Imine Hydrogenation Catalyzed by Ruthenium Complexes

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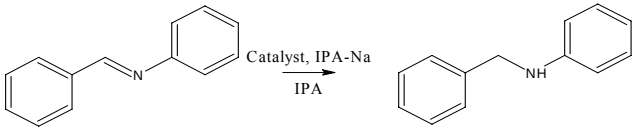
Introduction

In recent years homogeneous imine hydrogenation processes have undergoes significant developments.For example, good systems have been obtained *in situ* by addition of diphosphine over neutral or cationic precursors of the Rh(COD) or Ir(COD) type (COD = 1.5 – cyclooctadiene), as well as those from the di or trinuclear ruthenium species containing diphosphines or using derivatives from *ansa*-titanocene [1]. Imine hydrogenation is only lightly exothermic (about -14 kcal mol^{-1}) compared to alkene hydrogenation (about 31 kcal mol^{-1}), and require a η^2-coordinatiopn of the substrate, although the usual coordination mode of the imines is a η^1-coordination. For this reason the coordination effect of imines can produce the poisoning of the catalyst, decreasing the efficiency of the reaction. The presence of a polypyridine ligand in the complex as "innocent ligand" can prevent the unusual coordination favoring the η^1-coordinationof the imine.

The complexes dichlorodicarbonyl-1,10-phenantrolineruthenium (II) and dichlorodicarbonyl-2,2-bipyridineruthenium (II) were prepared and used as catalyst for the hydrogenation of *N*-benzylidenaniline using 2-propano (IPA) as hydrogen source



Materials and Methods

All chemicals were reagent-grade (Aldrich) and used as received. 2-propanol and the different solvents used in the synthesis of the complexes and for the catalytic runs were dried and distilled prior to use.

Catalytic runs were performed in a reactor provided with a condenser connected to the Schlenk line, magnetically stirred and heated using a silicone bath. In a typical run, the catalyst (10^{-2} mmole) and sodium 1 M isopropoxide (1 mL). dissolved in 2-propanol (8 mL) were added. Using the Schlenk line an inert atmosphere was provide to the reactor. After adding *N*-benzylidenaniline (1 mmol) to the reaction vessel, the system was refluxed. Samples were extracted every 15 minutes and analyzed in a GC-chromatograph

Analyses of liquid phase were done on a Agilent Technologies Model 6890 N programmable gas chromatograph fitted with a HP-INNOWAX (30 m x 0.248 mm x 0.25 μm) column and flame ionization detector, and using N_2 as the carrier gas.

The complex precursor of the catalyst, diclhorodicarbonyl-1,10-phenantrolineruthenium (II) was made according the following procedure : the dichlorodicarbonylruthenium(II) polymer (0,46 mmol), and the ligand 1,10-phenanthroline (0,51 mmol) dissolved in ethanol/water mixture were refluxed during three hours. After recrystallization of the solid obtained, the product was collected as a yellow powder. Yield 73 %. The complex was characterized by IR (Bruker IFS-66V FT IR spectrophotometer, KBr),^{1}H-NMR (400 MHz Bruker spectrometer, $CHCl_3$), UV-Visible (Shimadzu UV-160 spectrophotometer) and measurements of the melting point. The complex diclhorodicarbonyl-2,2-bipyridineruthenium (II) was made by following the same procedure.

Results and Discussion

The complexes diclhorodicarbonyl-1,10-phenantrolineruthenium (II) and dichlorodicarbonyl-2,2-bipyridineruthenium (II) are precursors of active catalytic system for the imine hydrogenation reaction. 2-Propanol was used as solvent and as hydrogen source for the transference reaction carried out in homogeneous condition and in basic media (sodium isopropoxide, IPA-Na).

The complex dichlorodicarbonyl-1, 10-phenantrolineruthenium (II) catalyzes the reaction with a conversion of 92% per hour of reaction while the complex containing thel ligand bipyridine shows a lower conversion at the same time, 78%. The catalysts are still useful in new refills reactors.

Significance

Chiral amines are very important products in pharmacological and agrochemical industry [2]. Antibiotics like amoxycillines can be prepared via catalytic processes mediated by transition metals. These processes can be accomplished by direct imine reduction or by imine and ketone

hydrogen transfer reactions. The design of actives catalysts for imine reduction could contribute to obtain best results in synthesis of useful pharmacological compounds.

Acknowledgments

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References

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