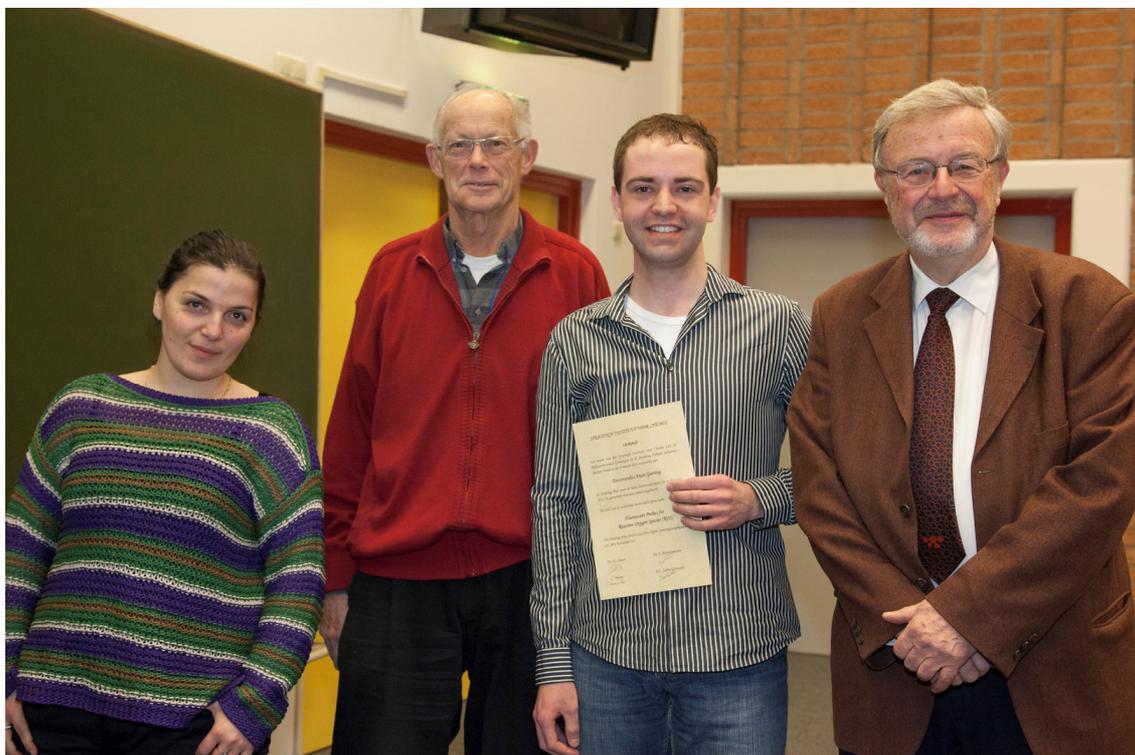




Strating Prize 2012



On March 15th, 2013 the prestigious Stratingh Award for the best colloquium in the year 2012 was announced. This award has been established in 1996 by (now emeritus) Prof. Albert van Leusen in recognition of his PhD supervisor, Prof. Jan Strating. The award is supported by the Backer foundation.

Selection of the three nominees, out of ten colloquia, was performed by the jury consisting of Dr. Syuzanna Harutyunyan (Chair), Dr. Edwin Otten, Claudia Poloni and Beatrix Calvo. The three nominated colloquia were of excellent quality and therefore the jury had a difficult task in selecting the best piece of work. After serious consideration the jury unanimously decided to award the prizes as follows: third prize went to Anouk Lubbe for her colloquium on cascade reactions in total synthesis. The second prize was given to Edwin Kroon for his colloquium on stereogenic-at-metal complexes in catalysis.

The first prize, the prestigious Stratingh award and 300 euros, was awarded to Arjan Geersing for his excellent colloquium titled “Fluorescent Probes for Reactive Oxygen Species (ROS)”.

Congratulations to all the winners! Almost the entire Stratingh Institute including Prof. Albert van Leusen, the founder of the Strating Award, joined in with the celebrations of these awards after the ceremony with cake and coffee (thanks goes to Hilda for arranging that). The winners enjoyed a lunch on the same day together with the jury and the Backer foundation committee members.

News from the library: Chemworks

The American Chemical Society has published a new tool: **ChemWorx**

It is an on-line and desktop application that enables you to search, find, collect and manage your literature. ChemWorx also features a microsoft Word plugin with which you can cite while you write your paper. With the help of the online tool you can also keep track of your submitted paper (s) for a ACS journal.

Highlights by Prof. dr. Jan B.F.N.Engberts

How cells know where they are. In a recent review, Arthur Lander argues that development, regeneration, and day-to-day physiology require plant and animal cells to make decisions based on their location. Successful strategies to do this need a high reliability and rely, among others, on diverse diffusible molecules, control circuits, and gene regulatory networks. The question has been asked whether steady-state diffusion gradients can provide sufficient reliability and whether transport, uptake, receptor synthesis, and signaling do not give too large measurement errors. Although there is much that we still do not know, there has been considerable progress in identifying mechanisms for encoding and detecting positional information.

A.D. Lander, Science, 2013, 339, 923-927.

In a joint project of the groups of Butler (Galway, Ireland) and Coyne (Cambridge, UK) it was demonstrated that Huisgen cycloadditions in water (water soluble reactants) and on water (water insoluble reactants) gave a preference for the endo isomer in the first case but that this did not occur in the second case. It should be noted that successful synthetic reactions between two water insoluble organic solids can be achieved by the on-water protocol if one reactant is liquefied to provide an oily layer in the water mixture.

R.N. Butler, A.G. Coyne, W.J. Cunningham, E.M. Molony, J.Org.Chem. 2013, doi 10.1021/jo400055g.

A paper from the University of Osaka, Japan, reported the first example of chiral recognition and kinetic resolution of aromatic amine guests employing supramolecular nanocapsules assembled from cyclodextrin derivatives in nonpolar media. With 1-(1-naphthyl)ethylamine (**1**) in cyclohexane, high chiral recognition was achieved, with a binding selectivity of up to 41 for (S)-**1** over (R)-**1**. Furthermore, kinetic resolution of **1** through enantioselective N-acylation was accomplished with an enantiomeric excess of up to 91%.

T. Kida, T. Iwamoto, H. Asahara, T. Hinoue, M. Akashi, J.Am.Chem.Soc. 2013, 135, 3371-3374.

Scientists from the Georgia Institute of Technology, Atlanta, US, obtained novel insights into biologically important mutations of A/T-rich DNA. One-electron oxidation of these DNAs involves rate-determining C-H bond cleavage of methyl groups as indicated by large deuterium isotope effects. The radical cation (electron hole) generated by DNA oxidation, initially located on adenines, localizes on thymine as the proton is lost from the methyl group. This process is consistent with proton-coupled electron transfer. The proton transfer by structural diffusion apparently occurs along a segmented "water-wire" and culminates in proton hydration in the hydration environment that serves as an entropic reservoir, and inhibiting reversal of the electron transfer pro-

cess.

R.N. Barnett, J. Joseph, U. Landman, G.B. Schuster, J.Am.Chem.Soc., 2013, doi 10.1021/ja311282k.

A report by chemists from the University of Tartu, Estonia, described the hydrolytic and aminolytic kinetic resolution of terminal bis-epoxides using Jacobsen's catalyst (i.e. (salen)CoIII complexes). Epoxy-diols and N-protected epoxy-amino alcohols were isolated with excellent enantio- and diastereoselectivity and in good yields. This novel procedure provides compounds with remote stereocenters in enantiomerically pure form. The methodology may find useful applications in the synthesis of biologically valuable targets.

J. Bredihhina, P. Villo, K. Andersons, L. Toom, L. Vares, J.Org.Chem., 2013, doi 10.1021/jo3024335.

A recent article in *J.Phys.Chem.B* reported evidence of dynamical constraints imposed by water organization around a bio-hydrophobic surface. These insights were obtained using molecular dynamics simulations and elastic neutron scattering experiments. As models of protein surfaces, fully hydrated small peptides were employed. The data appear to show that the dynamics of the side chain has not only a crucial role in the whole flexibility as compared to the backbone, but also modifies the values of the transition temperatures. Water cluster organization around hydrophobic interfaces is playing a crucial role. The cluster size corresponds to a single layer of water molecules.

D. Russo, M.A. Gonzalez, E. Pellegrini, J. Combet, J. Ollivier, J. Teixeira, J.Phys.Chem.B, 2013, doi 10.1021/jp3094885.

A recent communication in *JACS* reports the isolation and structural characterization of a thermally stable compound with a Cu-B one-electron bond. Its oxidized (nonbonded) and reduced (two-electrons-bonded) relatives were also investigated. The degree of σ -binding and spin density were analyzed in some detail. Species with similar one-electron bonds have been described previously but they were highly unstable.

M-E. Moret, L. Zhang, J.C. Peters, J.Am.Chem.Soc., 2013, doi 10.1021/ja4006578.

Three scientists from Gujarat, India have developed a novel transamidation protocol using L-proline as a catalyst (10 mol %). L-Proline is inexpensive, readily available and can be used conveniently. Yields vary, but are usually good. A wide range of benzylic, aromatic, aliphatic, propargylic, and heteroaromatic amines can be effectively transformed into the corresponding transamidation products. Preliminary studies of the reaction mechanism indicate that both free N-H and –COOH groups of L-proline are required for good results.

S.N. Rao, D.C. Mohan, S. Adimurthy, Org. Lett., 2013, doi 10.1021/ol4002625.h

A quantitative comparison of protein dynamics in live cells and in vitro was performed by researchers from Kyoto and Tokyo using in-cell ^{19}F -NMR. Enzyme dynamics was clearly enhanced in live cells, most likely in part due to macromolecular crowding effects. It might positively affect an efficient substrate-product exchange, an essential factor for enzyme activity.

Y. Takaoka, Y. Kioi, A. Morito, J. Otani, K. Arita, E. Ashihara, M. Ariyoshi, H. Tochio, M. Shirakawa, I. Hamachi, Chem.Comm. 2013, 49, 2801-2803.

Gaunt and his colleagues at the University of Cambridge, UK, developed a novel synthetic procedure for the synthesis of complex heteroaryl ketones using an organocatalytic aldehyde C-H bond arylation procedure. The straightforward catalytic protocol makes use of the inherent electrophilicity of diaryliodonium salts, and a commercial N-heterocyclic carbene catalyst promotes the union of heteroaryl aldehydes with these heteroaromatic electrophile equivalents in good yields. A variety of ketones bearing an array of arene and heteroarene substituents was obtained which could be converted into molecules with structural motifs commonly found in medicinal agents.

Q.Y. Toh, A. McNally, S. Vera, N. Erdmann, M.J. Gaunt, J.Am.Chem.Soc., 2013, doi 10.1021/ja400051d.

Branching mechanisms in surfactant micellar growth were investigated by Tang and Carter. Using simulation techniques, two branching mechanisms were identified, i.e., a disk-to-cylinder shape transition and a tip bifurcation process for, respectively, disklike and cylindrical micelles. The results are relevant for understanding the mechanism of formation of branched wormlike micelles that are observed in many surfactant systems.

M. Tang, W.C. Carter, J.Phys.Chem.B, 2013, doi 10.1021/jp309204t.

Researchers from the Universities of Rostock (Germany) and Sassari (Italy) developed an efficient low-temperature aqueous-phase methanol dehydrogenation process, facilitated by ruthenium complexes. The generation of hydrogen did occur at 65-95 °C and ambient pressure with excellent catalyst turnover frequencies and turnover numbers. This makes it possible to use methanol as a material for the storage of hydrogen because it is a liquid at room temperature and contains 12.6% hydrogen. These new findings could enable the delivery of hydrogen on mobile devices, and hence make the use of methanol as a practical hydrogen carrier feasible.

M. Nielsen, E. Alberico, W. Baumann, H-J. Drexler, H. Junge, S. Gladioli, M. Beller, Nature 2013, 495, 85-90.

An interesting observation was made by Fraser Stoddard and his coworkers. They found that mechanical bonds are able to stabilize radical cations. A series of [2]rotaxanes was synthesized, in which cyclobis(paraquat-p-phenylene) served as the ring component, while the dumbbell components all contain single 4,4'-bipyridinium units, centrally located in the midst of oligomethylene chains of varying lengths. Diverse techniques showed that the BIPY.+ radical cations are stabilized against oxidation, both electrochemically and by atmospheric oxygen. The enforced proximity between the BIPY units in the ring and dumbbell components gives rise to enhanced Coulombic repulsion, destabilizing the ground-state co-conformations of the fully oxidized forms of these [2]rotaxanes. The findings are of direct relevance for producing highly stabilized radical cations of the types studied here.

H. Li, Z. Zhu, A.C. Fahrenbach, B.M. Savoie, C. Ke, J.C. Barnes, J. Lei, Y-L. Zhao, L.M. Lilley, T.J. Marks, M.A. Ratner, J. Fraser Stoddart, J.Am.Chem.Soc. 2013, 135, 456-467.

Jan Engberts

Invited lectures



Dr. Manuel Alcarazo

Max-Planck-Institut für Kohlenforschung

Title: **Synthesis and applications of cationic phosphines: Applications in Au and Pt Chemistry**

Day: Thursday, **April 11th, 2013**

Room: **5111.0022**

Time: **14:00 - PLEASE NOTE LECTURE AT 14:00**

New Personnel

- **Niek N.H.M. Eisink, AiO**—as of April 1st , under the guidance of Prof Adri Minnaard

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

- **April 4th**—Y. Huang—"A Novel Catalytic Asymmetric Route towards Skipped-Dienes with a Methyl-Substituted Central Stereogenic Carbon"
- **April 11th**—M. Vlatkovic—"Photoswitchable organocatalyst"
- **April 18th**—J. Buter—"Title to be announced"
- **April 25th**—B. Calvo Gonzalez—"Title to be announced"
- **May 2nd**— D. Fracasso—"Using EGaIn to Uncover New Phenomena in Molecular Tunneling Junctions"

If you have items for the next issue of this Newsletter, please send an e mail to the Stratingh Institute office: Stratingh@rug.nl