



Swiss Science Concentrates

A CHIMIA Column

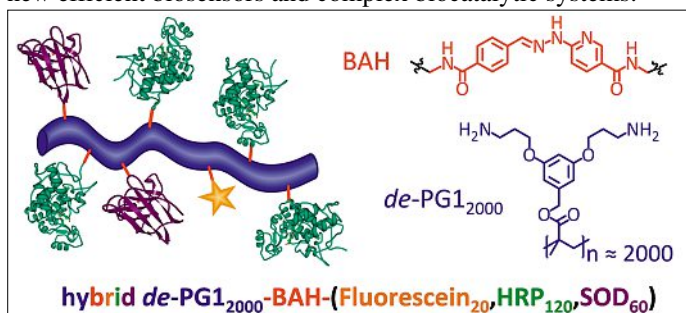
Short Abstracts of Interesting Recent Publications of Swiss Origin

A Fluorescently Labeled Dendronized Polymer-Enzyme Conjugate Carrying Multiple Copies of Two Different Types of Active Enzymes

A. Grotzky, T. Nauser, H. Erdogan, A. D. Schlüter, and P. Walde*, *J. Am. Chem. Soc.* **2012**, *134*, 11392.

ETHZ

Protein-polymer conjugates are hybrid molecules that find wide application in drug-delivery, biocatalysis and in biosensors. Binding multiple copies of more than one type of enzyme onto a polymer chain brings these enzymes into close spatial proximity and thus allows for efficient cascade reactions. However, such conjugation is difficult to achieve in a controlled and quantifiable way. The authors now report the application of a linker chemistry that results in the formation of covalent bis-aryldiazone (BAH) bonds with a distinctive, quantifiable UV absorption band. One hundred and twenty horseradish peroxidases and 60 superoxide dismutases were conjugated to a dendronized polymer of 2000 monomer units in length. The enzymes remained fully functional and catalyzed a cascade reaction. These results open the door to new efficient biosensors and complex biocatalytic systems.



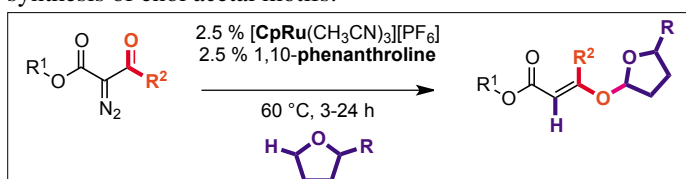
Enol Acetal Synthesis through Carbenoid C-H Insertion into Tetrahydrofuran Catalyzed by CpRu

C. Tortoreto, T. Achard, W. Zeghida, M. Austeri, L. Guénée, and J. Lacour*, *Angew. Chem. Int. Ed.* **2012**, *51*, 5847.

University of Geneva

Substituted tetrahydrofurans are readily accessible upon reaction of tetrahydrofurans with *e.g.* diazoacetates. This reaction is catalyzed by a variety of metal complexes. Such intermolecular transformations lead to the formation of a C-C bond, in α -position to the oxygen.

The kinetically favoured product resulting from C-O bond formation has now been reported by Lacour and coworkers. For this purpose, a {CpRu}-moiety catalyzes an unprecedented 1,3 C-H insertion reaction between an α -diazo- β -ketoester and tetrahydrofurans, yielding a novel and straightforward entry into the synthesis of enol acetal motifs.

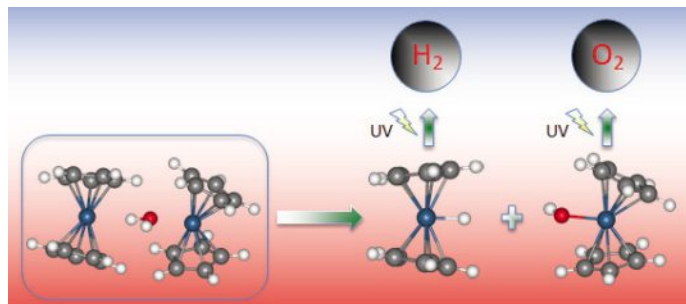


Biphasic Water Splitting by Osmocene

P. Ge, T. K. Todorova, I. H. Patir, A. J. Olaya, H. Vrubel, M. Mendez, X. L. Hu, C. Corminboeuf, and H. H. Girault*, *Proc. Natl. Acad. Sci.* **2012**, *29*, 11558.

EPFL

The photochemical splitting of water is a key technology to generate sustainable fuels for the future. The report by Girault and co-workers relies on osmocene as a photocatalyst for the splitting of water at the interface of dichloroethane and water. Detailed electrochemical, spectroscopic and computational studies indicate that osmocene can liberate an electron to produce H₂ from protons. The oxidized osmocene forms a dimer that reacts to split water forming an osmium hydride and an osmium hydroxide. Photolysis of the Os(IV) hydroxide species leads to an osmium peroxy species that further reacts to liberate O₂. This study suggests novel catalytic mechanisms relying on bimetallic dimers for the photocatalytic splitting of water.

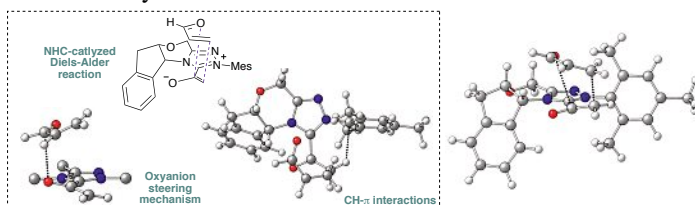


Oxanion Steering and CH- π Interactions as Key Elements in an *N*-Heterocyclic Carbene-Catalyzed [4 + 2] Cycloaddition

S. Allen, J. Mahatthanachai, J. W. Bode*, and M. C. Kozlowski*, *J. Am. Chem. Soc.* **2012**, *134*, 12098.

ETHZ and University of Pennsylvania, USA

Although *N*-heterocyclic carbenes are frequently used as organocatalysts, little is known about their mechanism of action. The authors performed computational studies on the mechanism of an *N*-heterocyclic carbene-catalyzed [4 + 2] cycloaddition. These give access to valuable γ,δ -unsaturated δ -lactones in excellent enantio- and diastereoselectivity. It was shown that a concerted, but highly asynchronous, Diels-Alder reaction occurs rather than a stepwise Michael- or Claisen-type pathway. Two critical interactions giving rise to high selectivity were identified: an oxanion-steering mechanism and a CH- π interaction. Furthermore, these calculations accurately predict the enantioselectivity of a number of *N*-heterocyclic carbene



Prepared by Nico Bruns, Adnan Ganic, Valentin Köhler, Fabien Monnard, Mark R. Ringenberg, Paolo Tosatti, and Thomas R. Ward
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