Ruthenium-catalyzed homogeneous hydrogenolysis of esters to alcohols

van Engelen, M.C.

Citation for published version (APA):
# TABLE OF CONTENTS

## Hydrogenation and hydrogenolysis: An introduction

1. Hydrogenation; definitions
   1.1 Transfer hydrogenation
   1.2 Functional groups in hydrogenation
   1.3 Hydrogen activation
   1.4 Substrates in hydrogenation

2. Hydrogenation of carbonyl compounds
   2.1 Hydrogenation of Aldehydes and Ketones
   2.2 Hydrogenation of Carboxylic acids
   2.3 Hydrogenolysis of Esters
      2.3.1 General considerations
      2.3.2 Stoichiometric methods
      2.3.3 Heterogeneous hydrogenolysis of esters
      2.3.4 Homogeneously catalyzed hydrogenolysis of carboxylic acid esters
      2.3.5 Neutral Ruthenium Complexes
      2.3.6 Anionic Ruthenium Complexes
      2.3.7 In situ generated catalysts

3. Objective and justification

4. Outline

5. References

## Ruthenium starting material and ligands for catalytic hydrogenolysis of esters

1. Introduction
2. Results and Discussion
   2.1 Selection of ruthenium precursor
   2.2 Ligand Selection
3. Conclusions
4. Experimental section
   4.1 Equipment
   4.2 Chemicals
   4.3 General hydrogenolysis experiment
5. References

## Scope of Ruthenium-Catalyzed hydrogenolysis: Selection of the solvents

1. Introduction
2. Results and Discussion
   2.1 Scope of the catalyst; substrates
      2.1.1 Hydrogenolysis of simple aliphatic di-esters

---

iii
Synthesis and characterization of novel ruthenium complexes and their application in the catalytic hydrogenolysis of esters

1 Introduction

2 Results and discussion
2.1 Ruthenium starting material
2.1.1 Synthesis and characterization of Ru(acac)$_2$(κ$^2$-triphos)
2.1.2 Synthesis and characterization of [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl
2.2 Hydrogenolysis of selected substrates with Ru(acac)$_3$ – triphos, Ru(acac)$_2$(κ$^2$-triphos) and [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl

3 Conclusions

4 Experimental section
4.1 Equipment
4.2 Chemicals
4.3 Standard hydrogenolysis procedure

5 References

Kinetic studies and a proposed mechanism of ruthenium-catalyzed hydrogenolysis of esters

1 Introduction

2 Results and discussion
2.1 Kinetic measurements
2.1.1 Assessing the order in catalyst precursor Ru(acac)₃ – triphos
2.1.2 Assessing the order in catalyst precursor [(triphos)Ru(μ-Cl)₃Ru(triphos)]Cl
2.1.3 The dependence of the reaction rate on the dihydrogen pressure
2.2 Mechanism of ruthenium(triphos)-catalyzed ester hydrogenolysis
  2.2.1 Formation of the precatalyst from Ru(acac)₃ – triphos
  2.2.2 Formation of the precatalyst from [(triphos)Ru(μ-Cl)₃Ru(triphos)]Cl
  2.2.3 Hydrogen dependence
  2.2.4 Mechanistic proposal

3 Conclusions
4 Experimental section
  4.1 Equipment
  4.2 Chemicals
  4.3 Kinetic Measurements
    4.3.1 Conditions for assessing the order in Ru(acac)₃
    4.3.2 Conditions for assessing the order in [(triphos)Ru(μ-Cl)₃Ru(triphos)]Cl
    4.3.3 Conditions for assessing the order in hydrogen pressure
5 References

Summary
Samenvatting
Evaluation of I.O.P.-Catalysis project IKA 97001
Dankwoord