

Asymmetric transfer hydrogenation of ketones using Ru(0) nanoparticles modified by Chiral Thiones

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The catalytic asymmetric transfer hydrogenation (ATH) of acetophenone in isopropanol by Ru(0) nanoparticles (NPs) obtained by the *in-situ* reduction of Ru (II) half-sandwich complexes of chiral 2-oxazolidinethiones and 2-thiozolidinethiones was examined and compared with the catalytic activity of Ru(0) NPs formed *in-situ* by the reduction of [Ru(*p*-cymene)(Cl)₂]₂ in presence of optically active ligands such as (S)-4-isobutylthiazolidine-2-thione, (S)-4-Isopropyl-2-(2-pyridinyl)-2-oxazoline, (8S, 9R)-(-)-cinchonidine, (S)-leucinol, (S)-phenylalaninol, and (S)-leucine. Three of the best catalytic systems were then examined for ATH of thirteen aromatic ketones with different electronic and steric properties. A maximum of 24% ee was obtained using NPs generated from the Ru (II) half-sandwich complex with (S)-4-isobutylthiazolidine-2-thione in the TH of acetophenone. The NPs were characterized by TEM and DLS measurements. Kinetic studies and poisoning experiments confirmed that the reaction is catalyzed by the chiral NPs formed *in-situ*. Complete characterization of the complexes, including the X-ray crystallographic characterization of two complexes, was also carried out.

KEYWORDS

asymmetric transfer hydrogenation, chiral nanoparticles, Ru half-sandwich complexes

1 | INTRODUCTION

Metal nanoparticles (NPs) particularly those of Pt, Ru, Rh, and Pd have been widely explored as catalysts for olefin hydrogenation, arene hydrogenation, polymerization, oxidation, and C–C coupling.^[1–3] A variety of ligands, surfactants, polymers, dendrimers, cyclodextrins and ionic liquids have been used to stabilize the NPs in solution or on the surface of a support.^[4–10] In each case, the stabilizing ligand binds to the metal atoms on the surface via a donor atom providing electronic, electrostatic and/or steric stabilization.^[2] These nanoparticle catalysts provide an opportunity to realize the efficiency of homogeneous catalysts along with the ease of separation as in the case of magnetic nanoparticles^[11,12] or when they

are stabilized by ionic liquids.^[13] The presence of numerous active sites on the surface, coupled with their ease of preparing makes NPs attractive catalysts.^[2] A significant value addition to the catalytic utility of NPs is achieved using chiral stabilizers. The metal NPs modified by chiral compounds, sometimes referred to as chiral NPs can catalyze the reactions in an enantioselective manner.^[14–18] Thus, NPs of Pt, Ir, and Pd modified by cinchona alkaloids have been used for the hydrogenation of ethyl pyruvate^[10,13,16,18–23] and other prochiral substrates to give chiral products with over 97% ee in some cases.^[24] However, cinchona alkaloid ligands appear to be unique. Platinum NPs modified by DIOP, aminoalcohols, and oxazoline ligands have also been used for catalyzing the hydrogenation of ethyl pyruvate but the ee of the product