Chiral phosphorous ligands for homogeneous, rhodium catalysed, asymmetric hydrogenations

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Abstract

Because of its high activity and selectivity, the enantioselective catalysed hydrogenation has a tremendous scope in technical chemistry. However, it is necessary to optimise reaction conditions to every substrate, whereas ligand tuning is essential.

The ambition of this work was the synthesis of sterically and electronically modified axial chiral phosphites with Cl-MeO-biphenol backbone and their use in the rhodium catalysed, asymmetric hydrogenation of itaconic acid dimethylester. These new phosphites proved to be very active ($Y \leq 100$ %) and enantioselective (*ee* ≤ 99 %) in hydrogenation.

Additionally, the effects of reactivity and selectivity caused by different bisphosphinites and phosphoramidites with pinen framework were studied in the same rhodium catalysed, asymmetric hydrogenation. Unfortunately, the hydrogenations gave out poor results. Different conversions ($Y = 0 - 97$ %) and low enantioselectivities (*ee* ≤ 17 %) were obtained.

Furthermore, transition states of catalytically active species during hydrogenation conditions with $[(nbd)_2Rh]PF_6$ as precursor and Cl-MeO-BIPHEP as well as two phosphites originate from Cl-MeO-biphenol as ligands should be investigated. Metal-hydride-complexes of the used catalysts could be successfully observed. Regrettably, it was impossible to determine a structure of the catalytically active species with the measured data. Modified acquisitions, high pressure IR spectroscopy and computer supported simulations are necessary to assign a structure.