ENANTIOSELECTIVE AND NANOSTRUCTURED CATALYSTS DERIVED FROM ARENE-METAL-CARBONYL COMPLEXES
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The element of originality of this project consists in the synthesis of chiral tricarbonyl-metal-aromatic (TMA) complexes, which can be employed as enantioselective catalysts. As such, we present the structure, syntheses, structural and stereochemical characterization of several types of chiral TMA complexes and also the screening of their potential enantioselective catalytic activity.

In conformity with the research plan approved for the year 2007, the following results were obtained:

1.Synthesis and structural characterization of some ligands with stereocenter

We describe the obtaining of ligands with stereocenter and without planar chirality bearing hydroxy-, acetoxy- and amino- groups and ligands posessing besides the stereocenter and functional groups mentioned above a planar prochirality element generated by introducing substituents such as methyl and methoxy in the 2,5 positions. The last category includes ligands with two equivalent stereocenters. In this way we have the means for accomplishing the second objective of 2007 and also some objectives of 2008 and 2009.

1.1.Synthesis of chiral ligands with stereocenter

The syntheses were accomplished following a methodology which implies in most cases the obtaining of chiral compounds first in racemic form. Such a procedure is cheaper and utilizes common reagents, and in the same time is useful for preliminary tests (reaction yield, physical and structural properties measurement).

In the next step, synthetic methods for optically pure compounds were developed and their optical purity was checked (enantiomeric excess, e.e.).

Compounds with alcohol structure and their corresponding acetates were synthesized in racemic form by a reaction sequence consisting of the acetylation of the aromatic compound, the reduction of acetophenones with $LiAlH_4$ to the corresponding 1-phenylethanols, followed by esterification with acetic anhydride/pyridine to acetoxy derivatives.

For the synthesis of optically active 1-phenylethanol, acetophenone was reduced with diborane in the presence of *S*-Z-oxoborolidine[2], and for the synthesis of optically active alcohols 2b and 2c, the corresponding ketones were reduced enantioselectively using (-)-diisopinocampheylborane[3].

An alternative means for obtaining alcohols having 85-90% optical purity was the enzymatic hydrolisis (PLE) of the corresponding racemic acetates following a method described in the literature[4].

The compounds with 1-phenylethylamine structure were obtained in racemic form starting from the corresponding ketones which were treated with ammonium formiate (Leukart reaction) or by reducing their oximes with $LiAlH_4$ [5]. Optically active compounds belonging to this series were obtained by resolution of the diastereomeric salt with (-)menthyl hydrogen sulfate[7] or by reducing the oxime with *S*-Z-oxaborolidine[2].

1.2. Structural characterization of the obtained ligands using modern physical methods

All syntesized compounds were characterized employing the following methods:
^{1}H-RMN spectroscopy; ^{13}C-RMN spectroscopy; FT-IR spectroscopy;GC-MS analysis

1.3. Stereochemical characterization of the obtained ligands

Optically active compounds were characterized by determining the enantiomeric excess using the following methods:

Optical rotation determination $[\alpha]_D^{20}$; *e.e. determination by chiral gas chromatography*; *e.e. determination by chiral HPLC; e.e. determination by ^{1}H-RMN.*

2.1.Synthesis of TMA complexes by direct complexation or stereoselective condensation reactions

The synthesis of optically active TMA compounds by direct complexation was performed by refluxing (diglyme, 150 ^{o}C) the optically active ligand in the presence of chromium hexacarbonyl (or molybdenum hexacarbonyl)[8].

The synthesis of TMA complexes by stereoselective condensation follows a procedure developed in our laboratory consisting of the acid catalysed condensation of benzyl acetates with reactive arenes[9].

2.2. The structural characterization of the obtained complexes was performed by the methods and employing the equipment described under Section 1.2.

2.3. The structural characterization of optically active complexes was performed following the methodology described in Section 1.3.

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