



Swiss Science Concentrates

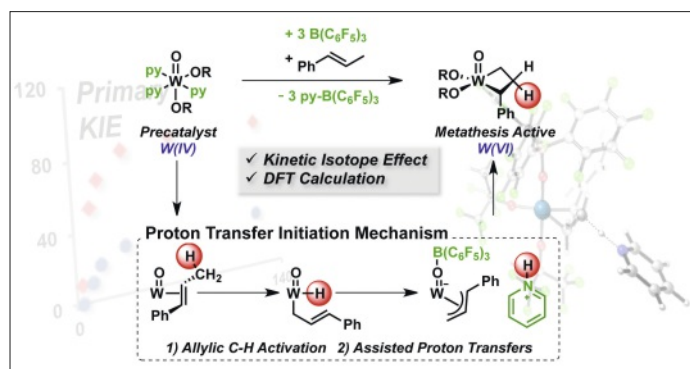
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

C–H Activation and Proton Transfer Initiate Alkene Metathesis Activity of Tungsten(IV)-Oxo Complex

K. W. Chan, E. Lam, V. D'Anna, F. Allouche, C. Michel, O. V. Safonova, P. Sautet, and C. Copéret*, *J. Am. Chem. Soc.* **2018**, *140*, 11395. ETH Zurich and Paul Scherrer Institute.

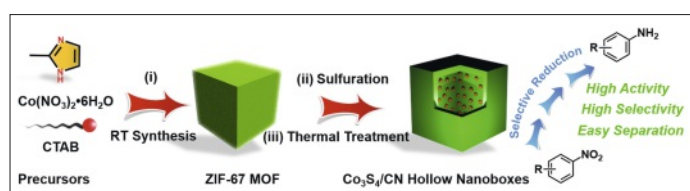
Alkene metathesis is typically carried out using high-oxidation state (VI) Mo or W alkylidenes as catalysts. Copéret and co-workers have demonstrated how a tungsten(IV)-oxo bisalkoxide complex is capable of alkene metathesis upon activation with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). Deuterium labelling studies support the presence of allylic C–H activation as a key step for converting the tungsten(IV) precatalyst to the active tungsten(VI) species. DFT calculations highlighted the importance of the synergistic effects of the Lewis acid ($B(C_6F_5)_3$) and Lewis base (pyridine) to activate the pre-catalyst by facilitating proton transfer.



Metal–Organic-Framework-Derived Co_3S_4 Hollow Nanoboxes Reduce Nitroarenes

S. Yang, L. Peng, D. T. Sun, E. Oveisi, S. Bulut, and W. L. Queen*, *ChemSusChem* **2018**, *11*, 3131. EPFL

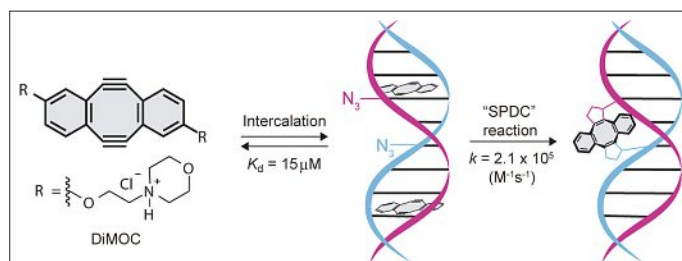
Queen and co-workers have developed metal–organic framework (MOF) derived cobalt sulphides for the catalytic reduction of nitroarenes. Their strategy is based on the preparation of hollow, MOF-derived Co_3S_4 nanoboxes and their utilization as catalysts in hydrogenation reactions. The unique nanobox architecture was found to inhibit both dehalogenation and vinyl hydrogenation reactions, which are common limitations to Pd-based catalysts. A wide variety of nitroarenes could be reduced to pure aniline products that were isolated without the need of tedious purification steps.



Intercalation-Enhanced ‘click’ Crosslinking of Cellular DNA

M. Tera, Z. Harati Taji, and N. W. Luedtke*, *Angew. Chem. Int. Ed.* **2018**, *57*, 15405. University of Zurich

Bifunctional electrophiles were initially developed as chemical weapons and later, certain derivatives were recognized as having important chemotherapeutic activities. The low chemoselectivity of these drugs (ex. cisplatin, chlorambucil, cyclophosphamide) contributes to their undesirable side effects. To overcome the poor chemoselectivity of traditional cross-linking agents Tera and co-workers developed a cationic Sondheimer diyne derivative ‘DiMOC’ that exhibits weak, reversible intercalation into duplex DNA where it undergoes tandem strain-promoted cross-linking of azide-containing DNA to give DNA-DNA interstrand crosslinks (ICLs) with an exceptionally high apparent rate constant $k_{app} = 2.1 \times 10^5 M^{-1}sec^{-1}$.



Copper-Catalyzed Arylation of Remote $C(sp^3)$ -H Bonds in Carboxamides and Sulfonamides

Z. Li, Q. Wang, and J. Zhu*, *Angew. Chem. Int. Ed.* **2018**, *57*, 13288. EPF Lausanne

The Hofmann-Löffler-Freytag reaction is an established procedure for making pyrrolidines from *N*-halo amines. After homolytic N–X bond cleavage, a 1,5-hydrogen atom transfer takes place allowing for functionalization of the resulting δ -carbon radical. Li, Wang and Zhu present an unprecedented copper-catalyzed cross coupling of this type of δ -carbon radical with arylboronic acids. *N*-halo carboxamides and sulfonamides can be employed as starting materials in this reaction that exhibits a high degree of functional group tolerance with good-to-moderate yields. The regioselectivity of the reaction is determined by the kinetics of 1,5-hydrogen atom transfer, and its utility was demonstrated in the late-stage functionalization of natural product derivatives.

