university of groningen

Newsletter

Stratingh Institute for Chemistry



March 2015

Netherlands Catalysis and Chemistry Award 2015 for Ben Feringa



The Netherlands Catalysis and Chemistry Award is a special Award for significant achievements in the fundamental and practice of catalysis, and is based on accomplishments and contributions over the last ten years. It is awarded every five years to an active researcher from academia, research institutes, or industry working in the Netherlands or Belgium, and consists of a certificate and a prize of €10,000.

The jury of the Netherlands Catalysis and Chemistry

Award 2015 consisted of Dr. Peter Berben, Dr. Martin Lok, Prof. Roeland Nolte, Prof. Roel Prins, Prof. Eelco Vogt, Prof. Thomas Weber, and Prof. Bert Weckhuysen. The jury received nine nominations, each for candidates of very high quality, spread over the various fields of catalysis, and from academia as well as from industry.

After careful consideration, the jury has decided to award the Netherlands Catalysis and Chemistry Award to Professor Ben Feringa, Jacobus H. van't Hoff Distinguished Professor of Molecular Sciences at the University of Groningen, for his ground-breaking research in Catalysis; more specifically asymmetric carbon-carbon bond formation, switchable chiral ligands, and the introduction of phosphoramidites as privileged chiral ligands for catalysis.

<u>Here</u> you can read more about this prize for Ben Feringa.

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

- In the first of two essays, Bruce Gibb (Tulane University, New Orleans) provided us with a chemistry-themed guided tour around the Solar System, informing us with details about the organic molecules that have been detected in space. Their number is relatively small (about 110), and their presence depends strongly on the conditions, particularly at the surface of the solar body. One of the most important questions is, of course, is life possible somewhere in outer space? It is assumed that there are three necessary and sufficient criteria for life: (i) a fluid medium, (ii) a source of energy and (iii) constituents and conditions compatible with polymeric chemistry. We are waiting for the second essay! *Gibb*, *B.C., Nature Chem.2015*, *7*, 91-92.
- A joint Swedish-American communication reported an unexpected efficient catalysis by N,N-diethylurea (DEU) in DMSO for the amidation reaction of phenylacetaldehydes with electron-deficient phenyl azides. Evidence was obtained for a 1,3-dipolar cycloaddition between DEU-activated enols and electrophilic phenyl azides, especially perfluoro azides, followed by rearrangement of the triazoline intermediate. Of special importance is here the activation of the aldehyde under near-neutral and very mild conditions. The final yields are often high. *Xie, S., Ramström, O., Yan, M., Org.Lett. 2015, DOI 10.1021/ol503655a*.
- Compound Q is a key intermediate in the conversion of methane to methanol by an enzyme called soluble methane monooxygenase. It is the most powerful oxidant found in

nature. John Lipscomb and coworkers have now solved the structure of Q for the first time. The essential feature is a "diamond core" in which two iron ions in the +4 oxidation state are bridged by oxygen atoms. A mixed isotopic form of dioxygen (16O-18O) was used to probe the formation of the apparent diamond core. Rosenzweig wrote a brief review. *Banerjee, R., Proshlyakov, Y., Lipscomb, J.D., Proshlyakov, D.A. Nature 2015, DOI 10.1038/* nature14160. Rosenzweig, A.C., Nature 2015, DOI 10.1038/nature14199.

- The presently available methods for the preparation of heteroaromatic compounds containing carbon-silicon bonds often have limitations, including functional group incompatibility. Groups at CalTech, Pasadena, USA and at the ETH, Zürich, Switzerland, have now developed a new and general catalytic approach to heteroaromatic C-Si bond construction avoiding many of such limitations. A cross-dehydrogenative heteroaromatic C-H functionalization catalyzed by an Earth-abundant alkali metal species induced the desired silylation, furnishing heteroarylsilanes in a single step. The novel synthetic protocol can be performed under mild conditions, in the absence of hydrogen acceptors, ligands or additives. It is also scalable to greater than 100 grams under optionally solvent-free conditions. The products are starting materials for a number of important synthetic applications. *Toutov, A.A., Liu, W-B., Betz, K.N., Fedorov, A., Stoltz, B.M., Grubbs, R.H., Nature 2015, 518, 80-84*.
- Three organic chemists and one inorganic chemist at the University of Duisburg-Essen, Germany, designed and synthesized molecular machines that perform unidirectional, fourstate switching cycles that bear similar characteristics to the arm movement of a human breaststroke swimmer. A peptide macrocyclic scaffold controls the direction of motion. The arms performing the swimming movements are rotated around one hinge and are stretched and folded by another hinge. The first hinge can be switched by light, the other by Cu2+ ions. Alternating addition of chemicals and irradiation with light control the movement of these machines. Despite practical problems, the results are a small step towards an artificial nanoswimmer. *Haberhauer, G., Burkhart, C., Woitschetzki, S., Wölper, C., J.Org.Chem.* 2015, DOI 10.1021/acs.joc.5b00026.
- Xiao and collaborators at the University of Nebraska, USA, have shown that the migration of ions under the effect of an external electric field are able to locally modify the doping of organometal halide perovskite films. The effect can be employed to reversibly switch the photocurrent direction in very simple photovoltaic architectures and may have a number of applications. These may involve the realization of electrically and optically readable memristors based on organic-inorganic perovskites. The results have been briefly reviewed by Park. *Xiao, Z., Yuan, Y., Shao, Y., Wang, Q., Dong, Q., Bi, C., Sharma, P., Gruverman, A., Huang, J., Nature Mater. 2015, 14, 193-198. Park, N-G., Nature Mater. 2015, 14, 140-141.*
- Catalytic Ir/SiO2 Janus micromotors, powered by hydrazine, have been described by Wang et al. of the University of California, San Diego, USA. N2, H2, and NH3 molecules are generated at the Ir surface, resulting in a zone of high product concentrations. Fluid flows from the SiO2 spherical particles to the Ir hemispheric layer because of the product gradient, thereby driving the motor toward the SiO2 side. The micromotors are self-propelled at very high speed in a 0.0001% hydrazine solution due to osmotic effects. These novel results hold considerable promise for a number of practical applications. *Gao, W., Pei, A., Dong, R., Wang, J., J.Am.Chem.Soc.* 2015, DOI 10.1021/ja413002e.
- A chemoselective and efficient catalytic system for the reduction of tertiary amides to the corresponding tertiary amines has been developed at Stockholm University by Adolfsson and his coworkers. A rather cheap polymeric silane was employed at room temperature as the hydride source. Addition of a substoichiometric amount of LiCl is crucially required for

the catalytic activity. A series of structurally different amides could be reduced in good-to-excellent yields. *Kovalenko, O.O., Volkov,A., Adolfsson, H., Org.Lett.*2015, DOI 10.1021/ 01503430t.

- Silicene has made its debut as a transistor. After all the world-wide interest in graphene, Peplow has now described the history of the rise of silicone in a brief Nature communication. After the first calculations on its two-dimensional crystal structure in 1994, its name was coined in 2007. Silicene nanoribbons were first fabricated in 2009 and six independent reports of silicone sheets, formed on silver, appeared in 2012. Now the first silicone transistor has been reported and its possible applications have been discussed. Handling silicone in the lab is a challenge, and Le Lay commented: "It should not be seen as a dream material, it is a practical thing". *Peplow, M., Nature 2015, 518, 17-18.*
- Pavel Jungwirth and coworkers at the Czech Academy of Sciences in Prague have studied what is exactly happening when we toss a lump of sodium or potassium metal into water. As you all know, often an explosion occurs, most vigorously for potassium. We are used to attribute this phenomenon to an ignition of the hydrogen gas that the alkali metals release from water. That may indeed happen eventually, but the first process is far stranger: what initially occurs is a rapid exodus of electrons that is followed by an explosion of the metal as a result of electrical repulsion. Quantum-mechanical computer simulations indicated that the atoms at the surface of the cluster lose an electron within just several picoseconds which shoot into the surrounding water to produce solvated electrons with a deep blue color. The metal cluster now carries a large number cations that strongly repel each other resulting in an explosion. Rather unexpected results, also lively reviewed by Phil Ball. Sijbren Otto's advice: don't try it out at home! *Mason, P.E., Uhlig, F., Vanek, V., Buttersack, T., Bauerecker, S., Jungwirth, P. Nature Chem.* 2015, DOI 10.1038/nchem.2161. Ball, P., Nature 2015, DOI 10.1038/nature.2015.16771.

Jan Engberts



Stratingh Seminars

Tuesday, March 17th

Prof. Nicolai Cramer - Ecole polytechnique fédérale de Lausanne Institut des sciences et ingénierie Chimiques, Lausanne, Switzerland
Room: 5111.0022
Time: 16:00 hrs
Title: ASYMMETRIC C-H BOND FUNCTIONALIZATIONS: A QUEST FOR EFFICIENT LIGAND SYSTEMS

PhD Defences

Friday, March 13th

@ 12:45 Peter Fodran will defend his PhD thesis. Title: "Stereoselective Synthesis of Glycerolbased Lipids". Promotor: Prof. dr. A.J. Minnaard

Friday, March 30th

@16:15 Maria Bastian will defend her PhD thesis. **Title:** "Synthesis and Aggregation Behaviour of Nature-Inspired Amphiphiles". **Promotores:** Prof. dr. B.L.Feringa, Prof. dr. A.J. Minnaard

New appointments



Tjalling Canrinus 1 February—**PhD** Group Roelfes

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

March 12th— Francesco Lanza (Haratyunyan) "Title to be announced" March 19th— Milon Mondal (Hirsch) "Title to be announced" March 26th—Jonas Lohse (Witte) "Targeted diazotransfer reagents"

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