



Digest paper

Upgrading and expanding the scope of homogeneous transfer hydrogenation

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This article is dedicated to the late Professor Takao Ikariya, Tokyo Institute of Technology, deceased on April 21, 2017.

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ABSTRACT

Transfer hydrogenation using inexpensive and safe hydrogen sources of alcohols and formic acid has been studied thoroughly over the decades. In particular, the asymmetric version offers the state-of-the-art methods to obtain optically active alcohols and amines, which are valuable synthetic intermediates in the field of pharmaceutical and agrochemical industry. This digest paper highlights the recent notable advances in homogeneous transfer hydrogenation using transition metal complexes, especially in direction to establish practical greener processes by upgrading the catalyst performance or by expanding the scope of reducible functional groups.

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Introduction

Transfer hydrogenation (TH) is an advantageous transformation being free from hazardous pressurized hydrogen gas or metallic

hydrides, and could be operated without special setups. In successful applications of metal-mediated hydrogen transfer from alcohols, 2-propanol has been widely employed as a safe, nontoxic, environmentally friendly hydrogen source; however, the reversible process between alcohols and ketones/aldehydes sometimes results in limited conversion. Formic acid is another attractive reducing agent which is amenable to the reduction with releasing

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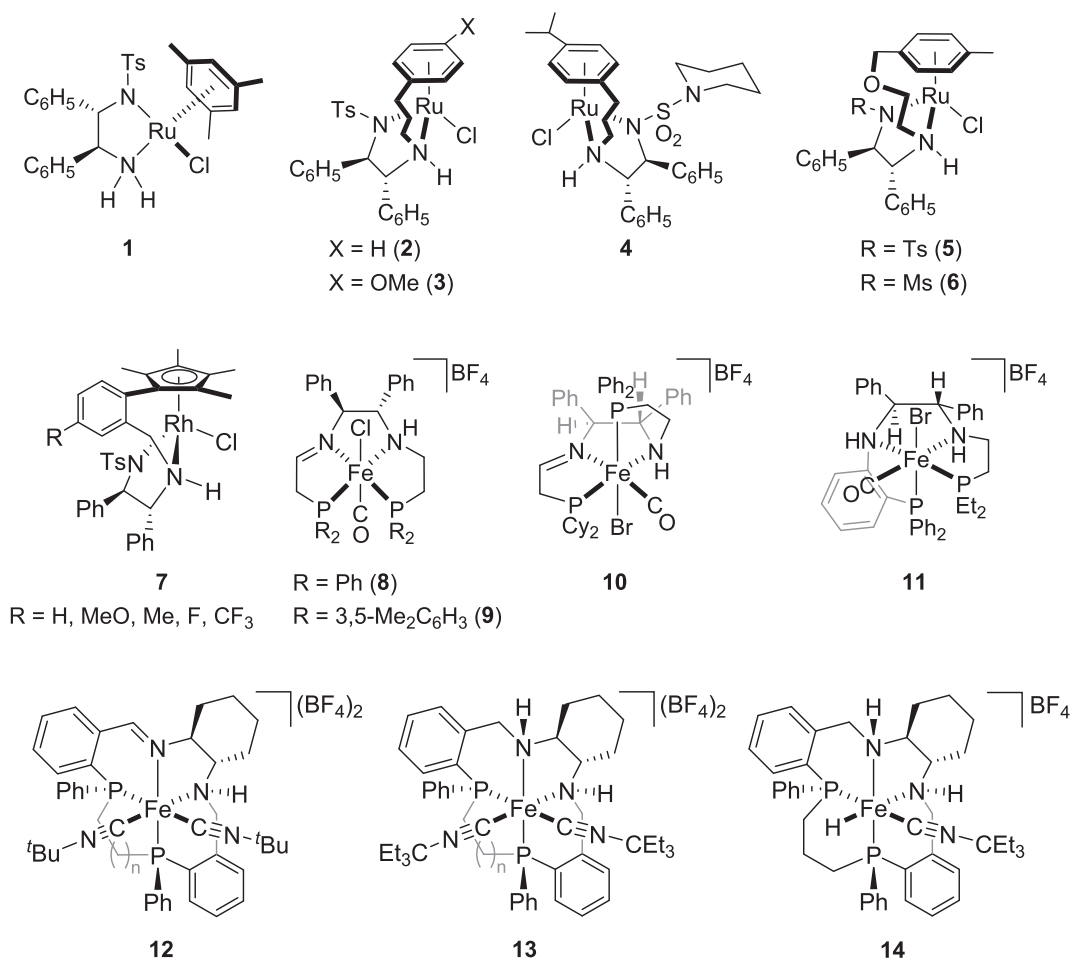


Fig. 1. Advanced transition metal complexes for ATH of ketones.

CO₂ in an irreversible fashion leading to 100% conversion. The significant progress in the design of molecular catalysts has made in the course of the application to asymmetric reduction.

Asymmetric transfer hydrogenation (ATH) of unsaturated polar C=O and C=N bonds have emerged as powerful synthetic methods for optically active alcohols and amines both in a laboratory scale and an industrial scale. In most of these enantioselective reactions, a number of chiral Ru, Rh, and Ir complexes have been designed as the effective catalysts. Among them, metal–ligand bifunctional molecular catalysts with proton-responsive NH ligands are now realized to be promising systems to assist the delivery of H⁺ and H[−] from the hydrogen donor to the acceptors. Not only the central metal but also the coordinating amine proton cooperatively facilitates the smooth and precise hydride reduction with remarkable stereochemical control. Regarding the history and background of the catalyst design for TH reactions, many excellent papers have been published and summarized to date.^{1,2} Herein, we focus on the continuous progress in the area of TH using transition metal based molecular catalysts, mainly for the last five years.

ATH of ketones

ATH of ketones has been most widely used among a large number of synthetic applications of TH. In the mid-1990s, Noyori and Ikariya successfully developed the efficient ATH of aryl ketones catalyzed by a chiral Ru complex **1** with a protic amine chelating ligand in 2-propanol (Table 1, entry 1)³ or an azeotropic mixture (5:2) of formic acid and triethylamine (entry 2).⁴ After

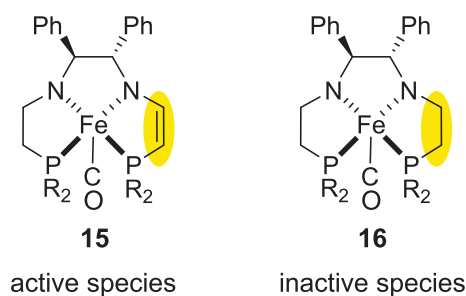


Fig. 2. Catalytically active and inactive PNNP-Fe species.

these pioneering works, various ATH catalysts providing prominent results have been reported.² Fig. 1 shows the recent achievements in catalyst design for the ATH of simple ketones. These catalytic performances are usually evaluated by reduction of acetophenone as the model substrate (Table 1/entries 1–10).

Continuing efforts have been made over the last decade to establish robust ATH catalysts. With regard to structural modification of the chiral amine-Ru complex, three-point coordination of the *N*-sulfonyl-1,2-diamine covalently linked to the η⁶-arene ligand gives rise to enhancement of catalytic activities and stabilities relative to the prototype catalyst **1**.^{2g} The bifunctional Ru complexes having such a tethered diamine structure **2–6**, which have been developed independently by Wills,⁵ Mohar,⁶ and Takasago International Corporation,⁷ proved to be effective for the ATH of aromatic ketones in HCOOH and NEt₃ (entries 3–6). The iso-

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