



Swiss Science Concentrates

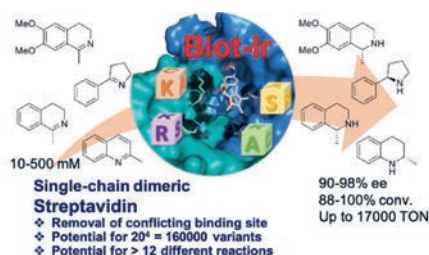
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Breaking Symmetry: Engineering Single-Chain Dimeric Streptavidin as Host for Artificial Metalloenzymes

S. Wu, Y. Zhou, J. G. Rebelein, M. Kuhn, H. Mallin, J. Zhao, N. V. Igareta, and T. Ward,* *J. Am. Chem. Soc.* **2019**, *141*, 15869. University of Basel

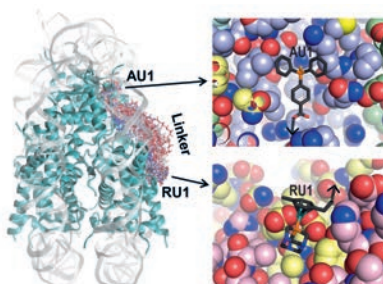
The high affinity of biotin for streptavidin (Sav) has been used to prepare artificial metalloenzymes (ArMs) that catalyse over a dozen reactions. However, their homotetrameric nature severely limits their genetic optimisation potential and their activity often depends on the cofactor:Sav ratio. The authors engineered and evaluated the activity of single chain dimeric streptavidins (scd-Savs) in the asymmetric transfer hydrogenation (ATH) of challenging substrates. With a single biotinylated cofactor precisely localized within the biotin-binding vestibule, these ATHases outperformed homotetrameric Sav-based ATHases. Moreover, their synthetic utility was demonstrated by the preparation of (*R*)-salsolidine in 90% ee and >17000 turnover numbers.



Crosslinking Allosteric Sites on the Nucleosome

L. K. Batchelor, L. De Falco, T. von Erlach, D. Sharma, Z. Adhireksan, U. Roethlisberger,* C. A. Davey,* and P. J. Dyson,* *Angew. Chem. Int. Ed.* **2019**, *58*, 15660. EPFL

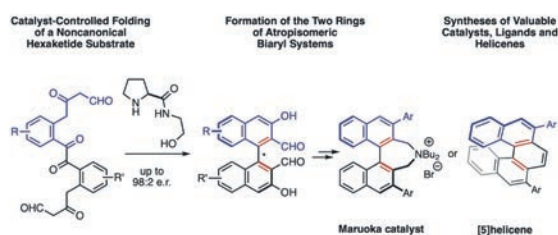
The 'acidic patch' is an interesting target in epigenetics as it is essential for the folding of the nucleosome into chromatin fiber, the repression of transcription and as a docking area for regulatory proteins. Inspired by the nucleosomal allosteric effect of the metal complexes RAPTA-T and auranofin, the authors designed a new hetero-bimetallic Ru(II)-Au(I) compound wherein the two metallic species are connected by a PEG linker. This compound was able to crosslink the two allosteric binding sites on the acidic patch at a distance over 35 Å, resulting in a significant increase in stability of the nucleosome.



Atroposelective Synthesis of Tetra-ortho-Substituted Biaryls by Catalyst-Controlled Non-Canonical Polyketide Cyclizations

R. M. Witzig, V. C. Fäseke, D. Häussinger, and C. Sparr,* *Nat. Catal.* **2019**, *2*, 925. University of Basel

The biosynthesis of aromatic polyketides is governed by the polyketide synthase-controlled cyclization of poly- β -carbonyl-substrates. Performing analogous small-molecule-catalyzed cyclizations of non-canonical polycarbonyl substrates would allow access to valuable molecules distinct from natural polyketides. Sparr and co-workers now report a stereoselective secondary amine-catalyzed twofold cyclization of non-canonical hexacarbonyl substrates, furnishing tetra-ortho-substituted binaphthalenes in high yields and atropo-enantioselectivities. This method was applied to the synthesis of valuable enantioenriched molecules such as a chiral diene ligand, a [5]helicene and the Maruoka ion-pairing catalyst. This study showcases the virtues of selective nonenzymatic polyketide cyclizations for the synthesis of complex polyaromatics.



Low-Valent Homobimetallic Rh Complexes: Influence of Ligands on the Structure and the Intramolecular Reactivity of Rh-H Intermediates

P. Jurt, O. G. Salnikov, T. L. Gianetti,* N. V. Chukanov, M. G. Baker, G. Le Corre, J. E. Berger, R. Verel, S. Gauthier, O. Fuhr, K. V. Kovtunov, A. Fedorov, D. Fenske, I. V. Koptuyug, and H. Grützmacher,* *Chem. Sci.* **2019**, *10*, 7937. ETH Zurich, Novosibirsk State University, University of Arizona, Université de Rennes and KIT

The mode of interaction between supported Rhodium nanoparticles and H₂ in heterogeneous catalysis for hydrogenation-dehydrogenation reactions is not fully understood, despite numerous applications in various industrial processes. To gain further insight, Grützmacher and collaborators designed and synthesized a new family of low-valent homobimetallic Rh(I)-Rh(I) complexes based on a polydentate trop-based ligand containing two alkyne moieties. They were able to identify two distinct modes of intramolecular semihydrogenation of the ligand and a Rh hydride species was characterized by advanced NMR methods upon stabilization with a diphosphine ligand

