



Digest Paper

Recent topics of transfer hydrogenation



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ABSTRACT

A number of transition metal catalysts have been developed for transfer hydrogenation of organic molecules. This method provides a useful process for the reduction of unsaturated molecules without the need for explosive hydrogen gas. An important development in this area is the design of new ligands that improve activity and selectivity under mild reaction conditions. Polydentate ligands are good candidates for producing high performance metal catalysts. This digest describes recent developments in transfer hydrogenation as well as asymmetric reactions using metal catalysts containing polydentate ligand systems.

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Introduction

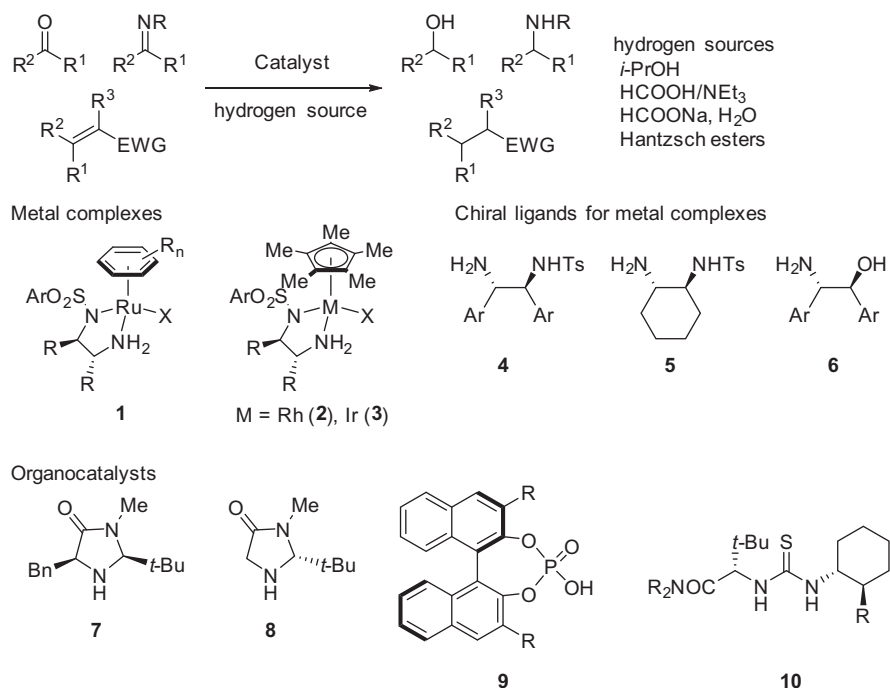
Transfer hydrogenation of unsaturated compounds is an important catalytic reduction reaction for preparing the corresponding saturated products without the use of explosive hydrogen gas or moisture-sensitive hydride reagents.^{1–15} Since the seminal improvement in asymmetric reduction of ketones using η^6 -arene Ru catalyst **1** containing a chiral diphenylethylenediamine (DPEN) ligand was reported by Noyori et al., a number of chiral Ru, Rh, and Ir catalysts containing a chiral diamine, amino alcohol, or amino acid derivative have been developed as active and selective catalysts for asymmetric transfer hydrogenation (Scheme 1). Recently, Ir catalyst **3** with DPEN and an iodide anion have been utilized as a highly efficient catalyst for the reduction of imines.^{13,14} In addition, a reusable immobilized catalyst based on polymer- and silica-supported DPEN ligands and micelle catalysts was examined in

an investigation of environmentally friendly 'green' reaction. In those systems, 2-propanol, formic acid/triethylamine, and sodium formate/water were commonly selected as hydrogen sources. Usually a dilute 2-propanol solution is required to achieve high product yields because of equilibrium between a reactant and a product. In contrast, reactions using formic acid/triethylamine and sodium formate can be conducted at high concentrations under mild reaction conditions. Another approach is the use of organocatalysts, which have been extensively studied for the reduction of α,β -unsaturated carbonyl compounds and imines using Hantzsch esters as a hydrogen source.^{16–20} Chiral secondary amines **7** and **8**, BINOL-derived chiral binaphthyl phosphoric acid derivative **9**, and the chiral thiourea **10** have been developed as active and highly enantioselective catalysts.

Because the activity and selectivity of transition metal catalysts strongly depend on their structures, ligand design is important. Extensive studies on (η^6 -arene)Ru and Cp*M (M = Rh, Ir) catalysts containing Ts-DPEN and related derivatives, such as cyclohexanediamine **5** and β -aminoalcohols **6**, have been reported. The development of metal catalysts containing polydentate ligands, such as tridentate and tetradentate ligands, has led to advancements

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Scheme 1. Transfer hydrogenation mediated by metal catalysts and organocatalysts.

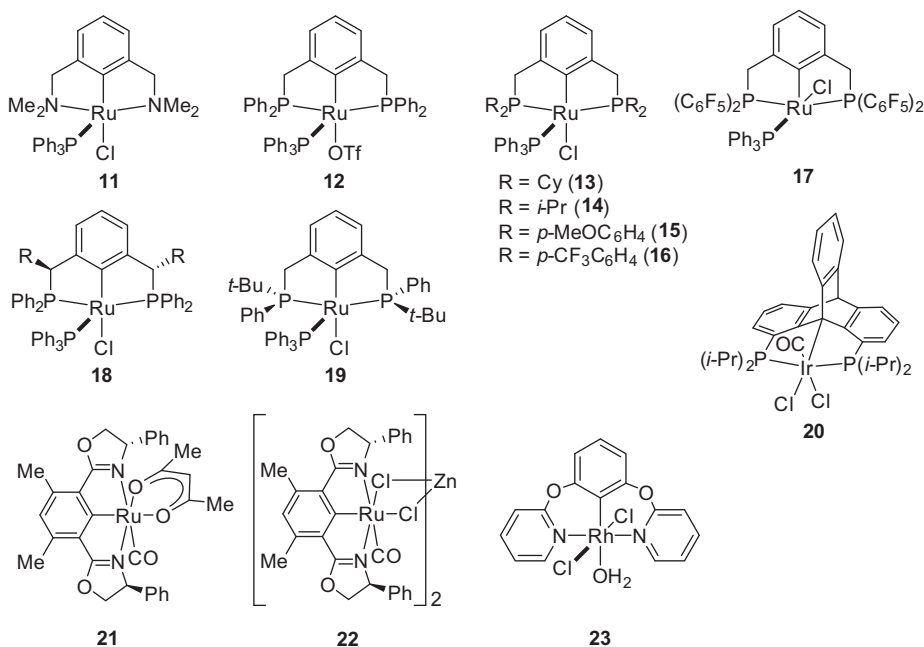


Figure 1. *E,C,E* pincer type metal complexes.

in the field. A number of transition metal complexes act as highly active and robust catalysts that are also highly enantioselective. Recently, Fe catalysts with tridentate and tetradentate ligands were applied to transfer hydrogenation to develop an environmentally friendly process. The present report describes a recent work on transfer hydrogenation mediated by structurally well-defined transition metal catalysts containing tridentate or tetradentate ligands. Since details of the complexes **1–3** and related catalysts and organocatalysts have been summarized in reviews previously, they are not included here.

Metal catalysts with tridentate ligands

Transition metal complexes with pincer type ligands are attractive in terms of the remarkable stability as well as high tunability of their electronic and steric properties.^{21,22} These advantages have led to the development of variable monoanionic *E,C,E* (*E* = P and N) scaffolds (Fig. 1). A pioneering work of pincer Ru catalysts containing *P,C,P* and *N,C,N* pincer ligands was reported by van Koten and co-workers (Table 1, entries 1–4).²³ The complexes were effective catalysts for the transfer hydrogenation of ketones using

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