

Università degli Studi di Salerno

Dipartimento di Chimica e Biologia “Adolfo Zambelli”



Tesi di dottorato in Chimica- XXX Ciclo

ABSTRACT

**New metal catalysts for the synthesis
of polyolefins and bioderived polymers**

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A.A 2016-2017

ABSTRACT

The aim of PhD project is the synthesis of new metal catalysts active in the polymerization of polar monomer and α -olefins. In the last decade, transition metal complexes bearing tetradentate bis(phenolato) ligands are widely studied for their high polymerization control and activity.¹ The bis(phenolato) ligand is composed of two phenoxide groups linked by a bridge comprising two donor heteroatoms; when the donors are two sulfur atoms, the ligand is called of OSSO-type (see Figure 1).

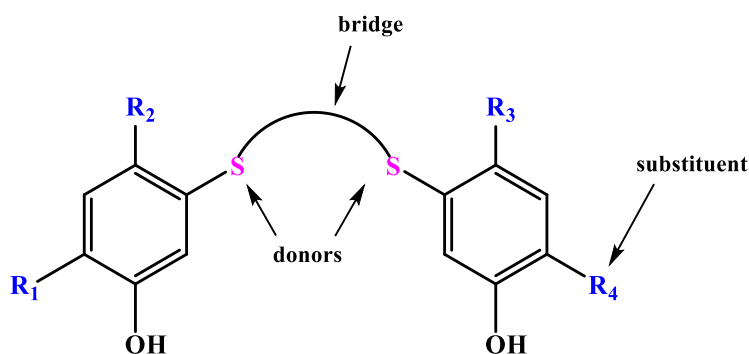


Figure 1. General structure of OSSO-type bis(phenolato) ligand

The tetradentate OSSO-type bis(phenolato) ligands are easy to prepare² and show high affinity to coordinate Group IV metals. We prepared a new series of OSSO-type Group 4 metal complexes of general formula $(OSSO_x)M(OR)_2$ (**1-5**) via protonolysis reaction between a metal alkoxide precursor and an appropriate proligand, Figure 2. The complexes **1-5** are active in the ring opening polymerization (ROP) of *rac*-lactide under the typical reaction conditions (toluene, 90 °C), showing catalytic performances comparable to the most active complexes reported in literature.³ In presence of hexogen alcohols, the polymerization proceeds by an “activated monomer mechanism” alternative to the common coordination-insertion process.

¹ a) Meppelder, G.-J. M.; Halbach, T. S.; Spaniol, T. P.; Mülhaupt, R.; Okuda, J. *Journal of Organometallic Chemistry*, **2009**, 694, 1235–1237. b) Si, G.; Zhang, L.; Han, B.; Duan, Z.; Li, B.; Dong, J.; Li, X.; Liu, B. *Polym. Chem.* **2015**, 6, 6372-6377.

² Nakata, N.; Toda, T.; Ishii, A. *Polym. Chem.*, **2011**, 2, 1597-1610.

³ Sauer, A.; Kapelski, A.; Fliedel, C.; Dagorne, S.; Kol, M.; Okuda, J. *Dalton Trans.* **2013**, 42, 9007–9023.

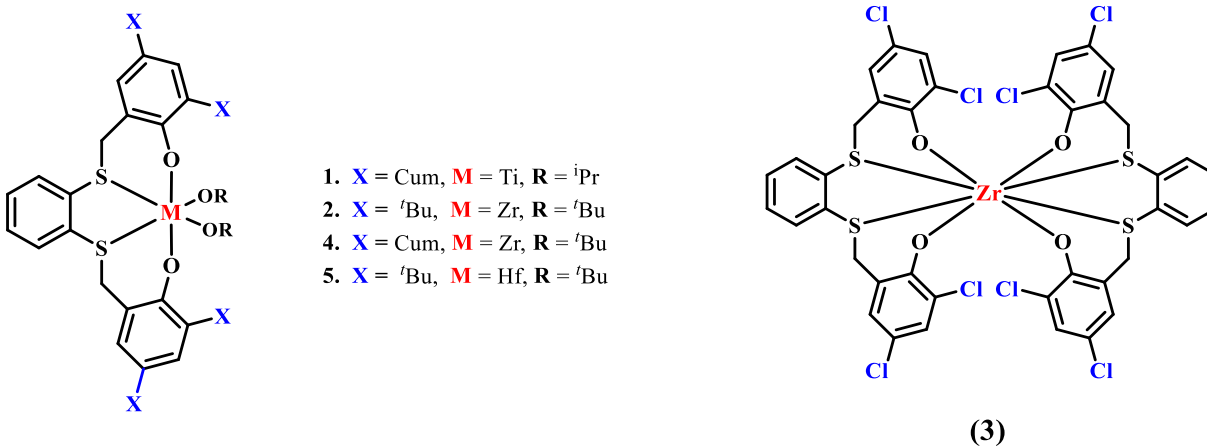


Figure 2. Complexes **1-5** active in the ROP of *rac*-lactide

The versatility of (OSSO)-type Group IV metal complexes is further investigated by analogues dichloro titanium derivatives of general formula $(\text{OSSO}_X)\text{TiCl}_2$ (**6-8**) (Figure 3). The precatalyst **7** is the most active in the polymerization of ethylene using $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{Al}(\text{tBu})_3$ activators ($\text{TOF} = 238 \text{ Kg}_{\text{PE}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{bar}^{-1} \cdot \text{h}^{-1}$); the obtained PE is linear with a T_m of 122°C and M_w of 107 KDa. The same precatalyst (**7**) is also active in propylene polymerization, yielding atactic oligomers terminated with unsaturated end-groups.

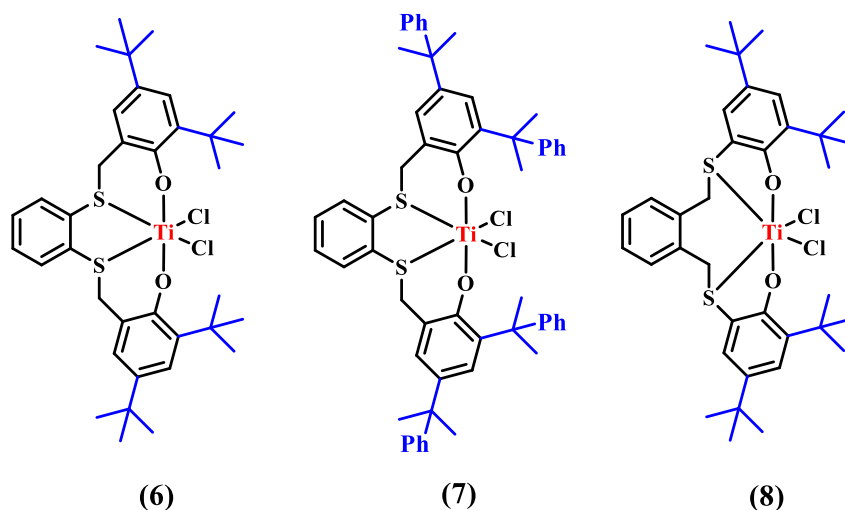


Figure 3. Complexes **6-8** active in the ethylene polymerization

Although mononuclear Group IV metal complexes are widely explored in the ROP of cyclic esters, few example of analogues dinuclear complexes remain little studied so far. Aiming to develop new bimetallic complexes, we prepared a new dinuclear-zirconium complex featuring calix[8]arene 1,5-bridged with a *m*-xylene-diyl functionality (**9**, Figure 4), in collaboration with the group of Prof. Neri in the same department. The complex **9** is active in the ROP of *rac*-lactide (LA), ϵ -caprolactone (ϵ -CL) and β -butyrolactone (β -BL), producing highly selective formation of macrolactones for the cooperative effect of the two proximal zirconium centers.

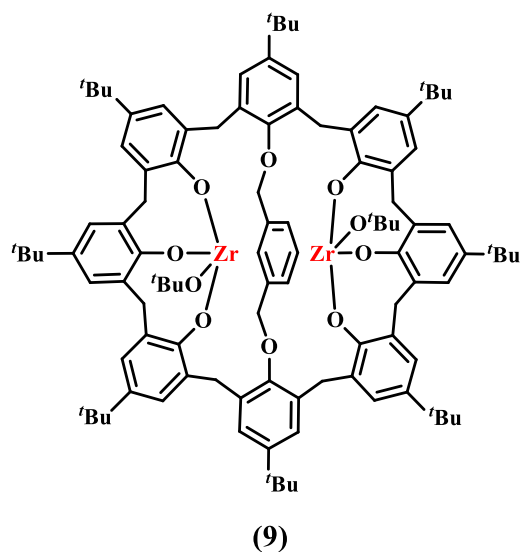


Figure 4. Dinuclear zirconium complex bearing 1,5-bridged-calix[8]arene ligand in the ROP of cyclic esters.

An alternative synthetic route to prepare biocompatible and biodegradable polyesters is the ring-opening copolymerization (ROCOP) of epoxides with cyclic anhydrides. Among the most efficient catalysts in this reaction, there are bimetallic zinc complexes for their catalytic performances and high control of polymerization.⁴ A series of robust dinuclear zinc *N*-Heterocyclic carbene complexes variously substituted on the nitrogen atoms (**10-12**) are synthesized during my stay in Strasbourg under the supervision of Dr Dagorne. All complexes are active in the copolymerization of propylene oxide (PO) or cyclohexene oxide (CHO) with succinic anhydride (SA) and the best performances are observed for **11**. The addition of TBACl cocatalyst improves the activity of **11**, but the molecular weights of the polymers are low (1 KDa).

⁴ a) Wu, L.-y.; Fan, D.-d.; Lu, X.-q.; Lu, R. *Chin. J. Polym. Sci.* **2014**, 32, 768–777. b) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. *Polym. Chem.*, **2014**, 5, 6068-6075.

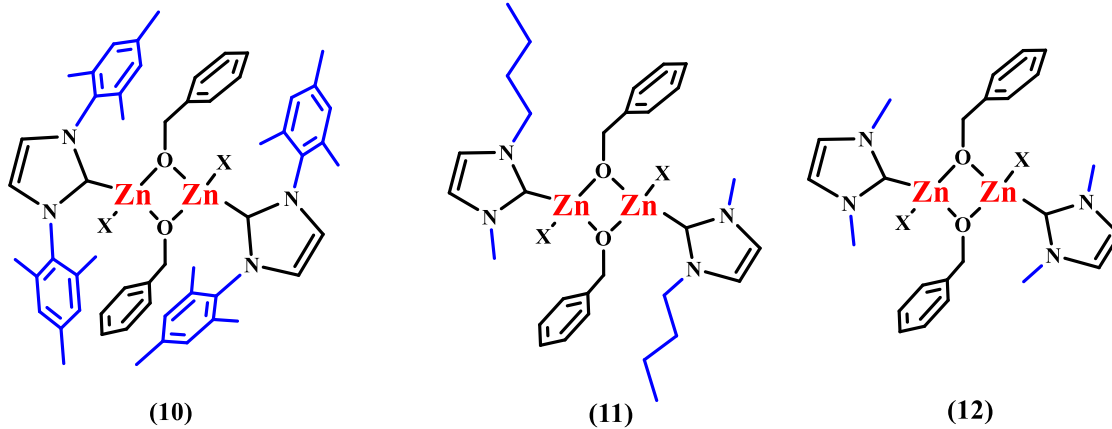


Figure 4. Dinuclear Zinc-*N*-Heterocyclic carbene complexes active in the ROCOP of CHO or PO with SA