

# Iron(III) complexes as efficient catalysts for the synthesis cyclic carbonates and polycarbonates from carbon dioxide and oxiranes

by

***Carminé Capacchione***

## Abstract

The incorporation of the carbon dioxide into chemicals as the organic carbonates, cyclic, acyclic or polymeric, represent undoubtedly a value added utilization of this abundant and cost effective chemical.[1] The selective and effective synthesis of organic carbonates and polycarbonates under mild conditions, as well as, the rationalization of the process catalyzed by metal complexes is currently challenging and in the focus of interest of industrial and academic researchers.[2] We have recently reported that a new family of thioether-triphenolate iron(III) complexes act as highly active catalysts for the coupling of carbon dioxide with epoxides affording cyclic organic carbonates under solventless condition.][3 Following these results that underline the crucial role of these sulphur containing ligands, we have also introduced a new family of [OSSO]-type iron(III) complexes and used them in combination with suitable nucleophile as catalysts for the coupling of carbon dioxide with various epoxides. [4] The catalytic systems resulted quite robust, tolerating the atmospheric oxygen and non-dry conditions during the catalytic tests.. The steric and electronic properties of ligand were modulated by, changing the substituents of the aromatic rings, in order to get a deeper knowledge of the relationship between complex structure and catalytic performance/selectivity for this new class of catalysts. Notably these catalysts are able both to promote the formation of cyclic carbonates and polycarbonates depending on the reaction conditions and on the type of epoxide employed. Finally Insights into the mechanism were obtained by means of kinetic studies and DFT calculations.

## References

[1] M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2013, 114, 1709.

[2] a) C. Martin, G. Fiorani, A. W. Kleij, *ACS Catal.*, 2015, 5, 1353. b) Donald J. Darensbourg, S. J. Wilson, *Green Chem.*, 2012, 14, 2665.

[3] a) A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vagin, B. Rieger, *Catal. Sci. Technol.*, 2015, 5, 118; b) A. Buonerba, F. Della Monica, A. De Nisi, E. Luciano, S. Milione, A. Grassi, C. Capacchione, B. Rieger, *Faraday Discuss.*, 2015, 183, 83. c) F. Della Monica S. V.C. Vummaleti, A. Buonerba A.De Nisi, M. Nonari, S. Milione, A.Grassi, L.Cavallo, C.Capacchione *Adv. Synth. Catal.* 2016, 358, 3231-3243.

[4] F. Della Monica, B. Maity, T. Pehl, A. Buonerba, A. De Nisi, M. Nonari, A. Grassi, B. Rieger, L. Cavallo, C. Capacchione *ACS Catalysis* 2018, 8, 10.1021/acscatal.8b01695.