CHIRAL RHODIUM COMPLEXES OF THE DIMENTHYLPHOSPHINE GROUP ATTACHED TO POLYSTYRENE FOR ASYMMETRIC HYDROGENATION OF Z-α-ACETAMIDOCINNAMIC ACID

H. W. Krause

Central Institute of Organic Chemistry, Department of Complex Catalysis, Rostock, GDR

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New chiral rhodium complexes of a set of dimethylphosphine-substituted, crosslinked styrene-divinylbenzene copolymers have been tested for the enantioselective hydrogenation of Z-α-acetamidocinnamic acid. The supported catalysts have been found to give optical yields up to 60% but suffer with respect to the catalytic activity.

INTRODUCTION

Chiral transition metal complexes attached to supports were synthesized only in recent years /1-5/. Apart from a polymeric benzylmenthylmethylphosphine /2/ and an anchored ethoxysilylpropylphenylmenthylmethylphosphine /3/, which have been used as mixtures of diastereomers, to date only ligands of the DIOP type have been investigated. We now wish to report some results utilizing the dimethylphosphine group as chiral ligand attached to crosslinked polystyrene giving supports of the type

\[ \begin{align*}
\text{P} & \quad \text{DMP} \\
\text{P} & \quad \text{MEDMP}
\end{align*} \]
Each of the polymers contained two identical chiral groups, thus avoiding the phosphorus to become chiral by attachment of the phosphine to the polymer backbone and hence the formation of diastereomers. The anchored complexes were prepared by the reaction of Rh$_2$(C$_2$H$_4$)$_4$Cl$_2$ or Rh$_2$(COT)$_4$Cl$_2$ with P$_2$DMP and P$_2$MEDMP. Their effectiveness was tested in the hydrogenation of $\alpha$-acetamidocinnamic acid.

EXPERIMENTAL

Crosslinked polystyrenes (2, 5.5, 10% DVB) were purified following the procedure of Relles /6/. The brominated or chloromethylated polystyrenes were transferred to polymeric lithium compounds either by direct metalation /7/ or by cleavage of the corresponding benzyl ethers /8/. By further reaction with chlorodimethylphospine, the polymer-attached chiral ligands were obtained.

Anchored rhodium- P$_2$MEDMP complex.

P$_2$MEDMP (7 g, 5.7 mmol) suspended in 35 ml benzene was treated with Rh$_2$(C$_2$H$_4$)$_4$Cl$_2$ (549 mg, 1.25 mmol) dissolved in 40 ml benzene for 30 min with stirring. The brown beads were filtered off and extracted with benzene (25 times), dried under vacuum and stored under argon. Anal. Cald. for Rh 4.0% (P:Rh = 2:1), Found 3.4%. The catalyst may be stored under argon for at least 6 months without deactivation.

The hydrogenation was performed at 10 atm H$_2$ and room temperature using a Rh: substrate ratio of 1:100. The optical rotation was measured in ethanol using a Polamat A, Carl Zeiss polarimeter.

RESULTS AND DISCUSSION

As can be seen from the Table 1, the dimethylphosphino group proved to be inducing optical activity. Applying the neutral rhodium complexes of the polymer-attached ligands in a mole ratio (p) between 2 and 3, an enantioselective hydrogenation...