



Swiss Science Concentrates

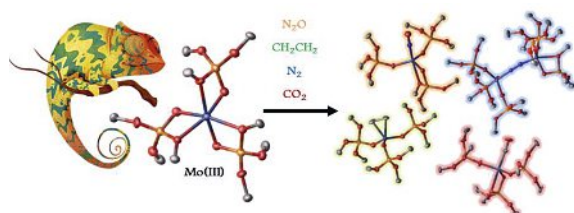
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

A Reactive Coordinatively Saturated Mo(III) Complex: Exploiting the Hemi-lability of Tris(*tert*-butoxy)silano-late Ligands

M. Pucino, F. Allouche, C. P. Gordon, M. Wörle, V. Mougel,* and C. Copéret,* *Chem. Sci.* **2019**, *10*, 6362, doi: 10.1039/c9sc01955c. ETH Zurich

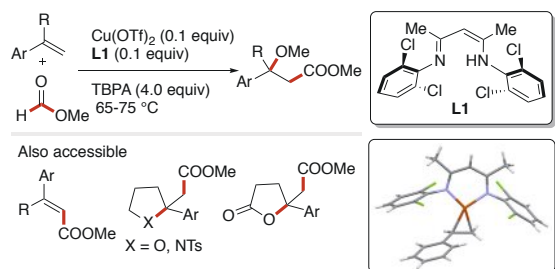
Unlike coordinatively unsaturated Mo(III) complexes, coordinatively saturated octahedral Mo(III) complexes are in general relatively unreactive towards small molecules. In this work, the authors exploit the hemi-lability of tris(*tert*-butoxy)silano-late (TBOS) ligands and report an isolable, yet highly reactive mononuclear octahedral Mo(III) complex. TBOS ligands are not very sterically demanding, and are able to adopt different binding modes. [Mo(TBOS)₃], wherein the ligands are bound in a κ^2 -fashion, proved to be competent for the cleavage of N–N and C–O bonds. This complex promotes the six-electron reduction of N₂ at a faster rate than other tri-coordinated Mo(III) complexes.



Copper-Catalyzed 1,2-Methoxy Methoxycarbonylation of Alkenes with Methyl Formate

B. Budai, A. Leclair, Q. Wang, and J. Zhu,* *Angew. Chem. Int. Ed.* **2019**, *58*, 10305, doi: 10.1002/anie.201904263. EPFL

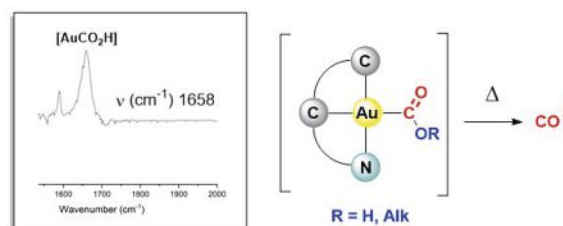
Zhu and co-workers report the copper-catalyzed 1,2-methoxy methoxycarbonylation of styrenes using the abundant methyl formate as the source of both methoxy and methoxycarbonyl groups. Applying their protocol, β -methoxy alkanates, cinnamates, as well as several valuable five-membered heterocycles can be obtained in good yield starting from easily accessible styrenes. They propose that the complexation of the electron-rich alkene by copper(I) accelerates the addition of nucleophilic radicals, which should pave the way to the development of new radical-based transformations.



κ^3 -(N[^]C[^]C)Gold(III) Carboxylates: Evidence for Decarbonylation Processes

H. Beucher, E. Merino, A. Genoux, T. Fox, and C. Nevado,* *Angew. Chem. Int. Ed.* **2019**, *58*, 9044, doi: 10.1002/anie.201903098. University of Zurich

Gold-based heterogeneous catalysts rank among the most effective systems towards the water-gas shift reaction at low temperature. Despite their efficiency, both intermediates and mechanisms underlying these transformations are still the focus of intense debate. In this context, Nevado and co-workers succeeded to characterize the first η^1 -Au^{III}-CO₂H complex under cryogenic conditions. This was enabled by the stabilization provided by a κ^3 -(N[^]C[^]C) pincer ligand template. The thermal decomposition of these species proceeds by an unusual decarbonylation pathway, hence showing the importance of the ligand template in modulating the reactivity of metalcarboxylate species.



Oligoprolines Guide the Self-assembly of Quaterthiophenes

N. A. K. Ochs, U. Lewandowska, W. Zajackowski, S. Corra, S. Reger, A. Herdlitschka, S. Schmid, W. Pisula, K. Müllen, P. Bäuerle, and H. Wennemers,* *Chem. Sci.* **2019**, *10*, 5391. ETH Zürich, Max Planck Institute for Polymer Research, University of Ulm, Lodz University of Technology

Supramolecular assembly of π -conjugated oligothiophenes and the control over their molecular organization is key to their use in organic electronics, but challenging as they have a pronounced tendency to aggregate. Wennemers and co-workers report that oligoprolines, which do not self-assemble, control the self-assembly of quaterthiophenes. Changing the length of the oligoprolines allows to induce the formation of mono- or double-layered sheets or helically twisted ribbons of micrometric dimensions. These correlate with the molecular dimension of the building blocks, hence paving the way to the rational design of supramolecular architectures

