



Swiss Science Concentrates

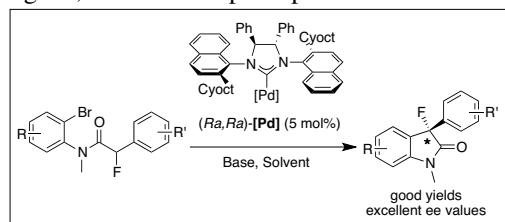
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Synthesis of 3-Fluoro-3-aryl Oxindoles: Direct Enantioselective α -Arylation of Amides

L. Wu, L. Falivene, E. Drinkel, S. Grant, A. Linden, L. Cavallo, and R. Dorta*, *Angew. Chem. Int. Ed.* **2012**, *51*, 2870

University of Zürich, University of Western Australia
N-heterocyclic carbene (NHC) ligands are well-established as an effective ligand motif in organometallic chemistry and catalysis. Due to inherent structural design constraints it has so far proven challenging to create chiral NHCs whose corresponding complexes induce very high enantiomeric excesses in catalytic transformations. One particular design was employed in Pd-mediated direct asymmetric α -arylation for the generation of fluorinated oxindoles, a hitherto unexplored reaction. The resulting fluorine-substituted quaternary stereocenters are produced with excellent enantioselectivity. An interesting feature of the ligand, which can in principle exist as a mixture of atropisomers,



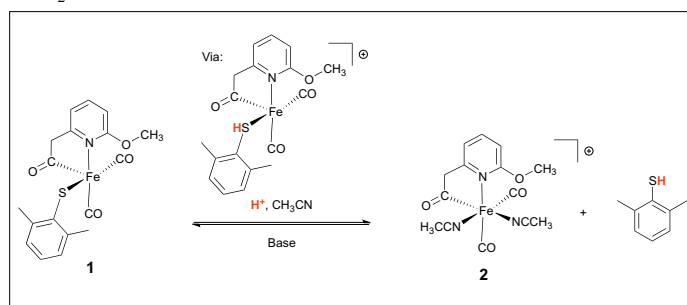
consists in the easy synthetic access of the single diastereomeric form used in catalysis.

Reversible Protonation of a Thiolate Ligand in an [Fe]-Hydrogenase Model Complex

D. Chen, R. Scopelliti, and X. L. Hu*, *Angew. Chem. Int. Ed.* **2012**, *51*, 1919.

EPFL

Hydrogenases (H_2 -ase) reversibly interconvert protons/electrons with hydrogen. In addition to the well-characterized hydrogenases bearing iron-iron and nickel-iron active sites, a third H_2 -ase active site was recently described. Spectroscopic and crystallographic data suggests a mononuclear Fe^{II} complex with *cis*-CO, a thiolate from a cysteine, and a chelating pyridyl-acyl ligand from a cofactor. A suitable mimick has been developed by Hu and coworkers. This model was probed for mechanistic insight as it relates to the function of the mono-iron H_2 -ase. Protonation of **1** liberates the thiol and forms the solvated complex **2**. This process can be reversed by the addition of a strong base. These studies shed light on the mechanism of this important new form of H_2 -ase.

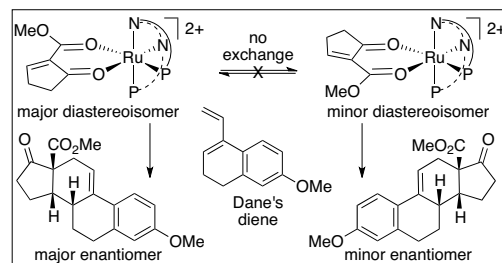


Asymmetric Diels–Alder and Ficini Reactions with Alkylidene β -Ketoesters Catalyzed by Chiral Ruthenium PNNP Complexes: Mechanistic Insight

C. Schotes, M. Althaus, R. Aardoom, and A. Mezzetti*, *J. Am. Chem. Soc.* **2012**, *134*, 1331.

ETH Zürich

Cyclic α -unsaturated β -ketoesters are challenging substrates for cycloaddition reactions, since they are prone to polymerization and exist as keto-enol tautomers. Following on recent reports of enantioselective cycloaddition reactions between alkylidene β -ketoesters and dienes or ynamides, the authors show here that such alkylidene β -ketoesters form well-defined dicationic ruthenium(II) complexes in combination with a chiral tetradentate PNNP ligand. These complexes offer the rare opportunity of studying the individual steps of the catalytic cycle and give mechanistic information that is pivotal for catalyst optimization. Thus, the diastereoisomers of the substrate/catalyst adduct were separated and characterized. Their stoichiometric reactions with Dane's diene revealed the stereochemical course of the cycloaddition reaction and showed that product release is slow.



A Two-Dimensional Polymer Prepared by Organic Synthesis

P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Götzinger, A. D. Schlüter, and J. Sakamoto*, *Nature Chem.* **2012**, *4*, 287.

ETH Zürich, EMPA Dübendorf, University of Nevada, Reno

Two-dimensional materials have attracted much attention since the discovery of graphene. However, the synthesis of such materials with a richer chemistry than simple carbon is extremely challenging. The authors now report a strategy to synthesize two-dimensional polymers with a high degree of internal periodicity. First a photopolymerizable monomer was designed to crystallize in a layered structure. Next, the crystal was irradiated with light upon which polymers formed. They could be exfoliated to yield sheets of several microns in diameter, but with a thickness of only a single monomer unit. Applications that can be envisioned for such polymers are, e.g. filtration membranes and building blocks for nanostructured materials.

