



Swiss Science Concentrates

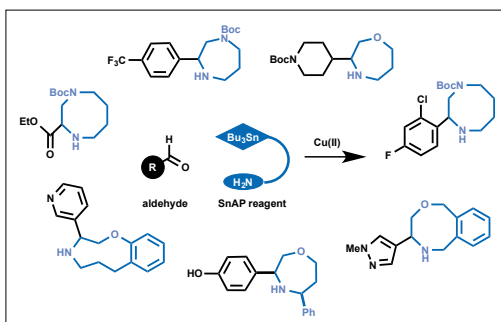
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

SnAP Reagents for the One-step Synthesis of Medium-ring Saturated N-Heterocycles from Aldehydes

C.-V. T. Vo, M. U. Luescher and J. W. Bode*, *Nature Chem.* **2014**, DOI: 10.1038/NCHEM.1878. ETH-Zurich

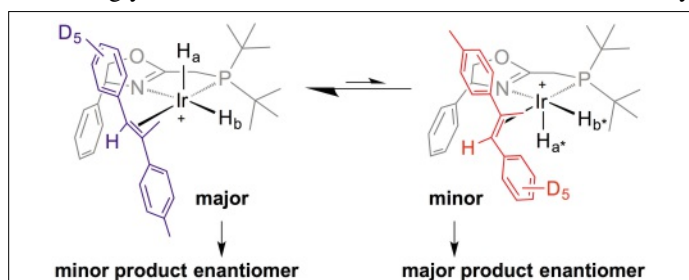
Saturated N-heterocycles are common scaffolds in biologically active molecules. However, these rings tend to be difficult to prepare, often requiring multistep protocols. A new method for the preparation of the medium-sized seven- to nine-membered ring analogues is presented by Bode and coworkers. To address this synthetic challenge, the authors rely on air- and moisture-stable aminostannanes (SnAP reagents), which are condensed with aldehydes to form the corresponding imines. In the presence of $\text{Cu}(\text{OTf})_2$, a highly *endo*-selective radical cyclization occurs under mild conditions to yield the N-heterocycles. The method displays a broad substrate scope, offers an easily recognized retrosynthetic disconnection, and may become a versatile tool for medicinal chemists as it affords the N-unprotected products by a single synthetic operation.



Asymmetric Hydrogenation with Iridium C,N and N,P Ligand Complexes: Characterization of Dihydride Intermediates with a Coordinated Alkene

S. Gruber and A. Pfaltz*, *Angew. Chem. Int. Ed.* **2014**, 53, 1896. University of Basel

Iridium complexes are important catalysts for the asymmetric hydrogenation of unactivated olefins. Their reaction mechanism is controversial: both $\text{Ir}^{\text{I}}/\text{Ir}^{\text{III}}$ and $\text{Ir}^{\text{III}}/\text{Ir}^{\text{V}}$ couples have been postulated in the catalytic cycle. The authors present convincing NMR studies which support a catalytic cycle involving an $\text{Ir}^{\text{III}}/\text{Ir}^{\text{V}}$ mechanism. Several intermediates were characterized spectroscopically, pointing towards a reaction pathway proceeding through rapidly equilibrating isomeric iridium dihydride alkene intermediates. Interestingly, a minor, less stable intermediate is ultimately

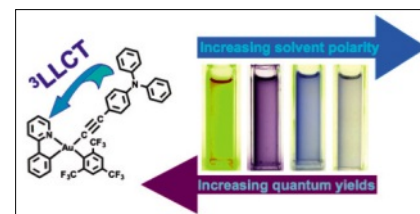


converted into the major product enantiomer, reminiscent of the 'Halpern' mechanism for the Rh-based hydrogenation.

Monocyclometalated Gold(III) Monoaryl Complexes – A New Class of Triplet Phosphors with Highly Tunable and Efficient Emission Properties

A. Szentkuti, M. Bachmann, J. A. Garg, O. Blacque, and K. Venkatesan*, *Chem. Eur. J.* **2014**, 20, 2585, University of Zurich.

Due to the phenomenon of triplet harvesting, phosphorescent organic light emitting diodes (PhOLEDs) can theoretically achieve 100% internal quantum efficiency. Therefore, they are subject of intense investigation. Au(III) complexes show promising properties in this context. To increase the stability and minimize the risk of reductive elimination, the introduction of the 2,4,6-tris(trifluoromethyl)phenyl ligand allowed the isolation of Au(III) monocyclometalated monochloro complexes for further modification. Up to 39% quantum yield was achieved, the highest reported for a monocyclometalated Au(III) complex. By using solvents of different polarity, it was possible to tune the emission spectrum from deep blue to red. These complexes display good thermal stability, which is an important requirement for practical applications.



Cyclic Carbo-Isosteric Depsipeptides and Peptides as a Novel Class of Peptidomimetics

S. M. Guéret*, P. Meier, and H.-J. Roth, *Org. Lett.* **2014**, 16, 1502. Global Discovery Chemistry, Novartis Institutes of Biomedical Research, Novartis, Basel

Peptides show a remarkable biological activity towards several pharmaceutically relevant targets. However, the poor bioavailability, permeability and metabolic stability of peptides represent a major challenge. Guéret *et al.* report on a powerful head-to-tail cyclization strategy to access carbo-isosteric depsipeptides and peptides as a novel peptidomimetic motif. Starting from linear precursors, a condensation reaction of a C-terminal methyl ketone and the free amine, followed by reduction of the imine resulted in a 'carbo-isosteric' depsipeptide. The scope ranged from cyclic penta- up to octa-pseudopeptides as well for synthetically challenging cyclic tetra-depsipeptides. In conclusion, a practical cyclization method was developed for the synthesis of pharmacokinetic improved depsipeptides and peptides.

