



Swiss Science Concentrates

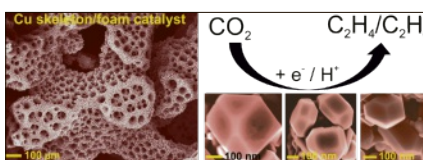
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Electrochemical CO₂ Conversion Using Skeleton (Sponge) Type of Cu Catalysts

A. Dutta, M. Rahaman, M. Mohos, A. Zanetti, and P. Broekmann*, *ACS Catal.* **2017**, 7, 5431. University of Bern

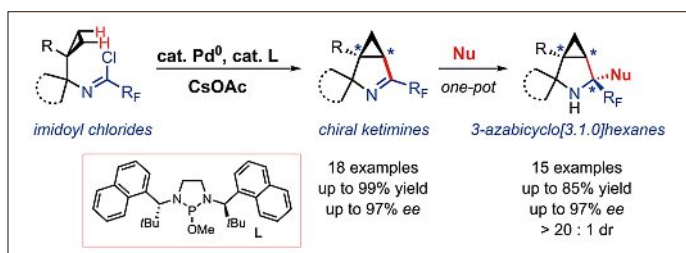
Electrochemical CO₂ reduction on Cu electrodes is considered as a promising approach for the conversion of CO₂ into valuable chemicals (CO₂ to value approach). Broekmann and coworkers demonstrate that highly porous 3D Cu skeletons (sponges) possess a greatly enhanced catalytic efficiency. Activation of the copper skeleton was performed by thermal annealing or copper foam electrodeposition. Both types of sponges were shown to favor C₂ product (C₂H₄, C₂H₆) formation. A detailed comparison between the annealed skeleton and the one modified by electro-deposition revealed that the preparation method has a significant influence on the activity, selectivity and surface morphology of the catalysts. The work introduces Cu skeleton substrates as a promising material for efficient CO₂ reduction catalysis.



Enantioselective C–H Functionalization-Addition Sequence Delivers Densely Substituted 3-Azabicyclo[3.1.0]hexanes

J. Pedroni and N. Cramer*, *J. Am. Chem. Soc.* **2017**, 139, 12398. EPF Lausanne

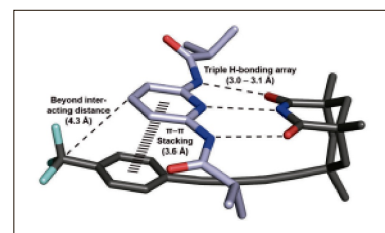
Nitrogen-containing heterocycles are prevalent in biologically active compounds. 3-Azabicyclo[3.1.0]hexanes are a group of saturated *N*-heterocyclic scaffolds which exhibit diverse biological activities and great potential for pharmaceutical use. However, modification of the pyrrolidine moiety remains limited and enantioselective methods are scarce. Pedroni and Cramer present an enantioselective entry to 3-azabicyclo[3.1.0]hexanes using trifluoroacetimidoyl chloride electrophiles in a Pd(0)-catalyzed C–H cyclization reaction. The resulting chiral ketimines represent a convenient synthetic platform for the access to secondary pyrrolidines by addition of various nucleophiles. Perfect diastereocontrol in the nucleophilic additions is ensured by the cyclopropane unit. The presented strategy consists of an enantio- and diastereoselective modular approach for highly substituted perfluoroalkylated 3-azabicyclo[3.1.0]hexanes.



Substituent Effects in Parallel-Displaced π - π Stacking Interactions: Distance Matters

L.-J. Riwar, N. Trapp, B. Kuhn, and F. Diederich*, *Angew. Chem. Int. Ed.* **2017**, 56, 11252. ETH Zurich and F. Hoffmann-La Roche Ltd. Basel

Non-covalent interactions between aromatic rings play an important role in biological and chemical recognition, but the mechanism by which substituents affect parallel π - π stacking interactions remain a much debated topic. Diederich and coworkers investigated the substituent effect in parallel-displaced π - π stacking interactions using host-guest systems with Rebek imide type receptors and a 2,6-di(isobutyramido)pyridine ligand. Substituent effects were strongly dependent on the intermolecular distance between the aromatic *para*-substituent of the receptor and the pyridine ring of the guest. The results indicate an electrostatic influence of the substituent on the aromatic platform of the receptor, which dominates the stacking strength when the substituent is displaced away from the guest. A linear correlation between $\log K_a$ and the Hammett substituent constant σ_{para} was observed, confirming predictions by the Hunter–Sanders model experimentally.



Beyond inter-acting distance (4.3 Å)

Triple H-bonding array (2.0–3.1 Å)

π - π Stacking (3.6 Å)

Biomimetic Strategy to Reversibly Trigger Functionality of Catalytic Nano-compartments by Insertion of pH-Responsive Bio-valves

C. Edlinger, T. Einfalt, M. Spulber, A. Car, W. Meier*, and C. G. Palivan*, *Nano Lett.* **2017**, 17, 5790. University of Basel

Bio-nanoassemblies combine the activity of biomolecules with the architecture of a synthetic assembly. Of particular interest are catalytic compartments which are based on the encapsulation of active compounds in the cavity of compartments. Meier, Palivan and coworkers describe a bioinspired strategy to generate catalytic compartments by combining pH-reversible bio-valves and enzyme-loaded synthetic compartments. The genetically modified channel porin serves as bio-valve and triggers the reaction inside the cavity of enzyme-loaded polymersomes by switching the *in situ* activity of the enzyme *on/off*, based on a change of the membrane permeability. This approach advances the development of catalytic compartments, which efficiently produce target molecules in a controlled, stimuli-responsive manner.

