



Swiss Science Concentrates

A CHIMIA Column

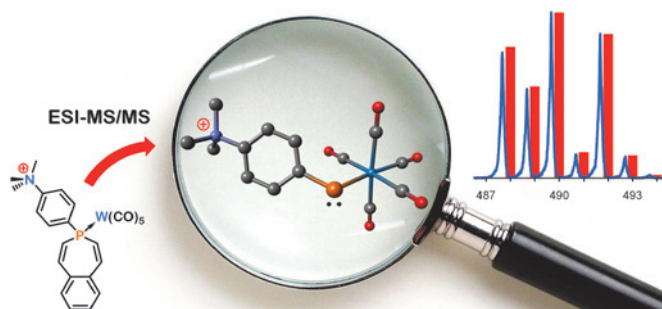
Short Abstracts of Interesting Recent Publications of Swiss Origin

Reactive Intermediates: A Transient Electrophilic Phosphinidene Caught in the Act

H. Jansen, M. C. Samuels, E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, P. Chen,* and K. Lammertsma*, *Chem. Eur. J.* **2010**, *16*, 1454

ETH Zürich; VU University Amsterdam.

Transient electrophilic phosphinidenes [R-P=W(CO)₂] have emerged as versatile intermediates that are highly valuable in the synthesis of a plethora of organophosphorus compounds. However, their existence had never been unequivocally established. Herein, employing electrospray ionisation tandem mass spectrometry (ESI-MS/MS) on substrates tagged with a NMe₃⁺ group, this low-valent species has now been detected and its gas-phase reactivity perfectly matches the well-established solution-phase data.

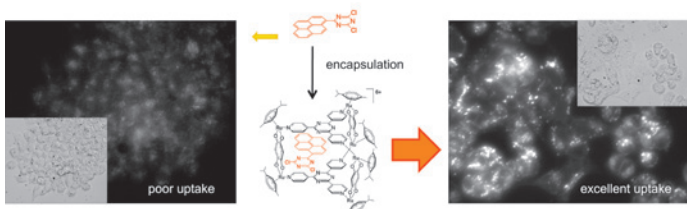


Evidence for Drug Release from a Metalla-Cage Delivery Vector Following Cellular Internalisation

O. Zava, J. Mattsson, B. Therrien,* and P. J. Dyson*, *Chem. Eur. J.* **2010**, *16*, 1428

EPF Lausanne; University of Neuchatel

Efficient intracellular release of a fluorescent hydrophobic molecule (1-(4,6-dichloro-1,3,5-triazin-2-yl)pyrene) from a ruthenium-based metalla-cage has been reported by the authors affording a new delivery vehicle for medicinal applications. Fluorescence microscopy has illustrated the potential of this kind of water-soluble metalla-cage to act as drug carrier as well as that the entry of the compound into the cell is, at least in part, dependent on an assisted diffusion pathway.

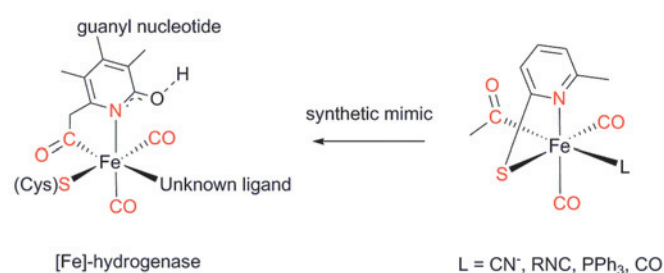


Synthesis and Reactivity of Iron Acyl Complexes Modeling the Active Site of [Fe]-Hydrogenase

D. Chen, R. Scopelliti, and X. Hu*, *J. Am. Chem. Soc.* **2010**, *132*, 928

EPF Lausanne

[Fe]-hydrogenase is the third type of hydrogenase and the only hydrogenase that requires only one metal center for H₂ activation. Few reactive synthetic mimics of [Fe]-hydrogenase have been reported. Herein, the authors detail the synthesis and reactivity of a [Fe^{II}Fe^{II}] dithiolate complex, which reacted with phosphine, cyanide, isocyanide, and CO to give monomeric Fe^{II} complexes reproducing the first coordination sphere of the active site of [Fe]-hydrogenase. All the acyl and carbonyl carbons in the di-iron complex underwent facile isotopic exchange with ¹³CO via monomeric Fe tricarbonyl intermediates..



Intramolecular Schmidt Reaction Involving Primary Azidoalcohols under Nonacidic Conditions: Synthesis of Indolizidine (–)-167B

A. Kapat, E. Nyfeler, G. T. Giuffredi, and P. Renaud*, *J. Am. Chem. Soc.* **2009**, *131*, 17746

University of Bern

In this article, the authors describe a modified version of the intramolecular Schmidt reaction involving such primary azidoalcohols. This process is run under nonacidic conditions, and it allows resolution of the regioselectivity problems caused by rearrangement of carbenium ions. The utility of the method is demonstrated by a concise synthesis of dendrobate alkaloid (–)-indolizidine 167B.

