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Conference Report

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Homogenous Catalysis – New Paradigms, Wonderful Applications

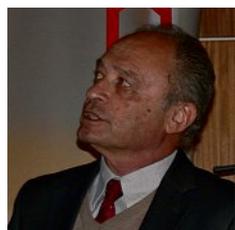


The 2017 Spring Meeting of the Swiss Chemical Society (SCS) took place in University of Bern, Switzerland on the 21st April. The theme of homogeneous catalysis was introduced by conference chair Prof. **Martin Albrecht**, along with the impressive line-up of six plenary speakers, as well as the recipients of this year's prestigious Alfred Werner Prize.

Plenary Talks



Prof. **John Hartwig** (University of California, Berkeley, USA) opened the meeting with a lecture on selective C–H bond activation, summarizing the elegant strategies his group has pursued. By installing temporary functional groups into substrates (e.g. boronate esters, silyl ethers), a range of products can be accessed from a single catalytic bond activation. With the goal of bringing enzymatic levels of selectivity to organometallic catalysis, and inspired by cytochrome P450 reactivity in particular, the protein myoglobin was expressed without the native Fe–porphyrin (heme) cofactor. Specific non-natural catalytic activity was conferred on the system by introducing different metal–porphyrin cofactors. Introduction of different transition metal systems into myoglobin and P450 gave increased catalytic rates and in the latter case allowed for enzymatic-like selectivity.



The novel pincer system presented by Prof. **David Milstein** (The Weizmann Institute of Science, Rehovot, Israel) was based on a new concept of *metal–ligand cooperation* (MLC) where the aromatization of an initial de-aromatized pyridine is the driving force in a wide variety of bond activation processes with direct participation of the metal center. Building on the concept of MLC, *Template Catalysis* was presented as an approach for C–C bond formation. This paradigm is in between organic and metal-organic catalysis where the metal center is not directly involved in the catalytic bond formation but instead in binding and activating the substrate. Further applications of these catalysts include regeneration of liquid organic hydrogen carriers (LOHCs) and dehydrogenative transformations such as the coupling of ethylene amine with ethanol. This pincer

system has also been used successfully in new environmentally benign (green) catalytic reactions; for example, acceptorless dehydrogenation reactions of different organic compounds not only release hydrogen gas but also constitute a new synthetic methodology with no waste generation.



Dr. **Rocco Paciello** (BASF, Ludwigshafen, Germany) presented some work of the homogeneous catalysis research department at BASF, giving the audience a fascinating insight into the R&D department of one of the world's largest chemical companies. The main focus was on the successful collaboration between industry and academia in form of the 'Catalysis Research Laboratory' (CaRLa). This partnership between BASF and the University of Heidelberg shows the importance of knowledge transfer in both directions for the development of new homogeneous catalysts with potential applications in industrial processes. The high demands of industry on a catalytic system was explained and underlined with several examples that showed the long journey from the first idea to laboratory experiments, followed by the scale-up process up to the actual production plant. A remarkable example of his work was shown with the production of L-menthol at BASF where the well-studied Rh-chiraphos catalyst is used for an asymmetric hydrogenation in a continuous process. The ingenious invention of a catalyst recycling procedure leads to a highly efficient homogeneous catalysis with up to 10 million turnovers, allowing the production of a large quantity of L-menthol with high purity using simple starting materials. An outlook was given on the ongoing development of catalysts permitting the use of CO₂ as starting material for a more sustainable and economical production of acrylates.

Alfred Werner Prize Talks



Before and after lunch, the Alfred Werner prize winners delivered their award presentations. The Swiss Chemical Society awarded the Werner Prize 2017 to Prof. **Kevin Sivula** (EPF Lausanne) and to Prof. **Christof Sparr** (University of Basel). This Prize comprises CHF 10,000 and a bronze medal and is awarded every year to promising young Swiss scientists, or scientists working in Switzerland, for outstanding independent chemical research. At the time of the award the candidate may not be a tenured professor or someone in a higher position in industry, and should be younger than 40.

Prof. **Kevin Sivula** (EPF Lausanne, Switzerland) was awarded for his significant contributions to the advancement of materials and methods for photoelectrochemical energy conversion. In an enthusiastic presentation, he explained the importance of developing robust and inexpensive materials that are able to directly convert solar energy to fuel by photoelectrochemical cells in an economically viable process. He showed recent achievements in the development of delafossite CuFeO₂ materials

enhancing their performance for photoelectrochemical water oxidation. Furthermore, he presented a method to fabricate high-quality thin films of two-dimensional layered dichalcogenides at low cost. These films efficiently convert solar energy to hydrogen as well as perform water redox catalysis. In the last part of the talk, he took some inspiration from natural materials and explored the activity of a fragment from the Gibeon meteorite as a water oxidation electrocatalyst. Electrodes prepared from this iron-based mineral exhibited a state-of-the-art performance for the oxygen evolution reaction comparable to the top-performing synthetic Fe–Ni catalysts.



Prof. **Christof Sparr** (University of Basel, Switzerland) was recognized for his very creative contributions to the asymmetric synthesis of single atropisomers of hindered aromatic compounds using organocatalysis. He presented a range of strategies towards selectively accessing atropisomers of molecules with restricted rotation around

aryl–aryl bonds. Inspired by the biosynthesis of polyketides, such as orsellinic acid, he showed organocatalytic approaches for the synthesis of specific enantiomers of atropomeric biaryls and oligoarylenes using a proline-tetrazole based catalyst. These rotational isomers are stable up to high temperatures. This catalyst also allowed for the formation of aromatic amides, and even allowed an elegant sequential strategy to be pursued for the formation of atroposelective oligonaphthalenes.

Plenary Talks



The theme of homogeneous catalysis, new paradigms and wonderful applications was resumed by Prof. **Morris Bullock** (Pacific Northwestern National Laboratories, USA) with a talk on ‘*Cheap Metals for Noble Tasks*’. He showed how to design molecular electrocatalysts for the production and oxidation of molecular hydrogen. Using

abundant, inexpensive metals (such as Ni, Fe and Mn), his group synthesized complexes containing diphosphine ligands with pendant amines. These pendant amines acted as proton relays that lower the barriers and overpotentials for catalytic evolution of H₂. The catalytic activity of Ni systems in the heterocoupling process of protons and hydrides was shown to be dependent on the protonated amine position with respect to the metal hydride. Amazingly the amine position could be controlled by elongation of peripheral chain in the ligand structure. Mn and Fe complexes were shown to be more effective as electrocatalysts for oxidation of H₂. Additionally, Mn complexes showed rapid reversible heterolytic cleavage of H₂.



Prof. **Hansjörg Grützmacher** (ETH Zurich, Switzerland) brought some diversity into the symposium with his talk about ‘*Fun with Funny Organophosphorus Compounds*’. A major motivation for this topic is the fact that the production of organophosphorus compounds today completely derives from phosphorus halides – not a

particularly atom efficient process which consumes a lot of energy. He presented his work on the use of Na(OCP) as a potential phosphorus building block, a remarkably stable salt which can easily be obtained from NaPH₂ and CO. Furthermore,

he described the utilization of Na(OCP) in the synthesis of phosphorus heterocycles and explained his research on the formation of Au-, Co-, Cu- and Ir-PCO complexes. Another exciting insight was given into the synthesis and properties of new bis(acyl)phosphane oxide (BAPO) photoinitiators that can be excited even by weak light sources like LEDs. This very promising research field covers a wide range of possible applications including polymerization of dental resins, formation of surface coatings and 3D printing.



Prof. **Pedro Pérez** (University of Huelva, Spain) closed the meeting with a fascinating lecture about methane functionalization. He started the talk by emphasizing the challenges of exploiting methane, the primary component of natural gas, for the synthesis of fine chemicals, which remains a goal both scientifically and economically. He

presented exciting results on the functionalization of alkanes promoted by diazo compounds as the carbene source. This exhaustive study allowed his team to understand the most relevant aspects of the C–H bond activation process in alkanes and to move to the most ambitious goal of methane functionalization. The use of supercritical CO₂ as an inert solvent is key for the success of the catalytic reaction he and his team discovered. Different Ag and Cu complexes were presented as efficient catalysts for the insertion of a carbene unit from ethyl diazoacetate into the C–H bond of methane by using this inert medium.



Conclusions

It was a great success to have so many significant international leaders from the field of homogeneous catalysis showcase their work in a single one-day meeting. It was very valuable to the audience to see a broad range of cutting-edge research leading to new paradigms, as well as important practical applications being addressed. The Alfred Werner Prize winners also demonstrated clearly the high quality of current research within Switzerland. The talks, coupled with fruitful question-and-answer sessions and discussion over coffee and lunch resulted in a symposium that was memorable, enjoying and inspiring.