Compressing the spin ladder: reactivity of iron complexes based on redox-active ligands

Dragos-Adrian Rosca

[1]*Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany*
[2]*Institut des Sciences Chimiques de Rennes, Université de Rennes, France*

E-Mail : dragos-adrian rosca@univ-rennes.fr

Some of the most „sustainable“ metal-based catalysts are considered to be located in the first-row of the transition metal block. Unlike their heavier counterparts, their reactivity is governed by rapid oxidation state, spin state and geometry changes all of which are interdependent on eachother. This behaviour often renders their reactivity difficult to control, which is translated into poor selectivity or favourable deactivation pathways in catalytic runs. A successful tool to control their reactivity is the so-called “metal-ligand cooperativity” approach, which based on actively involving the ligand in the chemical and redox processes of the elementary steps in catalysis.

This talk will showcase two approaches used successfully in our group to design highly active catalysts based on open-shell iron and cobalt systems: redox metal-ligand cooperativity (*via* the use of redox-active ligands) and chemical metal-ligand cooperativity (*via* ligand-based activation of the catalytically active species). The focus will be on [2+2]-cycloaddition methodologies involving unactivated alkenes and alkynes,[1] the identity of catalytically active species in these reactions, the fixation of N_2 at iron centres[2] as well as on iron-ligand multiple bonds.[3]

References:

[1] (a) J. S. Doll, R. Eichelmann, L. E. Hertwig, T. Bender, V. J. Kohler, E. Bill, H. Wadepohl, D.-A. Roșca *ACS Catal.* **2021**, *11*, 5593. (b) L. E. Hertwig, T. Bender, F. J. Becker, P. Jäger, S. Demeshko, S. J. Gross, J. Ballmann, D.-A Roșca *ACS Catal.* **2023**, *13*, 6416; (c) L. S. Freitag, J. Zeh, L. A. Ziegenhagen. F. J. Becker, D.-A Roșca *Chem. Eur. J.* **2025**, *accepted. Doi:* 10.1002/chem.202502476

[2] (a) N. I. Regenauer, H. Wadepohl, D.-A Roșca *Chem. Eur. J.* **2022**, e202202172.

[3] J. Zeg, L. E. Hertwig, N. I. Regenauer, D.-A. Roșca *in preparation*