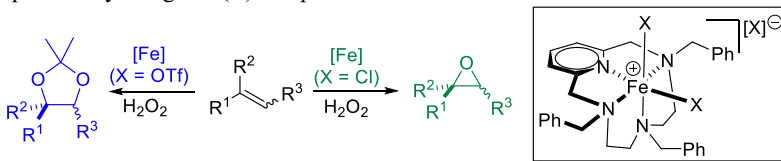


# Controlling selectivity in alkene oxidation and CO<sub>2</sub> cycloaddition reactions: fine tuning of Pc-L transition metal complexes

Alessandro Caselli and Nicola Panza

*Department of Chemistry, Università degli Studi di Milano and ISTM-CNR-Milano, Via Golgi 19, 20133 Milan, Italy. E-mail: alessandro.caselli@unimi.it*

Sustainable synthesis and green chemistry have become a fundamental tool when planning a new process. In catalysis this means to correctly design since the beginning the properties of the target metal complex. The cost and the availability of the metal ion, as well as its biocompatibility must be taken into account. Despite the fact that their greater reactivity makes more difficult their use, first row transition metals are to be considered as the first choice to plan a new catalytic cycle. In this lecture, I will provide a perspective on the catalytic applications of iron(III) and zinc(II) metal complexes of tetraaza 12-membered pyridine containing macrocyclic ligands.<sup>1</sup> I will focus on the selective iron(III) catalysed epoxidation or dihydroxylation of alkenes by using hydrogen peroxide as terminal oxidant.<sup>2</sup> Depending on the anion of the iron(III) metal complex employed as catalyst, a completely reversed selectivity was observed (Figure). Our approach towards the selective oxidation of alcohols by using the same catalytic system will also be covered. As for iron, catalytic applications of zinc complexes fall in the scientific community's effort to develop more eco-friendly chemical processes. CO<sub>2</sub> is the principal greenhouse gas, largely recognized as responsible for global warming, but it is also an abundant C<sub>1</sub> source. Limiting CO<sub>2</sub> emissions can only stem the problem but to solve it a circular economy based on carbon dioxide should be pursued and in this respect, research in the last decade has focussed on the design of systems able to promote the functionalisation of CO<sub>2</sub>. I will outline our approach towards the synthesis of cyclic carbonates by cycloaddition of CO<sub>2</sub> to epoxides by using zinc(II) complexes.



**Fig.** Controllable iron(III)-catalysed alkene epoxidation or dihydroxylation reactions are performed by judicious choice of anion in [Fe(III)(Pc-L)] catalysts (Pc-L = pyridine-based 12-membered tetraaza-macrocyclic ligands).

**Key words:** macrocyclic ligands, homogeneous catalysis, iron, zinc, oxidation, CO<sub>2</sub> functionalization.

## References

<sup>1</sup> G. Tseberlidis, D. Intriери, A. Caselli, *Eur. J. Inorg. Chem.* **2017**, 2017, 3589.

<sup>2</sup> G. Tseberlidis, L. Demonti, V. Pirovano, M. Scavini, S. Cappelli, S. Rizzato, R. Vicente, A. Caselli, *ChemCatChem* **2019**, doi:[10.1002/cctc.201901045](https://doi.org/10.1002/cctc.201901045)