photon ionization of valence electrons with circularly polarized synchrotron radiation [1]. These effects are a factor of 100-1000 larger than CD. This *photoelectron circular dichroism* (PECD) phenomenon makes angular-resolved photoionization studies of enantiomers very promising with regard to sensitivity and selectivity. During the last few years PECD in various chiral molecules was reported using a synchrotron XUV photon source [1].

Here, we report our first results using femtosecond multi-photon ionization in combination with mass-resolved photoelectron coincidence imaging [2,3] on chiral molecules. We demonstrate that a table-top chiral microscope can be used to detect mass-resolved enantiomers with high-selectivity and sensitivity. Our novel technique presented here opens new directions in analytical mass-spectrometric applications on chiral molecules. The details of our recent progress in our group at LaserLaB Amsterdam will be presented at the meeting [4].

References

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- [3] C. S. Lehmann, N. Bhargava Ram, D. Irimia and M. H. M. Janssen, *Faraday Discuss.*, **2011**, DOI: 10.1039/C1FD00047K.
- [4] N. Bhargava Ram, C. S. Lehmann, M. Rafiee Fanood, N. Ligterink and M. H. M. Janssen, (to be submitted) **2011**.

DETECTION OF SINGLE NON-ABSORBING PROTEINS USING A GOLD NANOROD

Peter Zijlstra, Pedro M.R. Paulo, Paul Ruijgrok, and Michel Orrit

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Most methods capable of detecting a single molecule rely on the fluorescence or absorption of the molecule or of a label attached to the molecule. However, label-free detection has definite advantages because the analyte cannot always be labeled, and because the properties of the molecule may be altered by a label. These notions have sparked large efforts in developing label-free sensors. Although ensembles of molecules can easily be detected with various label-free approaches, single-molecule sensitivity gives access to valuable information on dynamics and populations.

We demonstrate the label-free detection of single proteins by monitoring the surface plasmon resonance of a single metal nanoparticle. The electric field associated with a surface plasmon resonance (SPR) decays rapidly from the surface of the particle, into the surrounding medium. A perturbation of the local refractive index causes a shift of the SPR, allowing for the label-free detection of purely refractive molecules. As a sensor we employ a single gold nanorod, which can be produced by wet-chemical synthesis in large quantities with a low size and shape dispersion. We functionalized the nanorods with biotin to allow for the detection of biotin binding proteins. This functionalization was done specifically at the tips of the nanoparticle, where the sensitivity for protein binding is the largest. We employ photothermal microscopy to monitor the longitudinal SPR of a single gold nanorod immobilized in a flow cell. This approach allows for the real-time detection of single-molecule binding events in an integration time of 100 ms.

MODELING KEY PROCESSES IN PHOTOSYNTHESIS

Francesco Buda

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Modeling natural and artificial photosynthesis is a challenging task due to the intrinsic multiscale nature of the processes involved. A number of open questions still remain in the microscopic understanding of key processes, such as the first photo-induced charge separation, and the splitting of water into hydrogen and oxygen.

In this talk I will present some of the results we have obtained in the last few years in elucidating the structural and electronic properties of light-harvesting antennas and photosynthetic reaction centers. I will underline the importance of combining the computational work with crucial input from spectroscopic studies, in particular based on solid state NMR.

Ab-initio molecular dynamics has been used recently in our group to study the coupling between the electron density rearrangement and the vibrational motion in a bacterial reaction center model, which appear to be crucial in understanding the first photo-induced charge separation step.

Water oxidation catalysts constitute an important module in the design of artificial photosynthetic devices. The critical step of the oxygen-oxygen bond formation in the catalytic cycle has been investigated in recently synthesized ruthenium based catalysts. The results of our simulations clearly show the importance of an explicit inclusion of the water environment for a proper description of the reaction path and intermediate complex.

A MOLECULAR DYNAMICS STUDY OF CHAPERONE- PROTEIN BINDING

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Proteins produced in ribosomes emerge as long unfolded or partially folded polypeptide chains and need to acquire fully folded 3D structures to perform their respective functions. Special proteins, known as chaperones, are present at the exit tunnel of ribosomes or further downstream in the cells to assist in the folding of these nascent chains through direct guidance in folding or prevention of aggregation and misfolding. Triggerfactor is one such chaperone that interacts with polypeptide chains at various stages to guide protein folding, prevent aggregation, and facilitate protein translocation across membranes. However, direct influence of triggerfactor, or chaperones in general, on folding pathways remains poorly understood. This work employs molecular dynamics simulation methods to understand the relatively unknown binding mechanism of maltose binding protein (MBP) to the trigger factor (TF) chaperone. Contrary to popular belief, our results illustrate a crucial role for N-terminal of TF in its binding to various folding intermediates of MBP through hydrophilic interactions. This interaction is expected to stabilize MBP and prevent its aggregation/misfolding.

References

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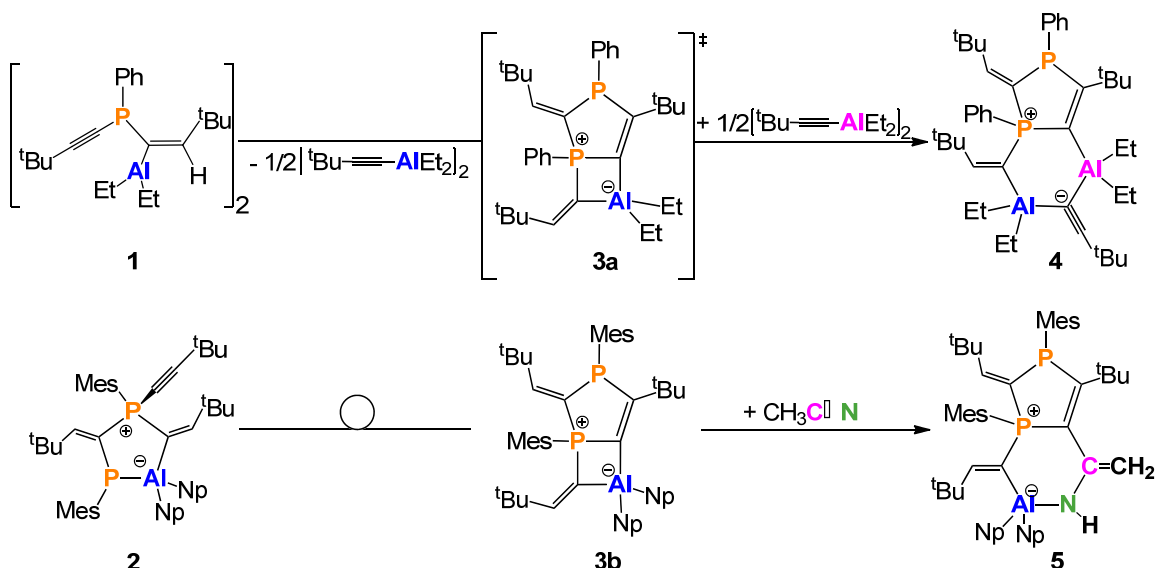
AL-P HETEROCYCLES AND THEIR REACTIVITY TOWARDS SMALL MOLECULES

Steffi Roters^a, H. Westenberg^a, Werner Uhl^a, J. Chris Slootweg^b
and Koop Lammertsma^b

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b: Department of Chemistry and Pharmaceutical Sciences, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Hydroalumination reactions are well-known procedures for the reduction of unsaturated organic compounds.¹ Treatment of alkynylphosphines with equimolar quantities of dialkylaluminium hydrides gave phosphinoalanes with basic donor (P) and acidic acceptor (Al) sites in close proximity that are able to activate small molecules.² The investigations in the influence of a second or a third alkyne moiety on the course of the hydroalumination reactions show that unprecedented secondary processes take place.³ Depending on the steric shielding by the substituents on aluminium and phosphorus the hydroalumination reactions lead to the heterocyclic compounds **1**, **2** or **3**. Reaction of **1** and **2** with small dipolar molecules (^tBuCCAIEt₂ and CH₃CN) give the insertion products **4** to **5** via the bicyclic intermediates **3a** and **3b** (Scheme 1).



Scheme 1: Reactions of **1** and **2**, rearrangement reaction and insertion of small molecules (Mes = 1,3,5-trimethylphenyl; Np = CH₂^tBu).

References

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LECTURE BY THE WINNER OF THE DICK STUFKENSPRIJS 2011 – 16:25 HOUR

SURFACE FORMATION ROUTES OF INTERSTELLAR MOLECULES

Sergio Ioppolo, Herma M. Cuppen^{*}, Claire Romanzin^{**}, Gleb Fedoseev, Thanja Lamberts, Ewine F. van Dishoeck, Harold Linnartz

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Today more than 160 different molecular species have been identified in the interstellar medium (ISM), in the gas phase and/or in the solid state. For decades astrochemists have tried to explain this chemical complexity in such a highly dilute environment as the ISM by combining astronomical observations, the outcome of dedicated laboratory experiments and astrochemical models. Gas phase reaction routes between reactive species were found to explain the observed abundances of many of the unstable species - radicals and ions - while solid state reactions on icy dust grains were proposed to play an important role in the formation of the more complex "organic" compounds. It is generally accepted now that interstellar grains provide a surface on which gas-phase species can accrete, meet and react and to which they can donate excess energy. In this way, icy dust grains act both as a molecular reservoir and as a catalytic site. Complex grain surface chemistry is then triggered by photon/cosmic ray irradiation, thermal processing and particle bombardment. In order to better understand the molecular complexity of the Universe, detailed laboratory experiments that simulate surface reactions triggered by these processes are highly needed.

Here, some of the latest research performed in the Sackler Laboratory for Astrophysics in Leiden, the Netherlands is reviewed. The focus is on the surface formation of some of the most abundant molecules detected in the solid phase in space, such as water and methanol, known to be both a chemical starting point for more complex species in space, and also carbon dioxide, formic acid, and formaldehyde. Formation reactions are triggered by hydrogenation (*i.e.*, non-energetic H-atom addition) of interstellar ice analogues at astronomically relevant temperatures ^[1-7].

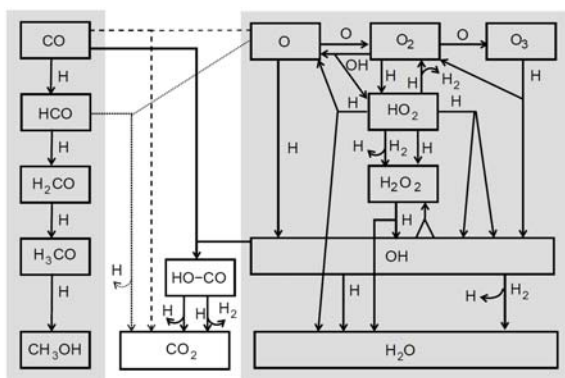


Fig. 1 Schematic representation of the investigated hydrogenation reactions in CO (left), O/O₂/O₃ (right) and CO:O₂ (center) ices. Experiments are performed using SURFRESIDE, an ultra-high vacuum set-up, in which ices are deposited on a gold substrate at low temperatures and subsequently (or simultaneously) exposed to hydrogen atoms in order to initiate possible surface reactions. Reaction products are monitored by means of reflection

absorption infrared spectroscopy (RAIRS) and mass spectrometry.

References

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ABSTRACTS OF POSTERS
IN ORDER OF POSTER NUMBER

THEME 1

SUBSTITUTED DIBENZOYLMETHANES AS ANTENNAE FOR LUMINESCENT Eu(III) COMPLEXES

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Thanks to the advent of LED chips emitting in the near-UV or blue spectral region (380-450 nm), solid state lighting (SSL) devices have attracted vast interest from the lighting industry. In SSL devices, the UV light emitted by the LED is converted to wavelengths in the visible range by a coating of appropriate phosphor materials. Superior robustness, high efficiency as well as improved environmental friendliness are the key advantages of SSLs over conventional lighting technologies.

Lanthanide complexes based on Eu(III) and Tb(III) ions are promising candidate materials for the phosphorescent coating. In these complexes, the line-like emission characteristic of the Ln(III) ion can be observed upon excitation in the ligand centered absorption bands, i.e. the ligand acts as an antenna. Unfortunately, only very few complexes are known that have the efficiency and stability required for application in SSL.

Beta diketonates are known to be efficient antennae, especially for Eu(III) centered luminescence. In particular, dibenzoylmethanate (DBM) gives highly efficient complexes. The anionic complex (HNEt₃)[Eu(DBM)₄] has a photoluminescent quantum yield of 75%, but is plagued by a poor stability [1-2]. Fortunately, this compound offers ample possibilities for improvement of its stability as well as its efficiency. Firstly, we have replaced the cation by other monovalent cations: NEt₄⁺, NMe₄⁺, NBu₄⁺, N(CH₂C₆H₅)Et₃⁺, and the alkali metal ions. These substitutions influence the geometry of the luminescent Eu(DBM)₄⁴⁻ centre, and via this route induce a profound effect on the luminescent properties of the compound. Secondly, we are tuning the antennae themselves to suit both Eu(III) and the excitation source. The antenna-effect is largely governed by the electronic structure of the ligand, which can be influenced by substitution on the aromatic moiety. Selected positions on the aryl rings have been substituted with halogens, methyl- and methoxy groups. The effects of these substitutions on the luminescent properties of the compounds are shown on the poster.

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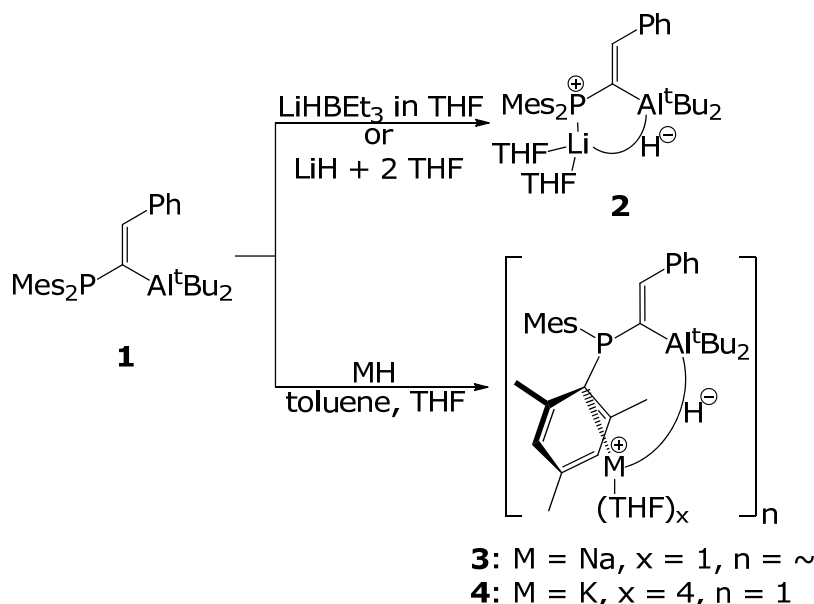
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ALKALI METAL HYDRIDE ADDUCTS OF AL/P BASED FRUSTRATED LEWIS PAIR AND THEIR APPLICATION IN PHASE TRANSFER CATALYSIS

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Frustrated Lewis Pairs (FLPs) with donor and acceptor sites in close proximity are of considerable interest for the dipolar activation of small molecules such as dihydrogen and carbon dioxide. The geminal Al/P based FLP **1**^[1] shows a high reactivity towards alkynes, CO₂, carbonyl compounds and Lewis base stabilized boranes (BH₃ * THF, BH₃ * NH₃). In addition, the reaction of **1** with alkali metal hydrides MH (M = Li, Na, K) leads to the formation of the corresponding alkali metal phosphanylalanates **2** - **4**^[2] (Scheme 1). The reaction of sodium hydride with triphenylchlorosilane using **3** as a phase transfer catalyst (10 mol %) gives triphenylsilane in good yields and indicates an increased reducing power of **3** compared to the free hydride.



Scheme 1: Synthesis of alkali metal phosphanylalanates **2** - **4**.

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ONE-POT FOUR-ENZYME CATALYTIC CASCADE TO PREPARE CARBOHYDRATES: SYNTHESIS OF D-FAGOMINE

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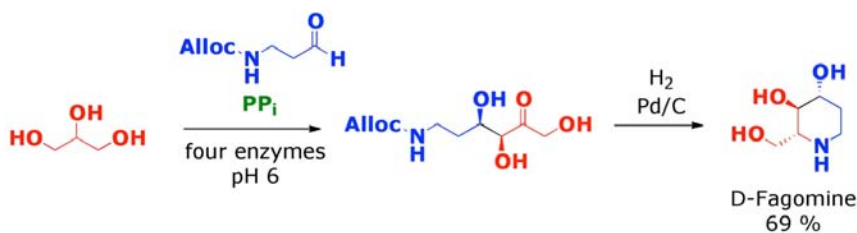
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In the search for more efficient, sustainable and greener synthetic strategies, chemists increasingly pursue approaches inspired by Nature. In particular chemoenzymatic cascades, mimicking the way Nature is constructing complex natural products, are progressively more applied in synthetic sequences [1]. In our group, a one-pot four-enzyme catalytic cascade has recently been developed in which glycerol is converted into carbohydrate fragments in enantio- and diastereomerically pure form starting from inexpensive reagents and without the need for protection and deprotection steps [2,3].

All four enzymes in the catalytic cascade act simultaneously at pH 6. Initially, three enzymes (PhoN-Sf, GPO and catalase) are involved in converting glycerol into the energy rich phosphate ester dihydroxyacetone phosphate (DHAP) at the expense of cheap pyrophosphate (PPi). In the same pot, the DHAP is then enzymatically coupled to various aldehydes by the DHAP-dependent aldolase RAMA. Finally, the cascade reaction is terminated by the irreversible dephosphorylation by PhoN-Sf of the aldol products to produce functionalized carbohydrate fragments in enantio- and diastereomerically pure form and reasonable yields. The advantage of this route is that many aldehydes can be used since the aldolase has a broad substrate tolerance, thus forming different carbohydrates.

The synthetic value of the catalytic cascade was demonstrated via a one-pot synthesis of the naturally occurring azasugar D-fagomine in 69% yield starting from glycerol and a protected 3-amino-propanal (Scheme 1).



Scheme 1

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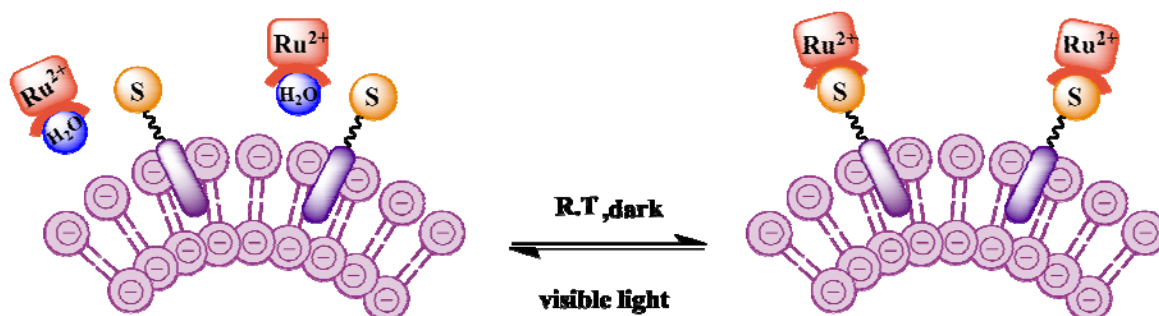
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LIGHT INDUCED REVERSIBLE BINDING AND UNBINDING OF RUTHENIUM(II) POLYPYRIDYL COMPLEXES AT THE SURFACE OF A LIPID BILAYER

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Large anionic unilamellar vesicles decorated with thioether ligands were prepared by incorporating into a dimyristoylphosphatidylglycerol (DMPG) lipid bilayer a thioether-cholesterol conjugate. Addition of $[\text{Ru}(\text{terpy})(\text{dcbpy})(\text{OH}_2)]^{2+}$ (terpy = 2,2';6',2''-terpyridine; dcbpy = 6,6'-dichloro-2,2'-bipyridine) to the vesicles is followed, in the dark, by thermal coordination of the ruthenium(II) complex to the sulfur atom of the membrane-embedded ligand, to form a membrane-bound ruthenium complex. Subsequently, irradiation of the sample with visible light breaks the Ru-S coordination bond to re-generate the unbound aqua ruthenium complex. Due to electrostatic interactions with the anionic lipid bilayer the "free" cationic ruthenium complex stays close enough to the surface of the lipid bilayer, which allows for back-coordination of the ruthenium center to the membrane-embedded ligand in the dark. As shown by UV-vis spectrophotometry binding and unbinding of the ruthenium complex to and from the surface of the lipid bilayer can be repeated up to four times without signs of degradation by switching off and on the source of visible light. Thus, back and forth hopping of the complex is obtained at the surface of the lipid bilayer.



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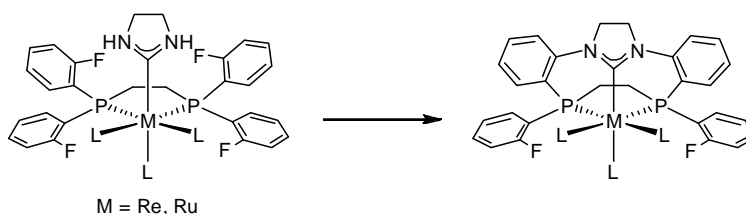
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TEMPLATE SYNTHESIS OF COMPLEXES BEARING MACROCYCLIC P₂C^{NHC} LIGANDS AND NH,NR- SUBSTITUTED CARBENE LIGANDS

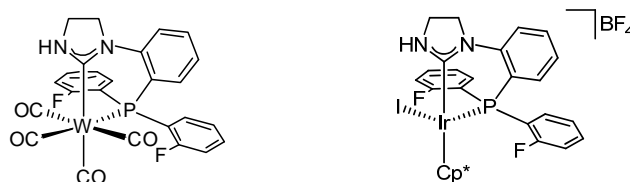
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N-Heterocyclic carbene complexes are well known and due to their diversity have become ubiquitous ligands in organometallic chemistry.^[1] For the generation of a macrocyclic ligand featuring both NHC and phosphine donor functions we selected a metal template controlled reaction. For this approach a suitable diphosphine as well as a reactive NHC ligand, all coordinated to the template metal, are necessary. The diphosphine ligand has to contain a potential linker to the carbene with a good leaving group. We used a fluorophenyl linker with fluorine as leaving groups in *ortho* position to the phosphorus atoms. After deprotonation of the NH-functions of the NH,NH-NHC ligand, the nitrogen atoms of the carbene ligand react under a nucleophilic attack at the fluorine substituted carbon atoms leading to the [11]ane-P₂C^{NHC} macrocyclic ligand at the metal template (M = Re^I,^[2] Ru^{II}).



Furthermore, metal coordination of a monophosphine and a NH,NH-NHC ligand followed by linkage generates a complex with a donor-functionalized NH,NR-stabilized NHC, which constitutes a new method for the preparation of such complexes. This reaction was first successfully carried out at the tungsten(0) and iridium(III) templates.



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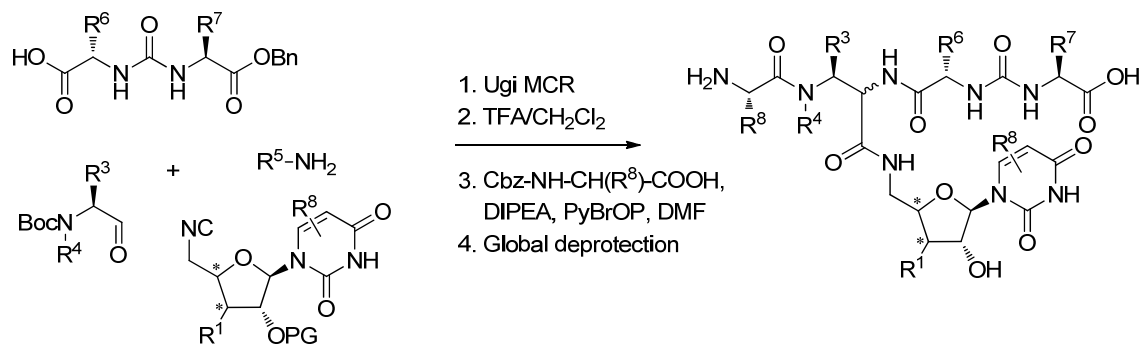
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DIVERSITY-ORIENTED SYNTHESIS OF URIDYL PEPTIDE ANTIBIOTICS USING MULTICOMPONENT REACTIONS

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Antibiotic resistance of pathogens is an urgent global problem that has recently become painfully clear by the life-threatening infections by enterohemorrhagic *E. coli* (EHEC) and carbapenem-resistant *Klebsiella pneumoniae* in Dutch hospitals. These examples underline the urgency of the problems caused by antimicrobial resistance and are illustrative for what awaits us if no actions are taken. Thus, our society dearly needs novel antibiotics targeting resistant pathogens. Especially, new classes of antibiotics with unexploited mode of action are desirable, since they are much less likely to encounter cross-resistance. The natural product class of uridyl peptide antibiotics (*e.g.* mureidomycins and pacidamycins) serves as an attractive starting point in the development of a new class of antibacterial drugs. They possess potent antibacterial activity against *P. aeruginosa* by inhibition of MraY (translocase), an essential enzyme in cell wall development.



As the exocyclic enamide function of these compounds is not essential for bioactivity,^[1] saturated derivatives of the natural occurring uridyl peptides are envisioned as suitable target molecules. We will discuss the synthetic challenges and recent progress using a multicomponent assembly approach, employing the Ugi reaction (see Figure) as a suitable strategy for the construction of a library of simplified or otherwise modified analogs of uridyl peptide antibiotics.

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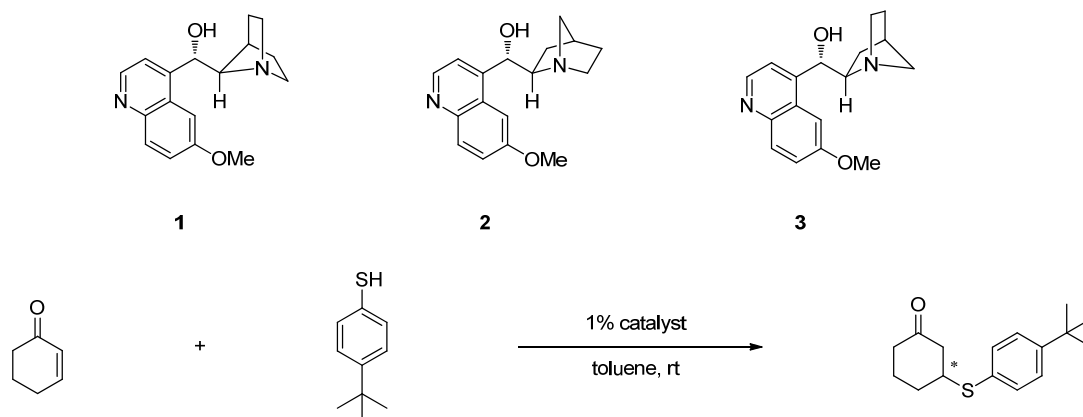
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TOTAL SYNTHESIS OF NOR-QUINIDINE-DERIVATIVES

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Cinchona alkaloids are an important class of organic molecules in the field of asymmetric organocatalysis. A significant development in organocatalysis was realized in 2005 by the synthesis of a modified *cinchona* alkaloid bearing a thiourea group at the 9-position.¹ Since then several different derivatives based on *cinchona* alkaloids have been reported.² However, no investigations have been performed with *cinchona* alkaloids that contain a modified quinuclidine group. Here we report the total synthesis of three isomeric nor-quinidine derivatives (**1** – **3**), each with a nor-azabornane functionality substituted at a different carbon atom. With these analogs of quinidine we want to examine the role of the direction of the lone pair of the tertiary amine in known organocatalytic reactions. As a model reaction we examined the suitability of these nor-quinidine derivatives as catalysts in the 1,4-addition of thiophenols on to cyclohexenones as this was one of the first *cinchona* alkaloid catalyzed reactions to be described in the literature.³



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N-HETEROCYCLIC CARBENE-FUNCTIONALISED IRIDIUM PHOSPHINIDENES: WHAT A DIFFERENCE A TWIST MAKES

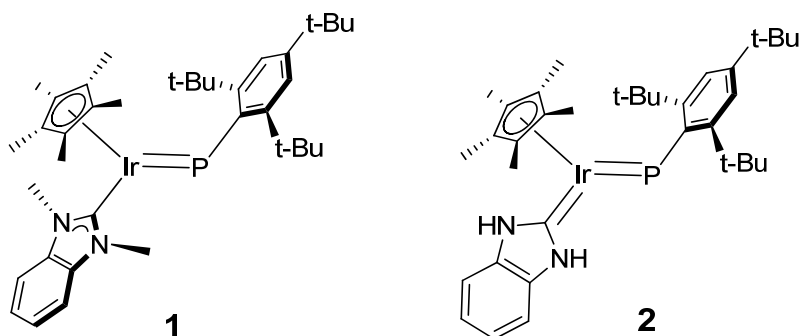
Andrei Chirila[†], Mark K. Rong[†], Carolin A. Dumke[‡],
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N-Heterocyclic carbenes (NHCs) are recognized as viable alternatives for the ubiquitous tertiary phosphine ligands (R₃P) used in homogeneous catalysis, and have often served as their replacement, mainly due to better results in improving the activity of specific catalysts. Although many studies have investigated the effects of NHCs and tertiary phosphines on carbene complexes, e.g. Grubbs' 1st and 2nd generation metathesis catalysts, little information is available about the effects that NHCs might have on the reactivity of analogous phosphinidene complexes. Furthermore, only few reports describe the reactivity of nucleophilic phosphinidenes coordinated to late transition metals. Bearing this in mind, the following question arises: Is it possible that a substituent-controlled conformational change of a coordinated NHC significantly modifies the reactivity of an organometallic catalyst, instead of having to use a totally different ligand?

As was previously reported by Lammertsma *et al.* [1], preliminary computational studies have shown that a simple *N*-substitution of the NHC modifies the σ -donor/ π -acceptor ability of the carbene, thus changing the electronic properties of the complex and consequently modifying the reactivity of the phosphinidene. As a direct result, the present work focuses on supporting these calculations by synthesising two new *N*-heterocyclic carbene-functionalised [2] iridium phosphinidene complexes, **1** and **2**, that may present different reactivity, directly correlated to the NHC conformation.



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RECYCLABLE PALLADIUM NHCS FOR SEMI-HYDROGENATION CATALYSIS

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Pd-NHCs **1** are highly efficient catalysts for the (transfer) semi-hydrogenation of alkynes to Z-alkenes^[1]. An important point of optimization of these systems is the development of recyclable systems. This can be achieved by attachment of homogeneous catalysts to a support. This method combines the rational design of homogeneous catalysts with the facile recycling and stability of a heterogeneous catalyst^[2].

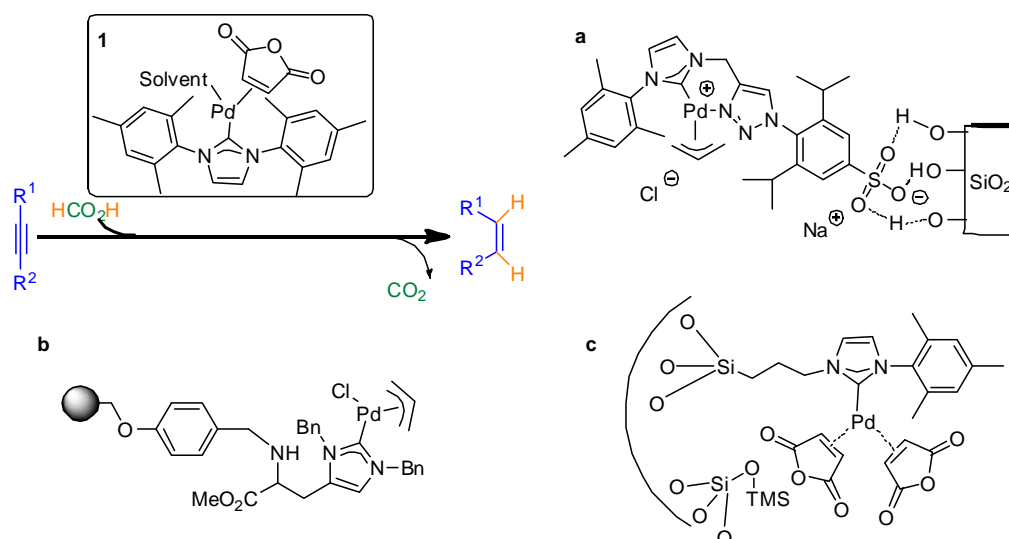


Figure 1: A homogeneous catalyst **1** and three heterogenization methods a,b,c.

Three methods of recycling are currently under investigation (figure1). The first (a) is a non-covalent method. Sulfonate functionalized NHCs are bound to silica through a hydrogen bonding interaction. Additionally a method with covalent linkage (b) is developed where the natural amino acid histidine is used as a precursor for NHCs, while the amine is used for attachment to a resin. As a third method, in cooperation with the Copéret group[†], a catalyst is developed on a highly regular hybrid TEOS silica (c).

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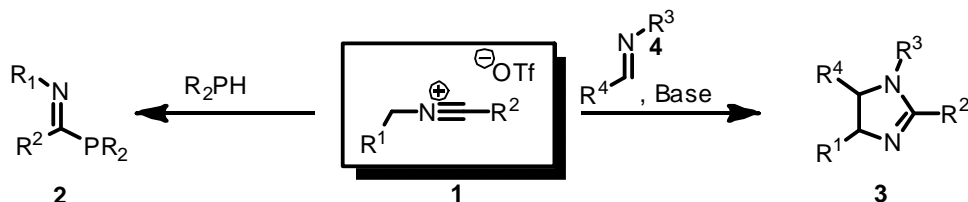
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NITRILIUM TRIFLATES: EASY ACCESS TO HIGHLY FUNCTIONALISED 2-IMIDAZOLINES

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Nitrilium ions and their corresponding ylids are versatile reactive intermediates.^[1] In our exploration of the use of nitrilium triflates **1** as versatile building blocks for the construction of heterocycles and transition metal ligands, we currently employ them for the synthesis of P,N-ligands **2** by nucleophilic addition of a secondary phosphine.



In the search for other applications we envisioned that the reaction of nitrilium triflates with imines **4** in the presence of a base would provide efficient access to functionalized 2-imidazolines **3**. Functionalized 2-imidazolines **3** are of great pharmaceutical interest^[2] and have potential as ligands in asymmetric transition metal catalysis.^[3] Although several methods for the synthesis of **3** have been reported, a direct route toward tetra functionalized 2-imidazolines in one step has not yet been described. Using **1** we were able to develop a simple route toward **3** in one step.

A deeper understanding of the reaction mechanism leading to **3** is essential for the determination of factors governing the scope and stereoselectivity of the reaction. Experimental and theoretical investigations to this end focus on the identification of possible reaction intermediates and plausible reaction pathways.

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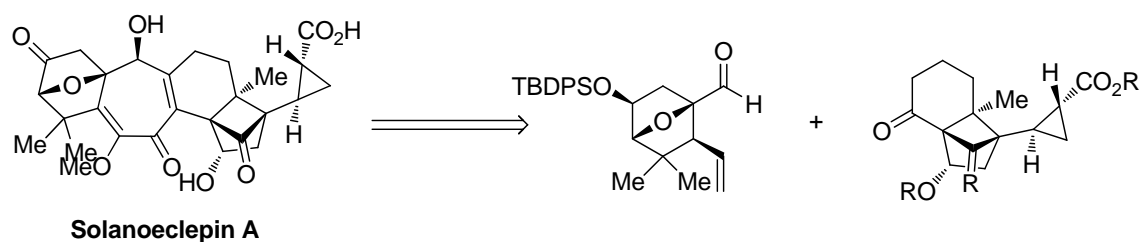
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STUDIES TOWARDS THE RIGHT-HAND SIDE OF SOLANOECLEPIN A VIA INDIUM/TIN MEDIATED ALLYLATION AND SUBSEQUENT [2+2]-PHOTOCYCLOADDITION

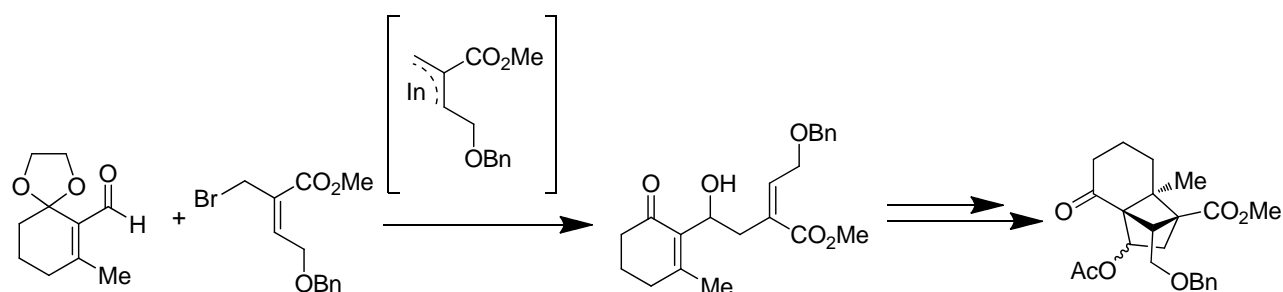
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Solanoeclepin A is a biologically active compound isolated from the roots of the potato plant. It is a potent hatching agent of the potato cyst nematode.^[1] Its unique structural features makes it a challenging synthetic target. The retrosynthetic analysis of solanoeclepin A reveals two synthetic fragments; the so called right- and left-hand side.^[2]



The poster deals with our efforts towards [2+2]-photocycloaddition precursors of the right-hand side structure involving an indium or tin mediated coupling between an aldehyde and an allylic bromide. Via this route complex tetracyclic structures could be synthesized in a limited amount of steps, making it a quick and versatile pathway towards the core structure of the right-hand side of solanoeclepin A.



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DEVICE COMPATIBLE WATER OXIDATION CATALYSTS FOR SOLAR TO CHEMICAL ENERGY CONVERSION.

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In 2001, the global energy consumption rate was 13.5 TW. In 2050 based on the increasing population and economic growth, this is estimated to reach 27 TW.¹ To meet these future demands, not relying on fossil fuels only, we need sustainable, carbon neutral ways of winning energy. The sun is the most abundant energy source on the planet (regarding current technology) as on average the energy of the sun reaching the earth's surface is estimated to be $1.2 \cdot 10^5$ TW. Part of this can be directly used by converting it to electricity using solar cell technology, but it is essential to at least partly convert to storable energy, by fixing it in chemical bonds. This can be achieved by using solar energy to convert water into hydrogen and oxygen.

Plants, algae and cyanobacteria already use photosynthesis to convert energy from the sun into chemical energy within Photosystem II at the water oxidation reaction center of the Manganese-Calcium cluster. With Nature serving as a model we try to develop new, rapid and efficient water oxidation catalysts based on Iridium.² Application of suitable ligands offer ease of synthetic modification such that these catalysts can be modified to have the ability to integrate them into devices, which are capable to split water into hydrogen and oxygen. This so called Artificial Leaf, if turnover numbers and turnover frequencies are sufficiently high, could provide us with a significant solution towards the upcoming energy problem. In this work we will discuss our endeavors in catalyst modification.

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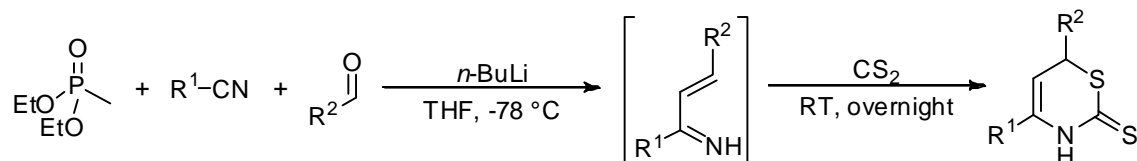
THE FORMAL HETERO DIELS-ALDER REACTION OF 1-AZADIENES WITH CARBON DISULFIDE

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Non-fused 3,6-dihydro-2*H*-1,3-thiazine-2-thiones constitute a so far rather unexplored class of compounds, as the latest reports date back more than two decades.[1] Thiazine-2-thiones contain an endocyclic dithiocarbamate group, which is often found in pesticides or in synthetic intermediates.

1-Azadienes are reactive species that can be generated by the multicomponent reaction (MCR) of diethyl methylphosphonate, nitriles and aldehydes (Scheme 1). In our group, several reaction partners for 1-azadienes were already developed.[2] We now wish to report the novel MCR of 1-azadienes with carbon disulfide. With this reaction a one step protocol towards the potentially interesting 3,6-dihydro-2*H*-1,3-thiazine-2-thiones was furnished, and a small library was subsequently synthesized.



In addition, possible reaction pathways were computationally investigated in order to gain further insight into the reaction.

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NEUTRAL PALLADIUM (II) COMPLEXES WITH SCHIFF-BASE P[^]N LIGANDS AS SUZUKI-MIYAURA COUPLING CATALYSTS

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Most common Suzuki-Miyaura catalysts in use are phosphine complexes with strong P-donors. The initial step in the coupling pathway is the oxidative addition of an aryl halide to a Pd(0) active species. A precatalyst such as Pd(PPh₃)₄, for example, would therefore need to enter the catalytic cycle through two successive ligand dissociations to give the 14-electron active complex Pd⁰(PPh₃)₂, which is extremely unstable and prone to deactivation by aggregation and formation of palladium black [1]. The use of hemilabile ligands is one way of stabilizing the active species. These ligands stabilize metal ions in various oxidation states and geometries, which normally form during the catalytic cycle [2]. The hard donor sites are weakly coordinated to the palladium centre, and can easily dissociate in solution, affording a vacant sites whenever demanded, whereas the chelate effect confers stability to the catalyst precursor in the absence of the substrate thereby preventing catalyst decomposition/deactivation [2,3].

We report here the use of well-defined neutral Pd(II) complexes with hemilabile iminophosphine ligands as pre-catalysts in Suzuki-Miyaura coupling reactions using low catalyst loadings under mild conditions. The tested compounds show tolerance of a wide variety of reaction conditions, including different solvents, bases, substituents on both the arylboronic acids as well as the aryl halides used.

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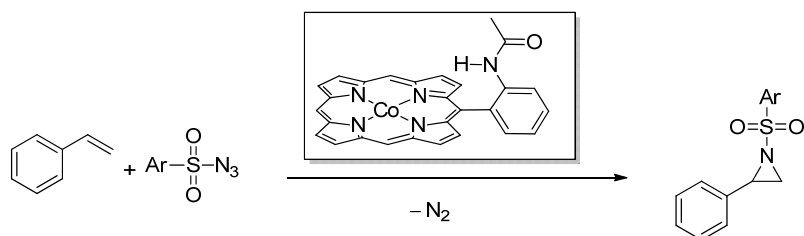
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THE RADICAL MECHANISM OF COBALT(II) PORPHYRIN-CATALYZED OLEFIN AZIRIDINATION AND THE IMPORTANCE OF COOPERATIVE H-BONDING

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Organic azides are among the most promising and environmentally friendly alternatives in olefin aziridination.^[1] Large substrate scope is already available, however the activation process is troublesome in most cases. Furthermore harsh reaction conditions are generally required for nitrene transfer from organic azides to organic substrates. Similar to diazo reagents, these compounds can generate nitrene ligands at transition metals by a simple loss of dinitrogen and afford a nitrogen source.^[2] Zhang and coworkers have tested several Co^{II}(por) based systems, and a novel N-H bond designed system proved so far the best catalyst for aziridination of various styrene derivatives with arylsulfonyl azides under mild conditions (Figure 1).^[3] However, the mechanism still remains unclear, and the understanding of it is important to expand the substrate scope.



In this contribution we present the mechanism of cobalt(II) porphyrin-mediated aziridination of styrene with PhSO₂N₃ by means of DFT calculations. We show that the mechanism of Co^{II}(por) mediated olefin aziridination proceeds via an unusual radical-type mechanism. The redox non-innocence of the nitrene ligand allows the formation of a nitrogen-centered nitrene radical, which plays a crucial role in the mechanism. We further computationally investigated the role of hydrogen bonding in this reaction.

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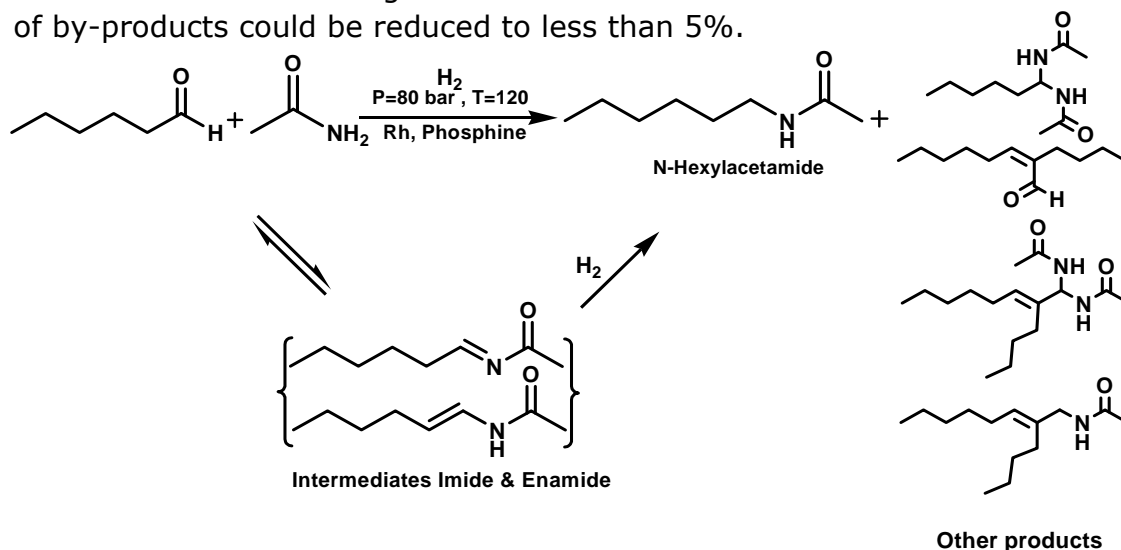
RHODIUM-CATALYZED HOMOGENEOUS HYDROAMIDATION OF ALDEHYDES

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The aim of our research is the development of a catalytic route for the selective conversion of biomass-derived levulinic acid to nylon precursors. The main challenge of this research is to develop a one-step intramolecular hydroamidomethylation reaction in which pentenamides are converted with syngas into caprolactam. The desired condensation between intermediate aldehyde and amide moieties to produce N-acylimine/enamide intermediates will be crucial to success. Therefore the one-pot catalytic intermolecular hydroamidation reaction to obtain N-alkylamide is currently studied.

Different rhodium precursors in combination with several monodentate and bidentate phosphine ligands with varying stereo electronic properties were studied in the catalytic hydroamidation reaction. The electronic and steric effects of the used phosphine ligands and reaction conditions in the reductive amidation reaction have been investigated. It appears that the reaction proceeds via the formation of enamide and imide intermediates. Best results in the catalytic hydroamidation of hexanal with acetamide reveal an overall hexanal conversion of higher than 85% with more than 80% selectivity for the desired N-hexylacetamide. In this reaction, the observed by-products are derived from aldol condensation; aldehyde hydrogenation and di-coupled amide. After optimization of the reaction conditions - such as using less concentrated reaction mixtures - the amount of by-products could be reduced to less than 5%.



Acknowledgements

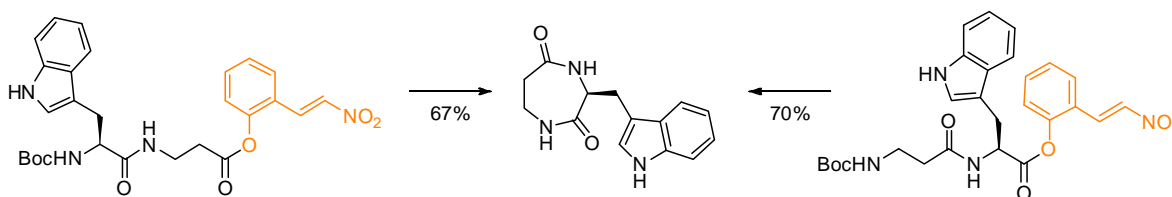
This research was performed within the framework of the CatchBio program. We gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

SYNTHESIS OF RING STRAINED CYCLIC PEPTIDES VIA INTRA-MOLECULAR AZA-MICHEAL/ACYL TRANSFER CASCADE

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Many cyclic peptides exhibit important biological activities [1]. Unfortunately, due to combination of ring-strain and the transoid character of the amide bond cyclization of small peptides is difficult. Over the years several methods have been developed to lactamize small peptides, but these still suffer from drawbacks such as epimerization or narrow synthetic scope [2]. In order to overcome these problems a new auxiliary mediated method for cyclization is under development. The auxiliary is esterified to the C-terminus of a small peptide and capable of undergoing an aza-Michael/acyl transfer cascade resulting in a new amide bond [3]. Using this this auxiliary, small peptides were cyclized under high dilution conditions resulting in highly strained lactams.



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CHIMERIC GNA/DNA METAL-MEDIATED BASE PAIRS

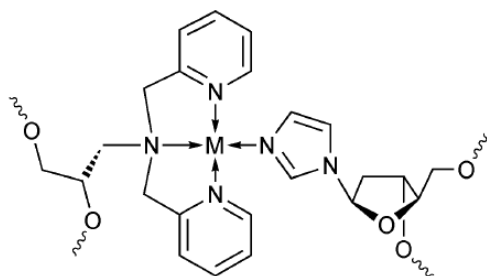
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The introduction of transition metals into either DNA or GNA *via* metal-ion-mediated base pairs is a promising strategy towards a functionalization of these supramolecules (GNA = glycol nucleic acid).[1,2] The possibility to combine different nucleic acid backbones within one metal-mediated base pair expands the applicability of metal-functionalized nucleic acids.

We report the introduction of chimeric GNA/DNA metal-mediated base pairs in DNA double helices. The base pairs are built from tridentate GNA dipicolylamine nucleoside and complementary monodentate DNA azole nucleosides (imidazole, 1,2,4-triazole and tetrazole). In this way, a planar complexation can be obtained (Scheme to the left with monodentate imidazole as example).



UV and CD spectroscopic data indicate a Ag(I)- and Au(III)-ion mediated stabilization of all three base pairs. Other transition metal ions do not lead to significant thermal stabilization. To verify the formation of a silver(I)-mediated base pair, theoretical calculations based on dispersion-corrected density functional theory were performed. The calculations support an incorporation of Ag(I) into oligonucleotides.[3]

Acknowledgements

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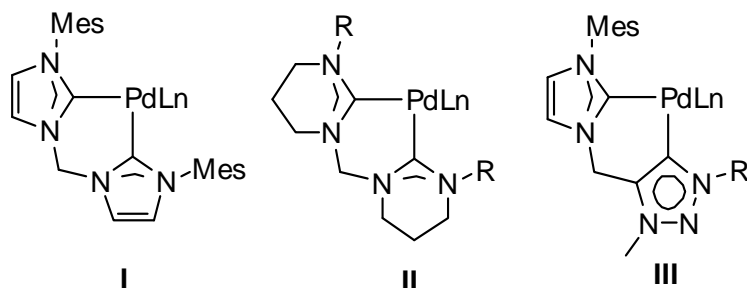
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EXPLORING CHELATING BIS-NHC LIGANDS

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N-heterocyclic carbenes (NHC) have proven to be very useful and versatile ligands in transition metal catalysis. Our group has recently developed zerovalent palladium NHC-complexes that are very active and selective in the transfer semihydrogenation of alkynes^{[1][2]}. In this project bidentate biscarbenes are explored as ligands for late transition metals, **I**, **II** and **III**. They are believed to enhance the stability as a result of the chelate effect as well as allowing fine tuning of steric properties and fluxional behavior^[3].



Next to the familiar biscarbene complexes^[3], **I**, we are also interested in making bidentate bis-expanded ring NHC complexes, **II**, as these have increased donating capacity. Additionally, a third structure is envisioned in which the NHC is connected to a triazole that coordinates in an abnormal fashion to the metal, **III**. In this system the different carbenes in synergy might lead to new reactivity patterns.

The synthesis of these ligands will be presented as well as preliminary results in their metal complexation and catalysis.

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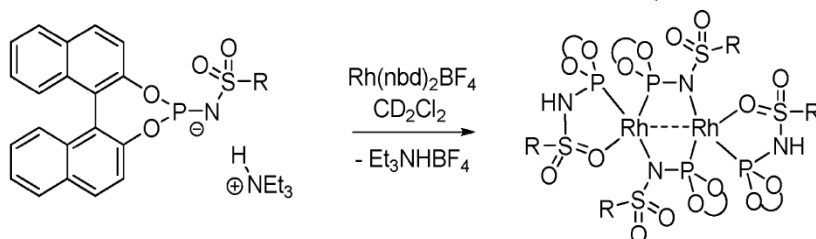
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HIGHER ORDER NONLINEAR EFFECTS IN ASYMMETRIC CATALYSIS USING RH-METAMORPHOS COMPLEXES

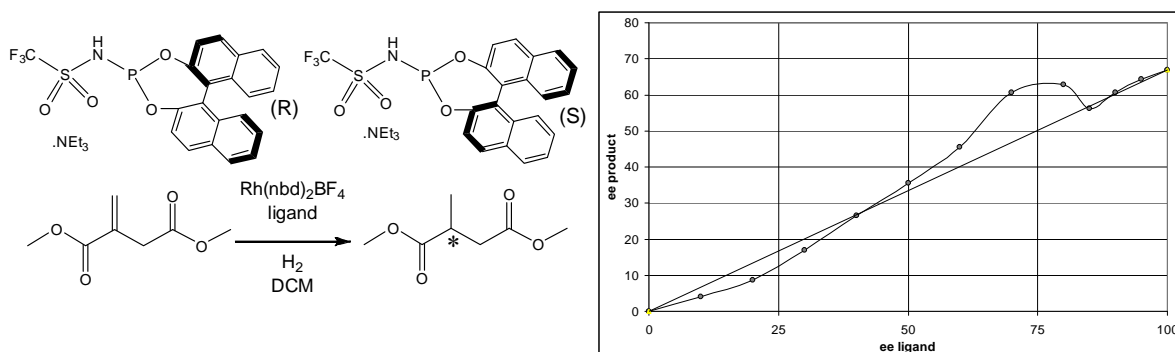
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The METAMORPhos family, a new class of sulfonamide-phosphorus ligand was recently discovered.^[1] Their coordination with rhodium can give rise to unique complexes consisting of two metal centers and four identical ligands. These complexes displayed high selectivity in the asymmetric hydrogenation reaction. Counterintuitively, the enantiomeric excess of the product may not be a linear function of the enantiomer purity of the ligand, an effect often referred to as nonlinear effect.^[2] Such nonlinear effects have not been studied for (dinuclear) rhodium complexes that contain more than two ligands, and this is interesting as higher order effects may be observed.



Indeed, these Rh_2 complexes show a higher order nonlinear effect in asymmetric hydrogenation of functionalized olefines. In several cases, a local maximum was observed. X-ray and NMR analysis were performed to get a better understanding of the system revealing the nature and relative population of the diastereomeric complexes, coordination behavior and dynamics.



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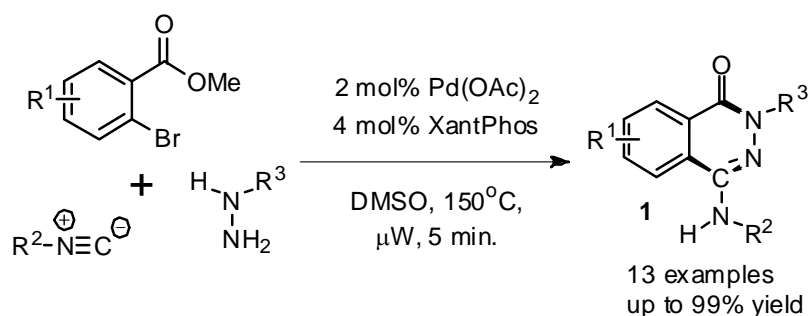
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PALLADIUM-CATALYZED SYNTHESIS OF 4-AMINOPHTHALAZIN-1(2H)-ONES BY ISOCYANIDE INSERTION

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4-Aminophthalazin-1(2H)-ones (APOs, **1**) are exceptional and structurally interesting heteroaromatics that have shown potential as anti-cancer agents and against various other diseases including stroke, myocardial infection and auto-immune diseases.^[1] Surprisingly, structural variation of APOs has only scarcely been studied, which might be explained by the tedious linear synthesis from phthalic anhydride. Furthermore, non-symmetric substitution of the phenyl ring is difficult due to formation of regioisomers.



Palladium-catalyzed iminoacylation by isocyanide insertion is a relatively unexplored methodology that has recently received a lot of interest.^[2] We now report an efficient one-step synthesis of APOs by palladium-catalyzed cross-coupling of *o*-bromobenzoates and hydrazines with isocyanide insertion followed by lactamization. The reaction proceeds to completion within five minutes under microwave irradiation with a wide range of substituted (pseudo)halobenzoates.

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THEME 2

SUBSURFACE OXYGEN ON Pt(111) AND ITS REACTIVITY FOR CO OXIDATION

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As a good catalyst for the oxidation reaction, platinum is massively used in the car exhaust systems and is considered as a promising candidate for the fuel cells applications. That is why interaction of platinum with molecular oxygen has not only fundamental but also applied value.

For the last four decades UHV surface science studied the formation and reactivity of atomic oxygen over-layer produced by dissociation of molecular oxygen on Pt [1, 2]. Recently it was shown that platinum surface is covered with a thin layer of platinum oxide after interaction with O₂ at realistic pressures and temperatures. This oxide was recognized as an active phase for the oxidation reaction [3].

In this work we demonstrate that by going to the catalytically relevant temperatures (400-700K) at UHV conditions, oxygen adsorbs not only on top of platinum surface but also migrates into the subsurface region. The amount of oxygen adsorbed at elevated temperatures can be double the maximum 0.25ML coverage routinely obtained at room temperature [1, 2]. At the same time, this extra oxygen is not detected on top of platinum surface in the STM and LEED measurements. Together with the reactivity measurements for CO oxidation, this suggests that additional oxygen is stored below the surface of Pt(111). We believe that our finding bridges the gap between the UHV and ambient pressure studies and sheds more light on the formation of platinum oxide during catalysis.

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BOOSTING UP THE EFFECTS OF MOLECULAR CHIRALITY

S. R. Domingos, C. L. M. Baij, D. Dunnebier, M. Finger, M. R. Panman, B. H. Bakker, F. Hartl, B. de Bruin, W. J. Buma, S. Woutersen

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The unambiguous assignment of the handedness of organic molecules is of essential importance in biochemistry and pharmacology. Vibrational Circular Dichroism (VCD), the infrared circular dichroism due to the vibrations of chiral molecules, is a relatively new spectroscopic technique that has proven itself very efficient as a probe to determine molecular handedness. However, the technique lacks of strong signal magnitudes. For biochemical compounds in solution, which aggregate at high concentrations, the VCD signals lack of enough absorption intensity and are often masked within the noise of the measurement. Therefore, with the aim of amplifying the VCD peak intensities of relevant Biomolecules in their naturally occurring environment, we re-engineer the electronic manifold of the molecules in order to induce an enhancement of the VCD signals.

The mechanism involved in the enhancement is based on vibronic coupling theory [1,2], and relies on the presence of low-lying electronically excited states. The mixing of these with the ground state eigenfunctions will add up to the total number of adiabatic electronic states contributing to the vibrational eigenfunctions, leading to strongly enhanced VCD signals. Manipulation of the electronic manifold has been proven possible by means of electrochemical reduction and complexation with paramagnetic metal ions (figure).

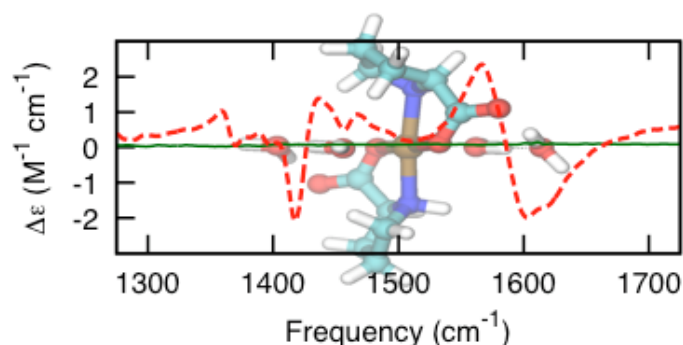


Fig. VCD spectra of L-valine (green) and L-valine complexated with Co(II) (red).

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CHARACTERIZATION OF LOW FREQUENCY MODES INVOLVED IN PHOTOSYNTHETIC CHARGE SEPARATION

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Using first-principles molecular dynamics we characterize the first step in the charge separation process in the reaction center of photosynthetic bacteria in a model including the special pair and closest relevant residues. This approach allows for a direct observation of the coupling between the nuclear motion and the electronic structure rearrangement in the ground state and after electronic excitation within the restricted open-shell Kohn-Sham method. In the ground-state a dynamical localization of the HO is found to be a defining characteristic of the special pair P. Two low frequency vibrational modes tune the orbital energy levels. After electronic excitation we demonstrate one specific mode that couples to P* and lowers the energy of the PM-dimer-half, representing the reaction coordinate along which the excited state develops into a PL+PM⁻ charge transfer intermediate. As such, the photosynthetic architecture effectively removes the barrier for charge separation.

Acknowledgements

Huub Adriaanse

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EMPLOYING A NI CYLINDRICAL SINGLE CRYSTAL IN STUDIES OF D₂ DISSOCIATION ON STEPS

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It is well known that steps at surfaces may strongly affect the barrier for dissociative adsorption of, *e.g.* H₂ and CH₄. Somorjai and co-workers found that especially the open side of the step may lower the activation barrier for H₂ dissociation on Pt¹. Much less is known how the width of adjacent terraces or the arrangement of atoms in the step influences the change in barrier height. Recently we have investigated how dissociative adsorption of H₂ on Pt is affected by terrace width employing a series of flat single crystals². This type of study is very time consuming and may be hampered by differences in quality between the individual crystals. It is preferable to use one cylindrical single crystal which can expose all relevant faces at the same time.

Previous use of cylindrical crystals was limited to analyze the surfaces by techniques involving electron beams³. In contrast to that we utilize a supersonic molecular beam to locally impinge molecules onto small identified surfaces areas. In this way we directly measure reactivities with the King and Wells-technique⁴ and obtain spatially resolved temperature programmed desorption (TPD) spectra.

We show that results obtained from the cylindrical single crystal are comparable to those obtained on flat crystals. We demonstrate the spatial resolution of at least 2° by displaying a series of TPD measurements. We provide results for a study of D₂ dissociation on surfaces with (111) terraces and (100) steps and varying step density. Results are interpreted in terms of dominance of direct and indirect reaction mechanisms and relate those to other metals where comparable studies have been performed.

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THE EFFECT OF A MEMBRANE-MIMICKING DETERGENT ON ALZHEIMER'S AMYLOID PEPTIDE AGGREGATION BY EPR

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The aggregation of the beta-Amyloid peptide into fibrils is the chief indicator of Alzheimer's disease. More intriguing is that oligomeric aggregates and protofibrils, rather than fully formed fibrils could be responsible for the toxicity of the beta-Amyloid peptide. We monitor the effect of a membrane-mimicking detergent on the aggregation of the beta-Amyloid peptide using EPR.

Continuous wave, 9 GHz EPR reveals that upon increasing the detergent concentration a transition from oligomers to a state in which a monomeric peptide binds to a micelle, occurs. The approach allows detection of oligomers on the timescale of aggregation.

OPTIMISING RAMAN SPECTROSCOPIC METHODS FOR THE DETECTION OF (PAST) LIFE SIGNATURES

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Was there ever life on Mars? Or maybe there still is. This study won't reveal the answer, but it could offer a range of Raman spectroscopic techniques for the detection of life in extreme environments, for example on Mars.

The challenge is *in situ* detection of biomarkers which unambiguously prove the evidence of (past) life. This poster presents the first period of the research project 'Optimising Raman spectroscopic methods for the detection of (past) life signatures'.

In Figure 1 a laboratory sample of a mineral with a microbial suspension is shown. This figure is produced with a Renishaw InVia Raman microscope equipped with a 785 nm StreamLine laser, used for a fast (<5 minutes) analysis of the sample area (approx. 400 data points). Two reference spectra of the mineral 'Calcite' (in red) and a suspension of a bacterial, iron and sulfide mixture (in green) were used to map the scanned area.

Acknowledgements

This project is funded by NWO, project **ALW-GO-PL/10-06**

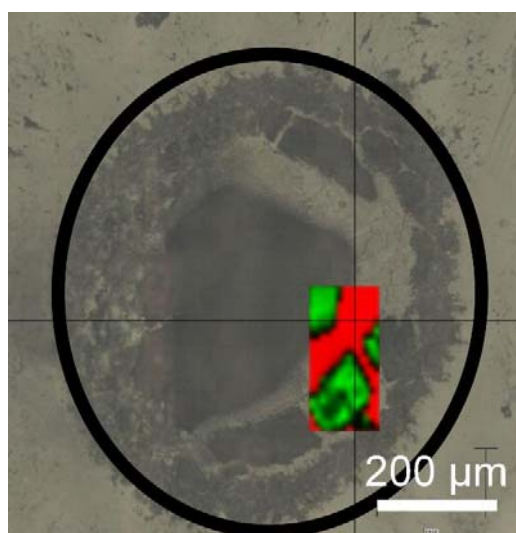


Figure 1: Calcite (CaCO₃) sample with a drop of a microbial suspension.

TIME-RESOLVED RAMAN SPECTROSCOPY THROUGH OPTICAL SKIN PHANTOMS AND SKIN

I.E. Iping Petterson, M. A. Fokker, V. E. van Eif, J. B. Buijs, G. van der Zwan, C. Gooijer, F. Ariese

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Time-Resolved depth Raman techniques are based on short laser pulses and the temporal discrimination between Raman photons emitted from the surface and Raman photons originating from a deeper layer within a sample. The relatively short gate width (~ 250 ps) of Time Resolved measurements using an Intensified Charged Coupled Device (ICCD) detector also considerably reduces fluorescence, as well as provides spatial selectivity in depth measurements.

The ability to obtain chemical information through opaque, diffusely-scattering layers shows particular promise for biomedical applications. Characterizing the nature of photon path and Raman photon migration through different materials is an essential step in the progression towards in vivo measurements.

Raman spectra were measured through optical skin phantoms with different compositions in order to determine how characteristics like the concentration of scattering particles, as well as sample thicknesses affect photon migration. These experiments were then compared with modeled Monte-Carlo simulations. Preliminary results from comparable measurements through porcine skin indicate that silicone optical skin phantoms with 0.4% (w/w) TiO_2 particles have similar scattering properties to skin, as representatively measured by Raman photon delay.

A MONONUCLEAR WATER SPLITTING MIMIC OF PHOTOSYSTEM-II WITH A FOUR-STEP PROTON COUPLED ELECTRON TRANSFER (PCET) REGIME

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Recent developments in water splitting by molecular catalysts are not mature enough to be exploited in fuel production system using solar energy hampered by catalytic instability, low turnover number and rate.¹ We here show a highly competent electrocatalytic water oxidation assembly based on new mono-site ruthenium complexes. This catalytic system mimics the photosystem-II in producing hundred thousands of rapid turnovers for dioxygen by consecutive 4-PCET steps for the first time (**Fig. 1**). In neutral water, the catalyst generates $>3 \times 10^5$ turnovers for O₂ at a rate of ~ 7 per sec, and more than 6×10^5 turnovers at $\sim 5.33 \text{ sec}^{-1}$ in aqueous acids were realized.² This leads to a water splitting device with the highest turnover numbers achieved till date for a molecular catalyst.

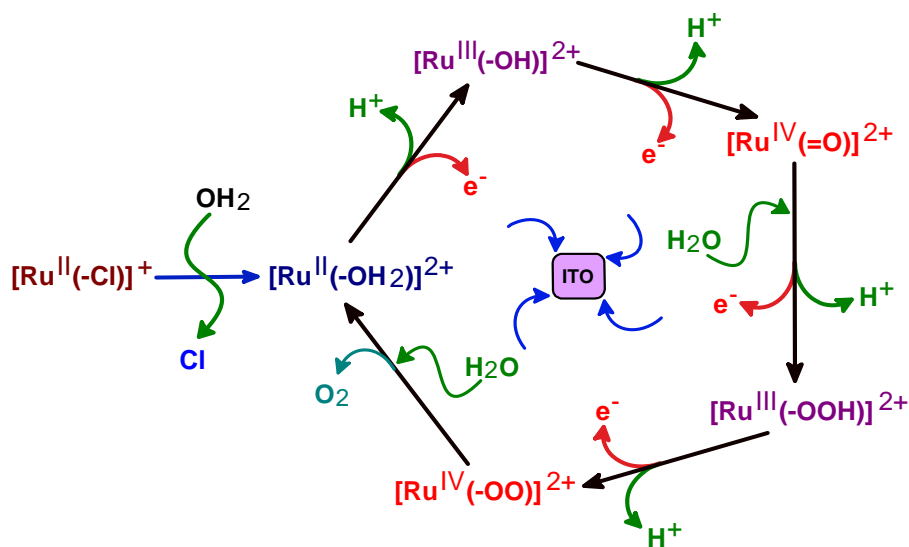


Figure 1. A pentacycle catalytic pathway for water oxidation.

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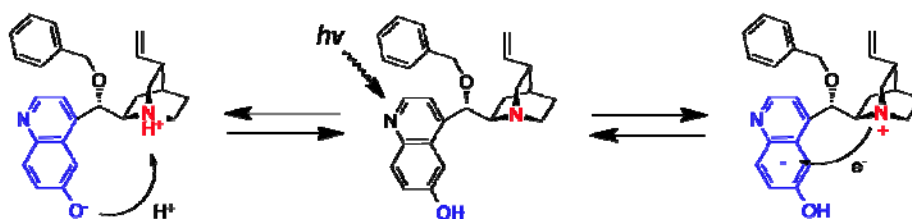
ELECTRON TRANSFER VS. PROTON TRANSFER: PROBING VERSATILE PHOTOPHYSICS OF CINCHONA BASED ORGANOCATALYSTS

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Cinchona based bifunctional catalysts have been widely utilized in asymmetric synthesis with high yield and enantioselectivity.^[1] It is generally recognized that bifunctionality of the catalyst arises from the interactions with the hydroxyl group (electrophile, hydrogen bond donor) and the basic quinuclidine nitrogen (nucleophile, hydrogen bond acceptor), but the understanding of the overall mechanism is limited.

On the other hand, these functional groups can facilitate different photophysical processes together with the built-in fluorophore, the quinoline moiety. For example, the quinuclidine nitrogen can act as electron donor and participate in a photo induced electron transfer to quinoline, or 6-hydroxyl can undergo excited state proton transfer to the quinuclidine in the presence of water. Understanding of these processes and how different hydrogen bonding and protonating agents will alter the behavior can open a new way to probe the substrate-catalyst interactions.



Some spectroscopic studies of these processes have been already reported, but these studies were mainly limited to steady-state methods.^[2,3] We now present the latest results from time-resolved studies with powerful analysis methods (global analysis and TRANES^[4]) for understanding the time-resolved fluorescence decays.

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PROBING THE ADSORPTION OF CARBON MONOXIDE ON TRANSITION METAL CLUSTERS USING IR PHOTODISSOCIATION SPECTROSCOPY

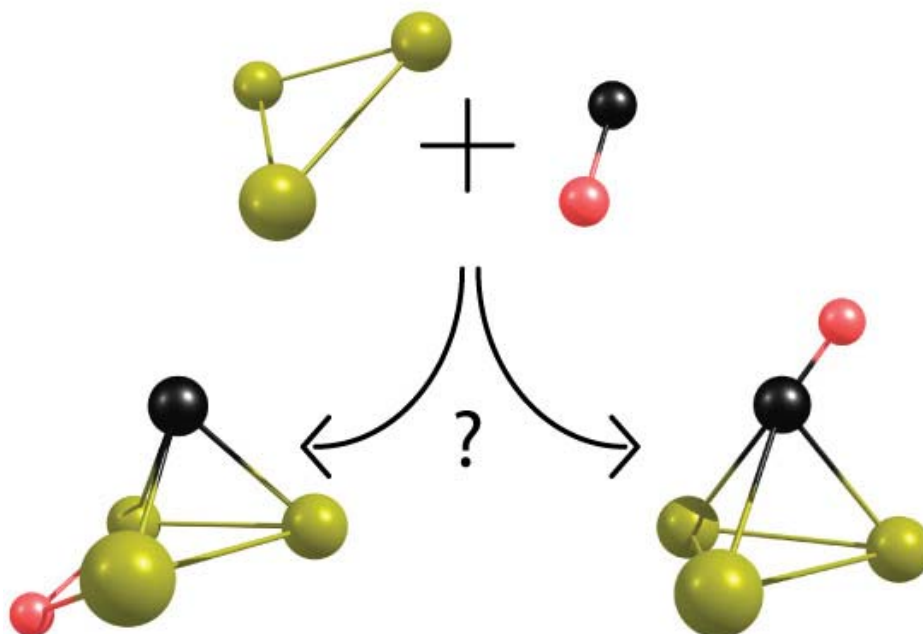
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Carbon monoxide is involved in many catalytic reactions, either as starting material or side-product. It is therefore of fundamental interest to understand the binding of CO to catalytic materials, for instance to transition metals. For niobium, CO molecules bind dissociatively to bulk material. However, despite the recent interest in enhanced catalytic activity of nanosized metal clusters, little is known on the adsorption of CO on niobium in the cluster regime.

We study the adsorption of CO on gas-phase niobium clusters. Using far-IR photodissociation spectroscopy in combination with mass-spectrometric detection, a size-selective IR fingerprint is obtained for cationic, neutral and anionic clusters. The combination of these spectra with DFT calculations allows for the structural determination of the adsorption product.



ABSOLUTE DENSITY-PROFILE MEASUREMENT OF MOLECULAR BEAM BY USING MULTIPHOTON IONIZATION OF XE

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We present a simple method to calibrate the density-profile of supersonic molecular beam, which is obtained by comparing the ion signal intensity between the molecular beam and bulk gas under the identical experimental conditions using MPI of Xe and velocity map imaging setup for Xe⁺ ions. This method relies on the fact that ions of interest are produced from the same interaction volume in both cases.

In determining the absolute density profile, issues like thermal broadening in the bulk gas are dealt with using selective discrimination of ion counts near the image center along the laser propagation direction. Details of the experiment are presented in this contribution.

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SINGLE MOLECULES AS OPTICAL TRANSISTORS

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A possible scheme for quantum computing is to transport qubits as photons and to switch and store them with electronic states. We propose to use a single molecule to switch a stream of photons. Because of the strong interaction of a single molecule with light at low temperature (cross section comparable to focused beam area), we intend to optically address a single molecule in a low-temperature fluorescence microscope¹. In its ground electronic state S_0 , the molecule strongly scatters the photons of the "blue" source beam (see Fig. 1Aa) because they resonate with the $S_0 \rightarrow S_1$ transition. When the molecule is switched to its triplet state T_1 (Fig.1Ab) upon absorption of a "red" gate photon, resonance with the "blue" photons is no longer possible and the molecule transmits the source beam into the drain channel (Fig.1Ac)². Similar switch mechanisms have been reported recently in a single molecule and NV-colored centers^{3, 4}. Here, we propose to demonstrate the feasibility of this experiment with a single phthalocyanine molecule as the switch. The singlet and triplet levels of the three phthalocyanine complexes (Cu, Zn and Pt) are known and present favorable spectroscopic properties. For future development of all-optical single-molecule transistors, optimization of the molecule's structure in view of its photophysical properties will be required.

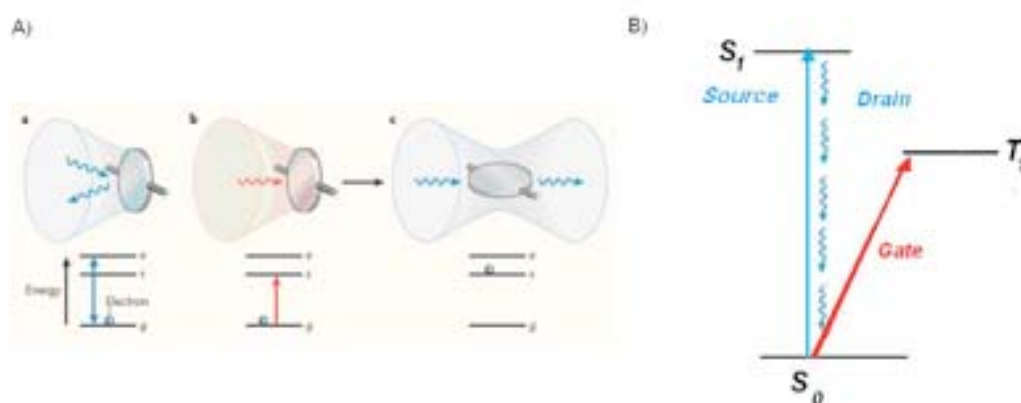


Figure 1. A) Cartoon of an all-optical single-molecule transistor. The molecule, upon absorption of one red photon (b, gate) can switch from a blocking state for blue photons (a, source) to a transmitting state (c, drain). B) Molecular electronic states diagram involved in the switch.

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VELOCITY MAP COINCIDENCE IMAGING AND PULSE SHAPING IN MOLECULAR DYNAMICS STUDIES

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Ultrafast photon induced dissociation dynamics can be probed in great detail with time resolved coincidence imaging of ions and electrons. Coincidence imaging is a technique in which both the ejected photo-electron and the ionic photofragment are measured, in coincidence, with two time- and position sensitive particle detectors. From the data the complete energetic and angular resolved distributions are obtained. Our coincidence apparatus (1, 2) has several technological advances. Such advances include three dimensional velocity map imaging of the particles and very high electron time and energy resolution.

To improve our understanding of coherent control mechanisms, we combine the technique of time-resolved three-dimensional coincidence imaging with adaptive femtosecond pulse shaping (3). Pulse shaping provides a tool to control the reaction pathway, thereby controlling the reaction outcome.

Moreover, the study of fast physical and chemical processes by time-resolved spectroscopy depends on the availability of ultrashort pulses. These pulses should have the center wavelengths suitable to the sample's emission and absorption bands. Many organic molecules have strong electronic absorption bands in the ultraviolet (UV) spectral region. Hence, it is essential to extend the available spectral range to shorter wavelengths. We use a Sum Frequency Mixing (SFM) scheme to generate the ultrashort tunable UV pulse.

In this contribution the latest experimental data on the ultrafast induced dynamics in small molecular systems will be presented.

ACKNOWLEDGEMENTS

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DYNAMIC ASYMMETRY IN THE SPECIAL PAIR OF
RHODOBACTER SPHAEROIDES OBSERVED BY
PHOTOCHEMICALLY INDUCED DYNAMIC NUCLEAR
POLARIZATION ^{13}C NMR

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Although the two branches of cofactors are almost symmetrically arranged [for review, see ref ¹], electron transfer in photosynthetic reaction centers (RCs) of the photosynthetic purple bacteria *Rhodobacter (R.) sphaeroides* occurs exclusively via the A branch. Also the primary electron donor of RCs of *R. sphaeroides*, the Special Pair, is symmetrically arranged from two bacteriochlorophyll *a* (BChl) cofactors, except for a few side groups of the macrocycles. Many progresses have been made by different spectroscopic techniques and by using mutants and also theoretical models have been proposed ¹. In the electronic ground state, photo-CIDNP (photochemically induced dynamic nuclear polarization) MAS has demonstrated that the break of symmetry between the two cofactors of the Special Pair and that one of the cofactors of the Special Pair is special ^{2, 3}. In the excited state, Stark spectroscopy provided evidence for a very large change in dipole moment in the Special Pair ⁴ which might be facilitating the charge transfer. Here we investigate the local mobility by ^{13}C photo-CIDNP solid-state magic-angle spinning (MAS) NMR using site-selective ^{13}C isotope enrichment of the Special Pair in the ground state. The solid-state photo-CIDNP effect leads to strong signal enhancement. Two-dimensional dipolar-assisted rotational resonance (DARR) MAS NMR experiments ⁵ at different mixing times allow for both, signal assignment and measurement of mobility information from the kinetics of the ^{13}C spin-diffusion process. We demonstrate that the Special Pair supermolecule is generally rigid but shows greater mobility towards the inactive branch. The observed dynamic symmetry break of the Special Pair might be related to the break of symmetry of electron transfer.

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STRUCTURE AND FIRST EPR CHARACTERIZATION OF HELICAL PEPTIDES WITH TOAC SPIN-LABELS: MODELS FOR SHORT DISTANCES

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For structural determination in biophysical systems, electron paramagnetic resonance (EPR) is rapidly gaining ground. Proteins labeled specifically with two identical nitroxide spin labels can be prepared, and several EPR methods are available for distance determination. To test such methods, rigid model compounds are needed. A series of peptides was synthesized with pairs of spin labels separated by two, three, four and five amino acids. To avoid flexibility, the unnatural nitroxyl containing alpha-amino acid TOAC that is rigidly connected with the peptide backbone is used. The EPR spectra of the peptides show a decreasing amount of coupling between the two spin labels within this series, providing a first characterization of these models.

HYDROGEN DISSOCIATION ON STEPPED PLATINUM SURFACE

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Dissociation of hydrogen on metals has been studied extensively because of its importance in catalytic reactions. Most of the important reactions are carried out on metal nanoparticles which have terraces, steps and defects. It is established that dissociation would process differently on steps when compared to terraces and also different steps would contribute differently. In order to understand the contribution of defects, steps and terraces and to identify the different mechanisms involved in an overall reaction researchers have used stepped surfaces with well defined terrace lengths¹. Here we present dissociation probability of hydrogen on Pt(553), denoted also as Pt(s)-[4(111)x(110)], as a function of kinetic energy and surface temperature. Results are compared with those of Pt(533)², denoted also as Pt(s)-[4(111)x(100)], another stepped surface which has same terrace length but different monoatomic step.

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THEME 3

MULTIPLE STATE TRANSITION INTERFACE SAMPLING OF ALANINE DIPEPTIDE IN EXPLICIT SOLVENT

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We applied the recently developed multiple state transition interface sampling (MSTIS) approach to alanine dipeptide in explicit water. We extracted the rate constant matrix for configurational changes between each pair of metastable states. The results are comparable with values from previous literature, and show that the method is applicable to biomolecular systems.

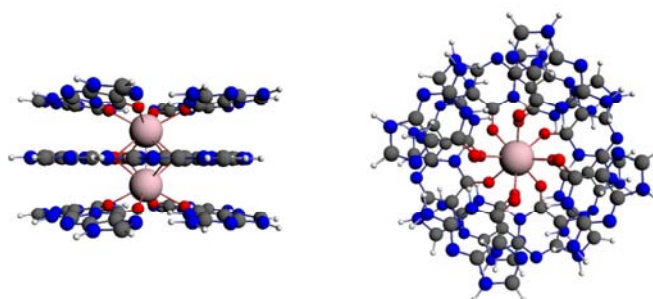
TELOMERE STRUCTURE AND STABILITY: COVALENCY IN HYDROGEN BONDS, NOT RESONANCE ASSISTANCE, CAUSES COOPERATIVITY IN GUANINE QUARTETS

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We show that the cooperative reinforcement between hydrogen bonds in guanine quartets is not caused by resonance-assisted hydrogen bonding (RAHB). This follows from extensive computational analyses of guanine quartets (G_4) and xanthine quartets (X_4) based on dispersion-corrected density functional theory (DFT-D). Our investigations cover the situation of quartets in the gas phase, in aqueous solution as well as in telomere-like stacks. A new mechanism for cooperativity between hydrogen bonds in guanine quartets emerges from our quantitative Kohn-Sham molecular orbital (MO) and corresponding energy decomposition analyses (EDA). Our analyses reveal that the intriguing cooperativity originates from the charge separation that goes with donor-acceptor orbital interactions in the π -electron system, and not from the strengthening caused by resonance in the π -electron system. The cooperativity mechanism proposed here is argued to apply, beyond the present model systems, also to other hydrogen bonds showing cooperativity effects.¹



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COMPUTING SOLVENT EFFECTS ON VCD SPECTRA: THE CASE OF 2BR-BINAPHTHOL IN DCM, ACN AND DMSO SOLVENTS

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The experimental VCD spectra of flexible chiral molecules depend sensitively on the solvent. Since when using VCD spectroscopy to determine the absolute configuration of chiral molecules, one compares experimental and calculated VCD spectra, it is very important to compute accurately the effects induced in the spectra by various solvents.

Using as example the experimental VCD spectra of Di-BromoBinaphthol measured in three different solvents, i.e. dichloromethyl, acetonitrile and DMSO, we have investigated:

1) the reasons inducing the observed changes in the experimental spectra by performing calculations for the free Di-BromoBinaphthol molecule and also for molecular complexes formed between one Di-BromoBinaphthol and two solvent molecules.

2) the structural parameters (related to the relative orientation of the solute and solvent molecules, e.g. length of intermolecular H-bonds, dihedral angles) that are the most critical to vary in order to reproduce the experimental spectra by performing linear transit calculations.

Besides identifying the most important reasons affecting the shape of the VCD spectra we also show that in order to obtain good agreement between computed and measured VCD spectra variation of the lengths of the intermolecular hydrogen bonds between solute and solvent is the most critical parameter.

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SOLVENT REORGANIZATION EFFECT ON ELECTRON TRANSFER TO A FLAVIN MOLECULE

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Flavin adenine dinucleotide (FAD) and flavin mononucleotide (FMN) are common cofactors found in redox proteins that use for their catalytic or photoactive function the special redox properties of these flavin molecules. The reduction potentials of the flavin are controlled by its environment. Using ab initio (DFT) molecular dynamics simulation, we have studied the redox properties of lumiflavin in water and in gas-phase. We find that the reduction potential, calculated using free energy perturbation, has the typical parabolic shape as predicted by Marcus theory on electron transfer. However the diabatic free energy curves for the flavin and the reduced semiquinone state exhibit different curvature, which indicates that the solvent reorganisation is not in the linear response regime, in contrast with Marcus theory. By mapping the changes in electrostatic potential and solvent structure we gain insight in how specific polarization of the flavin by its environment tunes the reduction potential.

THE ROLE OF WATER IN METAL CATALYZED TRANSFER HYDROGENATION OF KETONES, A COMPUTATIONAL STUDY

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Hydrogenation of a carbonyl bond is one of the most essential transformations in chemistry. With employment of transition metal catalysts highly enantioselective reactions can be achieved, which is of great importance for pharmaceutical industry. Specifically, Ru (II) based complexes with N-tosylated diamine ligands have been shown to give up to 99% enantiomeric excess[1].

The choice of solvent has been shown to be crucially important for the reaction rate and enantioselectivity of transfer hydrogenation for several transition metal catalysts [1]. Using water as solvent greatly increases the reaction speed in the case of Ruthenium complexes with N-tosylated diamine ligands [2]. Aqueous-phase catalysis is of special importance as it is environmentally friendly and the aqueous solvent is essential when mimicking biocatalytic mechanisms. Nevertheless, detailed insight of the molecular details of the role of water is absent. Nor experimental, neither computational studies have clarified the explicit role of the solvent. An earlier *ab initio* molecular dynamics study of Ru-catalyzed transfer hydrogenation in methanol has revealed that the solvent may play a crucial role in both the reaction rate and mechanism. [3]

Here we report a computational study of transfer hydrogenation of ketones with the Ruthenium complex mentioned above in bulk water. The study is performed with *ab initio* (Car-Parrinello) molecular dynamics (BLYP density functional and 70 Ry cutoff) of the reacting complex with 56 water molecules in a periodic system. Employing the constrained dynamics methods provides the reaction pathway and associated free energy profile in an accurate manner. Our results show a significant difference in the mechanism of transfer hydrogenation in water, compared to the studies in both gas phase and methanol.

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LARGE SCALE MODELING OF THE ELECTRONIC SPECTRA OF URANIUM-CONTAINING MOLECULES: UO_2 (SALDIEN) AND $[\text{UO}_2(\text{SALDIEN})]^-$ IN DMSO

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The uranium dioxocation (UO_2^{2+}) is an essential building block of many uranium species. This linear cation is then weakly coordinated in the equatorial plane by three to six ligands.[1,2] While the six-valued uranyl is very stable, the (also linear) V-valued uranyl is unstable and immediately disproportionates in acidic solution:



As a consequence only a few stable VI-valued uranyl complexes are known: $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ and $[\text{UO}_2(\text{salophen})_2\text{DMSO}]$. Recently, Takao and coworkers synthesized a new stable $[\text{UO}_2(\text{saldien})]^-$ complex that could be of interest for application in the nuclear fuel cycle.[3]

The aim of our work is to model theoretically the electronic spectra of $[\text{UO}_2(\text{saldien})]^-$ at different levels of theory (Time-Dependent Density Functional Theory (TD-DFT) and Equation of Motion Coupled Cluster Singles and Doubles (EOM-CCSD)) and analyze the experimentally observed transitions. Additionally, we study different partitioning schemes for a multilevel description of this and related systems in the condensed phase.

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THE EFFECT OF METAL VARIATION ON OXIDATIVE ADDITION *PERSPECTIVES FROM THE ACTIVATION STRAIN MODEL*

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The 2010 Nobel Prize in Chemistry was awarded to prof. Heck, prof. Negishi and prof. Suzuki for their work on palladium-catalyzed cross couplings in organic synthesis. The first step in these cross couplings is the activation of a bond in the substrate by a palladium catalyst. However, since palladium is expensive and scarce, it is desirable to investigate possible alternatives.

Using high-level DFT calculations and the chemically intuitive Activation Strain model, we are able to understand and explain how the energy profile of the oxidative addition is influenced if one varies for example the bond to be activated, the steric bulk on the substrate or the ligands attached to the catalyst. In this study we explain the influence of various metal centers on the energy profile of catalytic methane activation, and the interplay with ligand effects. To this end, we analyze the addition of methane to small model catalysts, where we interchange palladium with one of its surrounding metals in the periodic table, and explain the observed effects.

Our aim is to combine the knowledge of these studies to be able to rationally design catalysts with the desired efficiency and selectivity.

