

## More Robust Phenoxy-Amidine Ligands for Better Catalytic Performance

Phenoxy-imines (aka FI; **I**) and related bridged tetradentate Salen ligands (**II**) represent one of the most useful classes of ligands for metals (Chart 1). Their ease of access and structural modularity allow for the synthesis of a great variety of metal complexes, thus enabling thorough screening processes and identification of highly performant systems.

These compounds, also known under the broader name of Schiff base ligands, can coordinate almost all metal ions in the periodic table. Schiff base complexes have found utility in a plethora of fields ranging from catalysis to organic electronics.

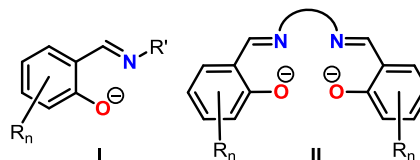


Chart 1: Phenoxy-imine (**I**) and Salen (**II**)

In catalysis, FI catalysts have proved to be particularly effective in olefin polymerization/oligomerization and for the ring-opening polymerization (ROP) of cyclic esters. In addition, FI complexes have been used to catalyze a wide array of reactions such as cyclopropanation, silylcyanation of aldehydes, hydroamination etc. The performances of Salen ligands are also impressive, notably their ability to control the stereochemical outcome of the reactions. Salen complexes have been widely used to initiate the stereocontrolled ROP of *rac*-lactide. Jacobsen-Katsuki catalysts (chiral Mn(III)Salen complexes) have proved to be among the best systems for the stereoselective epoxidation of non-functionalized alkenes.

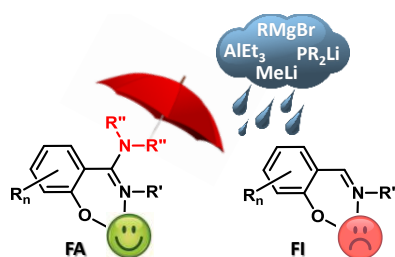


Chart 2: Phenoxy-amidine (FA) and related Phenoxy-imine (FI) ligands

The project is aimed at **the development of a related class of FI and Salen ligands in which the imine function is replaced by a trisubstituted amidine, giving rise to new phenoxy-amidine (FA) ligands** (Chart 2). Amidines differ from imines in that the nitrogen lone pair electrons of the amidine  $\text{NR}''_2$  group is involved in resonance, thus making them much more basic and more stable towards nucleophiles than imines ( $\text{pK}_a \approx 12$  and  $6$ , respectively). The additional  $\text{NR}''_2$  group in the amidine moiety shall thus bring steric protection and electronic density to the otherwise exposed electrophilic imine carbon atom. Hence, it should make FA ligands

and related metal complexes more robust against reducing agents or nucleophilic reagents as compared to FI or Salen analogues. In addition, the strong  $\sigma$  and  $\pi$ -donor character of the amidine function should provide additional stability to the metal ion. This is anticipated to **lead to a new class of robust catalysts with improved performances for a variety of processes of high academic and industrial interest.**

The PhD candidate will develop his/her skills in the synthesis of organometallic complexes using inert-atmosphere techniques (Shlenk line, glovebox), analytical and characterization techniques (NMR, XRD, GPC/SEC, DSC) and catalyst testing in high-pressure polymerization reactors.

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