

Rhodium Catalyzed Hydroformylation and Hydroaminomethylation reactions: Enantioselectivity and Flow processes

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Abstract

The hydroformylation and hydroaminomethylation reactions are important tools in organic synthesis since enantiomerically pure aldehydes and amines are of high interest as precursors for a variety of highly valuable products. Rhodium complexes modified with chiral phosphorus ligands are key catalysts in these asymmetric reactions. The metal catalyzed selective hydroformylation of [2.2.1]-bicyclic olefin is a challenging area due to the interest of the olefin desymmetrization upon one C-C bond formation which may lead to interesting building blocks in organic synthesis. Following our studies using Rh diphosphites and based on optimized conditions, this presentation focus on the results obtained in the asymmetric hydroformylation of norbornene. After catalyst immobilization and due to difficulties found for catalyst recycling, the process has been performed in continuous flow maintaining the enantioselectivity of the reaction.

Second part of the talk deals with the hydroaminomethylation reaction which involve hydroformylation, amine condensation and hydrogenation to obtain amines from alkenes. The successful rhodium catalyzed asymmetric hydroaminomethylation of alkenes using a single Rh catalyst bearing chiral diphosphine ligand will be presented. The preparation of a series of chiral γ -aminobutyric esters was performed through hydroaminomethylation of α -alkyl acrylates in the presence of amines as nucleophiles, achieving ee up to 86%. HP-NMR experiments show the coexistence of neutral and cationic species required to complete the hydroaminomethylation. Recent examples of asymmetric Rh catalyzed hydroaminomethylation achieving ee up 99% will also be included.