Asymmetric Transfer Hydrogenation of Prochiral Ketones in Aqueous Media with Chiral Water-Soluble and Heterogenized Bifunctional Catalysts of the RhCp*—Type Ligand

ANGÉLICA BARRÓN-JAIME, OSCAR F. NARVAEZ-GARAYZAR, JORGE GONZÁLEZ, VALENTÍN IBARRA-GALVÁN, GERARDO AGUIRRE, MIGUEL PARRA-HAKE, DANIEL CHÁVEZ, and RATNASAMY SOMANATHAN

Centro de Grados e Investigación, Instituto Tecnológico de Tijuana, Tijuana, Baja California, México
Facultad de Ciencias Químicas, Universidad de Colima, Colima, Compostellana, Colima, México

ABSTRACT  Asymmetric transfer hydrogenation (ATH) of prochiral aromatic ketones was carried out with a water-soluble complex of Rh

INTRODUCTION  Chiral secondary alcohols are valuable intermediates in the synthesis of physiologically active pharmaceuticals,1, 6  agrochemicals,7 and flavor ingredients.8 In response to the increasing demand for optically active secondary alcohols, a variety of powerful catalytic procedures have been developed. One such method involves the use of monosubstituted 1,2-diamines or monoalkyl amine ligands for ruthenium(II)-catalyzed asymmetric transfer hydrogenation (ATH) of ketones, a method developed by Noyori and coworkers.9-11 These bifunctional catalysts deliver the hydrogen in a concerted six-membered transition state to the aromatic ketone, and the enantioselectivity is induced by the proton-π interaction between the n ary ring proton and the aromatic ring of the ketone.

Since this discovery, a significant number of new ligands have been reported for the RTH with methylidene (II), iridium (III), and rhodium (II) complexes as catalysts in the ATH of ketones.12-13 More importantly, the hydride source for the reaction has been changed from isopropanol/KOH or HCOOH/NEt3 to a "greener" hydride source using sodium formate/water, a solvent system that is readily available, benign, and environmentally acceptable.14-15 This has triggered an intense search for new and efficient water-soluble ligands that could be used with Ru(II) and Rh(III) complexes as catalysts in the ATH of ketones. Addressing this, we recently reported the synthesis of a number of chiral bis- and monosulfonamide ligands L1, derived from trans 1,2-cyclohexane-1,2-diamine, which were efficiently used with Ru(II) and Rh(III) as catalysts in the ATH of ketones in aqueous sodium formate (Ref. 16). Continuing our search for a more efficient water-soluble catalyst, here we report the use of a ligand containing an aromatic nitro group in the homogeneous and heterogeneous ATH of prochiral ketones in aqueous media.

MATERIALS AND METHODS

Instrument and Measurements  Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra were taken on a Perkin-

SOMANATHAN*  *Correspondence to: Ratnasamy Somanathan, Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, Bvld. Industrial S/N, Mesa de Otay, Tijuana, BC 22520, Mexico. E-mail: somanatha@siituna.ite.tijuana.mx

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 764862).

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