

# Theoretical study of PhenoxyAmidine, Bis(salicylamidine) Ligands and their Zinc and Aluminum complexes

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Salen aluminum complexes are considered as benchmark catalysts for the stereocontrolled polymerization of rac-lactide.<sup>1</sup> Bis(salicylamidine) (FAlen) ligands are salen analogs in which the imine moiety is replaced by an amidine. Compared to phenoxy-imine (FI), amidine ligands are less sensitive to reducing or nucleophilic reagents. Also, the presence of the  $\pi$ -donor NR<sub>2</sub> group enhances the ability of the amidine moiety to stabilize electron-deficient metal ions such as Ti, Al or Zn.

Building on these properties, our group has synthesized different FA and FAlen ligands together with coordination complexes with aluminum and zinc metals.<sup>2</sup> Many structures could be resolved by X-Ray diffraction: they revealed a wide range of different coordination modes and geometries of the ligands around the metals. In particular, the FAlen ligand can adapt its denticity (from  $\kappa^2$  to  $\kappa^4$ ) to the electron density of the metal.<sup>3</sup>

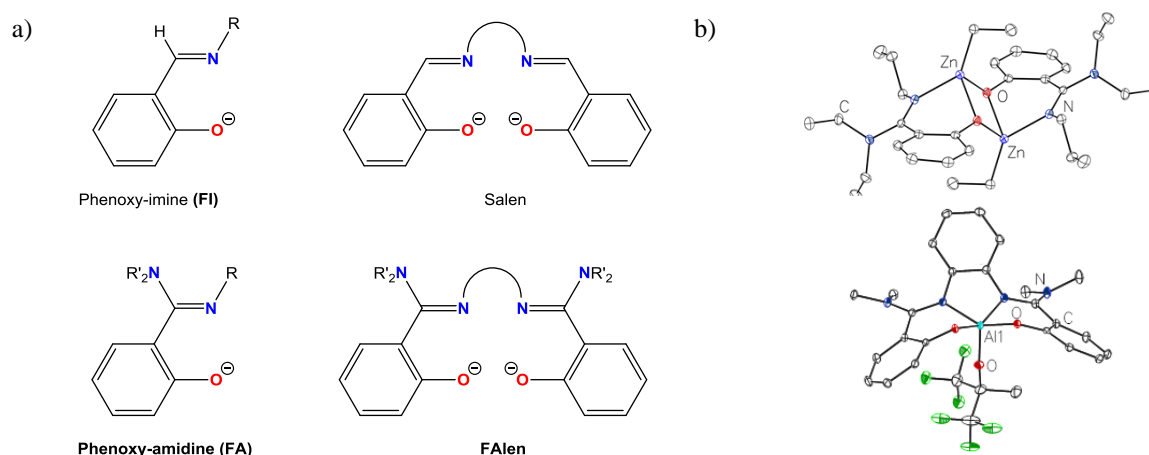


Figure 1. a) Molecular structures of the phenoxy-amidine and FAlen ligands. b) X-Ray structures of two complexes. Color codes: C in white, N in blue, O in red, Zn in blue, Al in turquoise, F in green.

In this communication, I will present our theoretical studies of these ligands and their complexes to illustrate the link between their electronic structure and their flexibility. In particular, we will discuss the impact of the cis/trans isomers of the amidine moiety on its coordinating ability.

Last, their unique coordination properties will be used in the controlled ring-opening polymerization (ROP) of rac-lactide.

**Keywords:** Amidine – NBO – Organometallic chemistry - ROP

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<sup>2</sup> Vaillant-Coindard, V.; Théron, B.; Printz, G.; Chotard, F.; Balan, C.; Rousselin, Y.; Richard, P.; Tolbatov, I.; Fleurat-Lessard, P.; Bodio, E.; Malacea-Kabbara, R.; Bayardon, J.; Dagome, S.; Le Gendre, P. Phenoxy-Amidine Ligands: Toward Lactic Acid-Tolerant Catalysts for Lactide Ring-Opening Polymerization. *Organometallics* **2022**, *41*, 2920–2932. <https://doi.org/10.1021/acs.organomet.2c00343>

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