Università degli Studi di Salerno

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Development of Iron-Based Catalysts for the Coupling of Carbon Dioxide with Epoxides

Tesi di Dottorato in Chimica - XXX Ciclo

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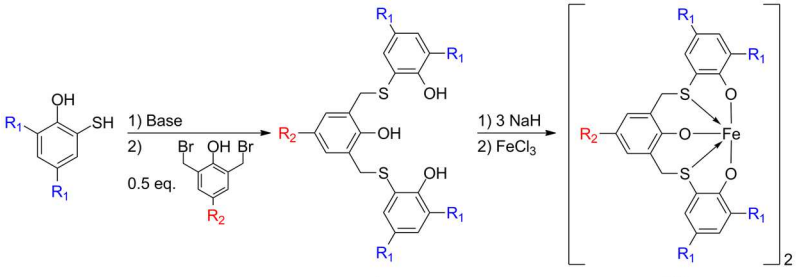
Thesis Abstract

Beside the environmental and energetic issues, carbon dioxide can be considered as a resource. Many chemical transformations based on CO_2 as C-1 building block have been developed. The coupling reaction of epoxides with CO_2 is one of the most attractive.[1] An overview on the state of the art for metal-mediated process is provided. Particular enphasis is given to the iron-based systems, because it is an ideal candidate for the development of environmental and economic sustainable catalytic systems.[2]

It is the aim of this thesis to investigate the application of sulphur containing ligand based iron complexes, starting from the encouraging results reported by the research group of Capacchione in the case of the bis-thioether-tri-phenolate ligand based bimetallic Fe(III) complex.[3] The synthesis and the complete characterization of five new thioether triphenolate ligands (**L2**-**6**), and of the corresponding bimetallic iron(III) complexes (**2**-**6**) is reported (Scheme 1).[4]

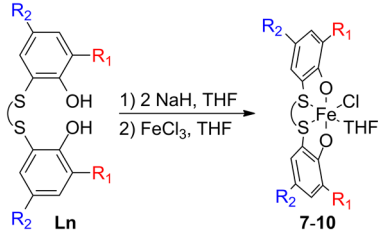


	1	2	3	4	5	6
R_1	$C(CH_3)_3$	$C(CH_3)_2Ph$	H	Cl	CH_3	CH_3
R_2	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$	$C(CH_3)_3$	Cl	$C(CH_3)_3$

Scheme 1. Synthesis of the pro-ligands **L1**-**L6** and of the reciprocal bimetallic Fe(III) complex **1**-**6**.

Their use in the cycloaddition of CO_2 to both terminal and internal epoxides leads to the selective formation of COCs, with the highest activity reported for an Fe-based system. In particular, complex **6** shows the best catalytic performance in terms of both activity and selectivity for several terminal epoxides with TOF values up to 5200 h^{-1} and 7000 h^{-1} for the conversion of PO and EPC respectively. The

DFT investigation of the reaction mechanism shows that, in spite of the dinuclear nature of the catalyst precursor, only one metal center is operative in the catalytic cycle and that coordination of the substrate and the subsequent reaction pathway can only take place by dissociation of a hemilabile S atom from one of the iron centers. The synthesis of a new group of mononuclear [OSSO]-type Fe(III) complexes is described (Scheme 2).



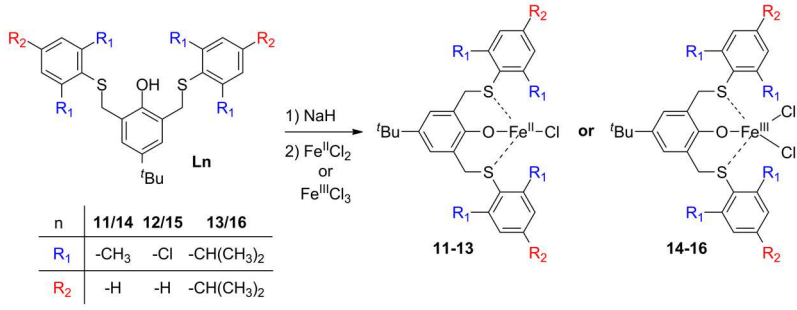
	⌒	R_1	R_2
7	$(CH_2)_2$	CPh_3	CH_3
8	$(CH_2)_2$	$C(CH_3)_2Ph$	$C(CH_3)_2Ph$
9	$(CH_2)_2$	CH_3	CH_3
10	*c*-Hex	$C(CH_3)_3$	$C(CH_3)_3$

Scheme 2 Synthesis of the [OSSO]-Fe(III) complex **7**-**10**.

The selective formation of cyclic organic carbonates was accomplished under very mild reaction conditions. In particular, the complex **10** shows the best catalytic performance, with a TOF of 108 h^{-1} for the PC formation at 35 °C and 1 bar CO_2 pressure. Only in the case of CHO, the selective production of perfectly alternate PCHC was obtained with the highest TOF of 420 h^{-1} in the case of the complex **8.** Kinetic investigations were conducted for the production of propylene carbonate and poly(cyclohexene carbonate).

The influence of the nuclearity and of the oxidation state of the metal centre on the catalytic activity were further investigted by comparing the catalytic performances of Fe(II) and Fe(III) complexes, supported by three new bis-thioether phenolate ligands (Scheme 3). The formation of monomeric or dimeric structures depending on the ligand was confirmed by magnetic moments measurements. When activated by TBAB, all the complexes resulted active in the cycloaddition of CO_2 to HO. Insights on the factors influencing the reaction were obtained by UV-Vis experiments, and comparison of the catalytic activity. The obtained results suggest the oxidation state

of the metal centre does play a prominent role into the modulation of the catalytic activity.



n	11/14	12/15	13/16
R_1	$-CH_3$	-Cl	$-CH(CH_3)_2$
R_2	-H	-H	$-CH(CH_3)_2$

Scheme 3 Synthesis of the bis-thioether phenolate complexes **11**-**16**.

In our ongoing search for active catalysts for the coupling of CO_2 with epoxides we have noticed that glycidol is sensibly more reactive than other epoxides. To get deeper insights into the reaction of glycidol with CO_2, we decided to investigate the reaction in the presence of [PPN]Cl and various ammonium salts.[5] The key role of the hydrogen bond in the activation of the epoxide ring was highlighted, also by means of DFT investigations (Figure 1).

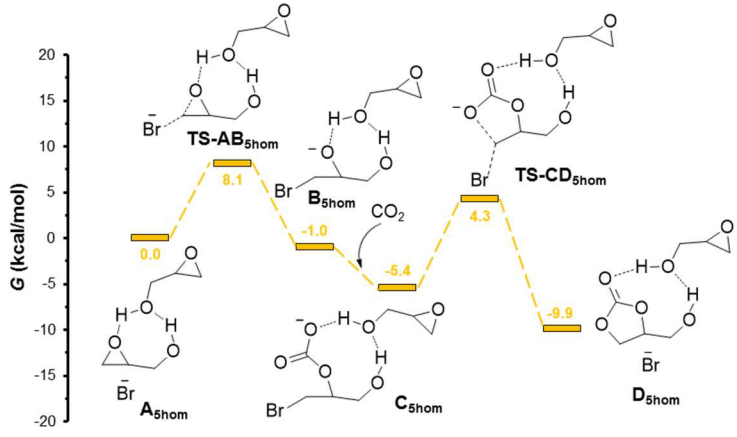


Figure 1 Relative free energy profiles for the cycloaddition of CO_2 to glycidol computed for the dimers of glycidol. Free energies are given in kcal/mol.

Glycidol in combination with a co-catalyst, was also used as an organocatalytic system for the cycloaddition of CO_2 to other epoxides.

References

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[3] Buonerba A., De Nisi A., Grassi A., Milione S., Capacchione C., Vagin S. and Rieger B., Catal. Sci. Technol., **2015**, *5*, 118-123.

[4] a) Buonerba A., Della Monica F., De Nisi A., Luciano E., Milione S., Grassi A., Capacchione C., Rieger B., *Faraday Discuss.*, **2015**, *183*, 83-95. b) Della Monica F., Vummaleti S.V.C., Buonerba A., De Nisi A., Monari M., Milione S., Grassi A., Cavallo L., Capacchione C., *Adv. Synth. Catal.*, **2016**, *358*, 3231-3243.

[5] Della Monica F., Buonerba A., Grassi A., Capacchione C., Milione S., *ChemSusChem*, **2016**, *9*, 3457-3464.