



Swiss Science Concentrates

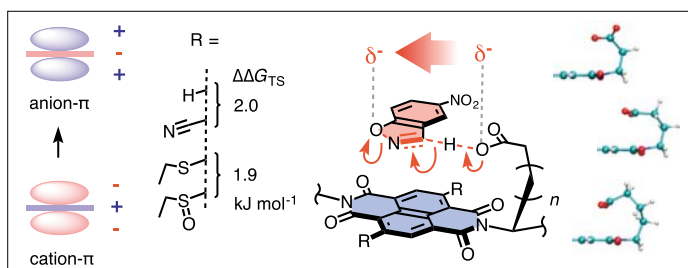
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Anion- π Catalysis

Y. Zhao, C. Beuchat, Y. Domoto, J. Gajewy, A. Wilson, J. Mareda, N. Sakai, and S. Matile*, *J. Am. Chem. Soc.* **2014**, *136*, 2101. University of Geneva

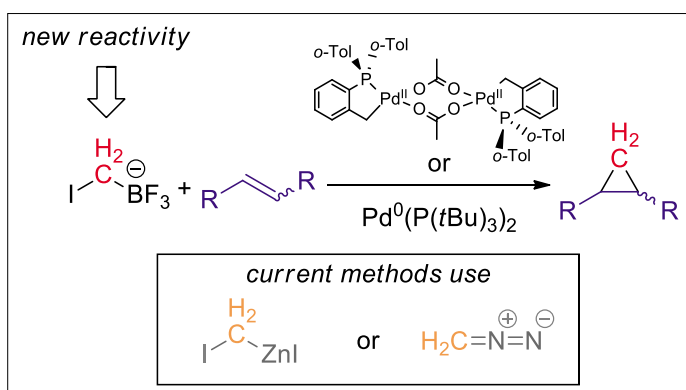
While cation- π interactions are widely recognized for providing stabilizing weak interactions, their anion- π counterparts have not received much attention. Herein, Matile and coworkers present conclusive experimental evidence for the importance of anion- π interactions in the catalytic Kemp elimination. The stabilizing effect on the anionic transition state of this reaction increases with the π -acidity of the catalysts, which are otherwise structurally similar. This insight could inspire the development of conceptually new catalysts with unprecedented activity.



A Palladium-Catalyzed Methylenation of Olefins Using Halomethylboronate Reagents

T. den Hartog, J. M. Sarria Toro, and P. Chen*, *Org. Lett.* **2014**, *16*, 1100. ETH Zürich

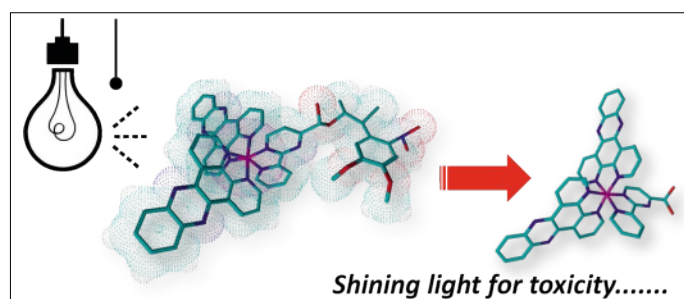
Methylenation reactions of electron-rich olefins are amongst the most challenging cyclopropanation reactions. Chen and coworkers report on a Pd-catalyzed methylenation of electron-rich olefins by using a halomethylboronate reagent. Initial studies showed, that both Pd(II)- or Pd(0) precursors can be employed in this transformation leading to high yields in both cases. Depending on the catalyst precursor, omission of base or water affected the yield of the desired cyclopropanated product. The authors thus suggest different mechanisms for both catalyst types. In conclusion, this novel methylenation method provides an attractive alternative to the use of diazomethanes or zinc carbenoids.



A Bis(dipyridophenazine)(2-(2-pyridyl)pyrimidine-4-carboxylic acid)ruthenium(II) Complex with Anticancer Action Upon Photodeprotection

T. Joshi*, V. Pierroz, C. Mari, L. Gemperle, S. Ferrari, and G. Gasser*, *Angew. Chem. Int. Ed.* **2014**, *53*, 2960. University of Zurich

Localized liberation of a cytotoxic compound from a less toxic prodrug is a promising strategy to reduce adverse side effects of anticancer drugs. Platinum- and ruthenium-based compounds are widely explored for their therapeutic potential, typically relying on liberation of a labile ligand to uncover their activity. Coordinatively inert metallodrugs on the other hand have only recently entered the arena. Masking a crucial carboxylate on the periphery of a hydrolytically stable Ru-complex with a photocleavable protecting group afforded the first example of a substitutionally-inert metal complex-based light-activated prodrug candidate displaying significant increase in cytotoxicity against cervical and bone cancer cells upon irradiation.



Photocurrent Generation Based on a Light-driven Proton Pump in an Artificial Liquid Membrane

X. Xie, G. A. Crespo, G. Mistlberger, and E. Bakker*, *Nat. Chem.* **2014**, *6*, 202. University of Geneva

The design of novel light-harvesting principles may eventually help to achieve solar cells with improved characteristics. A new chemical concept relies on the irradiation of a spiropyran (SP) that undergoes reversible photoisomerization to a merocyanine (MC). Exposure to either visible- or UV light on either side of the membrane results in both a proton flux and an electrical current as demonstrated by fluorescence and electrochemistry. This is the first example of a light-induced proton pump in a liquid membrane conceptually similar to the biological light-triggered proton pumps across a cell membrane.

