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Asymmetric Olefin Hydroamination Catalyzed by Ni(II)-Complexes

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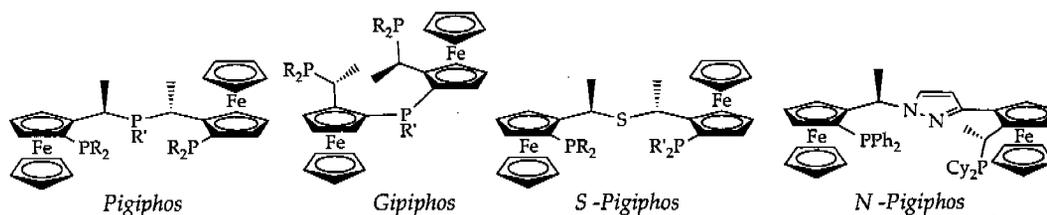
ABSTRACT

The asymmetric hydroamination of alkenes, catalyzed by transition metals, is one of the research's fields that up to date has not found a general solution for industrial applications. Aim of this work was to demonstrate that nickel(II) complexes are able to catalyze the addition of primary or secondary amines to a carbon-carbon double bond in an enantioselective manner, as predicted by *ab initio* theoretical studies.

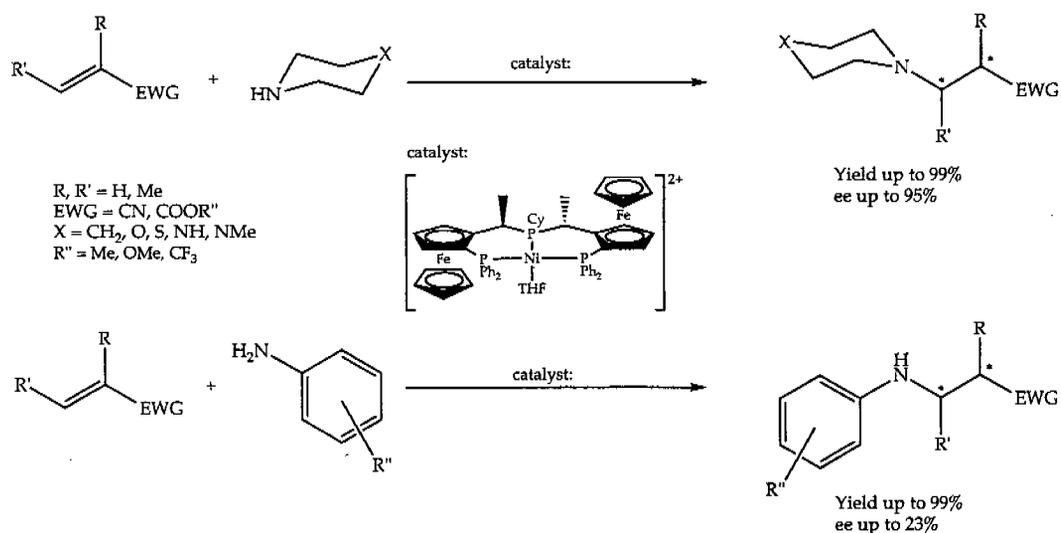
The first part of the thesis presents the bibliography (**Chapter 1**). The work on asymmetric hydroamination is reviewed, followed by the use of the ionic liquids as neoteric solvents in catalysis (specially for the hydroamination reactions), the theoretical studies on the hydroamination (basis of this work) and, finally, the synthesis and the applications of bidentate and tridentate ferrocenyl ligands.

The results (**Chapter 2**) have been subdivided into three sections reflecting the three main investigation fields of this thesis: the synthesis of new chiral ligands with ferrocenyl fragments (in particular the tridentate ones), the synthesis and characterization of the nickel(II) complexes containing such ligands, and their use as catalysts in intermolecular hydroamination reactions.

Three types of ligands have been synthesized and used in the hydroamination catalysis (**Chapter 2.1.2**): the triphosphane ligands derived from *Pigiphos*, the new *Gipiphos* and the ligands, which contain a different heteroatom (sulfur or nitrogen, giving the *S-* or *N-Pigiphos*).



The compounds $[Ni(PPP)L]^{2+}$ ($L =$ chloride, solvent or substrate) have been isolated. From the characterization it is possible to assert that all these complexes display a square-planar geometry, with the three phosphine coordinated to the metal center. This arrangement was confirmed by the solid-state structures as determined by X-ray diffraction analysis. Analogous results are presented also for the $[Ni(PXP)L]^{2+}$ complexes (**Chapter 2.2**). The efficiency of these complexes in asymmetric catalysis (**Chapter 2.3**) reaches high level when aliphatic or aromatic amines react with electron-poor olefins, especially with acrylonitrile derivatives.



This hydroamination reaction affords up to 95% of enantioselectivity at $-78\text{ }^\circ\text{C}$ for the addition of morpholine to methacrylonitrile (69% ee at room temperature). Scope and limitations (reaction conditions, ligand effects, substrates) of the catalysis are presented in **Chapter 2.3.3**.

The absolute configuration of the addition products of morpholine to methacrylonitrile and of aniline to crotonitrile was determined. In both cases the major enantiomer shows a (*R*) configuration for reactions that were conducted using (*R*)-(*S*)-*Pigiphos*. Additionally, the hydroamination products were utilized for the synthesis of optical active β -aminoacids, following standard hydrolysis and deprotection procedures.

Finally, in **Chapter 2.3.4**, the results of the catalytic addition of the amine to the alkenes carried out in ionic liquids are presented. The dicationic nickel(II) compounds are stabilized by the liquid salts, rendering the catalysis less sensitive to air and moisture. The selectivity in ionic liquids and classical solvents are comparable, whereas the activities are higher in the former solvents (TON's up to 300). Moreover, the nickel(II) complex dissolved in ionic liquid may be recycled in catalysis several times, thus increasing their total productivity.