



Swiss Science Concentrates

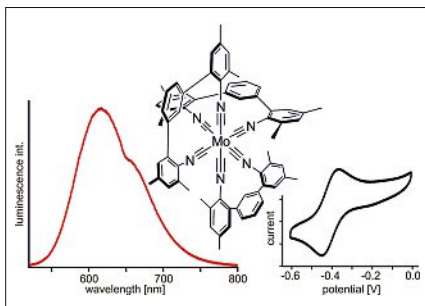
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

A Molybdenum(0) Isocyanide Analogue of Ru(2,2'-Bipyridine)₃²⁺: A Strong Reductant for Photoredox Catalysis

L. A. Büldt, X. Guo, A. Prescimone, and O. S. Wenger*, *Angew. Chem. Int. Ed.* **2016**, *55*, 11247. University of Basel

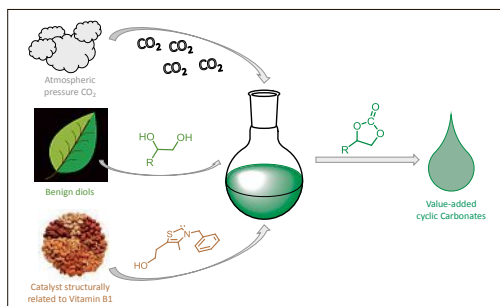
Ru(bpy)₃²⁺ serves as prototype for a large class of metal complexes with long-lived metal-to-ligand charge transfer (³MLCT) excited states. However, with a natural abundance in the earth crust of approx. 10⁻³ ppm, ruthenium is very precious and less expensive substitutes with similar photophysical properties are desirable. Wenger and coworkers now report the first homoleptic Mo⁰ complex with bidentate isocyanide ligands, which exhibits ³MLCT luminescence with quantum yields and lifetimes comparable to Ru(bpy)₃²⁺. This Mo⁰ complex is a very strong photoreductant, as manifested by diffusion-limited kinetics for reduction of ketones. The study provides the proof-of-concept for the use of chelating isocyanides to obtain Mo⁰ complexes with long-lived ³MLCT excited states.



Synthesis of Cyclic Carbonates from Diols and CO₂ Catalyzed by Carbenes

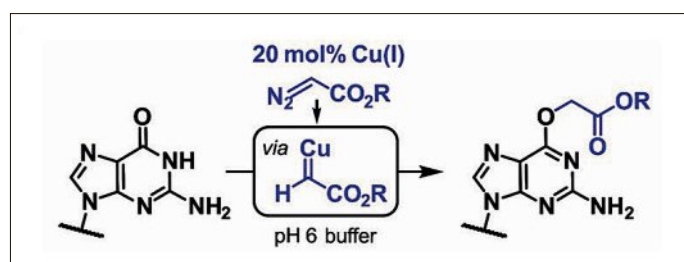
F. D. Bobbink, W. Gruszka, M. Hulla, S. Das, and P. J. Dyson*, *Chem. Commun.* **2016**, *52*, 10787. EPF Lausanne

The use of carbon dioxide in the production of fine chemicals and synthetic fuels would contribute towards a more sustainable chemical industry. Oxygenated cyclic carbonates are particularly suitable synthetic targets from CO₂. However, activation of the thermodynamically stable and kinetically inert CO₂ is challenging. In this paper, Dyson and co-workers describe heterocyclic carbene catalysts, including one derived from a cheap and efficient thiazolium salt, for the conversion of CO₂ and diols into cyclic carbonates. The reaction proceeds at atmospheric pressure in the presence of an alkyl halide and Cs₂CO₃. Plausible reaction mechanisms are discussed.



Copper Carbenes Alkylate Guanine Chemoselectively Through a Substrate Directed Reaction

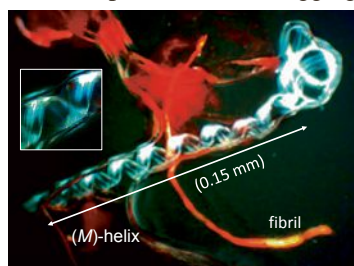
S. N. Geigle, L. A. Wyss, S. J. Sturla, and D. G. Gillingham*, *Chem. Sci.* **2016**, DOI: 10.1039/c6sc03502g. University of Basel
Catalytic reactions with metal carbenes are broadly applied in synthetic chemistry. Despite their high reactivity, the chemoselectivity of metal carbenes can be controlled by the choice of metal, ligand and carbene precursor. Gillingham and collaborators report that Cu(I) carbenes derived from α -diazocarbonyl compounds lead to the selective alkylation at the guanine O⁶ position (O⁶-G) in mono- and oligonucleotides. Mechanistic studies point to N7G as directing group. The results suggest that transition metals may increase the vulnerability of nucleic acids to alkylation damage. At the same time this method may serve as a synthetic tool for further research on O⁶-G adducts in biology and biotechnology.



Visible-Light Microscopic Discovery of Up to 150 μ m Long Helical Amyloid Fibrils Built of the Dodecapeptide H-(Val-Ala-Leu)₄-OH and of Decapeptides Derived from Insulin

M. Świontek, Z. J. Kamiński, B. Kolesińska*, and D. Seebach*, *Chem. Biodiversity* **2016**, *13*, 1111. ETH Zürich

The supramolecular aggregation of biopolymers is of fundamental importance for the understanding of biological processes. Amyloids have been associated with many types of human diseases, including neurodegenerative disorders and autoimmune dysfunctions. In this work, Seebach and collaborators demonstrate



for the first time the formation of helical amyloid fibrils from several small peptides. (M)- and (P)-superhelices were observed by visible-light microscopy from a dodecapeptide and two insulin-derived decapeptides. Importantly, the superhelices appear only after extended incubation periods at physiological pH and high peptide concentrations. The findings are discussed in the context of amyloid formation and polymorphisms *in vivo*.