CHEMICAL REVIEWS

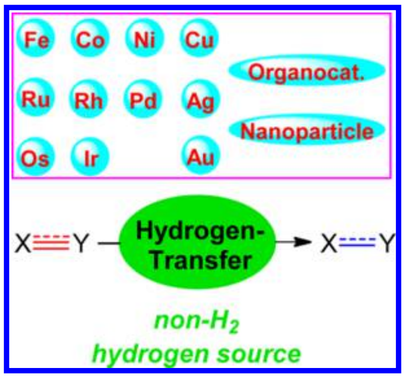
Review

pubs.acs.org/CR

The Golden Age of Transfer Hydrogenation

Dong Wang* and Didier Astruc*

ISM, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France



CONTENTS

1. INTRODUCTION

Hydrogenation is one of the most fundamental transformations in organic synthesis, and its industrial applications span from fine chemicals to pharmaceuticals synthesis.[1−3] Direct hydrogenation with a pressure of H_2 gas and transfer hydrogenation (TH) are the two employed strategies for hydrogenation. TH reaction, referring to the addition of hydrogen to a molecule from a non-H_2 hydrogen source, is a convenient and powerful method to access various hydrogenated compounds. It is an attractive alternative to direct hydrogenation, and it has recently become the center of research in hydrogenation science. The reasons for that are (i) the TH method does not require eventually hazardous pressurized H_2 gas nor elaborate experimental setups, (ii) the hydrogen donors are readily available, inexpensive, and easy to handle, (iii) the major side product can be recycled, and (iv) the catalysts that are involved usually are readily accessible and not sensitive.[4−14]

1.1. History, Basic Concepts, and Seminal Studies of Transfer Hydrogenation

The hydrogen transfer reaction dates back more than a century. In 1903, Knoevenagel[15] first demonstrated that palladium black smoothly promoted the disproportionation of dimethyl 1,4-dihydroterephthalate to dimethyl terephthalate and *cis*-hexahydroterephthalate in which hydrogen transfer was achieved between identical donor and acceptor units.[16] Braude and Linstead[17] classified hydrogen transfer reactions into three types: (i) hydrogen migration taking place within one molecule; (ii) hydrogen disproportionation, involving transfer between identical donor and acceptor units; and (iii) TH-dehydrogenation, occurring between unlike donor and acceptor units. Among them, TH-dehydrogenation, more simply called TH, is by far the most important and widely used subfield. TH reactions are divided according to the catalyst type in Meerwein−Ponndorf−Verley (MPV) reductions, late transition metal-catalyzed reactions, organocatalytic, enzyme-catalyzed, thermal, base-catalyzed, and uncatalytic processes. In this section, we discuss the history, seminal studies, and basic concepts of all of these categories.

The illustrious MPV reduction was first published independently by Meerwein and Verley in 1925, and it was the first TH reaction of carbonyl compounds.[18,19] Hans Meerwein (1879−1965) studied for his Ph.D. with Richard Anschütz in Bonn where he became a Professor in 1914 before moving to Königsberg in 1922, then to Marburg. Several

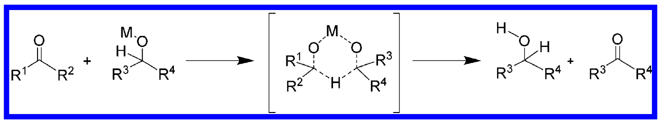
Received: April 8, 2015

DOI: 10.1021/acs.chemrev.5b00203

reactions and reagents bear his name including, in addition to the MPV reduction, the Wagneer−Meerwein rearrangement, the Meerwein arylation, and Meerwein's salt. Albert Verley (1867−1960) was, as a chemist, dedicated to perfume chemistry, aromatic synthesis, and synthetic rubber. He studied for his Ph.D. with Charles Friedel in Paris. At 22, he founded the first factory producing up to three tons per month of synthetic vanillin upon iso-eugenol oxidation by ozonized air, a revolutionary process. He was sent by President Paul Reynaud in 1940 as scientific ambassador to the U.S. near President Roosevelt, established a laboratory in New York, and proposed in 1943 an extremely efficient synthesis of butadiene from butane at atmospheric pressure that later produced 1 200 000 tons of synthetic rubber per year. He was also a known mathematician and a known composer who studied with Erik Satie and funded young musicians and composers including Arthur Honegger.

In the MPV process, an aluminum alkoxide acts as a promoter for the reduction of a ketone to the corresponding alcohol in the presence of a secondary alcohol as a hydrogen donor. Following the pioneering work, the MVP reduction of carbonyls over aluminum, zirconium, lanthanum, cerium, samarium, and ytterbium has been reported.[20] In the homogeneous MPV reduction, a direct TH through the formation of a cyclic six-membered transition state in which both the reducing alcohol and the carbonyl are coordinated to the same metal center was proposed to take place (Scheme 1),[21−23] and the reversibility of the catalytic cycle of the MPV reduction was exploited.[24]

Scheme 1. Hydrogen Transfer in the MPV Reduction via a Cyclic Transition State

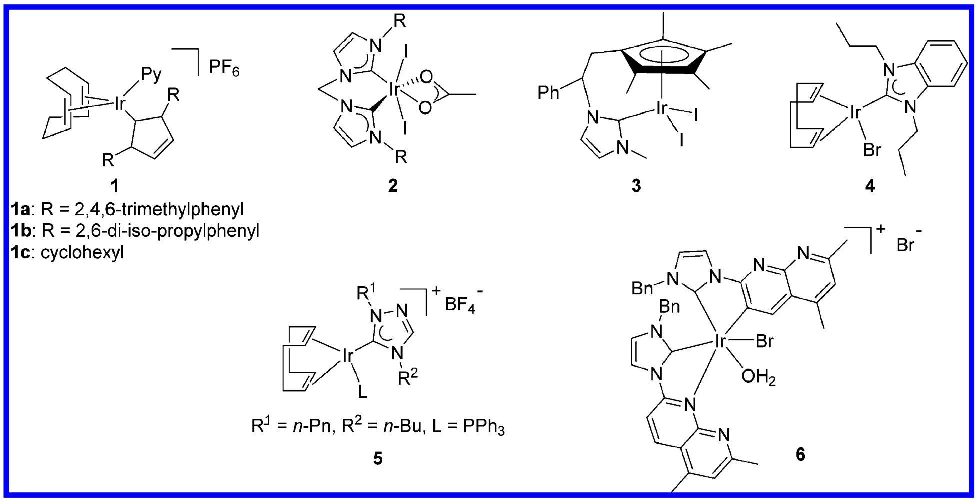


Furthermore, over the past decades, a number of heterogeneous Lewis acidic or basic catalysts including supported aluminum alkoxides, magnesium oxide, hydrotalcites, hydrous zirconia, supported ZrO_2, supported zirconium complexes, zeolites, and grafted lanthanide alkoxides have been utilized for promoting MPV reduction.[20,25] Among these easy-to-separate and regenerable catalysts, hydrotalcites, zeolites, and mesoporous material-anchored Al, La, Hf alkoxides showed high catalytic activities for MPV reduction. Some of them are even used in truly catalytic amounts. The MPV reduction has been extensively applied in both academic and industrial syntheses, particularly in the chemical manufacture of flavor agents, due to its chemoselectivity toward the keto functionality and the mild reaction conditions. The usual requirements of a large amount of reagents, undesired side reactions, and moisture sensitivity (especially for Al catalysts) are well-known drawbacks.[26]

The next milestone of TH was the discovery of late transition-metal catalysts involving first-, second-, and third-row transition metals of groups 8, 9, 10, and 11. The pioneering work reported by Henbest, Mitchell, and co-workers in the 1960s[27−29] showed that an iridium hydride complex catalyzed the hydrogenation of cyclohexanones and α,β-unsaturated ketones to alcohols with isopropanol. In the 1970s, Sasson and Blum[30−32] also provided seminal contributions to the development of transition metal-catalyzed TH. They demonstrated that the complex $[RuCl_2(PPh_3)_3]$ was active in the biphasic TH of acetophenone with isopropanol at high temperature. Two decades later, Chowdhury and Bäckvall[33] found that the $[RuCl_2(PPh_3)_3]$-promoted reaction was accelerated by 10^3−10^4 times upon adding a catalytic amount of NaOH. In the early 1980s, the first reports of the Ru-catalyzed asymmetric TH emerged.[6,34,35] Since then, asymmetric TH (ATH) has received significant attention as an essential branch of TH. Asymmetric hydrogenation (AH) is an important process in the fragrance and pharmaceutical industries,[36,37] culminating with the seminal work by Kagan and the award of the Nobel Prize to Noyori and Knowles for their contribution to the field in 2001.[38−41] ATH based on late transition-metal catalysts has proven to be among the most powerful methods for asymmetric reduction of various unsaturated substrates to produce chiral compounds.[7,8,10,11,42−45] This is due to the excellent stereoselectivities provided by these catalysts, the availability of various hydrogen sources, operational simplicity, and the use of readily accessible and little sensitive catalysts.

To date, great progress has been made in the development of late transition metal-catalyzed symmetrical TH and ATH. A

Scheme 2. Ir TH Catalysts Bearing NHCs



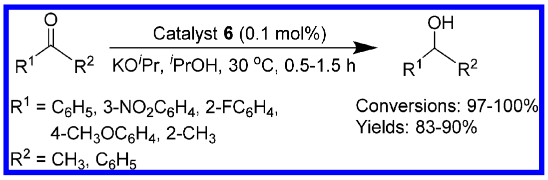
variety of transition metals, ligands, hydrogen sources, bases, reaction media, supports, and unsaturated compounds have been involved in the transformations, which makes the most important subtopic of TH.

Ir, Ru, and Rh complexes bearing N, P, O, S, C element-based ligands with various forms (such as metal-*N*-heterocyclic carbenes, half sandwich, multidentate metal complexes, and their combinations) are perhaps the most classic and popular catalysts for TH.

The family of *N*-heterocyclic carbene (NHC) ligands has shortly arrived at the forefront of coordination chemistry and organometallic catalysis[46−50] since the first isolation of a free NHC that was achieved by Arduengo et al. in 1991.[51] This is due to their strong coordination ability as σ-donors and remarkable adjustability of the steric and electronic properties on the metal center, and almost infinite possibilities of topological modifications. In Ir, Ru, and Rh catalysts for TH, NHC ligands were commonly incorporated into chelating, pincer, and chiral structures.[52]

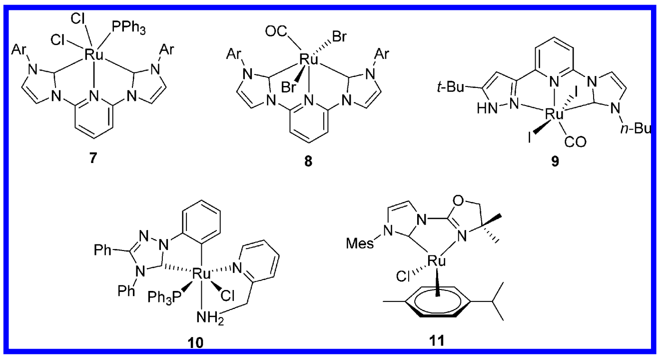
The use of transition-metal complexes containing NHC in catalytic TH was pioneered by Nolan et al.[53] who designed and synthesized the complexes $[Ir(cod)(py)(NHC)]PF_6$ **1a−1c** (Scheme 2). These complexes were further used as catalysts for the TH of several unsaturated substrates including ketones, olefins, and nitroarenes with 2-PrOH as hydrogen donor. All tested complexes were observed to be active for all involved THs, especially of ketones, with complex **1c** providing the best catalytic performance. After this pioneering research, many Ir−NHC complexes have been exploited.[54,55] Crabtree's group[56] reported the new air-stable and moisture-insensitive Ir catalysts **2** bearing a chelating bis(*N*-heterocyclic carbene) ligand for efficient TH of ketones. The first Cp*-functionalized NHC (Cp* = η^5-C_5Me_5) was prepared by Royo et al.[57] and coordinated to $[Ir(\mu\text{-}Cl)(cod)]_2$ providing complex **3**. This complex was employed at low catalyst loading down to 0.01 mol % for the TH of a series of ketones with up to a TON of 9900. The synthesis of the four-coordinate complex [IrBr(cod)(*C*-NHC)] **4** was reported by the groups of Hahn and Oro.[58−60] The catalytic performances of **4** were evaluated in the TH of cyclohexanone using 2-PrOH as hydrogen source in the presence of KOH, showing that excellent conversion was obtained in a few minutes with a TOF above 6000 h^{-1}. In 2007, Crabtree and co-workers[61] reported the first preparation and catalytic application of Ir(I) triazole-based NHC complexes. The TH of C═O, C═N, and C═C double bonds was successfully conducted in the presence of 1 mol % of **5** utilizing 2-PrOH or cyclopentanol as both hydrogen donor and solvent. A new "Ir^{III}-(C^N)(C^N)" complex **6** with a 1,8-naphthyridine (NP)−NHC hybrid ligand 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (BIN) was successfully synthesized.[62] The TH of carbonyl compounds catalyzed by **6** proceeded smoothly with 0.1 mol % catalyst loading using KO^{i}Pr as base and 2-PrOH as hydrogen source at 30 °C, providing the corresponding alcohols with 97−100% conversions and 83−90% isolated yields in a short time (Scheme 3).

Scheme 3. TH of Carbonyl Compounds over Ir−NHC Complex 6



Ru−NHC complexes were also applied as catalysts to greatly promote the TH processes.[63,64] The early pioneering work on TH using Ru−NHC catalysts was reported by Peris and Danopoulos.[65,66] These authors used 2,6-bis(1-alkylimidazolium-3-yl)pyridine salts as a new source of tridentate CNC bis(carbenes) to coordinate with Ru precursors, readily assembling the Ru "pincer" NHCs complexes 7 and **8** (Scheme 4). Both of these complexes exhibited high catalytic activities in the TH reduction of carbonyl compounds from 2-PrOH. In particular, **8** gave TONs up to 126 000 and a TOF of 15 200 h^{-1} when cyclohexanone was chosen as the reaction substrate. Later, Yu's group[67] prepared the new Ru(II) complex **9** containing a "pincer"-type pyridyl based (pyrazol-3-yl)-*N*-heterocyclic carbene ligand and revealed its good to excellent activity in the TH of ketones. A new orthometalated heterocyclic ruthenium carbene catalyst **10** with good thermal stability was synthesized by reaction of the commercially available NHC derivative 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene with the complex [Ru-2-(aminomethyl)-pyridine]. TOF values up to 120 000 h^{-1} were obtained in the TH of ketones with a broad substrate scope with the catalyst **10**.[68] In 2006, Gade et al.[69] described the synthesis and catalytic application of the first Ru complex bearing an oxazolinyl-carbene ligand with the half-sandwich structure. The obtained catalyst **11** showed a moderate activity in the reduction of ketones by 2-PrOH.

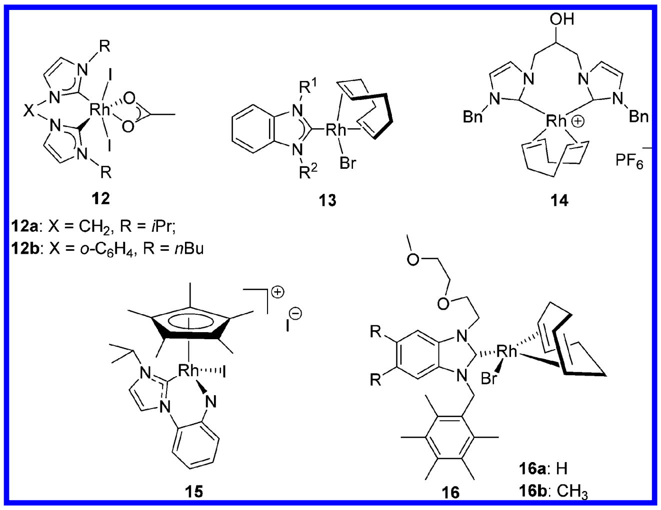
Scheme 4. Ru Catalysts Containing NHC Ligands for TH



The first example of Rh−NHC catalyst for TH was the robust and air-stable complex [Rh^{III}(bis-carbene)I_2(OAc)] (**12**) that was synthesized by Crabtree and Peris in 2002 by reaction of a bis-imidazolium salt with $[Rh(cod)ICl]_2$ in the presence of NaOAc/KI (Scheme 5).[70] These complexes displayed good catalytic performances in TH with both ketones and imines. However, the complexes **12** were inactive in TH of alkene C═C double bonds. After this groundbreaking report, several seminal studies on TH catalyzed by Rh complexes containing benzannulated NHCs (**13**),[59] bridged bis(NHC) (**14**),[71] amine-functionalized NHC (**15**),[72] and diether-functionalized NHC (**16**)[73] consecutively emerged, which drove the development of catalytic TH. For example, Kühn's group[71] synthesized the complex bis-Rh−NHC bridged with hydroxyl groups that is a potential anchoring point for immobilization onto different supports providing recyclable metal−NHC catalysts.

In 1995, Noyori and Ikariya introduced the synthesis of [RuCl(η^6-arene)(*N*-arylsulfonyl-DPEN)], **17** (named Noyori catalysts; DPEN = 1,2-diphenylethylene-1,2-diamine). This

Scheme 5. Rh TH Catalysts Bearing NHCs



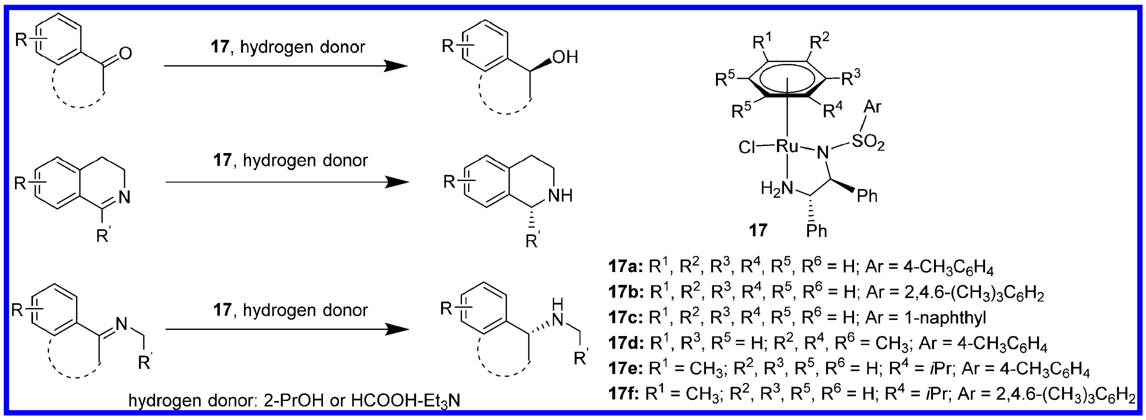
complex was reported to catalyze stereoselective TH of various aromatic ketones[39,74] and imines[40] (Scheme 6). Subsequently, TH using half-sandwich complexes including ruthenium arene and iridium/rhodium Cp* catalysts were much explored. The use of half-sandwich complexes as catalysts has been one of the most powerful strategies for asymmetric hydrogenations and other ATHs.

The well-established family of robust Noyori catalysts is very effective in terms of activity and stereoselectivity for ATH using either 2-PrOH or formic acid typically as the hydrogen source and for AH.[75] This robustness of the Noyori catalysts promotes numerous applications in total synthesis and synthetic methodology[76−87] as well as the development of many structural variations of these catalysts such as the introduction of the *N-R*-sulfonyl fragment, the sulfonamide moiety, the η^6-arene ligand, or the diamine unit.[37,88] For example, in 1999 Ikariya's group[89] reported that a Noyori catalyst efficiently promoted the asymmetric reduction of 1,2-diphenylethane-1,2-dione (benzyl) with a substrate/catalyst molar ratio of 1000−2000 in mixed solvents consisting of formic acid and triethylamine, giving a series of (*R,R*)-hydrobenzoin **18** quantitatively with high diastereomeric (97% de) and enantiomeric purities (>99% ee) (Scheme 7). As chiral 1,2-diols, the (*R,R*)-hydrobenzoins **18** are important building blocks in stereoselective organic syntheses as well as chiral ligands. The same group also reported the syntheses of the optically active alcohols **19** through ATH of the corresponding ketones in the presence of the Noyori catalyst in the same reaction media.[90] The obtained functionalized alcohols were further converted to optically active amino alcohols with excellent enantioselectivity.

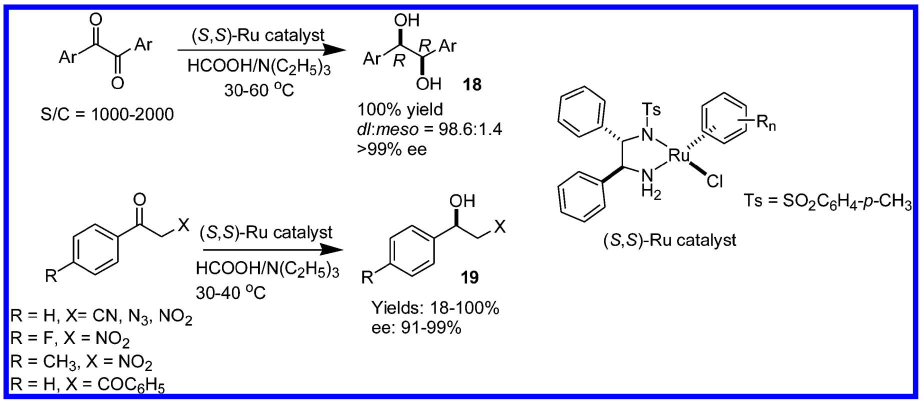
The selected variants of the Noyori catalyst based on Ru are gathered in Scheme 8. Süss-Fink and co-workers synthesized a new family of nine cationic organometallic complex **20** containing chiral 1,2-diaminocyclohexane ligand. The water-soluble and water-stable compound **20** provided good conversion and enantioselectivity for catalyzing TH of both prochiral aromatic ketones and imines in aqueous solution.[91,92] Zhu et al.[93,94] reported the first example on ATH of cyclic imines and iminiums in water with the assistance of cetyltrimethylammonium bromide (CTAB) using sodium formate as hydrogen source in the presence of the water-soluble catalyst **21**. Wills' group[95−100] provided initial reports on the synthesis of complexes **22** and **23**, a structural variation of Noyori catalysts containing a linking group (a "tether") between the η^6-arene and the diamine unit, which increased the complex rigidity. These complexes were found to be highly active catalysts for ATH of ketones in formic acid/triethylamine.

Various alternatives of monotosylated diamines in the Noyori catalysts have also emerged, such as N−O ligands (especially for amino alcohol ligands), N−P ligands, other related *N*-heterocycle-based dinitrogen ligands, and so on (Scheme 9). These half-sandwich η^6-arene Ru complexes generally showed excellent activities in the reduction of unsaturated compounds. One of the most significant breakthroughs reported by Noyori et al.[101] is that simple β-amino alcohols, for example, ephedrine, take the place of monotosylated diamines. This innovation largely improved the practical applications of the Noyori catalyst **17**, because chiral diamines are notoriously complicated to synthesize in contrast to the large variety and ready availability of chiral amino alcohols, and the new η^6-arene Ru complex **24** exhibited excellent catalytic behavior for TH in terms of enantioselectivity and catalytic activities. Since the initial discovery, plenty of amino alcohol ligands have been introduced into Ru-η^6-arene complexes and used as TH catalysts.[9,102−107] Mixed P,N-chelate ligands have attracted considerable attention in both coordination chemistry and catalysis, due to their unusual electronic properties and pronounced hemilabile character resulting from the presence of two very different binding sites.[108] In 2003, a half-sandwich

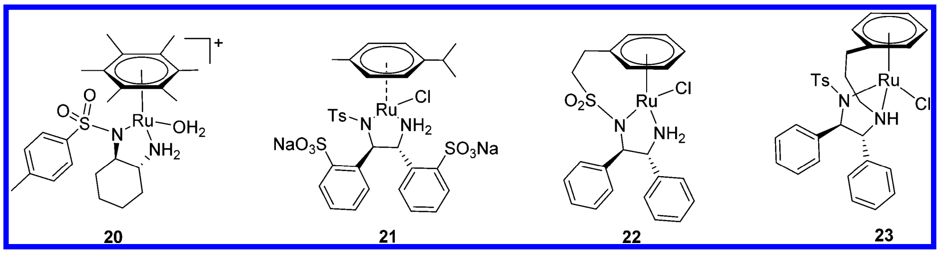
Scheme 6. ATH of Ketones and Imines Catalyzed by [RuCl(η^6-Arene)(*N*-arylsulfonyl-DPEN)] Using 2-PrOH or HCOOH-Et$_3$N as Hydrogen Donor



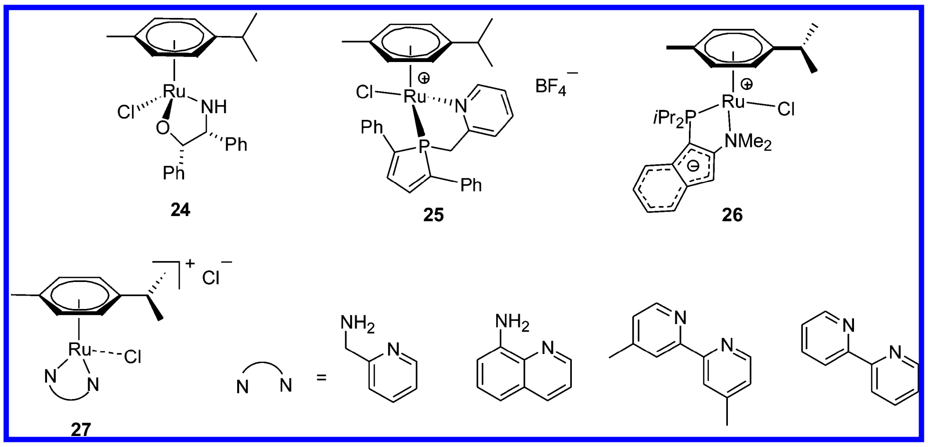
Scheme 7. Practical Syntheses of Hydrobenzoins and Optically Active Amino Alcohols via ATH Reactions Using the Noyori Catalysts



Scheme 8. Selected Variants of the Noyori Ru Catalyst

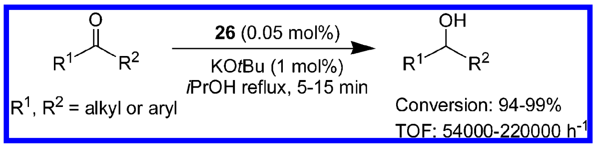


Scheme 9. Selected Half-Sandwich Ru TH Catalysts Containing N−O Ligands, N−P Ligands, or Related *N*-Heterocycle-Based Dinitrogen Ligands



[Ru−(cymene)Cl] chelate catalyst **25** bearing the 1-(2-methylpyridine) phosphole ligand was prepared and gave extremely high TONs (up to 2 × 10^7) and TOF (1.2 × 10^6 h^{-1}) for TH of ketones.[109] Another highly efficient half-sandwich Ru catalyst with P−N ligand was reported by Stradiotto and co-workers[110] who demonstrated that complex **26** with donor-substituted indenides remarkably promoted TH of a broad scope of ketones, and near quantitative conversions were detected within minutes with only 0.05 mol % of catalyst loading and high TOF values in the range of 54 000−220 000 h^{-1} (Scheme 10). Generally, the presence of a Ru−NH linkage in Ru catalysts is essential to give the highest levels of catalytic efficiency in TH of ketones, in particular in the cases of the Noyori catalysts. This is due to the well-established N−H effect that has been rationalized in terms of an outer-sphere TH mechanism involving the concerted transfer of H_2 from a {(*H*)Ru−N*H*$_2$R} intermediate to a ketone substrate.[14,39,111]

Scheme 10. TH of Ketones Catalyzed by the Highly Efficient Ru-Based Half-Sandwich Complex 26

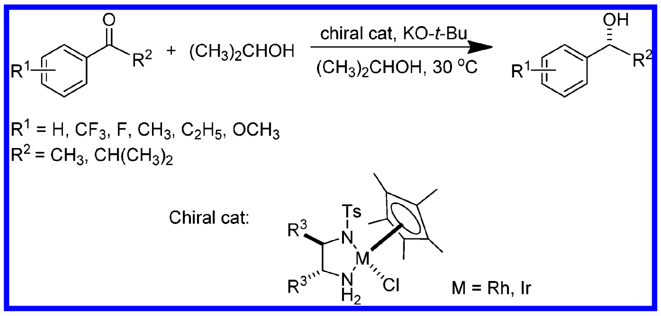


Interestingly, **25** and **26** did not rely on the N−H effect. Along this line, Stradiotto mentioned that in the case of **26** the anionic nature of the P−N ligand may play an important role in generating excellent catalytic activity.[110] Moreover, some pyridine-based dinitrogen ligands were also applied to assemble half-sandwich Ru complexes (Scheme 9, **27**).[112,113]

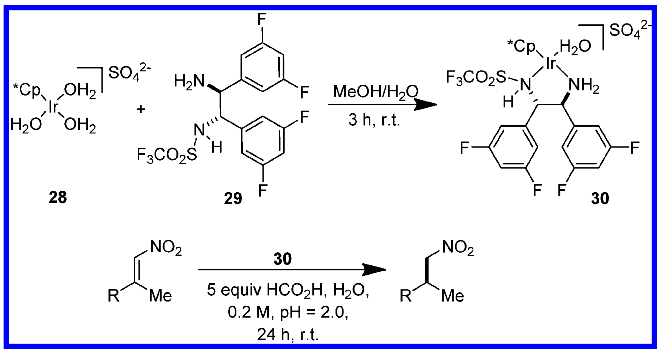
Half-sandwich Ir and Rh complexes with various combinations of ligands have also been explored in TH, but the number of complexes is less than those of Ru. In 1999, the group of

Ikariya[114] discovered the synthesis of new chiral Ir or Rh complexes containing Cp* and chiral diamine ligands. These complexes exhibited good catalytic activity and selectivity in ATH of aromatic ketones (Scheme 11), even comparable to those of their Ru counterparts. Since this discovery, Cp*Ir and Cp*Rh systems have received significantly increasing attention as catalysts in a wide variety of TH reactions in the 2000s.[115−133] For example, Carreira's group[118] prepared an air-stable Ir complex **30** containing a Cp* unit by combining the Ir(III) trihydrate precursor **28** with a donor ligand **29** in aqueous methanol at room temperature (rt). This complex **30** was then utilized as catalyst for the ATH of *β*, *β*-disubstituted nitroalkenes with a broad range of substituted groups in water at low pH and in open air, providing excellent yields and good selectivities (Scheme 12).

Scheme 11. First Examples of Chiral Rh or Ir Catalysts with Cp* and Chiral Diamine for ATH of Aromatic Ketones



Scheme 12. ATH of *β*,*β*-Disubstituted Nitroalkenes Catalyzed by the Half-Sandwich Ir Complex 30

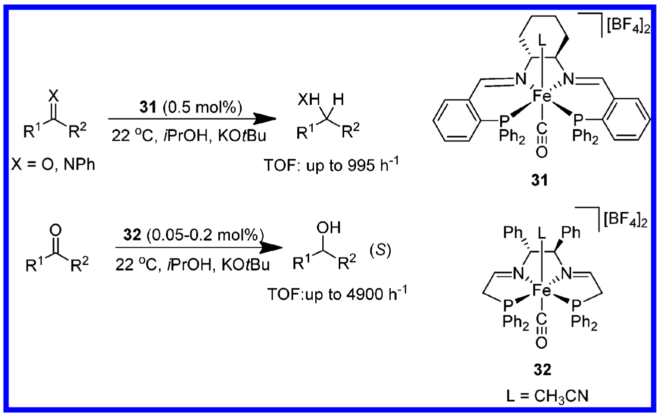


Ru, Ir, and Rh complexes containing bi- or multidentate ligands in the forms of [PN],[134] [NPN],[135,136] [NPO],[137,138] [NCN],[139] [NNN],[140−146] [PNP],[147−150] [PCP],[151,152] [CNN],[153−156] [NNNP],[157] [PNNP],[158−165] [SNNS],[166] [PPPC],[167] and [ONNO][168] backbone fragments have been extensively studied in catalytic TH due to their easy manipulations and high reactivity.[169] Among these units, phosphorus−nitrogen containing ligands have been particularly used to assist Ru, Ir, and Rh metals in TH where it is necessary for part of a ligand to dissociate to allow an organic fragment to coordinate and undergo transformations. Phosphorus−nitrogen-containing ligands are readily synthesized and structurally and electronically modified, and the coordination behavior and structural features of the corresponding Ru, Ir, and Rh complexes are tuned through small variations of these ligands. Moreover, the refined structure of these complexes enables one to probe the reaction mechanism straightforwardly.

Besides Ru, Ir, and Rh, the utilization of other late transition metals including Fe,[170−181] Co,[172,182] Ni,[183−185] Pd,[186−190] Re,[191] Os,[192−195] Pt,[196] and Au[197,198] in TH has also been widely explored.

In catalysis involving transition metals, Fe has been realized to be a fascinating candidate for a "greener" alternative to precious metals because Fe is abundant on earth, inexpensive, environmentally benign, and of low toxicity. The groups of Chirik[199−201] well established several iron-catalyzed TH systems. Shortly afterward, a pioneering breakthrough in the development iron-catalyzed ATH reactions was reported by Morris and co-workers[178,179] who designed the iron(II) complexes **31** and **32** containing tetradentate diiminodiphosphine "PNNP" ligands inspired by the high activity and enantioselectivity of Ru−PNNP complexes in TH and hydrogenation using H_2.[158,202] The new Fe complex [*trans*-Fe(CO)(NCMe)(CyP$_2$N$_2$)][BF$_4$]$_2$ (**31**) displayed a good activity in ATH of ketones, aldehydes, and imines under very mild conditions using 2-PrOH as the hydrogen donor, affording up to 995 h^{-1} TOF (Scheme 13).[178] On the basis of this result, in 2009 a modified Fe complex **32** was successfully prepared using a facile and economical two-step synthesis. This complex showed very high activity and enantioselectivity in ATH of ketones to enantioenriched alcohols with a broad scope of substituent groups, producing excellent ee values and up to 4900 h^{-1} TOF that are comparable to those of the Ru analogues.[179] In the past few years, significant progress in the field of iron-catalyzed TH has been witnessed.

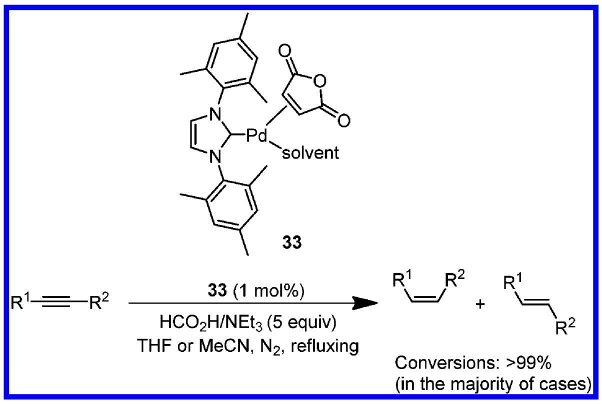
Scheme 13. ATH of Polar Bonds Using Iron-Based Catalysts



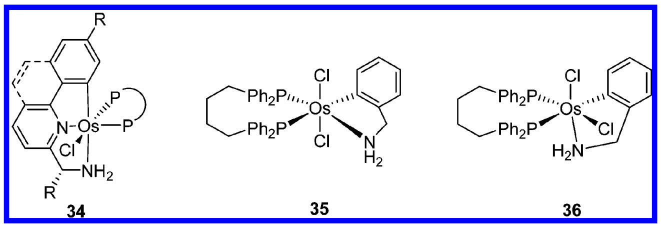
As one of the most frequently used transition metal catalysts, Pd has also been employed in catalytic TH. The first example of stereo- and chemoselective transfer semihydrogenation of alkynes to alkenes was reported by Elsevier's group.[188] In this work, the zerovalent Pd−NHC complex **33** was readily generated and utilized as catalyst in hydrogenation of aromatic and aliphatic internal alkynes by employing a 5-fold excess of HCO$_2$H/NEt$_3$ as the reductant in refluxing THF or CH$_3$CN under nitrogen atmosphere (Scheme 14). The transfer semihydrogenation proceeded smoothly with excellent conversions, and a series of *Z* alkenes were obtained with high stereoselectivities and chemoselectivities.[188]

Significant breakthroughs and developments of catalyst diversity in TH have been achieved by Baratta et al. in 2008 with pioneering studies of the osmium complexes [OsCl(CNN)P$_2$] (**34**)[192,193] and [OsCl$_2$P$_2$(Pyme)] (**35** and **36**)[194] containing CNN or CN pincer (Scheme 15). A remarkably high catalytic activity (up to 10^6 h^{-1} TOF) and enantiose-

Scheme 14. TH of Internal and Terminal Alkynes to *Z* and *E* Alkenes with HCO_2H/Et_3N as the Hydrogen Source in the Presence of the Pd Catalyst 33



Scheme 15. Baratta's Os Complexes for Efficient Catalytic TH



lectivity (up to 98% ee) was disclosed in the TH of ketones using 2 mol % of NaO*i*Pr as base, 2-PrOH as solvent, and hydrogen source with down to 0.001 mol % of the Os complexes. The authors mentioned that deactivation is retarded in these Os examples resulting in catalytic performances comparable to those of other elements including Ru.

In the field of transition-metal catalyst-promoted TH, various "sacrificial" hydrogen sources were employed such as cyclohexene, cyclohexadiene, alcohols (including 2-PrOH, MeOH, EtOH, glycerol), formic acid, Hantzsch esters,[203] hydrazine, benzothiazoles, dimethylamine-borane, sodium hypophosphitem, and alkanes. Because of their low costs, 2-PrOH and formate are the main used sources of reducing reagent. In some cases, the "sacrificial" hydrogen source was an alkane and the hydrogen acceptor an appropriate olefin ensuring favorable thermodynamics of the TH reaction. For instance, in 1979, Crabtree's group[204] demonstrated for the first time that $[Ir(Me_2CO)_2H_2(PPh_3)_2]^+$ efficiently catalyzed hydrogen transfer from cyclones to *t*-butylethylene, producing the corresponding cycloolefins and 2,2-dimethylbutane. Later, the complexes $[IrH_2(O_2CCF_3)(PAr_3)_2]$ and $[ReH_7(PPh_3)_2]$ were also shown to be active in the process of dehydrogenation of cyclones using *t*-butylethylene as the hydrogen acceptor.[205,206] In 2003, Goldman and co-workers[207,208] found that the "pincer"-ligated transition-metal complex $[Ir(^{t\text{-Bu}}PCP)H_2]$ ($^{t\text{-Bu}}PCP = \eta^3$-2,6-$(^tBu_2PCH_2)_2C_6H_3$) was an effective and robust catalyst for TH reactions between *t*-butylethylene and tertiary amines (or cyclooctane), and a series of enamines (or cyclooctene) were synthesized in acceptable yields.

Organic media in normal or supercritical state, ionic liquids,[209−212] and aqueous media were commonly employed for TH.[213] Most of the processes take place in an organic solvent that is generally used as hydrogen donor. Enzyme-catalyzed TH in aqueous media using formate as hydrogen donor has been occurring for billions of years. Since the initial research by the Peruzzini and Watanabe groups on transition-metal-catalyzed TH in aqueous media,[128,214] various catalytic systems involving aqueous solvents have been reported until recently.[215−218] Such systems involve the low-cost and environmentally benign property of water, the good water-solubility of the frequently used hydrogen sources, the great progress in the synthesis of water-soluble catalysts or ligands,[219−221] and the formation of water-soluble metal−hydride complexes as intermediates in catalytic cycles.[222] The catalytic performances of transition metal in aqueous media are critically affected by the pH value of reaction mixtures, allowing for fine-tuning of selectivity and limiting side reactions.[127,128,223] In addition, many reactions have been found to be significantly accelerated in water, as compared to organic solvents.[224,225]

A series of organic and inorganic bases have been employed in TH such as Et_3N, KOH, NaOH, Na_2CO_3, HCOONa, 2-PrOK, 2-PrONa, 2-PrOLi, KO^tBu, NaO^tBu, KHMDS (potassium hexamethylsilazane), K_3PO_4, Cs_2CO_3, CsOH, NaOAc, and NaOMe. The pK_a value and the cationic or anionic nature of the base influence the catalytic efficiencies of transition-metal catalysts.[226] Interestingly, in a few cases, TH proceeded smoothly without the use of any base.[227−230]

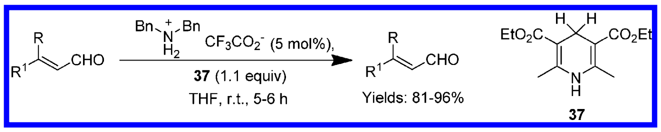
Various unsaturated compounds including ketones, aldehydes, imines, nitrocompounds, nitriles, oximes, α,β-unsaturated esters, α,β-unsaturated acids, α,β-unsaturated carbonyl compounds, heterocycles, alkenes, and alkynes have been reduced to the corresponding symmetric or asymmetric compounds through TH processes in the presence of either homogeneous or heterogeneous transition-metal catalysts. Moreover, transition-metal-catalyzed TH reactions have been applied to the synthesis of asymmetric products on industrial scale.[231]

An extensive exploration of mechanistic studies of transition-metal-catalyzed TH of unsaturated compounds has been witnessed in the last few decades. Taking the TH of ketones as an example, two mechanisms were most commonly demonstrated in the transformation. These are inner- (with substrate coordination) and outer-sphere mechanisms (with no substrate coordination). The inner-sphere mechanism implies insertion of the ketone reagent into an M−H bond with concomitant elimination of acetone. A new alkoxide is formed that is then protonated by the incoming hydrogen source, releasing the alcohol product from the metal.[14] The outer-sphere mechanism, initially proposed by Noyori[111] in the case of the Noyori catalysts, implies the existence of the strongly basic amido ligand that allows deprotonation of the alcohol by the nucleophilic nitrogen donor with simultaneous hydride transfer to the adjacent ruthenium atom via a highly ordered transition state. Transfer of the proton and hydride from the amine and ruthenium, respectively, to the ketone generates the alcohol product. In the outer-sphere mechanism, the ligand plays a critical role in activating the carbon of the unsaturated substrate to nucleophilic hydride. This provides a cyclic transition state for H^+/H^- transfer by adequate hyperconjugation. The metal serves as a source of proton to be transferred along with the hydride from the metal, offering a point of interaction for enantioselective recognition of the prochiral substrate.[111] These two mechanisms clearly differ from that of the direct TH proposed for the MPV reaction in which the ketone interacts with the metal alkoxide (Scheme 1).

Organocatalysis that dates back to more than 150 years ago offers several advantages. Organocatalysts are usually more robust, less sensitive, less toxic, and easier to synthesize than organometallic analogues and are immobilized onto a support and conveniently recycled. Moreover, organocatalysis can be performed under aerobic conditions.[232] Transition metal catalysts, in particular Rh, Ru, and Ir complexes, were widely and efficiently used in TH, affording high TONs and high enantioselectivity. On the other hand, the organocatalytic TH process has also been shown to be a promising means to reduce organic compounds containing C=O, C=N, and C=C bonds using dihydropyridines such as Hantzsch esters as the hydride source.[204,233]

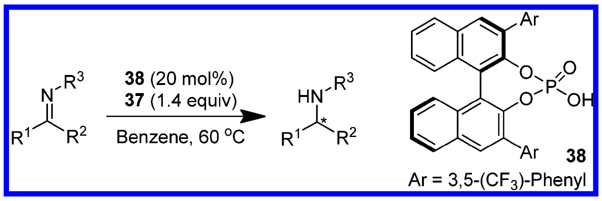
In 1989, Batra et al.[234] discovered the first metal-free ATH of imine with the use of Hantzsch esters as hydrogen sources in the presence of amino acid catalysts; up to 62% ee was obtained. The hydrogenation of *α*,*β*-unsaturated carbonyl compounds is a useful but challenging transformation. The first metal-free TH of olefins was discovered by List's group[235] who reported that iminium catalysts remarkably promoted the conjugate reduction of *α*,*β*-unsaturated aldehydes under TH conditions. A series of saturated analogues were synthesized upon using 5 mol % of the organocatalyst dibenzylammonium trifluoroacetate, Hantzsch ester **37** as hydrogen donor under mild conditions, with yields in the 81%−96% range (Scheme 16). Shortly afterward, the groups of MacMillan and Houk[236,237] found that imidazolidinone catalyzed ATH of cyclic *α*,*β*-unsaturated ketones smoothly at 0 °C using Hantzsch esters as hydrogen source, which provided the corresponding cyclic saturated ketones with good yields and excellent enantioselectivities.

Scheme 16. Iminium-Catalyzed TH of *α*,*β*-Unsaturated Aldehydes

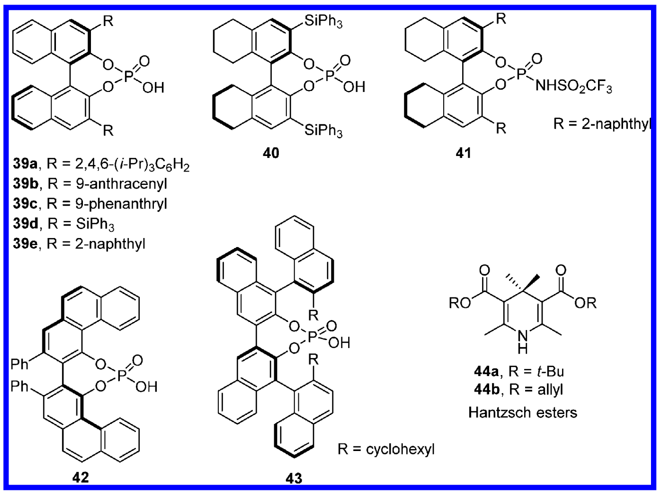


Over the past decade, Brønsted acids have become an important alternative to metal catalysts and are the most used organocatalysts for TH, in particular for ATH transformation.[238,239] After the initial report by Rueping and co-workers of the enantioselective Brønsted acids-catalyzed TH of *N*-aryl ketimines using a phosphoric acid catalyst (Scheme 17),[240] several phosphoric acid catalysts and Hantzsch esters (see some examples in Scheme 18) have been successfully utilized in the organocatalytic TH of nitrogen-containing substrates such as imines, quinolines, enamines, benzodiazepines, benzoxazines, and pyridines.[233,241−245]

Scheme 17. Phosphoric Acid-Catalyzed ATH of *N*-Aryl Ketimines



Scheme 18. Some Successful Phosphoric Acid Catalysts and Hantzsch Esters Employed in the Organocatalytic TH of Imines and Olefins



Although TH of carbonyls is achieved at high temperatures (220−400 °C) and supercritical alcohols under noncatalytic conditions,[246−248] these harsh conditions may not be viable for practical applications. Therefore, Varma et al.[249,250] reported that the addition of hydroxide bases to the mixture of carbonyls and alcohols improved the efficiency of TH processes. KOH and NaOH were shown to catalyze the TH of aldehydes and ketones to the corresponding primary and secondary alcohols in refluxing 2-PrOH. The method is simple, cheap, nontoxic, and easy-to-handle. However, it is only tolerant to a narrow range of carbonyls, and the mechanism is still debated.

Homogeneous TH plays a prominent role in the development of catalysis, and may be one of the most extensively studied type of homogeneously catalyzed reactions. However, the applications to industry of homogeneous TH catalysts are consumedly restricted by the difficulty of separating homogeneous catalysts from reaction media and reusing them. In this context, from both environmental and economic points of view, the heterogenization of catalysts has been widely explored and studied. Until now, numerous heterogeneous catalysts containing several supports such as polymers,[251−257] silica,[258−262] magnetic nanoparticles, graphene, TiO_2, and activated carbon have been prepared and employed in TH.

1.2. Scope of the Review

Many reviews have appeared on some subfields of TH catalysis.[4−14,217,263−270] In this comprehensive Review, a broad overview of TH is presented. We begin with an introductory discussion of the importance and significance of TH, including the historical background, basic concepts, catalysts assortment, and seminal discoveries. Given the explosive development, new catalytic systems and trends have appeared at a fast rate in the last 5 years. The key focus of this Review is then highlighted, that is, new breakthroughs, recent advances, and trends of TH involving homogeneous and heterogeneous transition-metal catalysts, organocatalysts, and other catalysts that have most recently appeared until 2015. At the end of this Review, we summarize the advantages and development of TH, demonstrate that TH is now in the golden age, and offer perspectives for further development.

2. RECENT ADVANCES AND TRENDS IN TH USING TRANSITION-METAL CATALYSTS

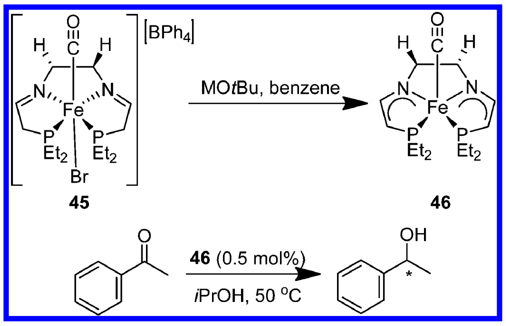
2.1. Homogeneous or Quasi-Homogeneous Transition-Metal Catalysts

2.1.1. Iron-Based Catalysts. In the field of catalysis, iron catalysts have recently appeared as a rising star.[271−274] In principle, iron catalysts are tolerant to a broad range of synthetic transformations, thanks to the distinct Lewis acid character and the facile change of oxidation state. Iron-catalyzed TH has kept growing in the last 5 years, and great progress has been achieved.[275]

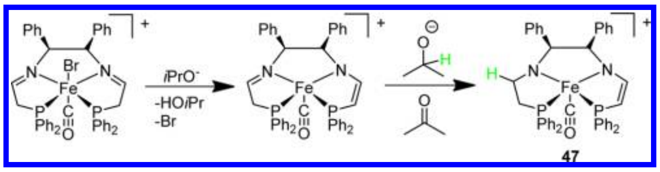
After their pioneering study on TH based on iron catalysts containing PNNP backbones, in 2010 Morris' group[276,277] prepared a series of new iron(II) precatalysts *trans*-[Fe(Br)(CO)($PPh_2CH_2CH{=}NCHRCHRN{=}CHCH_2PPh_2$)][$BPh_4$] with diamines containing various substituents through a one-pot synthetic route. These authors found that all of them showed excellent catalytic properties in the ATH of acetophenone with 2-PrOH and KO^{t}Bu under mild conditions. More importantly, a compared examination revealed that the catalytic activity of these complexes increased with increasing the size of the substituents in the backbone of the ligands.[276] Another report indicated that the steric and electronic properties of these complexes were tunable through change of the substituents of their phosphorus donors, resulting in seeking out more active and selective iron−PNNP catalysts.[278]

Along with catalytic examinations, many theoretical studies of the mechanism of TH of ketones using iron(II)−PNNP complexes have been conducted by Morris' group,[279−285] and these investigations led to the rational design of other well-defined iron hydrogenation catalysts. A five-coordinate iron(II) complex **46** was prepared by double deprotonation of the PNNP ligand of the precursor complex **45** by a base.[279] The new complex **46** with 0.5 mol % of loading amount displayed a good activity in ATH of acetophenone to 1-phenylethanol in isopropanol in the absence of added base (Scheme 19). Hence, it was inferred that complex **46** could be one of the intermediates in the catalytic cycle when its parent compound **45** was used for the TH with a base. If the ethyl group on phosphorus of **46** was replaced by bulky Cy or *i*Pr substituents, the corresponding complexes were inactive for TH, which was attributed to the inactivity of their parent compounds.[279] The same research group also reported that when activation of the complex *trans*-[Fe(CO)(Br)($Ph_2PCH_2CH{=}N$−((*S*,*S*)-C(Ph)H−C(Ph)H)−$N{=}CHCH_2PPh_2$)][BPh_4] with base resulted in the selective reduction of one of the imine groups of the PNNP fragment, the formed complex **47** showed extremely high activity for ATH of acetophenone (Scheme 20).[282] This result suggested that partial ligand reduction is the key for high catalytic activity and that an outer-sphere mechanism is more probable for iron−PNNP promoted TH.

Scheme 19. Catalytic TH of Acetophenone to 1-Phenylethanol in Isopropanol without Base



Scheme 20. Partial PNNP Ligand Reduction in the Complex *trans*-[Fe(CO)(Br)($Ph_2PCH_2CH{=}N$−((*S*,*S*)-C(Ph)H−C(Ph)H)−$N{=}CHCH_2PPh_2$)][BPh_4]



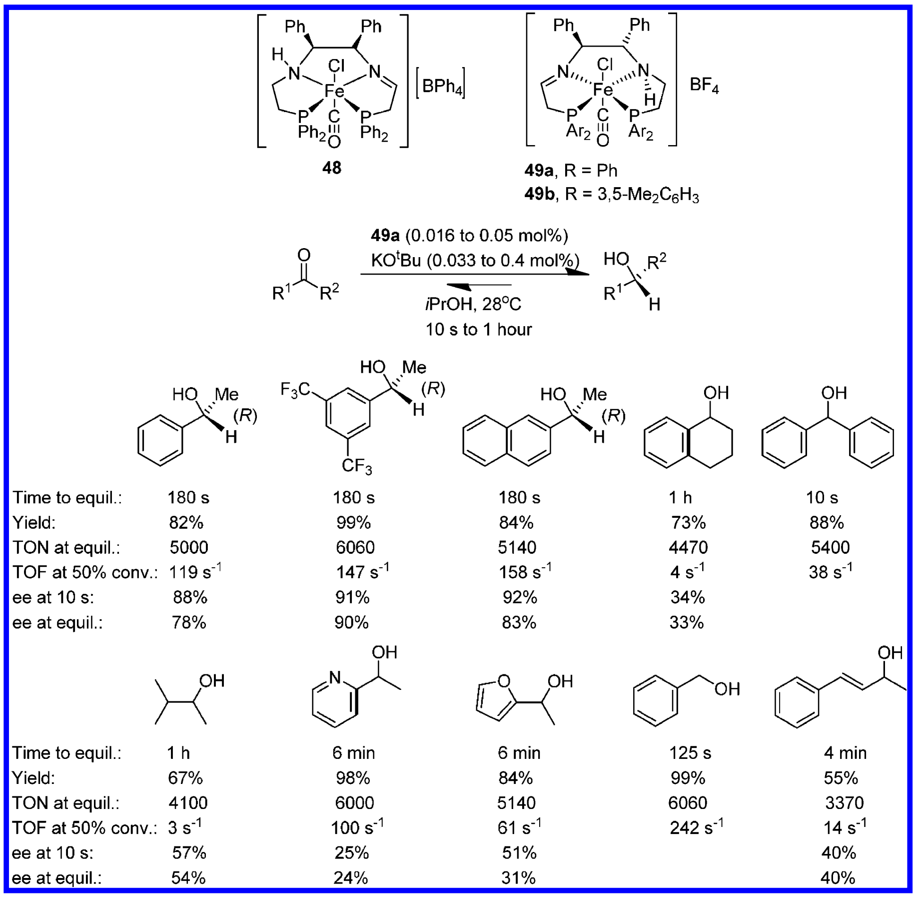
On the basis of this research, the iron complexes **48** and **49** that contain a partially reduced PNNP ligand with amine and imine functionality were constructed through a direct synthetic approach.[283,284] These complexes were two of the most active catalysts known for the ATH of polar bonds of ketones and imines, and the highest rate was obtained without requirement of an activation period. For example, **49a** bearing amine-(imine)diphosphine ligand exhibited unprecedented catalytic performance in TH of aromatic and aliphatic carbonyls with a broad range of substituent with 2-PrOH as hydrogen source and solvent using 0.033−0.4 mol % of KO^{t}Bu as base at 28 °C. Within reaction time down to 10 s, a series of alcohols were obtained at a TOF of 242 s^{-1} (Scheme 21).[284] Likewise, catalyst **49a** was also remarkably powerful for the reduction of imines under TH conditions. Within 3 min, two kinds of amines were produced with yields up to 99%, and high TONs, TOFs, and ee values (Scheme 22).[284]

During mechanistic investigation of the catalytic activity of the iron−PNNP complex *trans*-[Fe(NCMe)CO($PPh_2C_6H_4CH{=}NCHR{-}$)$_2$][BF_4]$_2$ for TH of ketones, Morris found that the real active species formed during catalysis are iron(0) nanoparticles modified with achiral PNNP-type tetradentate ligands (Scheme 23).[285] This proposed mechanism was given strong evidence by various analyses such as in operando techniques, poisoning experiments, scanning transmission electron microscopy (STEM) imaging with energy-dispersive X-ray spectroscopy (EDX) analysis, X-ray photoelectron spectra (XPS) analysis, superconducting quantum interference device (SQUID) magnetometry analysis, and a polymer supported substrate experiment.[285]

Other groups also reported crucial studies on iron−PNNP-catalyzed TH.[286−288] For instance, Beller and co-workers[286] provided in 2011 the first report of iron-mediated TH of imines. The use of the iron precursor [Et_3NH][$HFe_3(CO)_{11}$] and PNNP ligand **50** gives excellent results in ATH of a variety of *N*-(diphenylphosphinyl)ketimines; excellent enantioselectivities and high yields were observed in most cases (Scheme 24). This protocol holds many notable features such as high accessibility of the iron catalyst, safe and mild reaction conditions, and operational simplicity.

Because of the properties and applications of the NHC ligands in catalysis, a few well-defined iron−NHC complexes were recently designed and synthesized (Scheme 25). Compounds **51** and **52** are iron complexes bearing tethered Cp−NHC units in four- or three-legged piano-stool geometry; the existence of tethered systems may help to stabilize the complexes and bring some favorable catalytic behaviors.[289] The complex [Fe(IMes)$_2$Cl$_2$] (IMes = 1,3-bis(2,4,6-

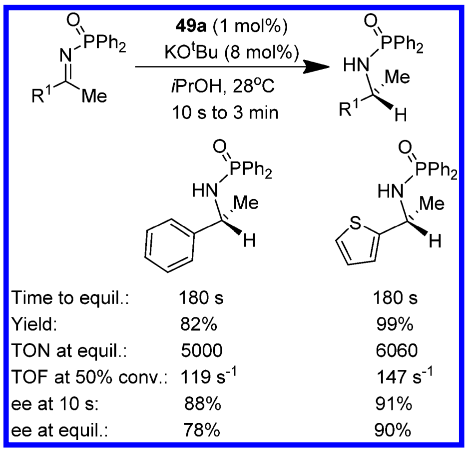
Scheme 21. Amine(imine)diphosphine Iron Catalysts for ATH of Ketones



Time to equil.:	180 s	180 s	180 s	1 h	10 s
Yield:	82%	99%	84%	73%	88%
TON at equil.:	5000	6060	5140	4470	5400
TOF at 50% conv.:	119 s^{-1}	147 s^{-1}	158 s^{-1}	4 s^{-1}	38 s^{-1}
ee at 10 s:	88%	91%	92%	34%	
ee at equil.:	78%	90%	83%	33%	

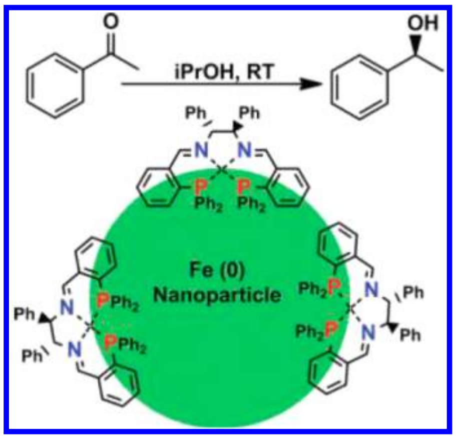
Time to equil.:	1 h	6 min	6 min	125 s	4 min
Yield:	67%	98%	84%	99%	55%
TON at equil.:	4100	6000	5140	6060	3370
TOF at 50% conv.:	3 s^{-1}	100 s^{-1}	61 s^{-1}	242 s^{-1}	14 s^{-1}
ee at 10 s:	57%	25%	51%		40%
ee at equil.:	54%	24%	31%		40%

Scheme 22. Amine(imine)diphosphine Iron Catalysts for ATH of Imines



Time to equil.:	180 s	180 s
Yield:	82%	99%
TON at equil.:	5000	6060
TOF at 50% conv.:	119 s^{-1}	147 s^{-1}
ee at 10 s:	88%	91%
ee at equil.:	78%	90%

Scheme 23. Iron Nanoparticles Catalyzing the ATH of Ketones[a]

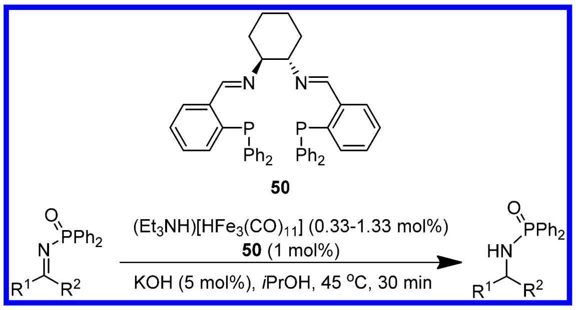


[a] Reprinted with permission from ref 285. Copyright 2012 American Chemical Society.

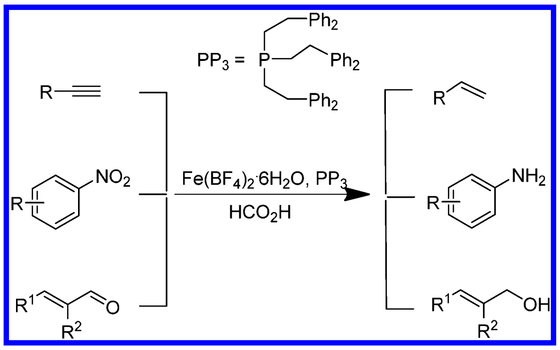
trimethylphenyl)imidazol-2-ylidene), **53a**, was straightforwardly prepared through reaction between [Fe{N(SiMe$_3$)$_2$}$_2$] and imidazolium salts. Further replacement of the chloride ligands by methyl groups resulted in the formation of the complex [*trans*-(IMes)$_2$FeMe$_2$] (**54**).[290] The iron–NHC complex **55** was generated in situ from [FeCp(CO)$_2$I] and the related 1,3-dialkylated imidazolium salts.[291] These iron complexes **51**–**55** were found to serve as good catalysts for the TH of ketones.

Besides carbonyls and imines,[292,293] iron catalysts also tolerate reduction of other nonpolar unsaturated organic molecules substrates via TH processes, such as alkynes, alkenes, and nitroarenes.[294–296] Beller's group[295,296] demonstrated that the in situ combination of [Fe(BF$_4$)$_2$·6H$_2$O] and tris[(2-diphenyl-phosphino)-ethyl]-phosphine (PP$_3$) achieved the catalytic TH of alkynes and nitroarenes, producing alkenes and anilines, respectively. In both processes, formic acid was employed as the reducing agent. In addition, no base was required (Scheme 26). With this protocol, a broad range of alkenes and anilines bearing various functional groups were isolated in excellent yields under mild conditions. Notably, this method was successfully extended to the selective hydrogenation of acroleins to allyl alcohols (Scheme 26),[297] which is

Scheme 24. First Example of Iron-Catalyzed TH of Imines



Scheme 26. TH Catalyzed by [$Fe(BF_4)_2$·$6H_2O$]/PP_3



very useful in both academic and industrial research. Another report showed that this transformation was also smoothly conducted using an iron oxide catalyst.[298]

2.1.2. Ruthenium-Based Catalysts.

Ruthenium catalysts are by far the most widely used ones to mediate TH. In the past few years, great improvements of ruthenium-catalyzed TH have been witnessed in several aspects including the development of the diversity of ligands and ruthenium catalysts with high efficiency, the use of "greener" and more economical catalytic systems, the mechanistic studies and theoretical calculations, and the exploration of practical applications in the synthesis of fine chemicals and pharmaceuticals.

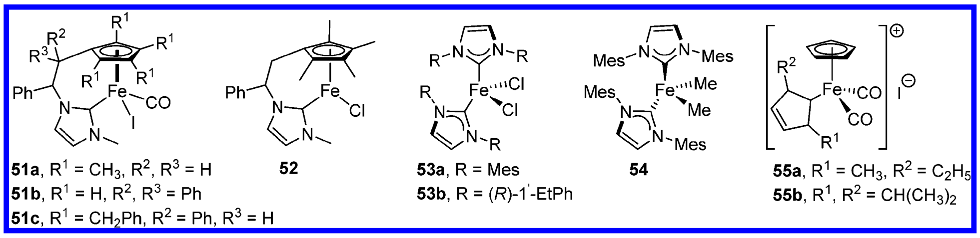
Ligand choice is a key issue toward both selectivity and activity of the metal center. As an ideal alternative of organophosphine ligands, NHCs have been shown to be indispensable for the synthesis of homogeneous organometallic catalysts. Ruthenium NHC complexes with a broad range of oxidation states, coordination geometries of ruthenium, and large structural motifs have recently disclosed good activity and selectivity in catalytic TH.[299−308] Particularly in catalysis involving ruthenium, NHC ligands functionalized with an additional donor group have been extensively explored, due to the potential hemilability of the new donor group involving reversible dissociation from the ruthenium center. These donor groups include pyridine, pyrimidine, phosphine, carboxylate, indenyl, oxazoline, thioether, and ether.

Ruthenium NHC complexes **56** and **57** that contain a pyridine moiety were well established as a promising new class of catalysts in TH (Scheme 27).[309−311] Remarkably, only 0.1 mol % catalyst loading of **57** appeared to be sufficient for the TH of a wide range of ketones and imines.[310] Albrecht's group[312,313] readily prepared a series of ruthenium complexes containing different donor substituent-functionalized NHCs (**58**−**61**). Among them, the olefin-tethered NHC ruthenium complex **58** was a very efficient and versatile catalyst toward TH of olefins to alkanes, alkynes to olefins, ketones to alcohols, nitrobenzene to aniline, benzonitrile to benzamide or benzylamine, and *N*-benzylideneaniline to *N*-benzylaniline under various conditions.[312] Furthermore, the study on the double TH of *α*,*β*-unsaturated ketones catalyzed by **58** revealed fast isomerization of the enol intermediate to its saturated ketone tautomer prior to the second hydrogenation. Recent research has also been devoted to the synthesis of ruthenium complexes bearing primary amine- (**62** and **63**),[314,315] phosphine- (**64**),[316] anionic benzimidazole (**65**)[317]-based NHC ligands, and NHC ligand without donor group (**66**),[318] and their catalytic performances and DFT studies of TH mechanisms of carbonyls were explored.

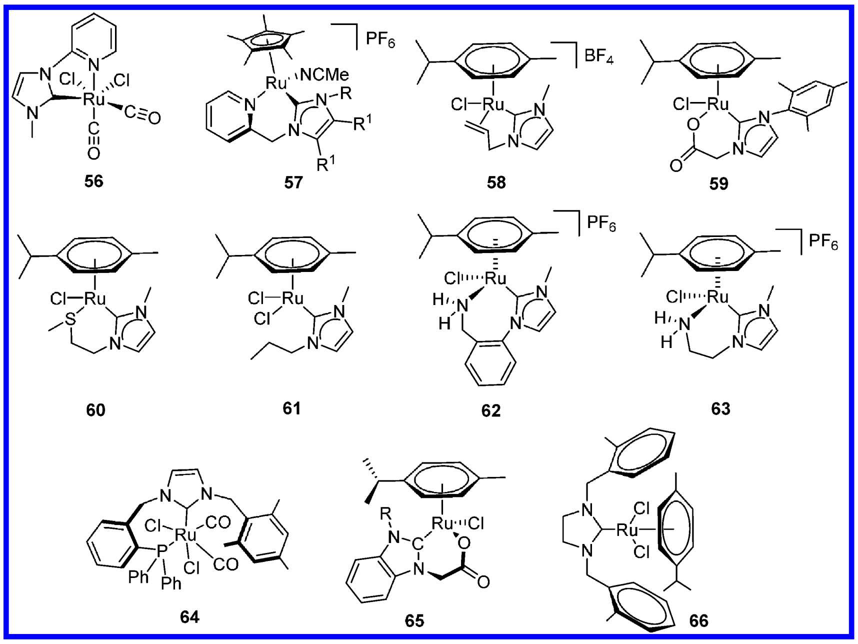
Most NHC ligands that are used in TH catalysis coordinate to the ruthenium center in a monodentate fashion. Chelating bis- or tetra-NHCs in general are of great interest, because they extend the range of possible NHC ligands, and their topological properties including bite angle, steric hindrance, and fluxional behavior have been delicately tuned. An alkane-bridged bis-NHC ligand was synthesized and used to support a ruthenium(II) carbonyl moiety, forming a new ruthenium complex with a six-coordinate octahedral geometry (**67**, Scheme 28). This complex showed an excellent activity in the reduction of ketones under TH conditions with 0.1 mol % of catalyst loading.[319] Peris and co-workers[320] reported that the complexes [Ru(η^6-arene)(bis-NHC)], **68**, gave good results in TH of carbon dioxide to formate using 2-PrOH as hydrogen source. A maximum TON value of 874 was measured when the reaction was conducted at 110 °C under 50 atm of carbon dioxide. These severe reaction conditions require a high stable catalyst. Apparently the existence of a bis-NHC ligand enhanced the stability of catalyst **68** resulting in satisfactory catalytic performances in this key TH.[320] A ruthenium complex **69** with octahedral geometry including four chelating NHCs and two acetonitrile ligands was synthesized and employed as catalyst in TH of ketones.[321] This process was efficiently promoted by down to 0.001 mol % of catalyst **69**, and exceedingly high TOFs (up to 56 000 h^{-1}) were provided.

An analogue of NHC, *N*,*S*-heterocyclic carbene (NSHC), was synthesized and used as ligand for the new ruthenium complex **70** (Scheme 28).[322] Its catalytic property toward TH

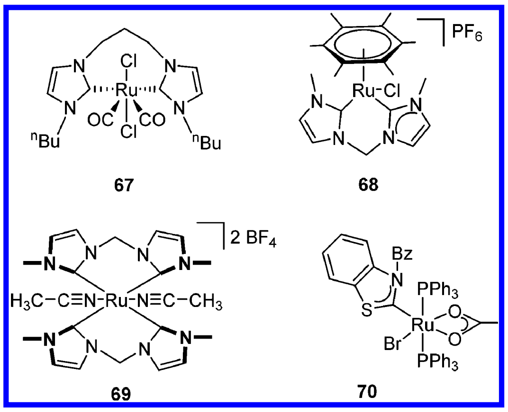
Scheme 25. Iron−NHC Catalysts for TH



Scheme 27. Ru Mono-NHC Catalysts in TH



Scheme 28. TH Ru Catalysts with Chelating Bis-, Tetra-NHC, and NSHC Ligands



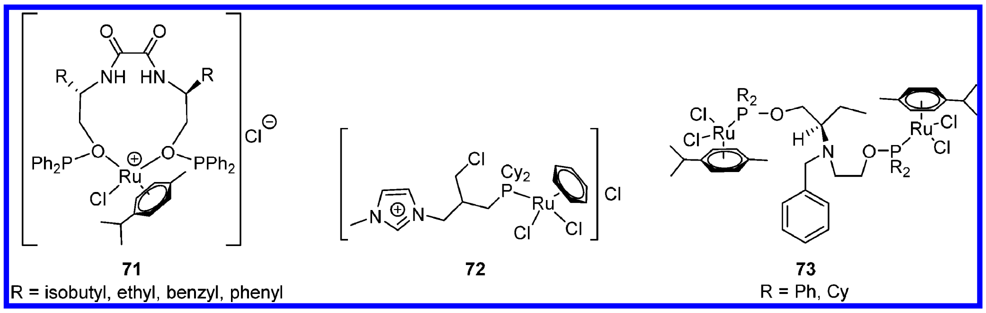
of ketones was examined, showing that this kind of catalyst allowed TH with relatively low efficiency.

On the basis of the previous reports, since 2010 a variety of half-sandwich ruthenium complexes containing arene (including benzene, *p*-cymene, and hexamethylbenzene), Cp, Cp*, or indenyl[323] have been extensively investigated in TH.[324−334] Slight modifications of ligands led to striking changes in their coordination behavior and properties of the resulting half-sandwich ruthenium complexes. By choosing an appropriate ligand system, their catalytic property was finely tuned.

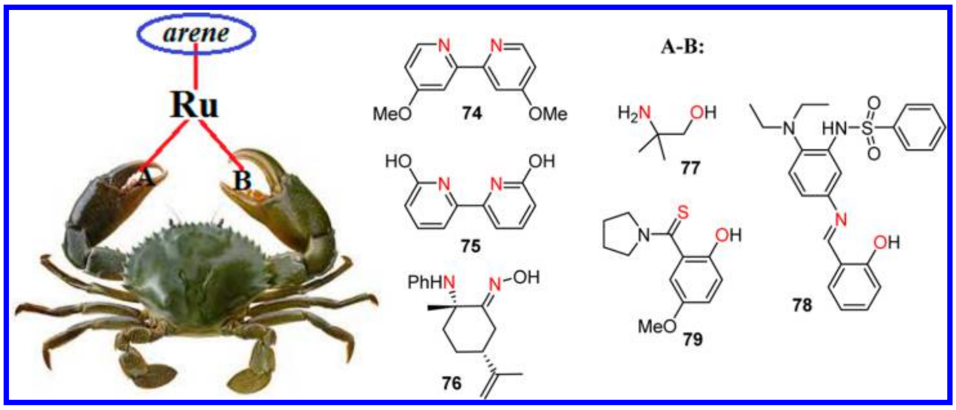
The discovery of the Noyori catalysts that was a milestone in TH still inspires the development of various analogues.[327,335−341] Indeed, the Noyori catalysts [RuCl(TsDPEN)(η^6-*p*-cymene)] and [RuCl(TsDPEN)(η^6-mesitylene)] are nowadays commercially available.

Versatile P-based ligands have also been introduced into half-sandwich ruthenium complexes (Scheme 29) that have been intensively explored in TH.[342] A series of new chiral *C*2-symmetric ligands *N*,*N*′-bis-[2-*O*-(diphenylphosphinite)ethyl]-ethanediamide bearing isobutyl,[343] ethyl,[343] benzyl,[344] and phenyl[345] groups have been synthesized and metalized with the precursor [Ru(*p*-cymene)Cl_2]$_2$ by Aydemir and co-workers who demonstrated that these corresponding ruthenium complexes **71** served as catalysts for ATH of acetophenone derivatives in 2-PrOH, providing high conversions (up to 99%) but somewhat low enantioselectivities (up to 75% ee). The same group[346] found that the ionic-liquid-supported Ru(II)−phosphinite compound **72** displayed extremely high catalytic performance in the TH of various ketones with excellent 98−99% conversions in 5 min, and up to 1188 h^{-1} TOF. A binuclear ruthenium complex **73** with P-donor ligand also gave good conversions and moderate to good enantioselectivities

Scheme 29. Ruthenium TH Catalysts Containing Arene and P-Based Ligands



Scheme 30. Ruthenium−Arene Complexes with Pincer Scaffolds

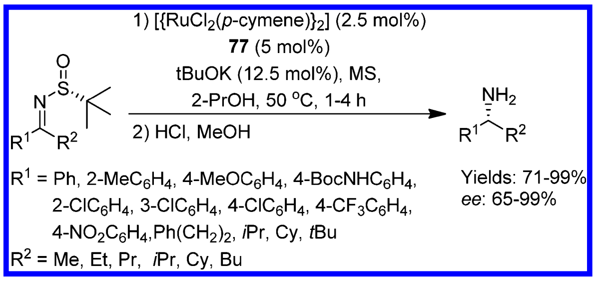


(up to 85% ee) when it was used as catalyst in the TH of aromatic ketones.[347]

The ferrocene moiety has been extensively explored as a backbone of phosphine ligands in asymmetric synthesis, because of its relative air stability, easy modifiability, highly electron-donating property, and unique structure. Recently, some ferrocene-derived phosphine ligands have been utilized in transition-metal-catalyzed TH reactions,[348] in particular for ruthenium arene catalysts. A new family of monodentate phosphinite ligands bearing both a ferrocene moiety and an NH bridging moiety adjacent to the stereocenter, and their half-sandwich ruthenium−arene complexes were synthesized.[349−351] These complexes were shown to be highly active for catalytic TH of aromatic ketones in the presence of 2-PrOH and NaOH. The corresponding alcohols were provided with up to 99% conversion and 97% ee.[349] The catalytic properties were obviously affected by substituent groups of the bridging moiety.

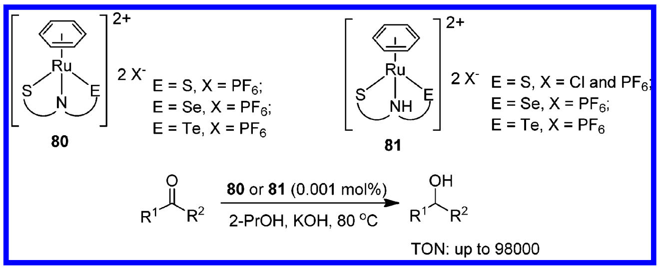
Half-sandwich ruthenium complexes containing pincer skeletons with P−N, bipyridine, α-amino-oximes, amino alcohol, Schiff base, thioamide backbones, and 1,3-diamines[352] have been recently described with applications in TH (Scheme 30). The ruthenium−arene complexes containing 4,4′-dimethoxy-2,2′-bipyridine (**74**) showed catalytic activity in the reduction of water-soluble and -insoluble ketones with the use of HCOONa as the hydrogen donor at pH 4.[353] The introduction of OH groups in the bipyridine moiety largely enhanced water solubility of the ruthenium catalyst. In addition, the hydrogen bond of the OH groups eventually induced metal−ligand bifunctional catalysis resulting in excellent performance in TH of ketones in aqueous media.[354] The new α-amino-oxime ligand **76** based on (*R*)-limonene provided an efficient route to a new ruthenium complex of α-amino-oxime that showed activity for enantioselective TH reactions of various ketones, giving high conversions but low ee values.[355] Yus et al.[356] reported that a cheap achiral, amino alcohol (2-amino-2-methylpropan-1-ol, **77**) was efficiently used as ligand in ruthenium−arene-mediated ATH of chiral *tert*-butylsulfinylimines to amines. Various primary amines were produced with up to >99% ee and excellent yields upon using both aromatic and aliphatic sulfinylimines with 2-PrOH as the hydrogen source (Scheme 31).[356] A new half-sandwich ruthenium compound readily prepared from $[RuCl_2(p\text{-cymene})]_2$ with the Schiff base scaffold **78** was examined as catalyst in the TH of ketones, and up to 1260 h^{-1} TOF was obtained.[357] Following the development of thio- ligand in ruthenium-catalyzed TH,[358] a new cationic half-sandwich complex of the type $[(\eta^6\text{-cymene})Ru(PPh_3)(L)]^+$ was synthesized as an air-stable salt. This complex contains a thioamide ligand **79** that is coordinated to Ru as a bidentate O, S donor with a typical piano-stool geometry.[359] Several ketones were hydrogenated to secondary alcohols in a TH process using this catalyst.[359]

Scheme 31. Ruthenium-Catalyzed ATH of Sulfinylimines



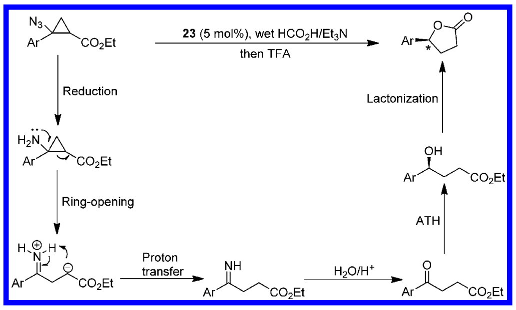
Singh's group[360,361] synthesized half-sandwich ruthenium(II) catalysts bearing tridentate (S−N−E or N−E−N)-type ligands (E = S, Se or Te). The catalysts **80** and **81** gave excellent results in the TH of ketones using 2-PrOH with TON values up to 98 000 (Scheme 32). The mechanistic study revealed that this process probably involved Ru−H bond formation.[361]

Scheme 32. TH of Ketones Using Half-Sandwich Ruthenium(II) Catalysts Bearing Tridentate Ligands



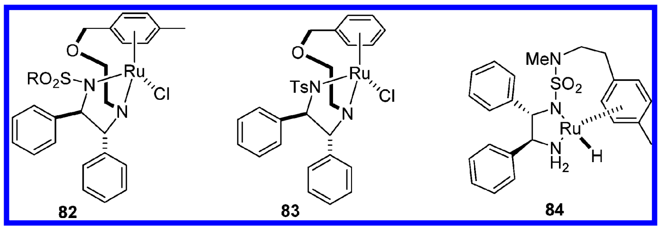
Recently, the early "tethered" Noyori catalysts were still important in TH,[362,363] mainly showing significant applications in the synthesis of functional compounds and in the exploration of new routes to "tethered" ruthenium catalysts.[364] The "tethered" half-sandwich catalyst **23** exhibited an unexpected directing effect in the ATH of hindered ketones. For example, a variety of alcohols were quantitatively formed with high ee values by reduction of hindered β-tetralones in the TH procedure.[365] The complex **23** was also found to be a good catalyst for the synthesis of enantioenriched γ-lactones with up to 94% ee through a four-step tandem process of azide reduction/cyclopropane ring cleavage/ATH of ketones/lactonization, using racemic *β*-azidocyclopropane carboxylates as starting materials (Scheme 33).[366]

Scheme 33. Synthesis of Enantioenriched *γ*-Substituted Lactones via ATH of *β*-Azidocyclopropane Carboxylates Using the Catalyst 23



The initial research on the synthesis and catalytic application of "ether-tethered" half-sandwich ruthenium complexes (**82** and **83**) was independently reported by the groups of Ikariya and Wills (Scheme 34).[367,368] The ATH of ketones was successfully conducted in 5:2 formic acid/triethylamine azeotropic mixture upon using compound **82** as catalyst. Remarkably corresponding chiral alcohols bearing a broad scope of substituents were enantioselectively synthesized with low catalyst loading, down to 0.0025 mol %.[367] Complex **83** also exhibited excellent catalytic performances for ATH of ketones under mild conditions.[368] Stephan et al.[369] observed that the new ruthenium(II) catalyst **84** featuring an enantiopure *N*,*C*-(*N*-ethylene-*N*-methyl-sulfamoyl)-tethered (DPEN-κ^2N,N')/η^6-toluene hybrid ligand was highly active and enantioselective in ATH of 1-naphthyl ketones to secondary 1-naphthyl alcohols in open air at rt in HCO_2H-Et_3N.

Scheme 34. "Tethered" Half-Sandwich Ruthenium TH Catalysts

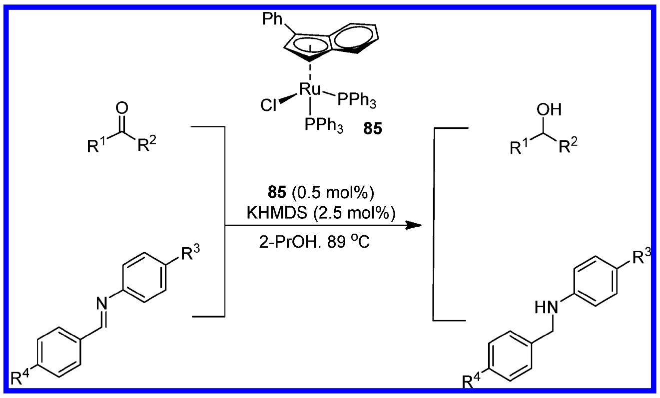


82 **83** **84**

In these reported "tethered" ruthenium−arene catalysts, both the persistent imposed coordination of the otherwise labile η^6-arene and the strong chelation of the sulfonamido-amine anchor led to prolonged life span of the active catalytic species. This resulted in a reinforced collective three-point ligation of the conjugate ligand to the ruthenium core, thereby decreasing the overall structure flexibility and rigidifing the stereoarray of the catalyst. These factors explain the enhanced catalytic performances.[370]

Besides Cp, Cp*, and arene, the indenyl moiety was also used as ligand in half-sandwich ruthenium TH catalysts. Indeed, the ruthenium phenylindenyl complex **85** was synthesized and employed as catalyst in TH of ketones, aromatic aldehydes, and primary imines.[371] In most of the cases, the desired alcohols and amine products were efficiently produced with excellent conversions when these reactions were carried out in 2-PrOH at 89 °C using catalytic amount of KHMDS as base (Scheme 35). Investigation of the tolerance to substrate variations showed that increasing the steric bulk of substrates caused the reaction to become more sluggish as expected; ketones with electron-withdrawing substituents displayed lower reactivity, and TH was faster for aliphatic than for aromatic ketones.[371]

Scheme 35. Efficient TH Catalysis Using a Ru Phenylindenyl Complex

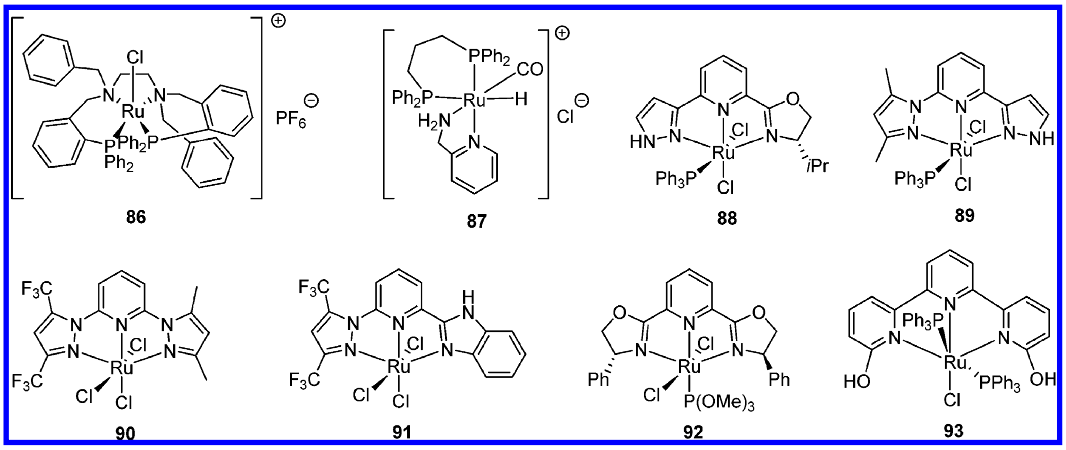


Not surprisingly, TH involving ruthenium complexes with bi- or polydentate backbones received ever-increasing attention in the past few years.[372−383] Numerous variations and modifications of conventional polydentate ligands including PNNP,[384−389] NNN,[390−396] CNN,[397−399] and NNO types,[400] NNP chelating fragments,[401] and PPPC[402] have been extensively investigated with the aim to explore more efficient ruthenium catalysts. Moreover, the tolerance of these conventional ruthenium catalysts to substrate variations, especially for the functional unsaturated compounds, has been investigated with polydentate ligands.

The TH of ketones, aldehydes, and imines using the well-established monofunctional (P^N^N^P)-ruthenium complex **86** possessing tertiary amines showed excellent activities with a diverse range of substrates at catalyst loadings down to the ppm level.[384] Comparison with the existing (P^N^N^P)-ruthenium catalysts revealed that the second functional part (usually provided by the secondary amine within the ligand backbone) was not needed in this catalyst.[384] Another new ruthenium complex **87** bearing a PNNP scaffold was synthesized through the reaction of $[RuHCl(CO)(PPh_3)(dppp)]$ (dppp = $Ph_2P(CH_2)_3PPh_2$) with 2-aminomethylpyridine. Catalyst **87** has been proven to be highly active in the TH of ketones using *i*PrOH as hydrogen donor in the presence of 2 mol % of NaO*i*Pr with low catalytic amount in the range from 0.2 to 0.004 mol %, giving TOF values up to 2.5×10^5 h^{-1}.[387]

The past few years have witnessed an extensive exploration of pyridine-based ruthenium catalysts for TH of a wide variety of substrates.[403−405] Yu and Pizzano et al. synthesized several symmetrical pyridine-based NNN-type ligands and the corresponding ruthenium complexes **88**−**93** (Scheme 36). Compound **88** containing a chiral pyridyl-based 1*H*-pyrazolyl−oxazolinyl ligand was shown to be a robust and productive catalyst for ATH of ketones under mild conditions, and a series of alcohols were obtained with good to excellent conversions and enantioselectivities within short times down to 5 min.[394] Furthermore, the activity of **88** was much higher than that of ruthenium pyridyl−pyrazolyl−oxazolinyl complexes featuring no NH functionality, which confirmed an outer-sphere mechanism for the involved "N−H" effect.[142] The "N−H"

Scheme 36. Selected Examples of Ru TH Catalysts with Polydentate Ligands

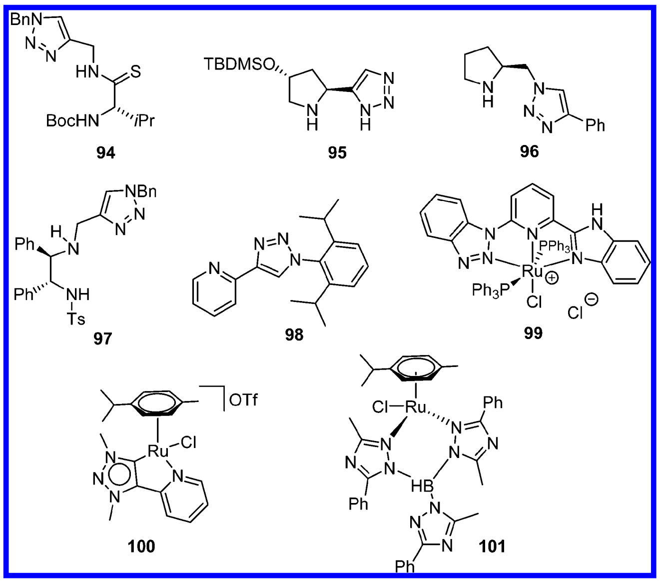


effect was also observed in the ruthenium pyrazolyl−pyridyl−pyrazole complexes **89** and **91**,[391,395] the catalyst **89** with β-NH functionality of the pyrazole arm amazingly reaching a final TOF up to 720 000 h^{-1}.[378] For the catalyst **91**, the use of the benzimidazol ligand with NH fragment provided 1.5−23 times higher TOF values than with the NCH_3-modified benzimidazole ligand.[391] The authors also showed that the compatibility of the trifluoromethylated pyrazolyl and unprotected benzimidazolyl was attributable to the high catalytic activity of catalyst **91**. In another report, the ruthenium complex **92** containing both a pybox (2,6-bis(oxazoline)pyridine) and a monodentate phosphite ligand was shown to be highly active in asymmetric TH of *N*-aryl imines using 2-PrOH as hydrogen source.[390] Szymczak's group[392] reported that 6,6′-dihydroxy terpyridine (dhtp), a rigid bifunctional ligand, was capable of directing proton transfer with metal-coordinated substrates. The formed ruthenium compound **93** showed good TH activities for many carbonyls and catalyzed the formation of a series of alcohol products, but the chemoselectivity was not satisfactory when a few carbonyl-containing olefins were tested.[392]

As complementary to an evolution of conventional polydentate ligands, several new ligand types have recently emerged, such as POP,[406] ONO,[407] CNC,[408] PPP,[409,410] SNS,[411] OPPS,[412] PNNNP,[413] and NOOPP.[414] These ligands were efficiently utilized to assist and activate ruthenium in TH processes.

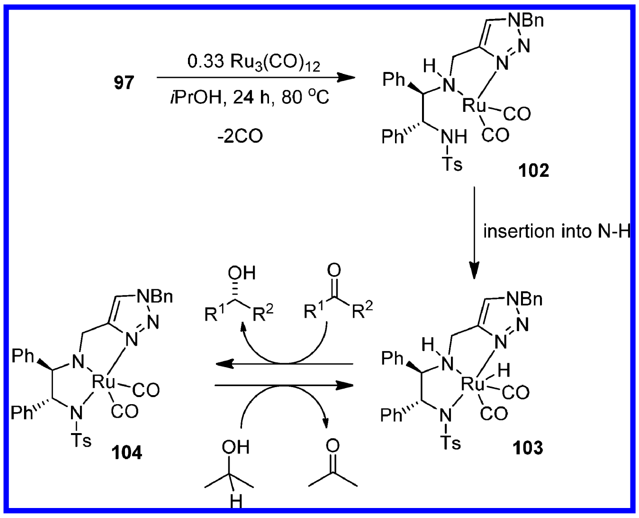
Mesoionic 1,2,3-triazoles, a subclass of NHCs and known as abnormal *N*-heterocyclic carbenes (aNHC), have recently found extensive use as ligands in coordination and organometallic chemistry, as well as in homogeneous catalysis. The use of 1,2,3-triazoles in catalysis has opened another vibrant field of research, because these ligands are accessible in a multitude of variations upon Cu^{I}-catalyzed azide alkyne cycloaddition (CuAAC click reaction). Moreover, these ligands benefit from specific σ-donor properties that are slightly stronger than those of classical imidazolium-derived systems.[415−417] TH with ruthenium complexes featuring a chelating triazolylidene ligand have appeared, and selected examples of ligands or complexes are gathered in Scheme 37. The 1,2,3-triazole-based ligands **94** and **95** displayed a good activity in assisting ruthenium-catalyzed ATH of ketones, but a closely related ligand **96** was less effective.[418,419] The tridentate diaminotriazole **97** in conjunction with $Ru_3(CO)_{12}$ in situ formed an efficient catalyst for ATH of ketones, and up to 93% enantioselectivities were determined with the use of 2-PrOH with the need for a base. Several alcohols were obtained with up to 99% conversions and 85% ee from *ortho*-substituted acetophenones.[420] A proposed mechanism for this catalysis involving **97** and $Ru_3(CO)_{12}$ is shown in Scheme 38. Starting from an initial reaction of **97** with fragmentation of $Ru_3(CO)_{12}$, a bidentate complex **102** was formed upon partial loss of CO, followed by insertion of ruthenium into the N−H(Ts) bond to form the ruthenium hydride **103** that transferred two hydrogen atoms to substrate to produce **104**. The completion of the catalytic cycle was achieved by treating **104** with 2-PrOH, which regenerates **103** (Scheme 38).[420]

Scheme 37. Triazolyl Ligands and Ruthenium-triazolyl TH Catalysts



The air- and moisture-stable ruthenium(II) complex **99** bearing an unsymmetrical benzimidazole-benzotriazole-pyridine ligand has been shown to be a robust and highly active catalyst for the TH of ketones in refluxing 2-propanol, reaching final TOFs up to 176 400 h^{-1}.[421] In addition, a RuH complex was isolated, and such a species was generally proposed as the actual catalytically active intermediate. The authors demonstrated that the excellent catalytic performances resulted from the hemilabile unsymmetrical coordinating environment around the central metal and "N−H" effect.[421] The two half-sandwich ruthenium complexes **100** and **101** containing a

Scheme 38. Proposed Mechanism of TH Catalysis by 97/$Ru_3(CO)_{12}$



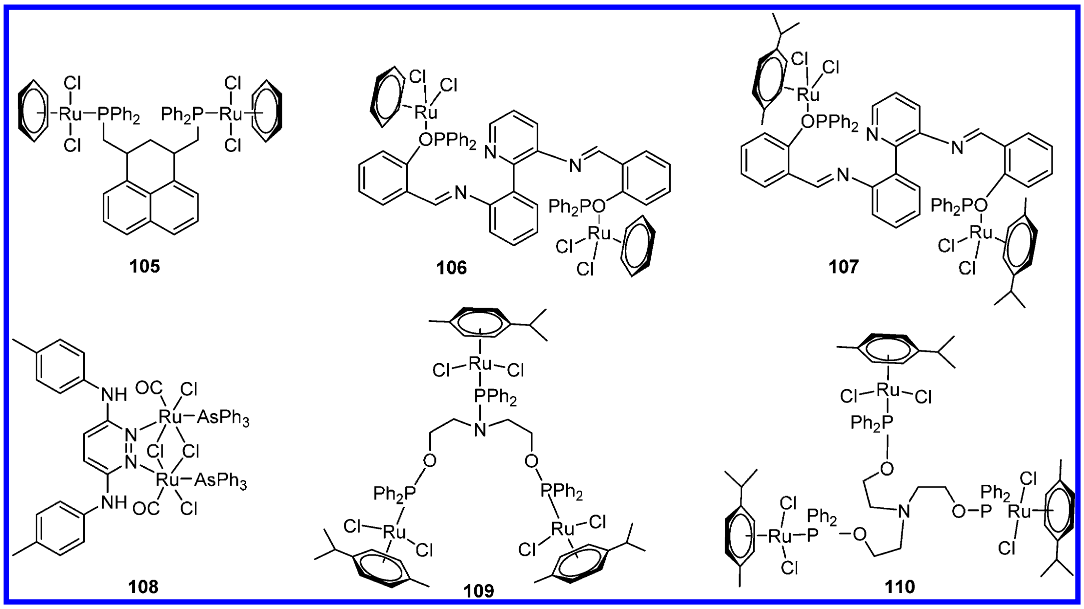
chelating 1,2,3-triazolyl or 1,2,4-triazolyl units also exhibited good catalytic behaviors in TH of carbonyls.[422,423]

Binuclear and trinuclear ruthenium complexes have been recently established as a promising new class of catalysts for TH (Scheme 39). The Li and Aydemir groups[424,425] obtained the new stable phosphinite-bridged dinuclear ruthenium arene complexes **106** and **107** prepared by metalation of the phosphinite-containing Schiff base ligand with $[Ru(\eta^6\text{-arene})(\mu\text{-}Cl)Cl]_2$. The investigation of their catalytic performances showed that **106** and **107** catalyzed TH of aromatic ketones giving TOF values as high as 530 h^{-1}.[425] A binuclear ruthenium(II) pyridazine complex **108** was found to be an efficient catalyst for the same transformation.[426] Two new versatile tridentate aminophosphine−phosphinite and phosphinite ligands and their trinuclear neutral ruthenium(II) dichloro complexes were synthesized and tested in TH of ketones in 2-PrOH solution, and when 4-fluoro acetophenone was employed a TOF of 1176 h^{-1} was obtained with catalyst **109**.[427]

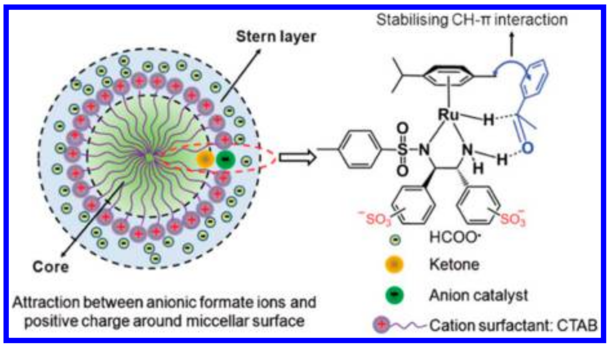
Water is an ideal reaction medium for catalysis, due to its inexpensive, "green", and totally innoxious properties. Moreover, the use of water can sometimes lead to remarkable rate acceleration in catalysis as compared to organic solvents, this phenomenon being called the "water effect". TH in water was relatively unstudied until a few years ago.[128,212,428] Various approaches using ruthenium catalysts containing water-soluble ligands, however, have been investigated; in particular, polyethylene-glycol-anchored[429,430] and aryl-sulfonated[91,221,431] TsDPEN-type ligands were synthesized. Subsequently some water-soluble polymer-supported,[252,432,433] chitosan-anchored[434] or surface-active[435,436] ruthenium catalysts have been used in TH reactions. Surfactants are useful to significantly improve the catalytic performances of water-soluble ruthenium catalysts.[437−439] A water-soluble anionic ligand derived from DPEN (DPEN = 1,2-diphenylethylenediamine) skeleton bearing two hydrophilic anionic sulfate groups was readily prepared and used to mediate ATH of ketones in aqueous formate in the presence of the ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$.[439] Considerable enhancement of activity was observed upon using a cationic surfactant such as CTAB (cetyltrimethylammonium bromide) or CPB (cetylpyridine bromide), presumably caused by accelerated transformation of formate ions from aqueous solution to micellar phases (Scheme 40). The water-soluble ligand was reused for 21 reaction cycles, and high conversion and enantioselectivity remained in the ATH of acetophenone with CPB as the surfactant.[439]

The synthesis of asymmetric or asymmetric functional products for various applications in medical science, bioscience, material science and environmental science is one of the ultimate aims of design and exploration of effective catalysts. Both development of substrate diversity[440−443] and synthesis of functional products are the most notable trends in the area of ruthenium-catalyzed TH in the past few years. A plethora of intermediates and final compounds with interesting properties have been successfully synthesized through TH using various ruthenium catalysts including chiral β-hydroxy sulfones,[444]

Scheme 39. Binuclear and Trinuclear Ru TH Catalysts



Scheme 40. Proposed Mechanism for ATH of Acetophenone in CTAB-Formed Micelle[a]



[a]Reprinted with permission from ref 439. Copyright 2013 Royal Society of Chemistry.

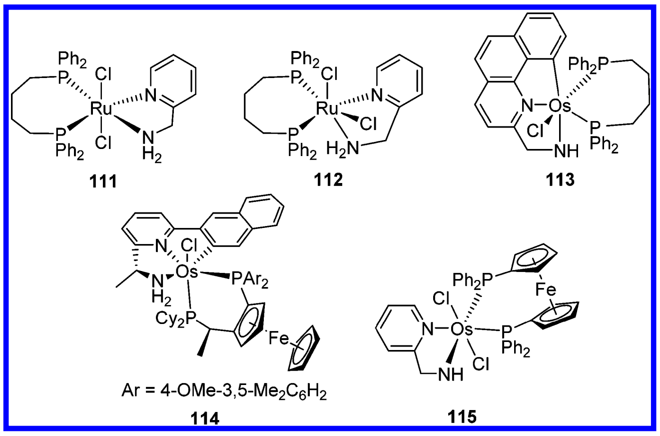
enantiopure (+)-yashabushitriol,[445] exocyclic 1,3-dienes,[446] γ-butyrolactones,[447] α-trifluoromethyl arylmethylamines,[448] acyclic α-trifluoromethylamines,[449] monoprotected 1,2-dihydroxyphosphonates,[450] *syn*-(*S*,*S*)-1,2-diols,[451] γ-valerolactone,[452] almorexant,[453] *anti*-β-amido-α-hydroxy esters,[454] functionalized 1-oxo-1-phenyl-2-acetic acids,[455] (*S*,*S*)-(−)-yashabushidiol B,[456] racemic or enantiomerically enriched *N*-benzyl-(3-aminomethyl glutarimide) derivatives,[457] *anti*-β-hydroxy-α-amino acids,[458] (*S*)-(+)-lennoxamine,[459] *anti*-β-hydroxy-α-amido esters,[460,461] chiral epoxy quinol,[462] anti Alzheimer's drug Ladostigil (TV3326),[463] tolvaptan,[464] *syn*-β-hydroxy amides,[465] and so on.

2.1.3. Osmium-Based Catalysts.

Osmium-catalyzed TH has been rarely studied, because osmium catalysts were generally regarded as less active than ruthenium, rhodium, and iridium analogues.[195] A few recent examples seem to indicate that certain osmium complexes exhibit high and comparable efficiency to ruthenium counterparts.

Baratta and co-workers devoted many efforts to this field (Scheme 41). They prepared the mixture of complexes **111** and **112** through reaction of $Ph_2P(CH_2)_4PPh_2$ with $[OsCl_2(PPh_3)_3]$ and Pyme (Pyme = 1-(pyridine-2-yl)methanamine). Up to 5.7 × 10^5 h^{-1} TOF was determined in TH involving ketones using 0.05−0.001 mol % of this mixed catalyst.[194] Several CNN pincer osmium complexes such as **113** and **114** with $Ph_2P(CH_2)_4PPh_2$ or Josiphos units were also designed and readily synthesized by the same group[192,193,466] who observed that these osmium catalysts exhibited exceptionally high efficiency for TH of ketones with very high TOFs (up to 1.8 × 10^6 h^{-1}) at very low loading (0.005−0.01 mol %). Indeed, the catalytic activity of **113** was even higher than that of its ruthenium analogue (1.8 × 10^6 vs 1.6 × 10^6 h^{-1}) when acetophenone was employed as test substrate.[192] The new osmium complex **115** containing both dppf (1,1′-bis-(diphenylphosphino)ferrocene) and ampy (2-aminomethylpyridine) fragments[467] was shown to efficiently reduce various ketones and aldehydes by means of TH using 0.005−0.1 mol % of catalyst at 82 °C with TOF values up to 3.0 × 105 h^{-1}. Interestingly, the reaction rate with the catalyst **115** was higher than that of its ruthenium analogue.[467]

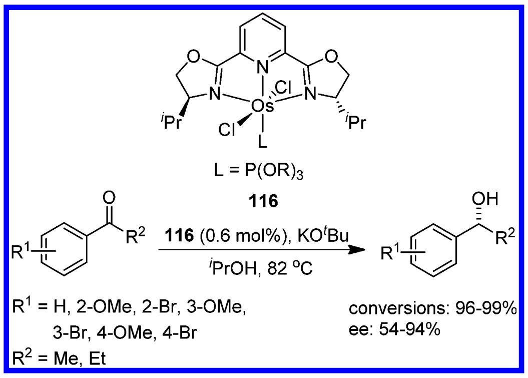
Scheme 41. Ru and Os TH Catalysts Synthesized by Baratta and Co-workers



Osmium(II)-half-sandwich complexes with L-α-amino carboxylate ligands in the forms of neutral mononuclear complex or cationic trimers were obtained and utilized as catalysts in ATH of ketones using 2-PrOH as hydrogen donor, and up to 82% ee value was obtained.[468] The authors took the enantiodifferentiation into account by assuming that Noyori's bifunctional mechanism was operating.

In 2013, Gamasa's group[469] reported that the presynthesized complexes *trans*-$[OsCl_2(L)\{(S,S)\text{-}^{i}Pr\text{-pybox}\}]$ (L = $P(OR)_3$; R = Me, Et, ^{i}Pr, Ph ; (*S*,*S*)-^{i}Pr-pybox = 2,6-bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine), **116**, served as catalysts for ATH of ketones (Scheme 42). When the reaction of acetophenone was conducted in 2-PrOH at 82 °C in the presence of 0.6 mol % **116** and 12% KO^{t}Bu, the corresponding alcohol was produced with 96−99% conversion and 86−94% ee. To probe the applicability scope of the catalysts, a series of aromatic ketones with various substituents were examined in the catalytic system, and within 60 min the desired alcohol products were obtained with nearly complete conversion and 54−94% ee.[469]

Scheme 42. ETH of Ketones Catalyzed by the Enantiopure Osmium(II) pybox Complexes 116

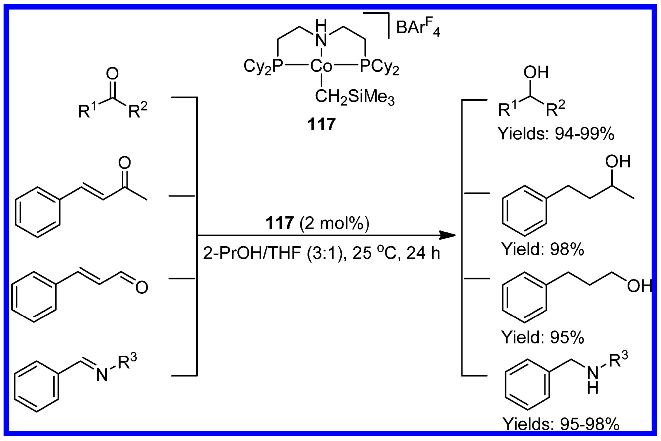


2.1.4. Cobalt-Based Catalysts.

Cobalt is one of the earth-abundant metals; thus cobalt catalysts are all the more appreciated as they provide precious hydrogenation performances,[470] even in the TH process.[471,472]

An easily accessible cobalt complex **117** showed excellent activity in diverse ranges of substrates including ketones, aldehydes, imines, and α,β-unsaturated carbonyls, and provided the alcohol and amine products in 94−99% yields with TH under mild conditions (Scheme 43).[473] Interestingly, the use of conjugated substrates including *trans*-4-phenyl-3-buten-2-one and cinnamaldehyde revealed that both C═C and C═O were completely reduced, affording the corresponding alcohols in 98% and 95% yields, respectively. Furthermore, mechanistic studies indicated that cobalt−ligand cooperativity was not

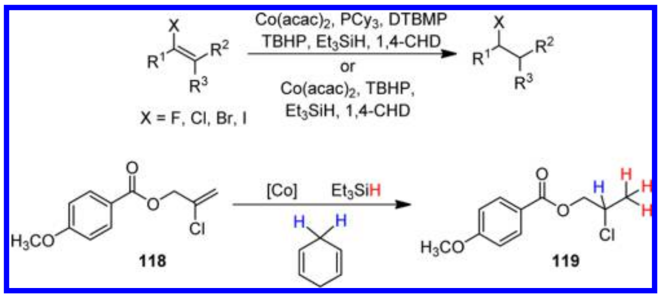
Scheme 43. Cobalt-Catalyzed TH of C=O, C=C, and C=N Bonds



required for catalysis that was conducted by a cobalt-monohydride intermediate.[473]

Herzon's group[474] reported a new route for the selective hydrogenation of alkenyl halides to alkyl halides catalyzed by $[Co(acac)_2]$ through a HT pathway using both triethylsilane and 1,4-cyclohexadiene as hydrogen donors. This procedure tolerated various alkenyl compounds with fluoro, chloro, bromo, and iodo substituents, and the desired alkyl halides were isolated in moderate to good yields (Scheme 44). Isotopic labeling experiments using **118** as test model suggested that the terminal hydrogen atom of the product **119** derived primarily from triethylsilane and that internal hydrogen atom derived from 1,4-cyclohexadiene (1,4-CHD) (Scheme 44).[474]

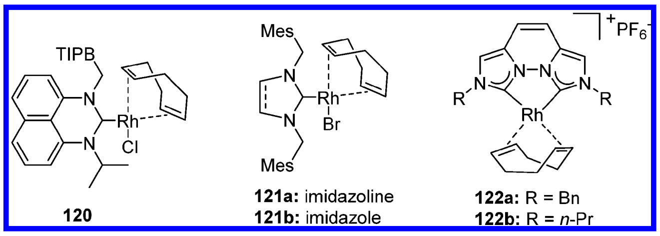
Scheme 44. Selective TH of Alkenyl Halides to Alkyl Halides over Cobalt Catalyst



These pioneered examples of homogeneous cobalt catalysts for TH should trigger the design, synthesis, and catalytic applications of effective cobalt catalysts.

2.1.5. Rhodium-Based Catalysts. On the basis of previous studies on rhodium−NHC catalysts for TH, some new counterparts were reported. Complexes **120** and **121** of the type [Rh(NHC)X(COD)] were well-established, and their catalytic properties have been evaluated in TH of ketones (Scheme 45).[475,476] Catalyst **120** that contains a perimidin-2-ylidene NHC exhibited low catalytic activity, probably due to the weak 6-donocity of the 1,3-disubstituted perimidin-2-ylidene ligand.[475] On the other hand, catalyst **121** bearing symmetric mesityl (Mes) substituents at N1 and N3 positions of imidazoline or imidazole efficiently promoted the TH reaction, giving almost complete conversion within 2 h with 0.5 mol % of catalyst loading.[476] Comparative studies of the efficiencies indicated that the introduction of the CH_2Mes group to the nitrogen atoms increased TH performances, and the catalyst **121a** with imidazoline induced a faster reaction than **121b** with imidazole. The pyridazine-annelated bis-NHC cationic rhodium complexes **122** showed a good activity in TH of ketones at 80 °C.[477] The IR stretching frequencies confirmed that the order of electron donor effect is triazole-derived biscarbene ibitz > pyridazine-annelated bis-NHC bearing *n*-Pr > 2,2′-dipyridine.[477]

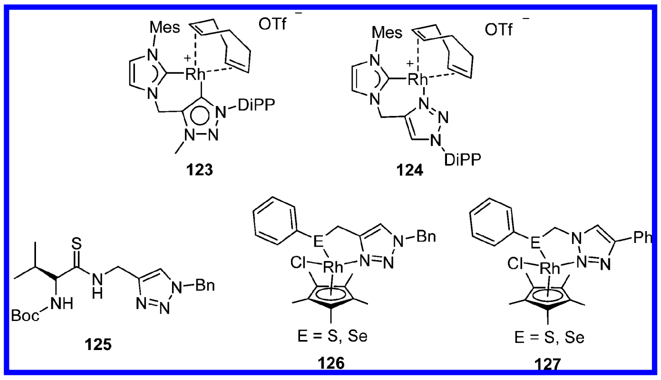
Scheme 45. Recent Examples of Rhodium TH Catalysts



Given the increasing interest in 1,2,3-triazolyl ligands in homogeneous transition-metal catalysis, the catalytic applications of these ligands were also investigated in rhodium-catalyzed TH. As mentioned in the section on “ruthenium-based catalysts”, the 1,2,3-triazol-5-ylidene (tzNHC) ligands have become a rising star in catalysis. A bidentate monovalent rhodium-cod complex (**123**) with square-planar geometry that contains tzNHC and an Arduengo-type NHC motif was synthesized. This tzNHC-NHC ligand possesses stronger electron-donating properties than classic di-NHC ligands. Complex **123** was successfully used as catalyst for the TH of carbonyls, imine, and diene using 2-PrOH as the hydrogen source.[478] More importantly, catalyst **123** was much more active than its analogue **124** in which the triazolyl moiety coordinates through a nitrogen donor. Adolfsson and Singh et al.[418,479] synthesized a series of 1,2,3-triazole-functionalized L-amino acid thioamide and organochalcogen ligands. The combination of the L-amino acid thioamide **125** with the half-sandwich rhodium precursor $[RhCl_2Cp^*]_2$ provided good catalytic results in the ATH of ketones, providing moderate to excellent conversions and up to 93% ee.[418] The complexes **127** having the N(2) atom of 1,2,3-triazole coordinated to the rhodium center have shown better activity in the TH of ketones than **126** in which N(3) is involved in ligation. Moreover, the reactivity with respect to the ligands is in the order Se > S.[479] The mechanistic studies indicated that the Rh species that had lost the Cp* ligand was an intermediate in the catalytic cycle. The iridium analogues of complexes **123**, **124**, **126**, and **127** were also synthesized and exhibited even better catalytic performances in TH reactions than these rhodium counterparts (Scheme 46).[478,479]

The half-sandwich rhodium complexes are the most extensively used rhodium TH catalysts (Scheme 47).[480−485] An easily accessible Rh(III)-η^5-Cp* complex **128** containing a bis(phosphino)amine ligand catalyzed TH of substituted acetophenones in 2-PrOH at 82 °C, and 94−99% conversions and 5−50 h^{-1} TOF values were obtained.[486] Treatment of $[Rh(\eta^5\text{-}Cp^*)Cl(\mu\text{-}Cl)]_2$ with the ligand 1,2-bis(phenylthiomethyl)benzene or 1,2-bis(phenylselenomethyl)benzene followed by reaction with NH_4PF_6 yielded the air- and moisture-stable complexes **129** that were the first rhodium TH catalysts of carbonyls in glycerol, a cheap, nontoxic, biodegradable, and easily available byproduct in biodiesel fuel production, obtained from the saponification of triglycerides of

Scheme 46. Rhodium TH Catalysts Containing Triazolyl Ligands



123 124 125

E = S, Se
126

E = S, Se
127

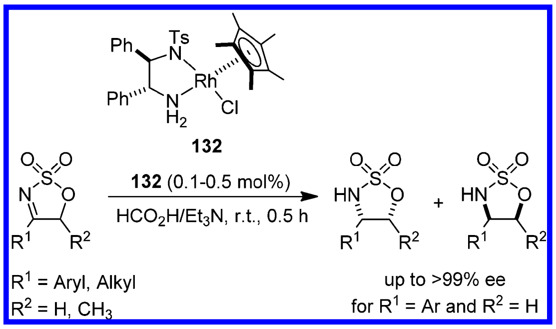
all natural fats and oils. Complex **129b** with Se atoms displayed better activity than the S-containing analogue **129a**.[487]

Complexes **130a** and **130b** having *ortho*- or *meta*-phenyl-bridged pyridinium and [RhCp*(NN)Cl]$^+$ centers and the complex **130c** without *meta*-phenyl-bridged pyridinium were shown to be TH catalysts of aromatic imines to amine compounds with formate ion acting as the hydride source and formic acid acting as buffer.[488] The catalytic results revealed that **130a** was far more active than the two other complexes. Indeed **130a** efficiently promoted the TH involving a variety of imines with excellent yields in most cases. On the contrary, **130b** and **130c** only gave less than 60% yields. Moreover, an inner-sphere TH mechanism, in which the imine binds to the rhodium center, was proposed upon observation of the considerably lower conversion of the electron-deficient 4-nitrophenylimine. Further investigation suggested that two issues are crucial for the TH of imines by **130a**: (1) the rhodium-catalyzed reduction of the phenyl-bridged pyridinium group to the corresponding dihydropyridine compound that provides the site for imine coordination, and (2) the TH from the formed dihydropyridine compound to the imines activated by the rhodium center.[488]

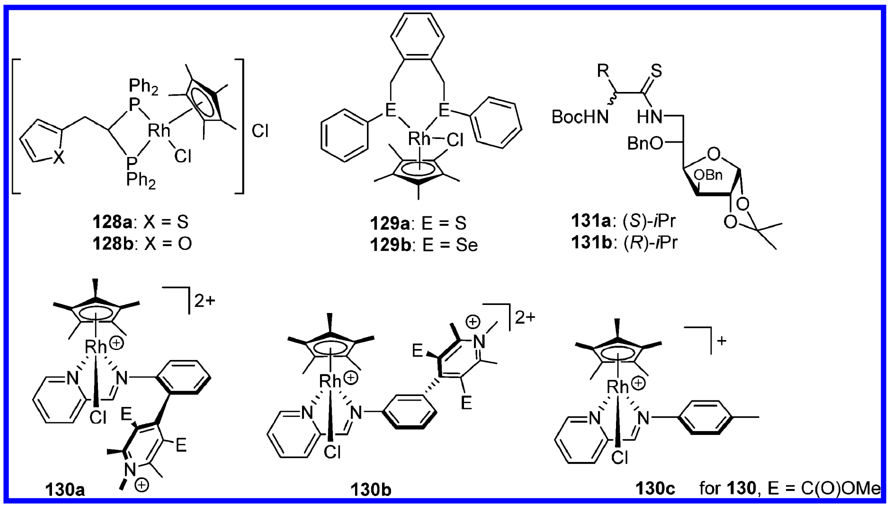
Diéguez and co-workers[489] prepared various new carbohydrate-based modular amino acid thioamide ligands and employed them in catalytic ATH of ketones with the use of Rh–Cp* or Rh–arene precursors. Compounds **131** were the most powerful ligands in the series, and it was found that quantitative transformation was achieved by combination of **131** with [RhCl$_2$Cp*]$_2$ for TH of acetophenone in 2-PrOH/THF at rt in the presence of NaO^{i}Pr and LiCl. To probe the tolerance of this system to substrate scope, a series of ketones including very challenging heteroaromatic ones were examined using this protocol delivering the corresponding alcohols with excellent conversions in most cases and high level of enantioselectivities. Interestingly, the changes of the absolute configuration of the α-amino acid preceded the formation of both enantiomers of the alcohols.[489]

Because of the nature of the nitrogen substituent and stereochemistry about the C═N double bond, the ATH of imines to chiral amines is relatively challenging. Cyclic sulfamidates bearing a chiral carbon functionalized by an amine moiety and a reactive cyclic sulfamidate group are useful precursors in organic synthesis. Lee's group[490] found that the half-sandwich rhodium catalyst **132** served as a highly effective catalyst in the ATH of cyclic sulfamidate imines with the mixture of HCO$_2$H and Et$_3$N as hydrogen donor within 30 min at rt, producing 16 cyclic sulfamidates with a wide range of substituents in excellent yields ranging from 91% to 99% and up to 99% ee's (Scheme 48). Moreover, the ATH of 4,5-disubstituted imines (R^1 = Ph, R^2 = CH$_3$) bearing preexisting stereogenic centers was accompanied by dynamic kinetic resolution, which indicated that the stereochemistry of the rhodium catalyst **132** controlled the stereochemistry of the ATH well.[490]

Scheme 48. Enantioselective Synthesis of Cyclic Sulfamidates Using Chiral Rhodium-Catalyzed ATH



Scheme 47. Half-Sandwich Rhodium TH Catalysts and Ligands



128a: X = S
128b: X = O

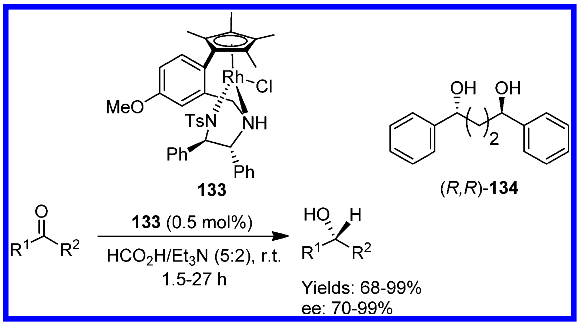
129a: E = S
129b: E = Se

131a: (*S*)-*i*Pr
131b: (*R*)-*i*Pr

130a **130b** **130c** for **130**, E = C(O)OMe

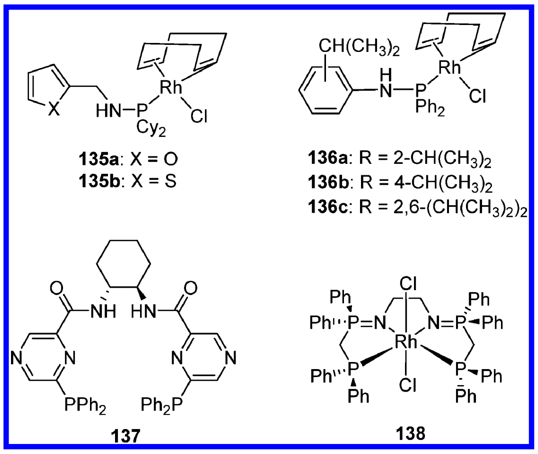
The new "tethered" half-sandwich rhodium complex **133** containing TsDPEN and a functionalized Cp* unit catalyzed ATH of ketones with the HCO_2H/Et_3N mixture as hydrogen source under mild conditions, giving various alcohols in 68–99% yields and 70–99% ee's (Scheme 49).[491] In this catalytic process, a diol (*R*,*R*)-**134** was effectively produced with an excellent 96:4 DL/meso ratio and >99% ee. (*R*,*R*)-**134** usually is a precursor of (2*R*,5*R*)-diphenylpyrrolidine that has extensive application in the area of asymmetric organocatalysis.

Scheme 49. Tethered Rh(III) Complex in ATH of Ketones



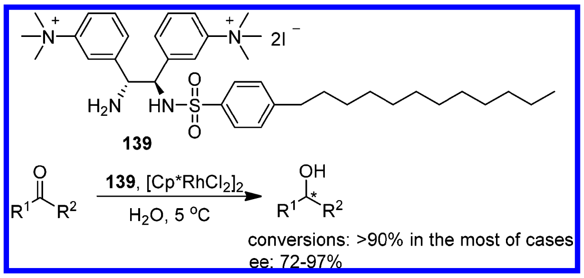
Given the considerably growing applications of functional P- and P–N-based ligands in catalysis, some rhodium complexes with these ligands were shown to be active in the TH of unsaturated compounds (Scheme 50). Aydemir's group[492,493] synthesized a series of rhodium complexes of aminophosphine containing the cyclohexyl moiety. Complex **135a** containing a furan unit exhibited good catalytic performances in the TH of acetophenone derivatives with 2-PrOH and NaOH, and 233–576 h^{-1} TOF values were measured with 4-fluoro-, 4-chloro-, 4-bromo-, 2-methoxy-, and 4-methoxy-acetophenones as starting materials. On the contrary, only 8–16 h^{-1} TOF values were determined when **135b** bearing a thienyl fragment was employed as catalyst in the same reactions.[492] Starting from $[Rh(COD)Cl]_2$, three new neutral rhodium complexes **136a**, **136b**, and **136c** with P-NH ligands were synthesized and applied to the catalytic TH of aromatic ketones. The catalytic performance of **136b** containing an *i*-Pr group at the *para*-position was superior to those of **136a** and **136c**. With the use of **136b**, complete conversions were observed, and the TOF values were as high as 588 h^{-1}.[493] The phosphane ligand **137** featuring a hydrophilic pyrazine was a good promoter in rhodium-mediated ATH of acetophenone in terms of both activity and enantioselectivity.[494] TH of polar bonds including C=O and C=N bonds was catalyzed by an iminophosphorane-based $[P_2N_2]$ rhodium complex **138**, although the reaction rate was relatively low.[495]

Scheme 50. P-Based Ligands and Rhodium TH Catalysts



Water-soluble ligands and catalysts were reported and applied in the field of rhodium-catalyzed TH, which proceeded smoothly in water and produced various functional compounds.[439,496,497] On the basis of the fact that the formation of micelles through addition of a cationic surfactant in water could improve the catalytic property of transition-metal catalysts in TH, a cationic amphiphilic surfactant-type ligand **139** and the corresponding chiral rhodium–Cp* catalyst were reported by Deng's group.[498] These authors observed that a chiral micellar rhodium catalyst formed in water by association of the in situ assembled surfactant-type rhodium catalyst was an excellent catalyst in ATH of aliphatic ketones, and more than 90% conversions (in most cases) and 72–97% ee values were obtained with this protocol (Scheme 51). The high level of enantioselectivity was taken into account by synergistic effects between the rhodium-catalyzed center and the hydrophobic microenvironment of the core. Specifically, the existence of a probable transition state stabilized by CH–π interaction between the substrate and the rhodium center was proposed. In the transition state, the steric interaction of the alkyl groups of the aliphatic ketones with the Cp* unit of the amphiphilic catalyst controlled the stereochemistry. In addition, the high enantioselectivity in the reduction may also benefit from hydrophobic interactions between the alkyl chains of the aliphatic ketones and the catalyst in the metallo-micelle (Scheme 52).[498]

Scheme 51. Rhodium Catalyst with a Chiral Surfactant for ATH of Aliphatic Ketones in Water



On the basis of the rhodium-catalyzed TH, several functional products or backbones showing potential applications in various areas have been successfully synthesized. These compounds include functional amines,[499] formanilides,[499] tetrahydropyridines,[500] piperidines,[500] chiral chroman-4-ol,[501] monosubstituted malononitriles,[502] and tetrahydroquinolines.[503]

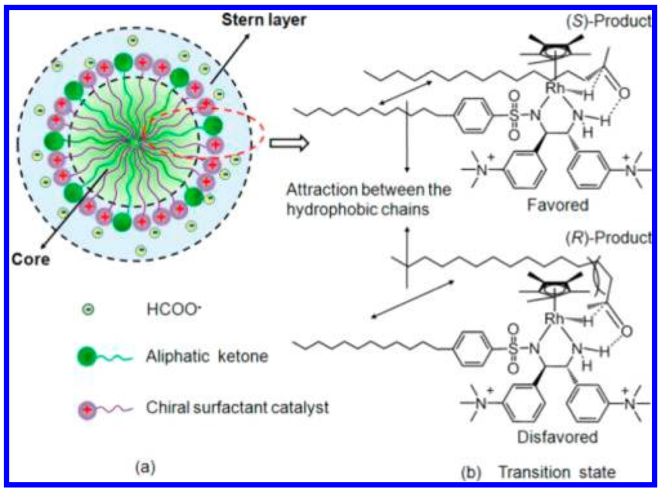
2.1.6. Iridium-Based Catalysts.

Iridium-based TH systems are the most active catalysts in TH, in particular ATH, and have thus recently attracted the attention of a number of research groups. Interest in this area is growing[54,263,265,504] since the pioneering work on iridium-catalyzed TH of ketones by Mestroni et al.[505,506] Various types of iridium complexes have been studied, and the catalytic systems will be presented here according to the structures of these unsupported iridium catalysts.

One of the most outstanding examples is the family of iridium–NHC complexes.[507] A series of new iridium–NHC

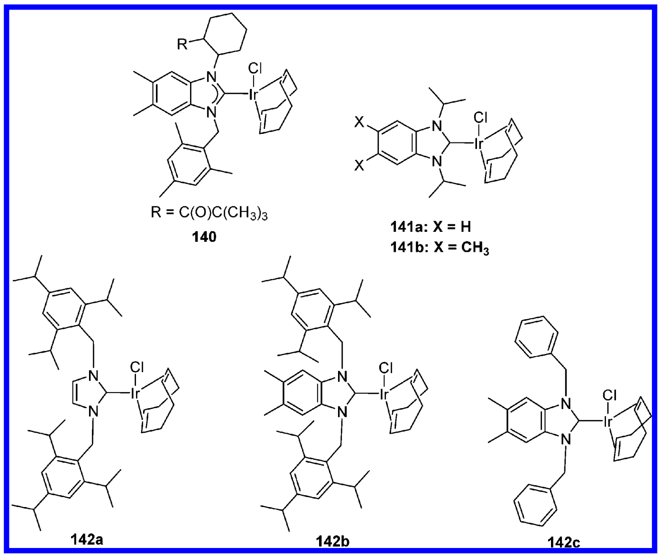
DOI: 10.1021/acs.chemrev.5b00203

Scheme 52. Proposed Mechanism for the ATH of Aliphatic Ketones in the Metallomicelle Formed with a Chiral Surfactant-Type Catalyst[a]



[a] Reprinted with permission from ref 498. Copyright 2012 American Chemical Society.

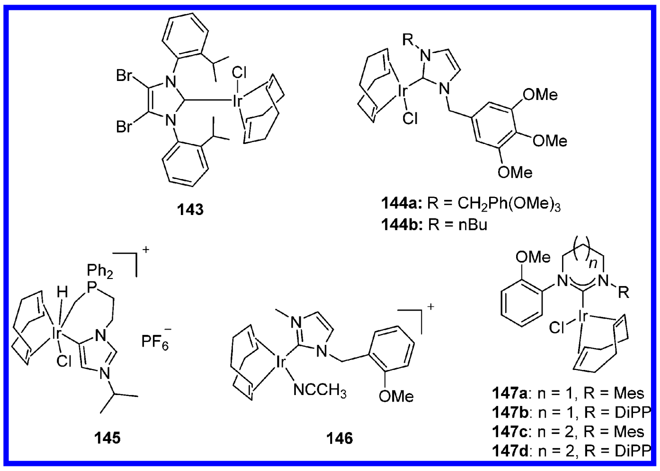
Scheme 53. Iridium−NHC Complexes Synthesized by Gülcemal's Group



complexes were synthesized through transmetalation reactions from the in situ prepared silver(I)−NHC complexes by Gülcemal's group (Scheme 53). Good results have been obtained in the reduction of carbonyls in the TH process using the ester-functionalized iridium(I) complex **140** as catalyst showing that >99% conversions and 96−99% yields were achieved, while various carbonyls were hydrogenated by 0.1 mol % of **140** using 2-PrOH as hydrogen source within 1.5−6 h.[508] The TH of carbonyls catalyzed by **141** and **142** was completed in very short reaction times down to 2 min, reaching 12 000 h^{-1} TOF. The influence of various substituents on the reactivity of the complexes was examined, and the complex **142b** showed the best activity.[509,510] Catalyst **142b** was also shown to be highly efficient in the TH of imines to amines with a TOF of 800 h^{-1}.[510] The high efficiency of catalyst **142** was attributed to the existence of both flexible and sterically demanding benzyl substituent(s) on the N atom(s) of NHC and a strong σ donor 5,6-dimethylbenzimidazol-2-ylidene skeleton. This study should bring about more attention to the use of alkylated benzyl-functionalized 5,6-dimethylbenzimidazole NHC ligands in homogeneous catalysis.

An air-stable NHC, IPrBr, and its iridium complex **143** were prepared, and the catalytic performance of this complex in TH of acetophenone was found to be comparable or to surpass that of the IPr-based iridium complex.[511] Colacino et al.[512] reported iridium−NHC conclexes bearing 3,4,5-trimethoxybenzyl *N*-substituents, taking **144a** and **144b** as examples (Scheme 54).

Scheme 54. Selected Examples of Iridium−NHC TH Catalysts

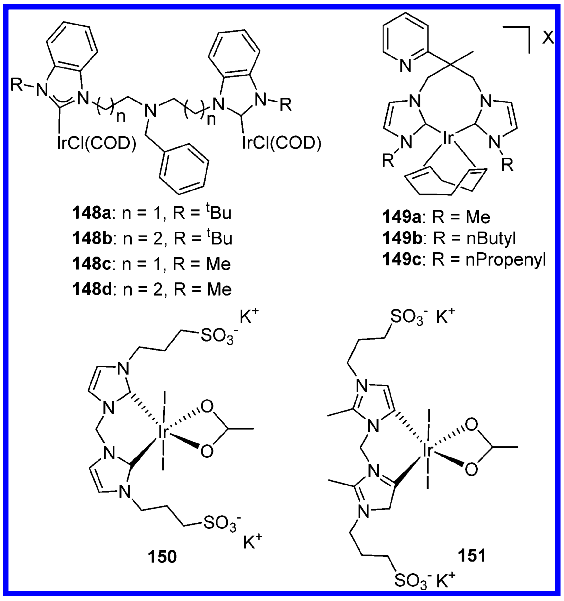


Catalytic studies indicated that the TH of ketones and aldehydes that were achieved using **144a** or **144b** as catalyst with glycerol disclosed higher activities than with other iridium−NHC complexes. In addition, tremendously increased reaction rates were observed with the aid of each of microwave and ultrasound techniques, in particular with the later. Interestingly, due to the strong reducing-agent nature of glycerol, iridium nanoparticles in the size of 2−3 nm with uniform and narrow size distribution were formed in the TH process, which was confirmed by both transmission electron microscopy (TEM) and UV−vis analysis.[512] Other iridium catalysts with various mono-NHC units were also successfully synthesized and used such as complex **145** containing an abnormal NHC,[513] **146** functionalized by a hemilabile NHC,[514] and **147** containing a NHC with an extended ring and a donor substituent.[515] Both **146** and **147** were extremely effective catalysts. TOF of 4622 h^{-1} was obtained in the reaction of cyclohexanone borrowing hydrogen from 2-PrOH using catalyst **146**; the methoxy group of the functionalized NHC ligands produced a positive effect on the catalytic activity.[514] The iridium catalysts **147** with various substituents provided almost 100% conversion with as low as 0.01 mol % catalyst loading.[515]

A series of new binuclear iridium complexes with a flexible linear linker connecting two NHC fragments was obtained by facile transmetalation of their silver analogues with the precursor complex [Ir(COD)Cl]$_2$.[516] The generated complexes **148** with axial chirality featured by 1-*tert*-butylimidazole or 1-methylbenzimidazole groups proved to be active in the catalytic TH of both acetophenone and *N*-benzylideneaniline in 2-PrOH in the presence of KO^{t}Bu.

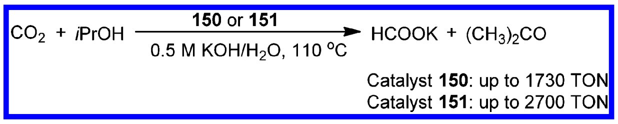
As a family of well-established powerful chelating ligands, bis-NHCs have received increasing interest in homogeneous TH catalysis (Scheme 55). Metalation of the bis-NHCs produced iridium complexes having various CNC donor ligands. In these complexes, a chelating bis(NHC) core is supplemented by a hemilabile pyridyl donor.[517] The performances of the complexes **149** in the TH of ketones were evaluated under various reaction conditions with a variety of substrates allowing comparison of the influence of the NHC ligand on the catalytic performances. Several desired alcohols were obtained in 30−60 min using a catalytic amount of 0.01−0.3 mol %.[517]

Scheme 55. Dinuclear Iridium−NHC and Iridium−Bis-NHC TH Catalysts



CO$_2$ activation is an important challenge involving conversion of CO$_2$ to C1 building block toward the formation of organic molecules. Meanwhile, this transformation participates in addressing the question of global warming and a consequent series of environmental problems caused by the greenhouse gas CO$_2$. Peris' group[518,519] proposed for the first time that 2-PrOH could be utilized as the hydrogen donor for CO$_2$ activation by the TH methodology. Two new water-soluble iridium−bis-NHC complexes, **150** and **151**, incorporating sulfonate functionalities, were readily synthesized and tested as catalysts in TH of CO$_2$ to formate in 2-PrOH. The results revealed that complex **151** with up to 2700 TON value was the most active catalyst for the reduction of CO$_2$ under the TH conditions (Scheme 56).[518] These two versatile catalysts also catalyze the TH of several organic carbonyl compounds including olefins, alkynes, and *α*,*β*-unsaturated ketones using glycerol as both solvent and hydrogen donor; moderate activities were obtained.[520]

Scheme 56. TH of CO$_2$ Using 2-PrOH as Hydrogen Source in the Presence of the Iridium Catalyst 150 or 151



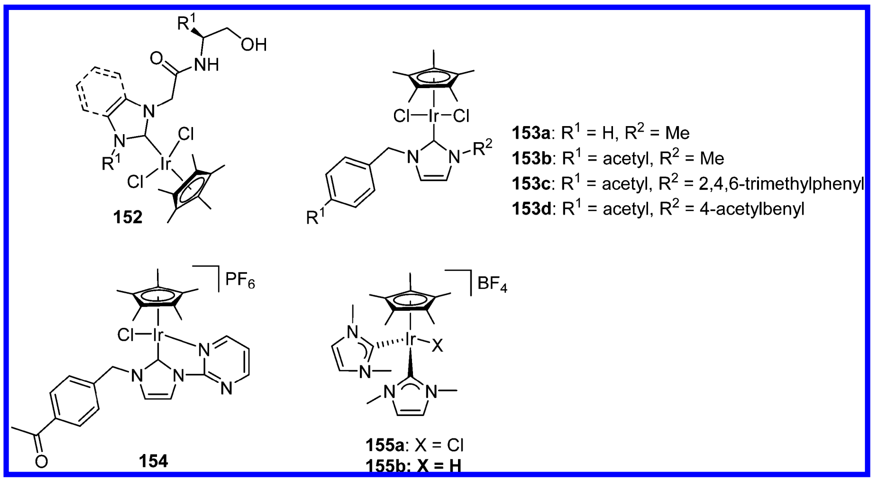
The family of iridium complexes with half-sandwich structure is an important component of the family of iridium catalysts that are used in TH (Scheme 57).[521−526] Recent examples of half-sandwich iridium catalysts incorporated a variety of coordinating ligands mainly based on N, P, C elements. These ligands included mono-NHC, bis-NHC, triazolyl, pyridyl, 2,2′-bipyridyl, *N*-[*p*-(trifluoromethyl)-benzenesulfonyl]-1,2-ethylenediamine) (CF$_3$TsEN), *N*-(camphorsulfonyl)-1,2-diphenylethylenediamine (CsDPEN), and *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN) scaffolds.

Iridium catalysts containing both NHC and Cp* units have proven to be active in reduction by means of TH. The new anionic monodentate iridium complexes **152** containing readily accessible and tunable chiral hydroxyamide-functionalized NHC ligands with various substituents were presynthesized or in situ constructed, and these complexes served as catalysts in ATH of ketones.[527] They were moderately active for this transformation at rt, and the ligand featuring both a *tert*-butyl group at the stereogenic center and a benzyl substituent at the azolium ring exhibited the best catalytic properties. Another new category of mono-NHC ligands smoothly generated the corresponding iridium complexes **153** and **154** with a Cp* group. These iridium complexes were found to act as highly active catalysts for the TH of ketones and imines involving a range of substrates with 1 mol % of catalyst loading.[528] When complex **153d** having two acetyl groups was employed in the procedure, the use of low catalyst loading (0.01 mol %) provided good catalytic results with up to 8000 TON. Importantly, these ligands with acetylbenzyl group in complexes **153** and **154** showed good stability in basic media.[528]

Crabtree and Hintermair et al.[529,530] conducted mechanistic studies that were focused on several points with the half-sandwich iridium complex **155** bearing two NHC ligands. It is known that some metal nanoparticles are active in the mediation of TH,[285,531] and in the case of the iridium catalyst it was found that iridium nanoparticles in situ assembled in the presence of base proved to be the real catalytic species in the hydrogenation of ketones under dinitrogen.[532] The authors questioned whether iridium nanoparticles were the true catalyst in TH. Control experiments and mercury poisoning tests showed that iridium(0) nanoparticles, although active in the reaction, are not responsible for the high activity observed for the catalyst **155**.[529] In addition, the replacement of both monodentate-type NHCs in complex **155a** by a bridging bis-NHC chelate ligand caused a significant decrease in activity. Therefore, the existence of two NHCs in mono forms is essential for high catalytic efficiency.[529] Both the results from H/D scrambling experiments and the findings of Cp* loss in a precatalytic activation step of TH catalysis with **155a** made the classic monohydride mechanism questionable.[530] A new catalyst activation mechanism that is suitable to [IrCp*]-promoted TH was proposed. In addition, to further enhance the catalytic acidity of **155a**, the feasibility of designing a modified version of catalyst **155a** with more bulky groups around the iridium center was confirmed.[530]

In the past few years, half-sandwich iridium complexes with chelating triazolyl units have been extensively developed because of their high activities, high accessibilities, high stabilities, easy modifications, and bis-coordinating sites of 1,2,3-triazoles. Iridium complexes functionalized by pyridyl-triazole (toward **156**), bis-triazole (**157**), or bis-abnormal

Scheme 57. Half-Sandwich Ir Catalysts Containing NHC Fragments



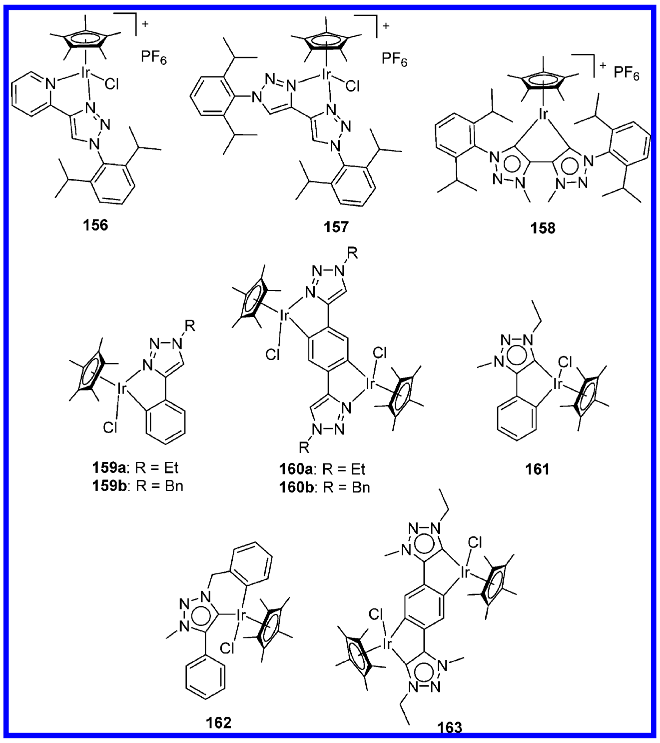
152

153a: R^1 = H, R^2 = Me
153b: R^1 = acetyl, R^2 = Me
153c: R^1 = acetyl, R^2 = 2,4,6-trimethylphenyl
153d: R^1 = acetyl, R^2 = 4-acetylbenyl

154

155a: X = Cl
155b: X = H

Scheme 58. Iridium TH Catalysts Bearing Triazolyl Ligands



156 **157** **158**

159a: R = Et
159b: R = Bn

160a: R = Et
160b: R = Bn

161

162 **163**

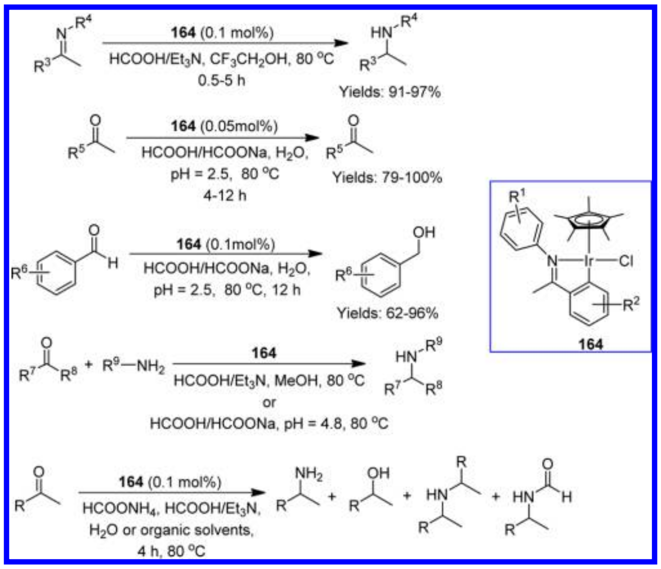
carbene (**158**) with half-sandwich and piano-stool configuration were assayed in the catalytic TH of nitrobenzenes using 2-PrOH providing aniline, azobenzene, and azoxybenzene compounds.[533] Investigations of ligand substitution, metal substitution (comparison with ruthenium counterparts containing each of the above-mentioned triazolyl ligands), and temperature variation on the catalytic behavior indicated that the selectivity was moderately controlled by tuning the metals, ligands, and reaction conditions. In addition, the iridium-based catalysts provided higher conversion of nitrobenzenes than their ruthenium analogues.[533] The same research group[534] reported a series of mono- and dinuclear orthometalated iridium complexes with both Cp* and triazolyl fragments either with C−N or with C−C donor sets to iridium centers with a central phenyl ring as C−H activation sites. All of these presynthesized complexes **159**−**163** were employed as catalysts for the TH of benzaldehyde and acetophenone revealing that the dinuclear iridium complexes **160** and **163** produced faster reactions than their mononuclear counterparts (Scheme 58). Moreover, the dinuclear cyclometalated iridium complex **163** with poly mesoionic carbene ligands gave the best catalytic performances.[534]

Xiao's group[535] explored the catalytic applications of a family of cyclometalated iridium complexes **164** containing Cp* unit in several TH processes. These complexes have been identified as versatile catalysts. They allowed the efficient and selective TH with a range of substrates including imines to amines,[535] ketones and aldehydes to alcohols,[536,537] and TH for reductive amination of ketones to secondary[535,538] and primary amines[539] using safe and inexpensive formate as hydrogen donor (Scheme 59). These reactions were carried out "on water"[540] or in organic solvents, and the pH values of solutions were shown to be critical for a high catalytic performance in terms of selectivity and activity.

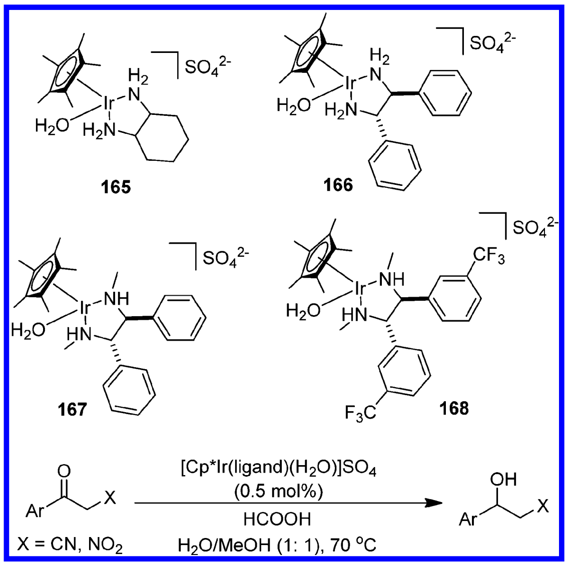
The reaction of $[IrCp^*(H_2O)_3][SO_4]$ with chiral diamines generated four chiral aqua iridium(III) complexes $[IrCp^*(ligand)(H_2O)][SO_4]$ (**165**−**168**) that were air- and moisture-stable.[541] Taking 2-cyanoacetophenone as the model substrate, TH catalyzed by these complexes proceeded smoothly with sodium formate using a 1:1 water/methanol solvent mixture in an open reaction flask. The desired alcohol was obtained with 90%, 79%, 63%, and 84% yields, and 47%, 43%, 83%, and 95% ee with catalyst **165**, **166**, **167**, and **168**, respectively. Considering both activity and selectivity, catalyst **168** functionalized with CF_3 substituents was chosen to investigate the substrate scope. Compound **168** was highly active for ATH of various aromatic cyanoketones, providing good to excellent yields and ee values. When α-nitro ketones were employed in the catalytic system, a series of 2-nitroalcohols were produced with 35−85% yields and excellent ee values (Scheme 60). Remarkably, the "ortho effect" was observed in these catalysis reactions, leading to orthosubstituted aromatic alcohols with high enantioselectivities.[541]

Besides these above-mentioned half-sandwich iridium catalysts containing NHC, some polydentate iridium complexes containing P, N, C-functionalized ligands have been also found to be active in TH of polar compounds, in particular, carbonyls.[542−547] In 2013, Meggers and co-workers[548] designed a very interesting iridium complex, **169**, featuring octahedral stereocenter. Such a stereocenter usually permits the straightforward generation of compounds with high stereo-

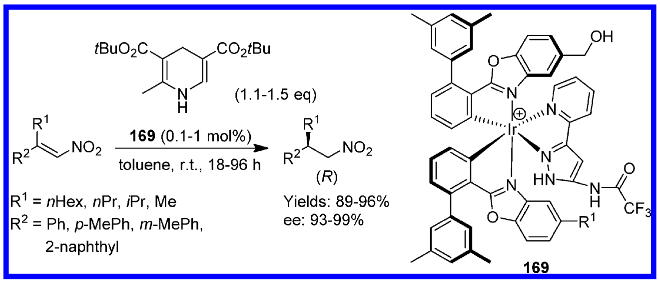
Scheme 59. Half-Sandwich Cyclometalated Ir Complexes as TH Catalysts



Scheme 60. Ir Diamine Catalysts for the ATH of Ketones



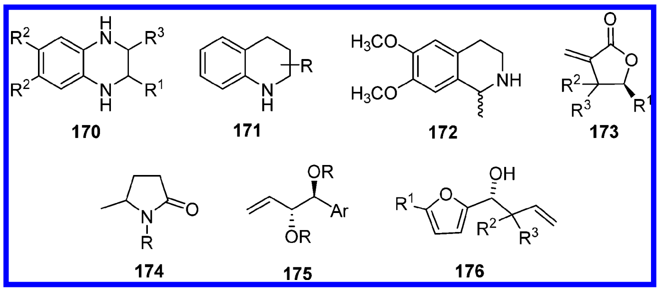
Scheme 61. ATH of *β*,*β*′-Disubstituted Nitroalkenes over Catalyst 169



chemical complexities. This complex showed excellent catalytic performances in terms of activity and enantioselectivity in ATH of *β*,*β*′-disubstituted nitroalkenes at rt using Hantzsch ester as the hydrogen source. The corresponding reduced nitroalkane products with a wide range of substituents were isolated in 89−96% yields and 93−99% ee values with 0.1−1 mol % of catalyst loading (Scheme 61). Interestingly, this catalytic process involving the inert and rigid complex **169** did not include any direct metal coordination, but operated exclusively through weak interactions of functional groups of ligand with substrates. More precisely, the chelated 5-amino-3-(2-pyridyl)-1*H*-pyrazole in the complex **169** acted as a double hydrogen-bond donor to a nitroalkene, whereas the hydroxymethyl substituent on the benzoxazole ligand played the role of a hydrogen-bond acceptor for the incoming nucleophile.[548]

In the field of practical applications of iridium-catalyzed TH reactions, several functional reduced chemicals with unusual properties and potential applications have been synthesized through direct TH or cascade reactions involving TH. The selected examples of the synthesized functional compounds are gathered in Scheme 62. They include tetrahydroquinoxalines (**170**) that are useful organic compounds with a wide range of key biological properties,[549] tetrahydroquinolines (**171**) that have significant substructures in many bioactive compounds,[550] (*R*)-salsolidine (**172**),[551] *α*-*exo*-methylene *γ*-butyrolactones (**173**) that show an enormous array of biological activities and constitute approximately 10% of the >30 000 known natural products,[552] pyrrolidinones (**174**) that are platform molecules for various applications in fuel and fine chemical industries,[553] 1-ene-2,3-diols (**175**),[554] and crotylation derivatives of 5-substituted 2-furan methanols (**176**).[555]

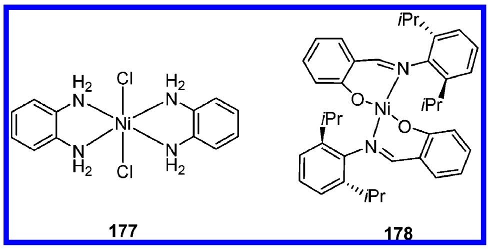
Scheme 62. Functional Derivatives Synthesized by Direct Iridium-Catalyzed TH or Cascade Reactions Involving Ir-Catalyzed TH



2.1.7. Nickel-Based Catalysts. As mentioned above, although ruthenium, rhodium, and iridium-based catalysts are powerful in TH, they are expensive, toxic, and damaging to the environment. Recently, there has been a renewed interest in developing cheap, abundant first-row metal catalysts for this transformation, and plenty of examples involving iron and cobalt have been described in both the Iron-Based Catalysts and the Cobalt-Based Catalysts sections. Nickel catalysts were also found active in the reduction of unsaturated compound with TH methodology.[556−558]

The easily accessible nickel complex **177** bearing diamine ligands was evaluated in the TH of acetophenone at 50 °C using 2-PrOH as hydrogen donor, but unfortunately a poor conversion was observed (Scheme 63).[559] A Schiff base was used to synthesize the organometallic compound **178** that acted as catalyst in the TH of 4-bromoacetophenone with 2-PrOH. Within 12 h, the corresponding alcohol 1-(4-bromophenyl)ethan-1-ol was obtained in 72% yield. However, the dehalogenations of both 4-bromoacetophenone and 1-(4-bromophenyl)ethan-1-ol also proceeded under these conditions, yielding the dehalogenated ketone and alcohol (Scheme 64).[560]

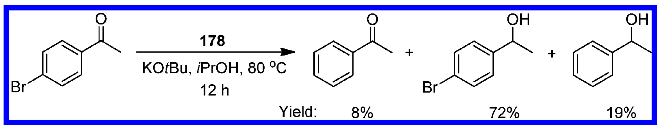
Scheme 63. Nickel TH Catalysts



177

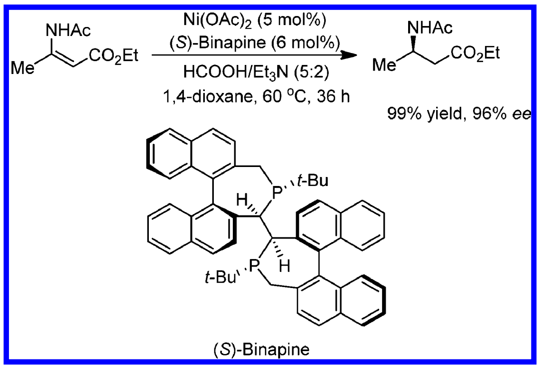
178

Scheme 64. Nickel-Catalyzed Dehalogenation/TH of Bromoacetophenone



Zhou's group[561] has reported a highly active nickel catalyst in ATH of olefins using formic acid for the synthesis of α- and β-amino acids. In the initial research, the ATH of α,β-dehydro-β-acetaminobutyrate was chosen as model reaction and conducted in the presence of [Ni(OAc)$_2$] and various highly electron-rich and sterically demanding bisphosphines, such as (*S*)-Binapine, TangPhos, DuanPhos, Mark Burk's ligands, Imamoto's P-chiral bisphosphine QuinoxP*, Josiphos ligand, BINAP, Segphos, DIPAMP, and PHOX. Among them, (*S*)-Binapine afforded the best results in terms of yield and ee value, respectively, 99% and 96% (Scheme 65).[561] The scope of olefins then was probed in the Ni/(*S*)Binapine system. A number of aryl and alkyl olefins were involved, showing that olefins with both electron-donating and electron-withdrawing aryl groups provided the corresponding products in very high ee. This process was also successfully extended to some compounds with heteroaryl rings (Scheme 66).[561] Only 30% ee and 10% yield were obtained using an olefin with a β-anilino group, perhaps due to the in situ hydrolysis of the enamine group. Interestingly, the *E*-isomer of the model olefin was reactive in the TH procedure, but with only 44% ee, the low enantioselectivity being attributed to the two competing insertion modes for hydride insertion at the nickel center. α-Acetamidoesters were also synthesized with this process, providing more than 80% ee. In addition, in this catalytic system, the enantioselectivity was tunable by changing the solvents or the ratio of formic acid and Et$_3$N.[561]

Scheme 65. ATH of α,β-Dehydro-β-acetaminobutyrate in the Presence of Ni(OAc)$_2$ and (*S*)-Binapine

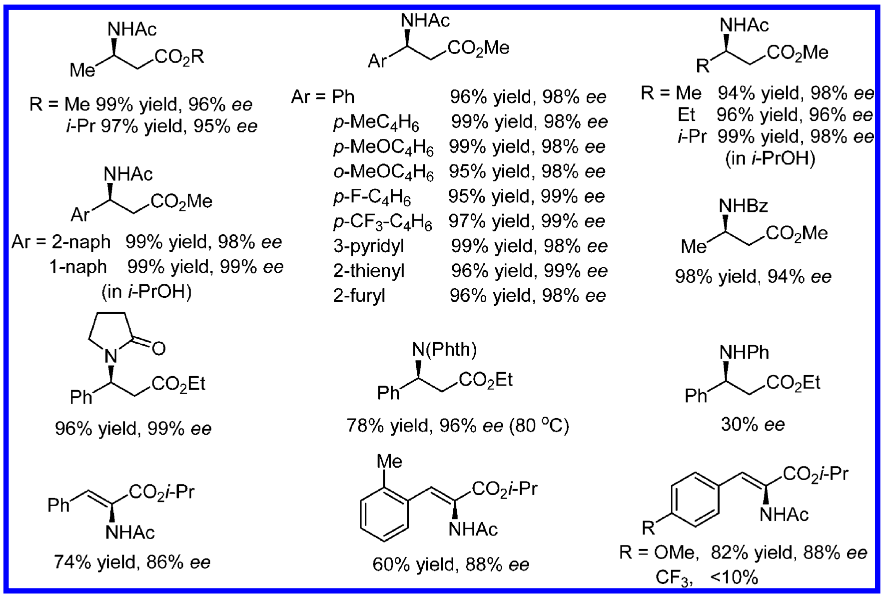


Nickel nanoparticles (NiNPs) catalyze the TH of olefins and carbonyl compounds and the reductive amination of aldehydes with 2-propanol as the hydrogen donor.[264] Yus and co-workers[562] demonstrated that the TH of olefins was catalyzed by NiNPs of 0.75−2.88 nm that were generated from anhydrous nickel(II) chloride. Numerous nonfunctionalized and functionalized alkanes were obtained with >99% yields in most of cases. The TH of dehydrobrittonin A to brittonin A (a natural dihydrostilbene) was successfully conducted using this strategy giving 100% conversion and 95% yield (Scheme 67).[562] These NiNPs also exhibited high activity in the TH of acetophenone, the concentration of acetophenone and isopropanol being one of the critical factors on the reaction rate.[563] The same authors[564] reported that the reductive amination of aldehydes by TH with 2-PrOH was catalyzed by 20 mol % of NiNPs at 76 °C, and a series of amines bearing a wide range of substituents were produced in 30−99% yields.

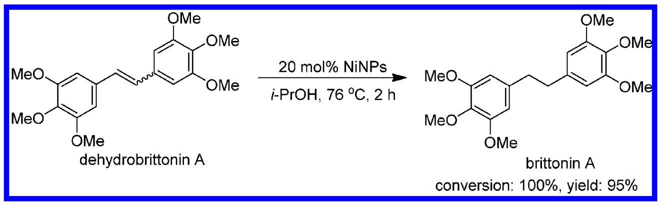
2.1.8. Palladium-Based Catalysts. The TH of carbonyls and imines is well-known, because these C═O and C═N bonds are easily hydrogenated to the corresponding alcohols and amines. In contrast, the TH of nonpolarized C−C multiple bonds has been scarcely reported, because it is far different to achieve. Although some homogeneous catalytic systems have been reported for this transformation, quite a few of them showed good results for the transfer semihydrogenation of alkynes to alkenes, as the initial alkenes products often are over-reduced to alkanes.

Elsevier's group demonstrated that several palladium(II) or palladium(0)−NHC precatalysts exhibited excellent activities in transfer semihydrogenation of alkynes to *Z* alkenes (Scheme 68), which are present in a plethora of biologically and pharmaceutically active compounds.[565,566] Compound **179** containing zerovalent palladium was the first catalyst for stereo- and chemoselective semihydrogenation of aromatic and aliphatic internal alkynes under TH conditions with formic acid/triethylamine.[188] A series of alkynes with a wide range of scope were employed in this catalytic system, and in most cases the desired *Z* alkenes were obtained with >99% conversions and >90% selectivities; meanwhile, both *E* alkenes and alkanes were found as side-products. Interestingly, the selectivity was tuned by solvent switch between MeCN and THF.[188] Later, a thorough investigation of the influence of the substituents on both the NHC and the pyrimidine was performed through the catalytic tests of their zerovalent palladium complexes **180** in transfer semihydrogenation of 1-phenyl-1-propyne. With 1 mol % of palladium loading, catalyst **180a** showed the best catalytic activity, and both **180c** and **180d** featuring the DiPP scaffold displayed the highest selectivity toward *Z* alkene.[567] Using complex **179** having MeCN molecule as model catalyst, mechanistic studies revealed a broken positive order in substrate and first order in catalyst and hydrogen donor. Both hydrogen atoms of HCOOH exhibited a primary kinetic isotope effect, indicating that proton and hydride transfers are separate rate-determining steps.[568] The identifications of a coordinated formate anion and part of the maleic anhydride (MA) during the reaction suggested a mechanism in which migratory insertion of hydride provided [Pd(0)(NHC)(MA)(alkyne)(H)], after which the alkene product was released by proton transfer from the triethylammonium cation. In the catalytic cycle, the selectivity depended on the result of the competition between the strongly coordinating solvent and the alkyne for the formation of a Pd(alkene)-intermediate.[568]

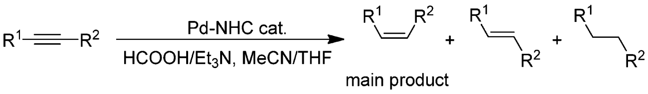
Scheme 66. Chiral α- and β-Amino Acid Derivatives Synthesized by $Ni(OAc)_2$/(*S*)-Binapine-Catalyzed ATH



Scheme 67. Ni Nanoparticles-Catalyzed TH of Dehydrobrittonin A to Brittonin A



Scheme 68. TH of Alkynes Using Palladium−NHC Catalysts



Numerous zerovalent complexes $[Pd(NHC)(alkene)_{1,2}]$ (**181**−**186**) functionalized by expanded-ring NHCs were used as precatalysts in this reaction of 1-phenyl-1-propyne by the same group.[569] These authors observed that the existence of these very bulky, strong σ-donor NHCs in complexes **181** and **182** significantly enhanced their catalytic activities. Although the initial selectivity of *Z*-alkene was high, both isomerization of the double bond and over-reduction to the corresponding alkane sequentially proceeded to consume all of the obtained *Z*-alkene.[569]

One of the disadvantages of these palladium−NHC precatalysts is that they are not shelf-stable and cannot be isolated, causing difficulty in precatalyst storage, which is not convenient for practical applications in synthesis. On the basis of that, the exploration of shelf-stable catalysts to improve the applicability of this catalytic methodology was conducted by Elsevier's group.[570] Indeed, the commercially available, highly stable complex $[PdCl(\eta^3\text{-}C_3H_5)(IMes)]$ **187** served as precatalyst in this transformation producing *Z*-alkenes (Scheme 69). With the addition of triphenyl phosphine, this new system was shown to be a robust catalytic method allowing excellent selectivities for a broad range of *Z*-alkenes. Notably, in the catalytic operation, all solvents and reagents were directly used without any drying or purification.[570]

The substitution of NHC catalysts has a significant influence on the selectivity of the transfer semihydrogenation reaction. To this end, Elsevier's group[571] prepared a series of NHCs ligands containing both an acid and an amino functionality using the amino acid histidine as precursor. Subsequently, the corresponding palladium−NHCs complexes **189** were synthesized and utilized as precatalysts in the *Z*-selective transfer semihydrogenation of alkynes. With this catalytic protocol involving robust palladium−NHC precatalysts containing additional donor functionalities, good selectivities were determined. Moreover, compound **189c** that possesses two picolyl functional groups provided the best catalytic performance.[571]

Hua's group[572] found that $[Pd(OAc)_2]$ was extremely active in the catalytic transfer semihydrogenation of internal alkynes bearing various functional groups, delivering the desired *Z*-alkenes in 86−99% yields and 86−99% selectivities, using DMF/KOH as hydrogen source (Scheme 70). With this procedure, the synthesis of the natural product *Z*-combretastatin A-4 (**190**) that is useful in organic and medicinal chemistry with important biological activities was achieved by performing the semihydrogenation of 1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl) acetylene in 94% isolated yield and >99% selectivity. The stability and commercial availability of the catalyst and the wide substrate scope are the most attractive advantages of this catalyst. On the other hand, the requirement of high reaction temperatures could more or less restrict its applications.[572]

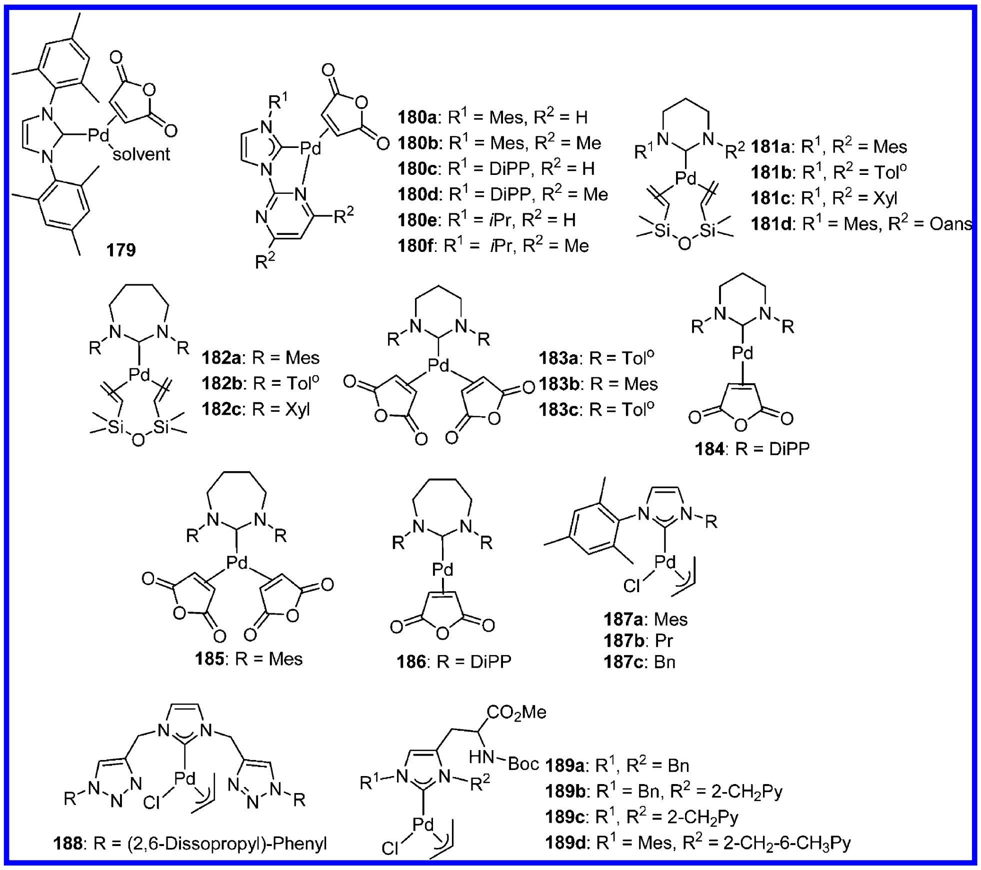
The versatile catalyst $[Pd(OAc)_2]$ is also active in the TH of nitrobenzene to anilines, carbonyls to alcohols, and alkenes to alkanes that were carried out in a surfactant-free catalyst system using 2-PrOH as hydrogen donor. In this process, the real catalytic species are in situ formed palladium nanoparticles.[573]

2.1.9. Gold-Based Catalysts.

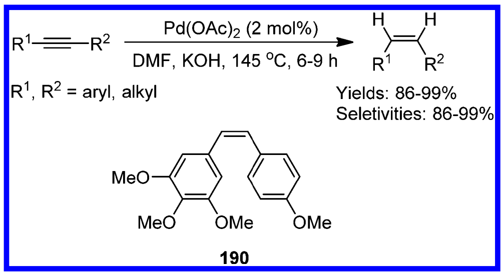
Gold complexes and catalysts have attracted considerable attention in organic transformations due to relativistic effects and soft Lewis acidity.[574] Recently, some gold-based complexes and nanoparticles were found to be excellent catalysts in homogeneous or quasi-homogeneous TH.

DOI: 10.1021/acs.chemrev.5b00203
Chem. Rev. XXXX, XXX, XXX−XXX

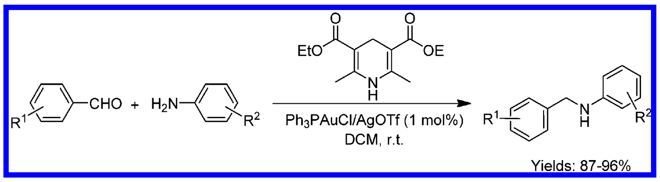
Scheme 69. Palladium−NHC Complexes for Transfer Semihydrogenation of Alkynes to Z Alkenes



Scheme 70. $[Pd(OAc)_2]$-Catalyzed Transfer Semihydrogenation of Internal Alkynes Affording Z-Alkenes



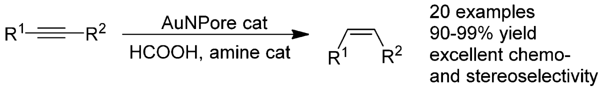
Scheme 71. Amination of Aromatic Aldehydes through TH Catalyzed by $Ph_3PAuCl/AgOTf$



A facile, highly efficient reductive amination of aromatic aldehydes by borrowing of hydrogen from an ethyl Hantzsch ester has been achieved by use of easy-to-get $Ph_3PAuCl/AgOTf$ catalyst.[575] The reaction between aniline and benzaldehyde was conducted in dichloromethane at rt in the presence of $Ph_3PAuCl/AgOTf$ and ethyl Hantzsch ester. Within 1 h, the desired product N-benzylaniline was synthesized in 95% yield. Under these conditions, aldehydes and primary amines functionalized by diverse groups were used to test the scope of this reaction, and 26 secondary amines were isolated in 86−96% yields (Scheme 71).[575]

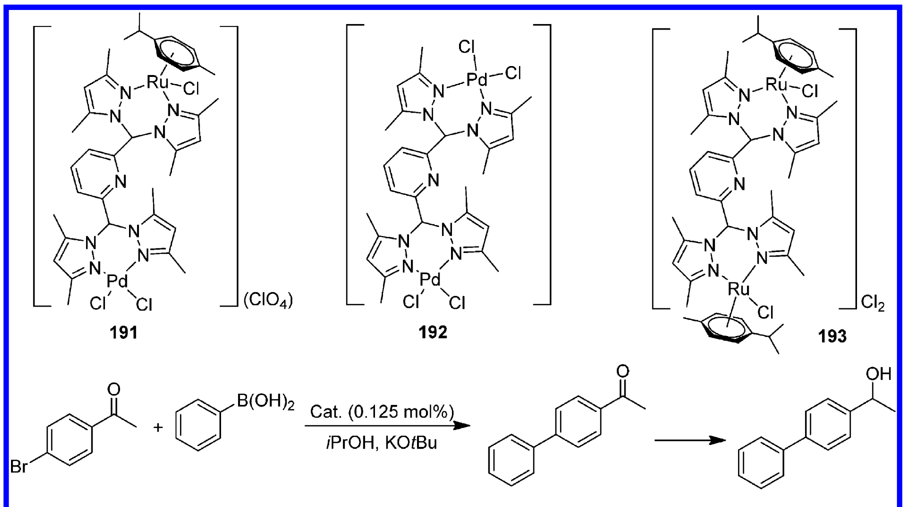
Unsupported nanoporous gold (AuNPore), prepared from Au alloys by selective leaching of less costly metals, is a potentially sustainable catalyst with rising interest, due to its high surface area, high stability for versatile chemicals, lack of toxicity, and high reusability.[576] This new-emerging material has been assayed in transfer semihydrogenation of alkynes producing the corresponding Z-alkenes using organosilanes as hydrogen donor.[577] In 2015, Asao[578] demonstrated that the much cheaper reagent HCOOH can also be utilized as hydrogen donor in this transformation. A variety of both internal and terminal alkynes were hydrogenated, delivering Z-alkenes bearing nitrile, ketone, and ester groups, with extremely high activity, stereo-, and chemoselectivity (Scheme 72).[578]

Scheme 72. Selective Transfer Semihydrogenation of Alkynes with Nanoporous Au Catalysts



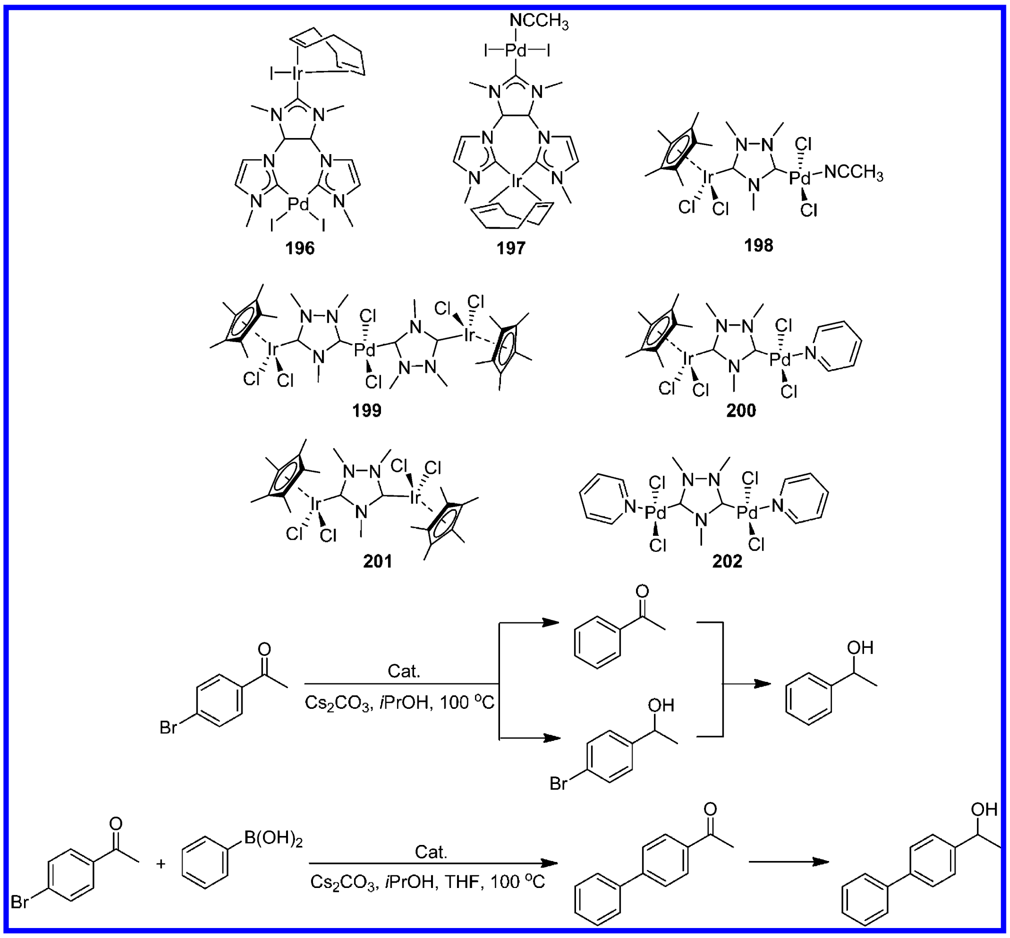
Recently, the vast majority of examples of nitrophenol reduction have been catalyzed by quasi-homogeneous gold nanoparticles using $NaBH_4$ as hydrogen source. Various stabilizers, synthetic methods, reaction conditions, and gold nanoparticles of various sizes were involved in this reaction, and review articles have been published.[579,580]

2.1.10. Bimetallic and Multimetallic Catalysts. Bimetallic and polymetallic catalysts have a bright future in catalysis because of their enhanced activities, stabilities, selectivities, Scheme 73. Tandem Suzuki–Miyaura Coupling/TH Reaction with a Bis-heteroscorpionate Pd–Ru Complex



		194	195
30 °C, 48 h	Cat. **191**:	16%	67%
	Cat. **192** and **193**:	24%	53%
80 °C, 2.5 h,	Cat. **191**:	0	97%

Scheme 74. Multifunctional Ir, Rh, and Pd Y-Shaped Catalyst with Tris-*N*-heterocyclic-carbene Ligand for Dehalogenation/TH of Haloacetophenones and Suzuki–Miyaura Coupling/TH of *p*-Bromoacetophenone



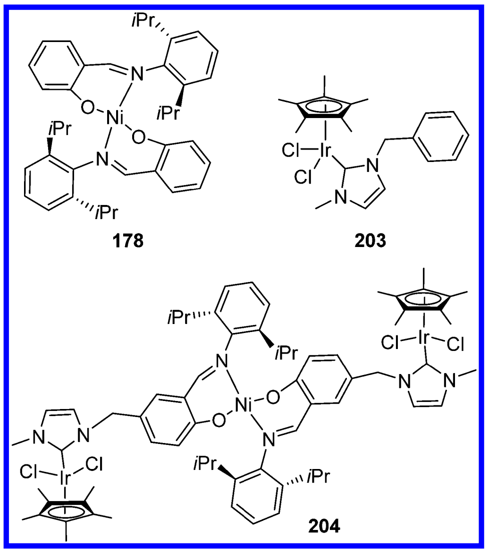
synergistic effects, and other properties as compared to their monometallic counterparts. Several bimetallic and polymetallic complexes and nanocatalysts recently appeared in TH processes.[581,582]

Patra's group[583] pioneered the synthesis and catalytic applications of heterobimetallic complexes bearing bis-heteroscorpionate ligands. Starting from α,α,α′,α′-tetra(pyrazol-1-yl)-2,6-lutidine (pz_4lut) bis-heteroscorpionate ligand, the heterobimetallic Pd–Ru complex **191** and the homobimetallic complexes **192** and **193** were prepared, and their catalytic behavior was checked in tandem Suzuki–Miyaura coupling/TH of 4-bromoacetophenone and borophenylic acid. As shown in Scheme 73, when the reactions were carried out at 30 °C for 48 h using complex **191** or the equimolar mixture of **192** and **193** as catalysts, as expected the heterobimetallic Pd–Ru complex provided higher yield for the TH product **195** than the mixed catalysts. This improved catalytic performance was accounted for by the single well-defined heterobimetallic catalytic system disclosing cooperativity at least to some extent.[583] With the use of **191** as catalyst, the final product was isolated in 97% yield when the reaction was conducted at 80 °C for 2.5 h. A few other alcohols were synthesized with 82–92% yields using this protocol.[583]

Several mono-, bi-, and trimetallic complexes based on Ir, Rh, and Pd including homo- (**201**, **202**) and heterobimetallic ones (**196**–**198** and **200**) and complexes **196** and **197** were featured by Y-shaped tris-NHC ligand. All of the complexes shown in Scheme 74 were employed as catalysts in two different tandem reactions: dehalogenation/TH of haloacetophenones and Suzuki–Miyaura coupling/TH of *p*-bromoacetophenone (Scheme 74).[584] In the former transformation, all hetero bi- and trismetallic catalysts (**196**–**200**) exhibited much better catalytic activities than the homobimetallic counterparts **201** and **202**. In particular, the uses of catalysts **197**, **199**, and **200** provided the dehalogenated alcohol product in more than 95% yield. The same phenomenon was also observed in the case of Suzuki–Miyaura coupling/TH. The better catalytic performance of hetero bi- and trimetallic catalysts was attributed to the catalytic cooperativity among different metal centers.[584]

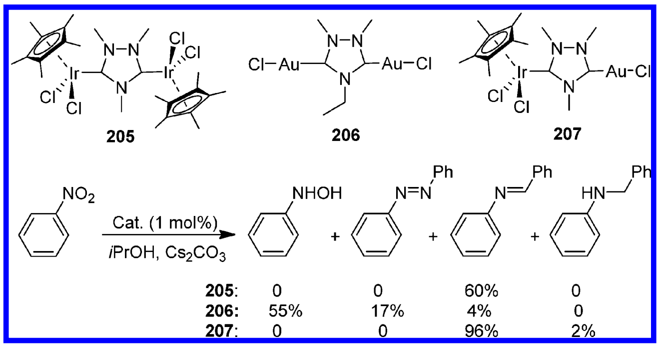
A sophisticated Schiff base–NHC ligand generated a heterotrimetallic organometallic complex **204** possessing one nickel and two iridium atoms (Scheme 75).[560] This complex served as a multifunctional catalyst in the reaction of dehalogenation/TH of haloacetophenones yielding excellent catalytic results. A comparative study demonstrated that the heterometallic species was more active than the physical mixture of the corresponding monometallic species **178** and **203**.

Scheme 75. Heterotrimetallic TH Catalyst Involving Ni and Ir, and the Corresponding Monometallic Catalysts



The homobinuclear complexes of iridium and gold **205** and **206** and the heterobinuclear complex **207**, prepared by metallization of the triazolyl-diylidene ligand,[585] were employed as catalysts in the reduction of nitroarenes by TH using benzyl alcohols giving four products with a catalyst-dependent ratio. A hydroxylamine was obtained as the main product when the catalyst **206** was utilized, and the heterodinuclear iridium–gold complex **207** facilitated the formation of an imine (Scheme 76). The preliminary catalytic study showed that the heterobinuclear complex **207** provided better catalytic performances than the two homobimetallic catalysts.[585]

Scheme 76. Reduction of Nitroarenes by TH Using Primary Alcohols Catalyzed by an Iridium–Gold Heterobimetallic Complex



Chikate's group[586] reported an iron–nickel bimetallic nanoparticle catalyst for catalytic TH of nitroarenes yielding amino derivatives. Without other additives under ambient conditions, 99% conversion and 100% selectivity were obtained with nitrobenzene. With this catalytic system, a series of desired amines with a wide range of substituents were produced with 88–100% conversions and 92–100% selectivities. It was suggested that the nickel sites on the bimetallic surface caused the catalytic activity and that these nickel sites did not only hinder the surface corrosion of the iron sites but also facilitated efficient electron flow from the catalyst surface to the adsorbed nitro compounds.[586]

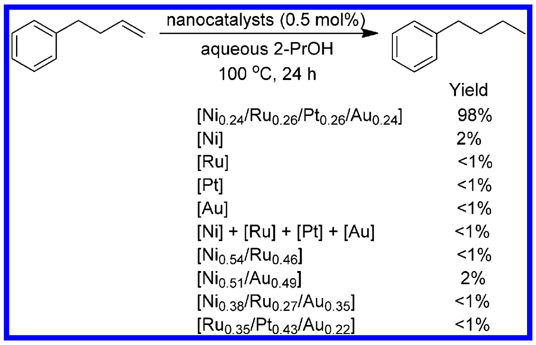
A variety of mono-, bi-, tri-, and tetrametallic alloy nanoparticles capped with trioctylphosphine oxide (TOPO) were assembled through a parallel combinatorial manner. Transmission electron microscopic (TEM) analysis revealed that the average diameter of these nanoparticles was 3.0 nm.[587] The catalytic activity was evaluated for TH of alkenes using 2-PrOH as hydrogen donor at 100 °C under atmospheric conditions. With 4-phenyl-1-butene as the substrate, the Ni/Ru/Pt/Au heterotetrametallic nanoparticles catalyzed the TH reaction in 98% yield. On the contrary, other mono-, bi-, and trimetallic nanoparticles were inactive or only slightly active (Scheme 77).[587]

2.1.11. Other Transition Metals Catalysts.

Beside these above-mentioned catalysts, other transition-metal complexes have been also recently explored in TH, such as those of copper,[588] zinc,[589] zirconium,[590–593] molybdenum,[594–596] rhenium,[597–599] etc.

Stoichiometric amounts of molybdenum compounds have been utilized to promote hydrogenation using hydrogen gas or silanes as reducing agents.[600,601] On the basis of previous examples, a well-established cubane-type cluster $[Mo_3S_4X_3(dmpe)_3]^+$ (dmpe = 1,2-(bis)-dimethylphosphinoethane) was applied as catalyst in the TH

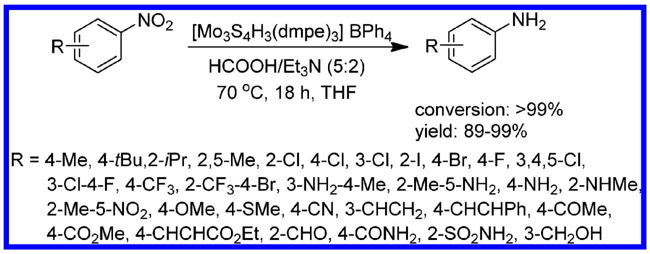
Scheme 77. TH of 4-Phenyl-1-butene (1) with Various Mono-, Bi-, Tri-, and Tetrametallic Nanoparticles



	Yield
$[Ni_{0.24}/Ru_{0.26}/Pt_{0.26}/Au_{0.24}]$	98%
[Ni]	2%
[Ru]	<1%
[Pt]	<1%
[Au]	<1%
[Ni] + [Ru] + [Pt] + [Au]	<1%
$[Ni_{0.54}/Ru_{0.46}]$	<1%
$[Ni_{0.51}/Au_{0.49}]$	2%
$[Ni_{0.38}/Ru_{0.27}/Au_{0.35}]$	<1%
$[Ru_{0.35}/Pt_{0.43}/Au_{0.22}]$	<1%

of nitroarenes with formate.[594] Reduction of a variety of nitroarenes to anilines was achieved with this means, and >99% conversions and 89–99% yields were obtained (Scheme 78).

Scheme 78. Mo-Catalyzed TH of Nitroarenes to Anilines

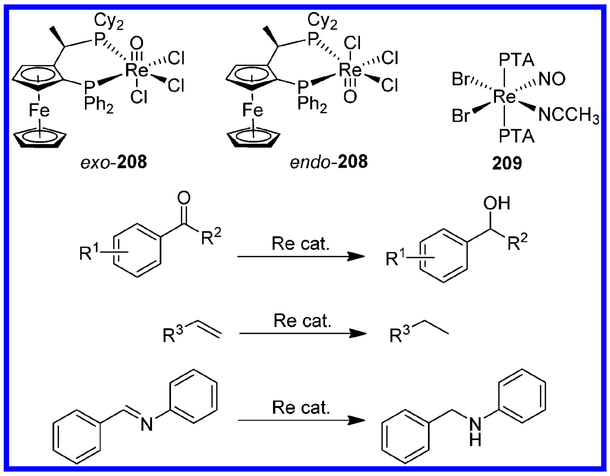


R = 4-Me, 4-*t*Bu,2-*i*Pr, 2,5-Me, 2-Cl, 4-Cl, 3-Cl, 2-I, 4-Br, 4-F, 3,4,5-Cl, 3-Cl-4-F, 4-CF_3, 2-CF_3-4-Br, 3-NH_2-4-Me, 2-Me-5-NH_2, 4-NH_2, 2-NHMe, 2-Me-5-NO_2, 4-OMe, 4-SMe, 4-CN, 3-$CHCH_2$, 4-CHCHPh, 4-COMe, 4-CO_2Me, 4-$CHCHCO_2$Et, 2-CHO, 4-$CONH_2$, 2-SO_2NH_2, 3-CH_2OH

Moreover, $[MoCp(CO)_3H]$ was shown to be active in the reduction of carbonyls using formic acid as reducing reagent.[595] The results obtained with these two molybdenum catalysts should trigger the further development of molybdenum-catalyzed TH.

Rhenium complexes have recently been reported as catalysts in TH of C═O, C═C, and C═N bonds (Scheme 79) since the pioneering work in this field by Toste and Kwong et al.[602,603] Togni's group[597] synthesized new air- and moisture-stable rhenium complexes such as **208** that have chiral ferrocenyldiphosphine ligands of the Josiphos family and used them as catalysts in the ATH of ketones using 2-PrOH as reducing reagent and substoichiometric amounts of triethylamine as base. A series of alcohols were obtained with up to 99% yields but moderate enantioselectivity. On the basis of the successful isolation of an alkoxido complex, the authors suggested a plausible reaction mechanism in which a direct TH between the simultaneously coordinated alkoxy and ketone substrate was involved, rather than through hydridic species.[597]

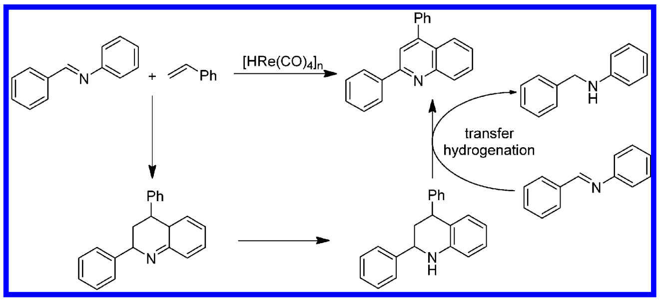
Scheme 79. TH of C═O, C═C, and C═N Bonds



TH of olefins over rhenium was also reported with the complex **209** (PTA = 1,3,5-triaza-7-phosphaadamantane) that showed high activity in the reduction of various terminal olefins with a broad range of substituents, using alcoholysis of amineboranes as a reducing agent. Moreover, alcoholysis was also catalyzed by this rhenium complex.[598] Addition of *t*-BuOK significantly improved the catalytic efficiency, reaching a TOF value of 396 h^{-1}.

The synthesis of 2-alkenylbenzylamines was achieved by $[HRe(CO)_4]_n$-catalyzed reaction of aromatic aldimines with terminal alkenes.[599] The catalytic process includes three steps including the insertion of the alkene into a C−H bond at the ortho-position of the imino group of the aromatic aldimine, the sequential *β*-hydride elimination from the formed alkyl rhenium intermediate, and the TH of the imino group of the aldimine (Scheme 80). This catalytic system tolerated various substituents, and several 2-alkenylbenzylamines were obtained in good to excellent yields.[599]

Scheme 80. Rhenium-Catalyzed Insertion of Terminal Alkenes into a C(sp^2)−H Bond and Successive TH



2.2. Heterogeneous Transition-Metal Catalysts

With the rapid development of "green" chemistry, heterogeneous catalysts are heavily favored in industry from an economic and technical point of view. Heterogeneous catalysis is preferable to homogeneous catalysis because of the improved handling, separation, and recycling possibilities. In the area of catalytic TH, the heterogenization of catalysts on/in various materials attracted considerable attention during the past few years.[217,604,605]

2.2.1. Magnetic Nanoparticle-Immobilized Catalysts.

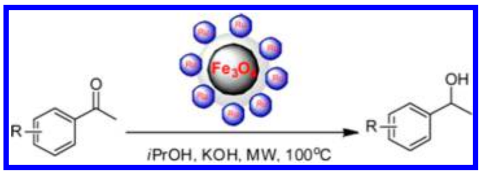
Research on magnetic nanoparticles (MNPs) has become one of the hottest fields and has experienced extremely fast growth in the past few years,[606−613] because MNPs were regarded as ideal catalyst supports due to their large surface area, controllable morphology and dispersity, straightforward and relatively low preparation cost, low toxicity, good stability, biocompatibility, facile separation by magnetic forces, as well as the unique interaction between the catalytic species and MNPs. The use of MNPs bridges the gap between homogeneous and heterogeneous catalysis, and combines catalytic activity with catalyst separation. MNP-immobilized transition-metal catalysts based on ruthenium, rhodium, iridium, nickel, palladium, silver, and gold have been widely explored and used in TH.[614]

MNP-ruthenium nanoparticles (MNPs-RuNPs) with spherical morphology and a size range of 15−30 nm were readily

DOI: 10.1021/acs.chemrev.5b00203
Chem. Rev. XXXX, XXX, XXX−XXX

assembled through tandem generation of $Fe_3O_4@SiO_2$ and immobilization of RuNPs in one pot.[615] The catalytic activity was initially evaluated in TH of acetophenone at 100 °C under MW irradiation in the presence of KOH and a catalytic amount of MNPs-RuNPs; using 2-PrOH as reducing reagent, the desired alcohol product was successfully obtained with over 99% yield in 30 min. The scope of carbonyl compounds was then investigated under optimal conditions. A series of acetophenones containing a broad range of substituents were smoothly transformed into the corresponding alcohols with high conversion and selectivity within 30−45 min (Scheme 81).

Scheme 81. TH of Carbonyl Compounds Catalyzed by Ru Nanoparticles Supported on Magnetic Silica[a]



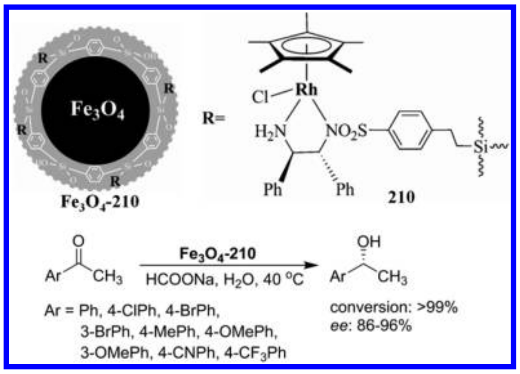
[a]Reprinted with permission from ref 615. Copyright 2013 American Chemical Society.

As a key feature of heterogeneous catalysts, the recyclability was tested in the MNPs-RuNPs-catalyzed TH based on acetophenone. It was shown that this catalyst was magnetically collected and reused at least three times without decrease of activity. Moreover, only 0.08% of Ru leached from the initial catalyst after three reaction cycles.[615]

A presynthesized half-sandwich ruthenium complex {[*N*-4-chlorobenzenesulfonyl-4,5-dichloro-*o*-phenylenediamine]-(*p*-cymene)-chloro-ruthenium(II)}chloride performed well to promote the TH of ketones in 2-PrOH, reaching a TOF value of 2192 h^{-1}.[616] More interestingly, this catalyst was anchored on the surface of Fe_3O_4 by sonication, forming a hybrid material that showed moderate activity in both TH of *p*-acetophenone and reduction of nitro compounds. The good reusability of this MNPs-immobilized ruthenium was confirmed in the later transformation.[616]

Liu and co-workers[617,618] reported organorhodium functionalized MNPs (**Fe_3O_4-210**) consisting of chiral 4-((trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-diamine, 1,4-bis(triethyoxysilyl)benzene, RhCp* fragment, and Fe_3O_4 nanoparticle core. Scanning electron microscopy (SEM) and TEM images revealed that **Fe_3O_4-210** exhibited core−shell morphology with an average particle size of about 370 nm, and a 30 nm thick organosilica layer (Scheme 82).[619] The catalytic efficiency of the obtained MNPs was screened in the ATH of aromatic ketones. Reactions were conducted over 1 mol % [Rh] in the presence of 50 equiv of HCOONa in aqueous medium, providing the corresponding (*S*) ethanol with quantitative conversion and high enantioselectivity (up to 96% ee). Taking acetophenone as an example, a compared investigation showed that **Fe_3O_4-210** offered a higher conversion than its homogeneous counterpart and comparable enantioselectivity.[619] This excellent catalytic performance was believed to benefit from the well-confined nature and the high hydrophobicity of the catalyst. After completion of the ATH involving acetophenone, the catalyst **Fe_3O_4-210** was simply removed from the reaction mixture using an external magnet and reused for another nine reaction cycles with only a slight decrease in both activity and enantioselectivity.[619] The analogues based on iridium were also applied as efficient catalysts in the same transformation.[617]

Scheme 82. ATH Reaction Catalyzed by the Rh Composite Fe_3O_4-210[a]



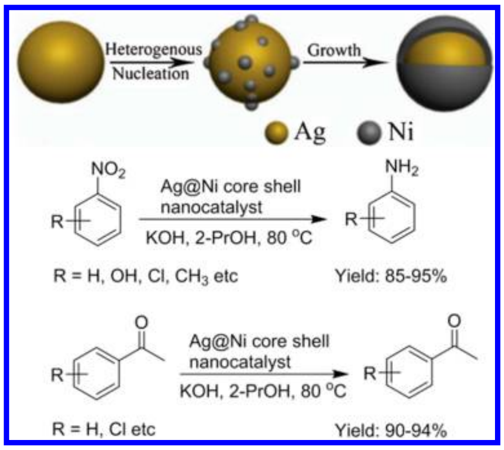
[a]Reprinted with permission from ref 619. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Varma's group[183] reported for the first time the synthesis and catalytic application of a nanoparticle-supported Ni material. This Ni catalyst with a size range from 10 to 13 nm was assayed in a series of hydrogenation and TH reactions. Several ketones bearing different substituents were employed in the Ni-catalyzed TH process that was carried out with 2-PrOH at 100 °C under MW-irradiation. In most cases, the corresponding secondary alcohols were synthesized in excellent yields. A good recyclability and reusability of this catalyst was obtained upon hydrogenation of phenylacetylene to styrene as model reaction.[183]

As the most interesting structure of bimetallic or multimetallic nanoparticles, the core−shell structure can be regarded as a kind of phase separation with a core metal surrounded by the shell composed of the other metal. The core/shell boundary has been shown to provide a tremendous impact in applications due to its unusual physical and chemical properties.[620,621] A facile, simple, and inexpensive Ag@Ni core−shell nanoparticle was readily prepared by a one-pot synthetic route using oleylamine both as solvent and as reducing agent and triphenylphosphine as surfactant (Scheme 83).[622] The TEM image showed the core−shell structure, a diameter of 14.9 nm (the diameter of the core and the thickness of the shell were around 8.1 and 3.3 nm, respectively), and a narrow size distribution with a standard deviation of 1.14 nm. The catalytic properties of these core−shell nanoparticles were disclosed in the TH of aromatic nitro and carbonyl compounds using 2-PrOH. With this catalytic protocol, diverse aromatic nitro and carbonyl compounds were successively converted to the corresponding amines or alcohols in 85−95% yield within only a few hours (Scheme 83). The recycling test revealed that these core−shell nanoparticles were magnetically separable and reused for at least eight cycles without obvious loss in activity.[622] It was believed that after the first report on Ag−Ni core−shell magnetically separable nanocatalyst for TH, such nanocatalysts would find applications in the context of "green" catalysis.

MNP-supported palladium catalysts have recently been shown to be effective in both hydrogenation[623] and TH.[624] Hermans' group[624] reported that a palladium catalyst supported on Fe_2O_3 performed well in the sequential TH/hydrogenolysis of furfural and 5-hydroxymethylfurfural to 2-methylfuran and 2,5-dimethylfuran with the use of 2-PrOH as reducing reagent.

Scheme 83. TH of Aromatic Nitro and Carbonyl Compounds Catalyzed by Magnetic Core−Shell Ag@Ni Nanoparticles[a]



[a]Reprinted with permission from ref 622. Copyright 2013 Royal Society of Chemistry.

This transformation has notable potential for the synthesis of liquid fuel-substitutes from renewable substrates. The palladium loading is a critical factor on both activity and selectivity; for instance, the use of 2 wt % of [Pd] offered the highest selectivity toward 2-methylfuran. A comparative study revealed that the activity of the Fe_2O_3-immobilized palladium catalyst was superior to that of its nickel and copper counterparts, which was taken into account by a stronger palladium−support interaction than with nickel and copper.[624]

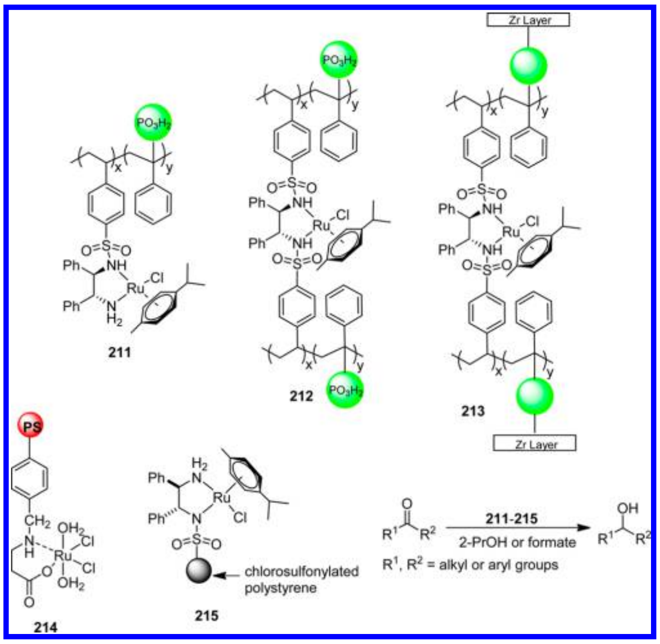
2.2.2. Polymer-Immobilized Catalysts. Polymers are considered as one of the most promising supports for transition metals, and polymer-bound metal complexes and nanoparticle catalysts have been found to be active in various reactions. The catalytic performance is affected by the polymer inherent properties such as solubility, functional groups, molecular weight, degree of cross-linking, hydrophilicity, or hydrophobicity.[625−628] In the past few years, various polymers have been used to immobilize transition metals, forming heterogeneous TH catalysts.[629] These polymers include mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine, mesoporous poly triallylamine, polystyrene, poly(diallyldimethylammonium chloride), polyethylene, polyethylene glycol, polypyrrole, poly(methyl acrylate), and several copolymers. A few examples of polymer-supported recoverable homogeneous TH catalysts are also included in this section.

Because of a remarkably high surface area and stability, functionalized mesoporous materials constituted by inorganic oxides, inorganic−organic hybrid silicas, or organic compounds have attracted increasing attention in numerous fields, in particular, catalysis. Islam and co-workers[630−632] prepared mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine and poly triallylamine and used them to immobilize palladium, ruthenium, and silver species; the latter two exhibited high catalytic efficiency in the reduction of ketones and nitroarenes by TH. Grafting of ruthenium(II) onto mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine was readily achieved. The obtained hybrid material was well characterized and successfully employed as catalyst in TH of ketones with a broad range of substituents using 2-PrOH as hydrogen donor. The corresponding aromatic and aliphatic alcohols were obtained with 65−97% conversions.[631] These good catalytic properties were attributed to highly dispersed and strongly bound ruthenium(II) sites at the mesoporous polymer surface. This heterogeneous ruthenium catalyst was easily collected and recycled several times with almost the same catalytic activity.[631] Silver nanoparticles (AgNPs) dispersed on mesoporous poly triallylamine also served as catalyst in the TH involving nitroarenes with 2-PrOH, and a series of desired anilines were obtained in 81−98% yields. A good reusability and recyclability of this silver nanocatalyst was clearly observed in the recycling tests.[632]

A mesoporous copolymer functionalized by *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN) units was synthesized through copolymerization of *N*-*p*-styrenesulfonyl-1,2-diphenylethylenediamine with divinylbenzene. Coordination with the ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$ provided mesoporous copolymer-anchored Noyori catalyst that displayed extraordinary catalytic performance in terms of activity, chemoselectivity, and enantioselectivity in ATH of ketones with formate.[633] Notably, comparative examination revealed that the activity of this heterogeneous ruthenium catalyst was much higher than that of its homogeneous counterpart. It was suggested that the unique features of high enrichment for the reactants in the superhydrophobic catalysts resulted from their good wettability and easy transfer of product from the catalyst into the water phase and was responsible for the observed higher activity.[633]

Polystyrene (PS) is an attractive and popular organic polymer support. Several phosphonate-containing single- or double-stranded PS copolymer supported ruthenium complexes (for example, **211** and **212**) were prepared initially by Ma and Peng et al.[634,635] who reported that aqueous ATH of carbonyls was efficiently conducted with compound **211** as catalysts, and 94−98% yields, 93.9−97.8% ee, and 100% chemoselectivity were observed with this catalytic system (Scheme 84).[634] In addition, a new hybrid material **213** prepared by coprecipitation of double-stranded PS copolymer-supported ruthenium complexes and NaH_2PO_4 with $ZrOCl_2$ also acted as good catalyst in the same transformation.[635]

Scheme 84. PS-Supported Ru Catalysts for the ATH of Carbonyls



Remarkably, catalysts **211** and **213** were easily recoverable from the reaction mixture by centrifugal separation and reused for at least five reaction cycles without appreciable loss of catalytic activity.[634,635]

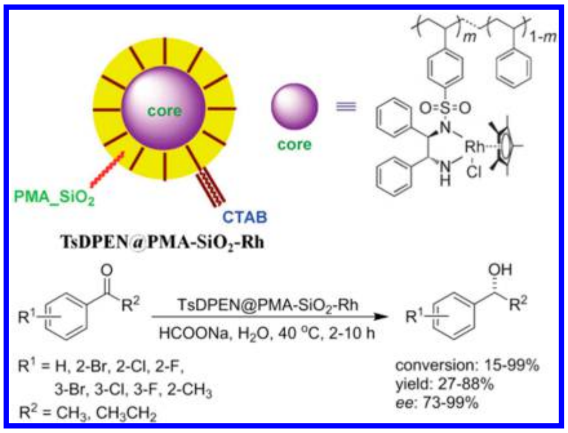
An efficient yet simple PS-supported ruthenium(III) complex **214** was reported, and its catalytic activity and recyclability were investigated in TH reactions of ketones in open air, utilizing 2-PrOH as reducing reagent.[636] Various aromatic and aliphatic ketones were converted to the corresponding alcohols in the presence of KOH and 0.1 mol % of [Ru], providing 84−99% isolated yields. The PS-supported ruthenium catalyst retained the same activity even in the fifth cycle, and no catalyst leaching was detected during the reactions.[636] A chlorosulfonylated PS-immobilized Noyori catalyst **215** was synthesized and used in ATH of ketones with formic acid-triethylamine at 40 °C.[637] The reaction of acetophenone proceeded smoothly with 0.67 mol % of catalyst loading, and chiral 1-phenylethan-1-ol was obtained with 99% conversion and 97% ee value. To probe the reaction scope with catalyst **215**, several ketones bearing electron-withdrawing or electron-donating groups, benzo-cyclic ketone, and ketones connected with naphthyl and furyl fragments were examined with this catalytic procedure. The results showed that in most cases the desired alcohols were quantitatively obtained with 86−99% ee values.[637]

Besides PS and mesoporous poly triallylamine, heterogenization of Noyori's catalyst with other polymers has been also disclosed very recently such as with poly(N^1-{4-vinylbenzenesulfonyl}-1,2-diphenylethylene-1,2-diamine-*co*-divinylbenz-*co*-vinyl),[638] polyethylene glycol,[639] and cross-linked poly(divinylbenzene) and poly(methacrylic acid-*co*-ethylene glycol dimethacrylate) microspheres.[640] These assembled polymer−organometallic materials have been shown to be active, recyclable, and reusable in ATH reactions of cyclic sulfonimine to sultam, carbonyls to alcohols, and imines to amines.

A polymer-bound ruthenium-based nanoparticle catalyst was synthesized and used in the TH of carbonyls.[641] First, the precursor of the ruthenium nanoparticles was provided through ion pairing of $[Ru_4H_3(CO)_{12}]^-$ with the quaternary ammonium groups of poly(diallyldimethylammonium chloride), and then the final nanocatalyst was obtained by reduction of the precursor with H_2 gas. Hydrogenation (of olefins and carbonyls) and TH (of carbonyls) were carried out over the synthesized nanocatalyst in water, and for TH the catalyst exhibited moderate to excellent activity. Unfortunately, an obvious decrease in conversion was found in the second cycle during the recycling study involving TH of acetophenone. On the contrary, the ruthenium nanocatalyst was reused at least five times with only slight loss in activity in the case of direct hydrogenation of cyclohexanone.[641]

Heterogeneous catalysts based on rhodium,[433,642] iridium,[643] and palladium[644] metals were also recently supported on polymers. Li and Yang groups[642] described the synthesis of new polymer−inorganic hybrid core−shell nanospheres containing *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine in the core and the poly(methyl acrylate) (PMA) polymer−mesoporous silica in the shell (Scheme 85). The addition of PMA and cetyltrimethylammonium bromide in the shell significantly increased the surface hydrophobicity, resulting in good catalytic performance of this nanosphere-encapsulated TsDPEN ligand with $[RhCp^*Cl_2]_2$ for the ATH of aromatic ketones in aqueous HCOONa. The recycling results in the first five cycles of the ATH of acetophenone indicated a steadily decreased activity and almost the same enantioselectivity.[642]

Scheme 85. Rhodium-Based Hybrid Core−Shell Nanosphere Catalysts for the ATH of Aromatic Ketones[a]



[a]Reprinted with permission from ref 642. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

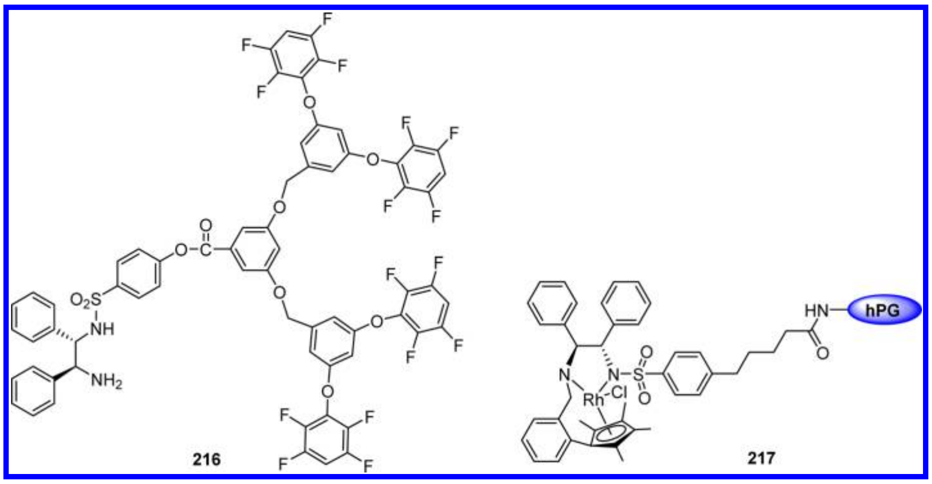
Polypyrrole-immobilized palladium nanoparticles were fabricated through in situ polymerization and composite formation method.[644] The composite possessed valuable catalytic properties in chemoselective TH. A wide range of halogenated α,β-unsaturated carbonyl compounds (olefins/acetylenes) were successfully converted to saturated carbonyl compounds with 77−97% yields and TOF values up to 1463 h^{-1}. In the process, no semihydrogenated product was observed when alkyne substrates were tested, no hydro-dehalogenation of the haloarene segment of the substrate was observed, and the carbonyl moiety was not touched.[644] Loss of activity was determined after two reaction cycles that could be caused by the loss of catalyst during washing revealed by inductively coupled plasma mass spectrometry analysis and the aggregation of the palladium nanoparticles, the particle size increasing from 2−3 nm to 5−15 nm after the third cycle.[644]

Dendritic polymers, a family of nanosized well-defined three-dimensional highly branched molecular frameworks, have been demonstrated to have essential and promising applications in catalysis.[645−649] A fluorinated dendritic chiral mono-*N*-tosylated 1,2-diphenylethlenediamine **216** has been used as metal catalyst carrier.[650] The in situ fabricated ruthenium complex with **216** was unprecedently active in aqueous ATH of ketones, delivering chiral secondary alcohols with complete conversion, and up to 97% ee. The ruthenium-**216** catalyst displayed excellent recyclability and stability, and it was recycled more than 25 times without significant loss of both activity and enantioselectivity.[650]

Experimental analysis and DFT calculation suggested that high stability and reusability of this catalyst benefited from a semirigid structure and chemical resistance in dendritic backbone. The semirigid structure and chemical resistance were caused by considerable intramolecular weak interactions such as $\pi-\pi$ stacking and hydrogen-bonding interactions provided by the presence of fluorine atoms.[651]

Hyperbranched polymers are versatile supports in catalysis due to their related structure with dendrimers. Hyperbranched polyglycerol (hPG), one of the most-used hyperbranched polymers, is well-known with good solubility, high stability, and weak chelating property to metal. Immobilization of tethered rhodium(III)-*p*-toluenesulfonyl-1,2-diphenylethylenediamine complex onto hPG was easily achieved through covalent attachment, and the formed metallorganic supported catalyst

Scheme 86. Dendritic Polymers and Hyperbranched Polymer-Supported Rhodium Catalyst for TH



217 provided excellent catalytic performances in terms of activity and enantioselectivity in ATH of aromatic ketones with formate (Scheme 86).[652] With **217** as catalyst, several alcohols were synthesized with 100% conversions and as high as 99% ee values. In addition, the catalyst was recoverable by ultrafiltration. However, the reusability of catalyst **217** was disappointing, as in the second cycle the conversion dropped from 100% to 65%. It was inferred that the significantly decreased activity was due to accumulation of the catalyst on the ultrafiltration membrane because of cross-linking between the polymers.[652]

2.2.3. Silica-Immobilized Catalysts. Silicic materials are classic and widely used immobilized supports, and they possess many valuable features such as low cost, easy functionalization, convenient separation, high stability, and biocompatibility. Many successful examples have currently been shown to anchor a series of organometallic complexes in/on silicic materials and presented excellent catalytic efficiency in various THs. These used silicic materials include conventional SiO_2 nanospheres, fibrous-structured silica nanospheres, conventional mesoporous siliceous materials, three-dimensional mesoporous siliceous materials, siliceous mesocellular foams, organosilicon frameworks, etc.

Because of their large surface area, pore volume, tunable pore dimension, special pore arrangement, and highly thermal and mechanical stability, mesoporous siliceous supports in heterogeneous catalysis have attracted a great deal of interest. Several mesoporous siliceous-bounded ruthenium, rhodium, iridium, and palladium catalysts have been constructed and used in the reduction of polar bonds by TH.[653−657]

Liu and co-workers[658,659] demonstrated that chiral *N*-sulfonylated diamine-based $[RhCp^*(TsDPEN)]^+$ was successfully encapsulated into the mesoporous siliceous materials Me-SBA-15 and Me-SBA-16, utilizing an ion-pair interaction as an immobilizing mode. The obtained composites exhibited heterogeneous nature, excellent catalytic activity, high enantioselectivities, and great substrate scope tolerance in ultrasound-promoted ATH of aromatic ketones (Figure 1).[658] The catalytic activities of these two heterogeneous catalysts were comparatively even higher than those of the homogeneous counterpart. In addition, their good reusability and recyclability were observed, and in particular the cationic rhodium functionality within Me-SBA-16 was recycled at least 10 times with only slight loss of activity and retained the same enantioselectivity.[658] Postgrafting, postmodification, and co-condensation were useful strategies to immobilize the homogeneous chiral rhodium catalysts within mesoporous silicate networks (SBA-15 and Me-SBA-15).[659] The results of catalytic tests in aqueous ATH indicated that all of the catalysts formed by postgrafting, postmodification, and co-condensation means exhibited notable catalytic behavior in terms of activity and enantioselectivity. The order of observed enantioselectivity was postgrafting method > co-condensation > postmodification. The outcome from the study is an example guiding the design and construction of mesoporous silica-bound homogeneous metal−organic catalysts.[659]

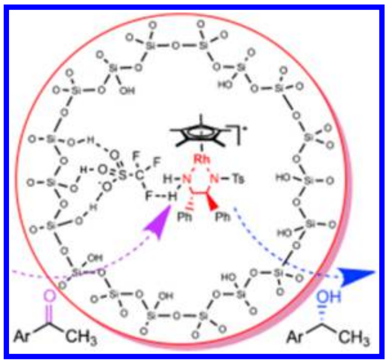


Figure 1. Ion-pair immobilization of $[RhCp^*(TsDPEN)]^+$ in Me-SBA-15 and Me-SBA-16 and their catalytic application in ATH of aromatic ketones.[658] Reprinted with permission from ref 658. Copyright 2012 Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim.

As a rising hybrid material, three-dimensional flowerlike mesoporous silica has attracted much interest in catalysis, because it does not only maintain the properties of traditional mesoporous silica. It also contains relatively short nanochannels of nanopores, like cavum of flowers and uniformly distributed active centers leading to easy accessibility/diffusion. These nanostructures accelerate reactions and mimic an homogeneous catalytic environment. Moreover, in some cases, the presence of cetyltrimethylammonium bromide (CTAB) within silicate network brings about a phase-transfer catalytic process. Flower-like mesoporous silica materials have been discovered for immobilization of rhodium-TsDPEN via a cooperative dual-template protocol followed by complexation with organorhodium complexes (Figure 2).[660] This three-dimensional spherical hybrid **220** with mesostructure and well-defined

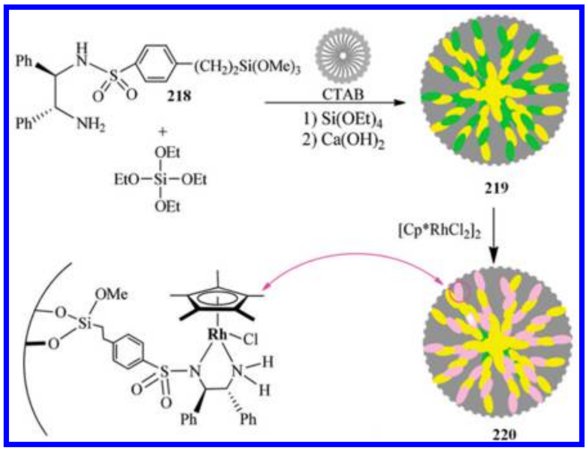


Figure 2. Synthesis of flower-like mesoporous silica-immobilized rhodium catalyst.[660] Reprinted with permission from ref 660. Copyright 2013 Royal Society of Chemistry.

single-site chiral organorhodium functionality acts as a bifunctionalized catalyst in the ATH of aromatic ketones with formate, and many chiral alcohols were synthesized in almost 100% conversions and up to 97% ee values. Furthermore, the heterogeneous catalyst **220** provided the same conversion and ee value in the 10th reaction cycle.[660] Unprecedented high activity, enantioselectivity, and recyclability of three-dimensional flowerlike mesoporous silica-encapsulated ruthenium-TsDPEN in the ATH of ketones and imines were also disclosed in 2013.[661]

A chiral rhodium catalyst (**211** in Figure 3) supported in core–shell structured mesoporous silica spheres was simply prepared.[662] Its core comprises plenty of chiral rhodium-TsDPEN functionalities, while its shell is beneficial to prevent the leaching of catalytic species. The material **221** performed well in the ATH of aromatic ketones using HCO_2Na/H_2O as hydrogen source, and a series of alcohols with a broad range of substituents were delivered in 1 h, showing >99% conversions and 89–97% ee values. This rhodium-based catalyst was recovered easily and reused repeatedly (12 times) without an obvious decrease in both activity and enantioselectivity.[662]

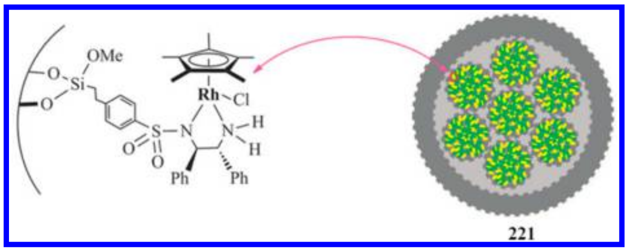
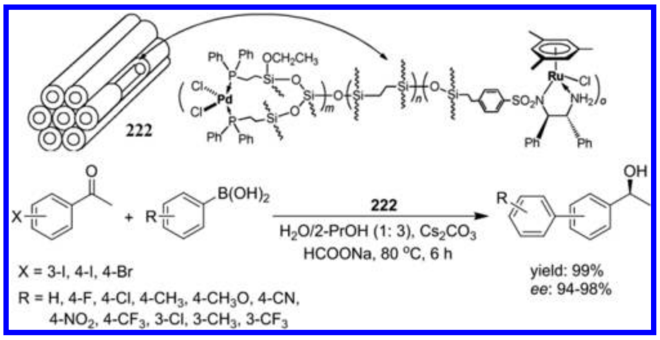


Figure 3. Core–shell structured mesoporous silica functionalized by [RhCp*(TsDPEN)(Cl)].[662] Reprinted with permission from ref 662. Copyright 2012 Royal Society of Chemistry.

Periodic mesoporous organosilicas (PMOs) that contain organic moieties embedded within their silicate networks are an improved variation of inorganosilicate mesoporous materials. PMOs have some unique features such as a highly hydrophobic inner surface and potential additional interactions with active centers (for example, $\pi-\pi$ interactions and hydrogen bonds).[663] POMs were used as immobilized supports for the synthesis of the site-isolated bifunctional organoruthenium-/organopalladium catalyst **222**, and its catalytic property was evaluated in a one-pot cascade involving ATH/Suzuki–Miyaura coupling reactions of haloacetophenones and arylboronic acids. With this procedure, various chiral biaryl alcohols were obtained with 99% conversions and 94–98% ee values (Scheme 87).[664] These authors demonstrated that the site-isolated,

Scheme 87. Cascade ATH and Suzuki–Miyaura Cross-Coupling Catalyzed by a Site-Isolated Organoruthenium-/Organopalladium-Bifunctionalized Periodic Mesoporous Organosilica[a]



[a]Reprinted with permission from ref 664. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

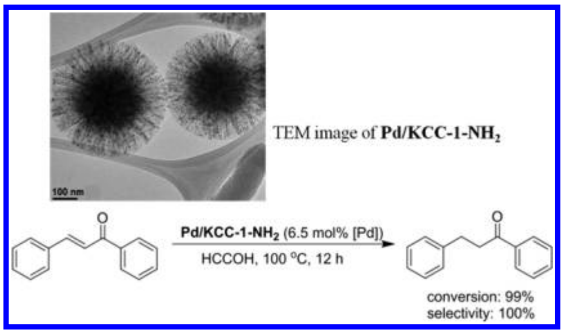
uniformly distributed, well-defined single-site morphology of palladium and ruthenium active species are responsible for the outstanding catalytic performance. Moreover, after the completion of the first cycle, the catalyst **222** was removed from the reaction mixture and reused another seven times without loss of both activity and enantioselectivity. These good results encourage the development of asymmetric cascade reactions that are a remaining challenge in organic synthesis due to the frequent intrinsic incompatibility of two types of distinct organometallic complexes in the same pot.[664]

Siliceous mesocellular foams are useful silica-based supporting materials in catalysis. Bäckvall and Johnston et al.[665,666] have reported a palladium nanoparticle supported amino-functionalized siliceous mesocellular foam. This heterogeneous catalyst that contains well-dispersed palladium nanoparticles with the size of 1–2 nm was utilized to catalyze TH of alkenes and nitroarenes using 1-methyl-1,4-cyclohexadiene and γ-terpinene as hydrogen donors, respectively. A variety of aromatic and aliphatic alkenes were chemoselectively reduced to the corresponding alkanes in 93–99% yields in 5–30 min with the aid of microwave irradiation.[665] Numerous anilines with various functional groups were also synthesized in 85–99% yields when TH of nitroarenes was conducted at 80 °C in EtOH without the use of microwave irradiation.[666] The siliceous mesocellular foam-immobilized palladium nanoparticles were recoverable and recyclable in both TH reactions, and no significant decrease in activity or leaching of palladium was found in several reaction cycles.[665,666]

Basset et al.[667–670] recently discovered new silica nanospheres with high surface areas, pore volumes, and pore sizes, good thermal, hydrothermal, and mechanical properties, as well as fibrous morphologies. In 2015, a fibrous silicananosphere (KCC-1)-supported palladium nanoparticle (named **Pd/KCC-1-NH$_2$**) with a mean size of 5 nm was prepared and used as catalyst in the TH of alkenes and α,β-unsaturated carbonyl compounds providing high yields of the corresponding products with excellent chemoselectivity.[670] For instance, the TH of 1,3-diphenyl-2-propen-1-one proceeded smoothly at 100

°C, producing the desired 1,3-diphenylpropan-1-one product with 99% conversion and 100% selectivity (Scheme 88). This catalyst was collected by centrifugation and recycled four times without a significant decrease in catalytic performance. Moreover, only minor changes in the oxidation state of palladium and in the morphology of the recycled catalyst were detected.[670]

Scheme 88. TH of 1,3-Diphenyl-2-propen-1-one Catalyzed by Pd Nanoparticles Supported on Fibrous-Structured Silica Nanospheres (KCC-1)[a]



[a]Reprinted with permission from ref 670. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

During the past few years, some silica-based polyoxometalate platforms[671] or organic–inorganic hybrid silica-bounded[672,673] TH catalysts involving iridium and rhodium metals were reported to display good catalytic performance and recyclability in the reaction of carbonyls, utilizing 2-PrOH or HCOONa/H_2O as reducing reagents (Figure 4). For example, the polyhedral oligomeric silsesquioxane-connected half-sandwich organorhodium complex **225** serves as an efficient bifunctional heterogeneous catalyst, and 84–99% of conversions and more than 91% ee values were observed. In 12 reaction cycles, the conversion and ee values for each cycle remained similar.[673]

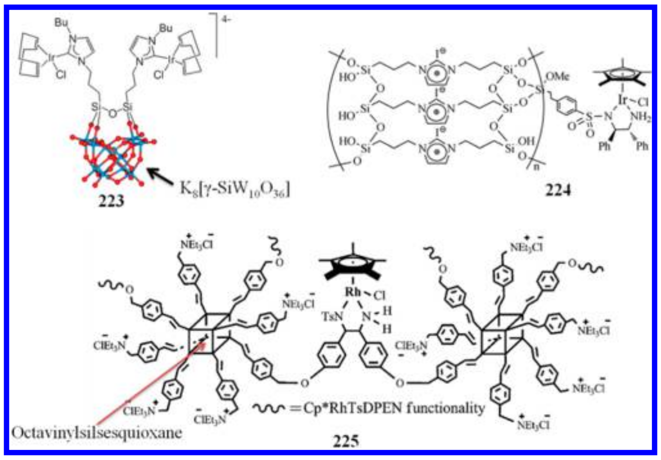
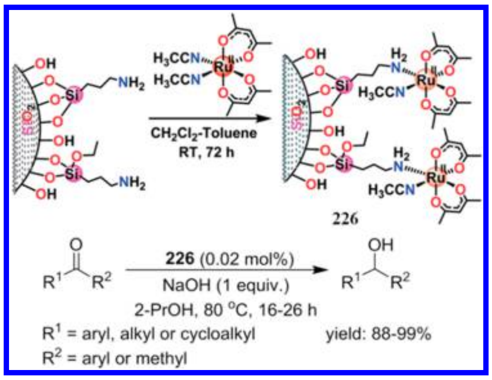


Figure 4. Organic–inorganic hybrid silica- and inorganic silica-immobilized TH catalysts.[671−673] Reprinted with permission from refs 671–673. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, and 2012 Royal Society of Chemistry.

Besides the above-mentioned late-model silica materials, conventional SiO_2 materials (including common SiO_2 nanosphere) were also widely used to support ruthenium, rhodium, and iridium complexes, and these composites presented good catalytic behavior in TH and ATH.[674−678] For instance, immobilization of presynthesized $[Ru(acac)_2(CH_3CN)_2]$ onto amine-modified SiO_2 was achieved, and the assembled solid hybrid **226** was applied as catalyst in the reduction of carbonyls under TH conditions.[674] Various substituted aryl secondary alcohols including heteroaryl alcohols were isolated in 88–99% yields using this procedure. The catalyst **226** exhibited good reusability, the yield of the sixth cycle slightly dropping from 99% to 90% (Scheme 89).

Scheme 89. Heterogeneous SiO_2-Supported Ru Catalyst for TH of Carbonyls[a]



[a]Reprinted with permission from ref 674. Copyright 2014 Royal Society of Chemistry.

2.2.4. Carbon Material-Immobilized Catalysts.

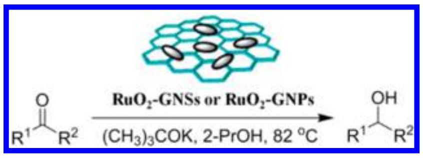
Transition metals immobilized on various carbon materials including activated carbon,[679] graphene, carbon nanotube, carbon nanosphere, and carbon nanofilber have been prepared and efficiently used as catalysts in TH in the past few years.

The reports on the catalytic applications of activated carbon-supported ruthenium, palladium, and iridium complex or nanoparticle composites in TH were frequently found. In particular, these easily fabricated, even commercially available, materials were extensively used in the synthesis of fine chemicals, fuels, and functional compounds, such as methyl furan,[680,681] dimethyl furan,[682,683] monoenes,[684] hexitols,[685] citronellal,[686] aromatic heterocycle-containing amines,[687] quinazolin-4(3*H*)-one and benzimidazoles,[688] and halogenated anilines.[689]

Graphene, consisting of one or a few overlapped graphite layers, is considered to be an ideal, two-dimensional catalytic support due to its high surface area, excellent electrical and thermal conductivity, and mechanical strength. Kim's group[690,691] described the synthesis and catalytic examination of ruthenium dioxides (RuO_2) nanorods decorated on graphene nanosheets (GNSs) or graphene nanoplatelets (GNPs). GNS-RuO_2 was obtained from a simple calcination of GNS-RuNPs that was assembled by a dry synthesis method,[690] and GNP-RuO_2 was prepared by a "mix and heat" method.[691] Both dry synthesis and "mix and heat" methods appeared for the first time in the synthesis of graphene-anchored ruthenium nanomaterials. The catalytic activity and reusability of both GNP-RuO_2 and GNS-RuO_2 toward the TH of aromatic carbonyl compounds were determined to be good (Scheme 90).[690,691]

Carbon nanotubes (CNTs) possess intriguing features, for examples, nanosize, large specific surface area, mechanical strength, high electrical conductivity, and high chemical stability. Recently, CNTs (especially functional CNTs) have

Scheme 90. TH of Carbonyls over GNSs or GNP-Immobilized RuO_2 Nanorods[a]



[a]Reprinted with permission from ref 691. Copyright 2013 Royal Society of Chemistry.

been used as an advanced support material for the immobilization of ruthenium and iridium-based catalysts that presented activity in TH reduction. Multiwall carbon nanotubes (MWCNTs)-[$RuHCl(CO)(PPh_3)_3$] composite that was constructed by modification-coordination process catalyzed C−C bond formation via TH. A series of β,γ-unsaturated ketones were generated in good to excellent yields; moreover, the catalyst recovery result revealed a steady decline of catalytic activity.[692] In another report, the preparation, characterization, and investigation of the catalytic activity of MWCNTs-RuO_2 nanoparticles hybrid were described.[693] The MWCNTs-RuO_2 nanoparticles with a high specific surface area of 189.3 $m^2\ g^{-1}$ were remarkably effective in the heterogeneous ruthenium-mediated TH of aldehydes and ketones using 2-PrOH as hydrogen donor, and this catalytic system tolerated a broad scope of substrates. Recycling experiments involving acetophenone showed that the GC yield slightly decreased from 95% to 87% between the first and eighth cycles.[693]

Iridium-NHC organometallic complexes have been successfully immobilized on oxidized MWCNTs by covalently bonding. The iridium-functionalized nanomaterials performed well in the heterogeneous iridium-catalyzed TH of cyclohexanone to cyclohexanol in the presence of 2-propanol and KOH. Indeed, up to 5500 h^{-1} TOFs were determined, illustrating higher catalytic efficiency than the homogeneous unsupported iridium-NHC counterpart (Figure 5).[694] Furthermore, this air-stable iridium catalyst retained the same activity after five reaction cycles.

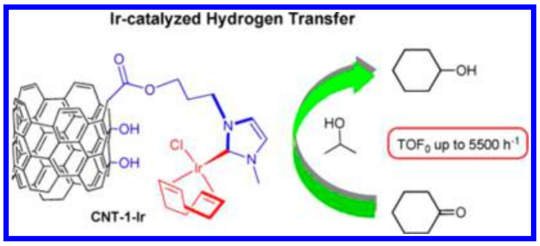
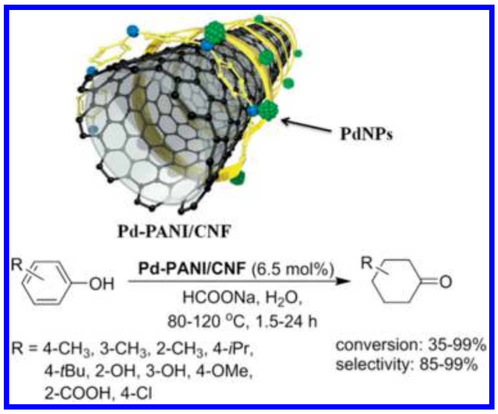


Figure 5. TH of cyclohexanone to cyclohexanol catalyzed by CNT-immobilized iridium−NHC.[694] Reprinted with permission from ref 694. Copyright 2013 American Chemical Society.

Yu and co-workers[695] reported the synthesis and application of palladium nanocrystals supported on carbon nanospheres. The uses of sodium tetrachloropalladate and palladium chloride as palladium precursors led to the formation of palladium nanocrystals with sizes of 5.4 and 18.1 nm, respectively. The immobilized palladium nanocrystals with a size of 5.4 nm were highly efficient for TH of nitroaromatics to anilines with hydrazine hydrate as hydrogen donor. 83.1−100% conversions and 72−100% selectivity toward anilines were observed when the reactions were carried out under ambient conditions. However, an obvious loss of activity, 3.4% palladium leaching, and aggregation of nanoparticles were found during the recycling study.[695]

A few polymer-functionalized carbon-nanofibers (CNF) have been found to be good supports for palladium nanoparticles. The polymers involved include polyaniline (PANI), polypyrrole (PPY), poly(4-vinylpyridine) (PVP), and poly(1-vinylimidazole) (PVI).[696] The catalytic performances of these supported palladium-based nanomaterials were checked in the selective hydrogenation of phenol and derivatives to cycloketones using formate as the hydrogen donor. In the initial experiment, when palladium supported on PANI-functionalized carbon nanofibers (Pd-PANI/CNF) was used as catalyst, phenol was smoothly converted to cyclohexanone with >99% conversion and >99% selectivity. Pd-PANI/CNF showed both higher activity and selectivity than palladium immobilized on other polymer-functionalized CNF. With Pd-PANI/CNF as catalyst, several hydroxyl aromatic derivatives were selectively hydrogenated in high yields and excellent selectivities (Scheme 91). In addition, a good recyclability of Pd-PANI/CNF with slightly decreased activity and the same selectivity was observed.[696]

Scheme 91. Pd-PANI/CNF-Catalyzed TH of Hydroxyl Aromatic Derivatives to Ketones[a]



[a]Reprinted with permission from ref 696. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2.5. Titanium Dioxide-Immobilized Catalysts.

Titania photocatalysis has attracted intensive research interest and has been extensively applied in several fields, in particular organic synthesis due to relatively low cost, long-term stability, perfect biocompatibility, and sustainability of the energy source (solar light) employed. In addition, the catalytic properties of TiO_2 are largely enhanced upon doping TiO_2 with other elements.

A new photocatalytic TH system based on the use of TiO_2 loaded palladium−platinum bimetallic alloyed nanocrystals has been discovered.[697] In the catalytic system, solar light was utilized as the energy input, and methanol was employed as hydrogen source. A series of ketones, aldehydes, and styrene oxide were transformed by TH into the corresponding alcohols in the presence of a TiO_2−Pd−Pt composite, showing good conversions and selectivities. Moreover, this TiO_2−Pd−Pt composite exhibited remarkably superior photocatalytic performances as compared to Pd or Pt alone loaded on TiO_2.[697] The proposed mechanism is shown in Figure 6. This transformation was shown to be triggered by the existence of Pd−Pt with photoinduced electrons, these electrons being generated by irradiation and transfer from TiO_2 crystals to the Pd−Pt alloy.

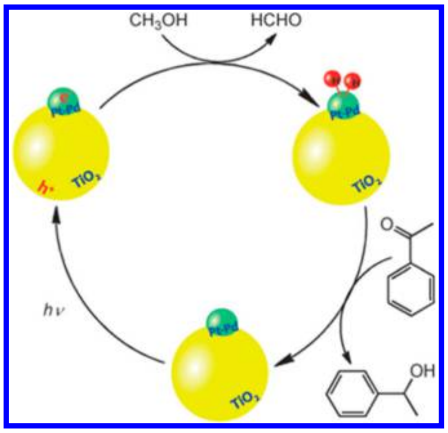


Figure 6. Proposed reaction mechanism for the photocatalytic TH reduction of acetophenone in the presence of a TiO_2-supported Pd−Pt alloy.[697] Reprinted with permission from ref 697. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

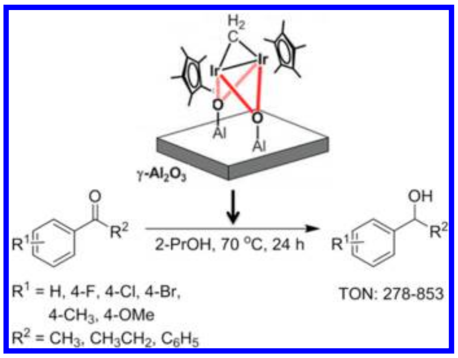
Supported gold nanoparticles have recently emerged as extraordinary catalysts for a broad range of organic transformations.[698] The vast majority of examples have shown that supported gold nanoparticles were highly efficient in the reduction of carbonyls, *N*-alkylation of amines, reduction of nitro compounds and subsequent transformation of amines, photochemical reduction of nitroarenes, as well as reductions via activation of boron−hydride bonds, by the "borrowing hydrogen" means. In 2014, Lykakis[699] prepared mesoporous TiO_2-stabilized gold nanoparticles that displayed a good catalytic activity in TH of nitroarenes to anilines, utilizing $NaBH_4$ or 1,1,3,3-tetramethyl disiloxane (TMDS) as hydrogen-donor molecules. A mechanistic study suggested that B−H or Si−H bond cleavage occurred in the rate-determining step, and [Au]−H active hybrids were formed; moreover, hydroxylamines were the only intermediate products in the catalytic cycle.[699]

2.2.6. Aluminum-Immobilized Catalysts.

In the field of TH catalysis, a number of aluminum-containing materials in the forms of AlO_x, $MgAl_2O_4$, γ-Al_2O_3, Al_2O_3, AlO(OH), and Al-pillared clay were very recently used to load copper,[700,701] iridium,[702] ruthenium,[703] palladium,[704] and bimetallic catalytic species.[705,706]

A γ-Al_2O_3-anchored dinuclear iridium complex (**Ir_2/γ-Al_2O_3**) was readily synthesized starting from the precious iridium complex $[Ir_2Cp^*_2(\mu_2\text{-}CH_2)_2]$ (Scheme 92).[702] In catalytic TH of aromatic ketones, the formed hybrid exhibited a good activity that was remarkably superior to heterogeneous SiO_2- and MgO-supported iridium dimer, and homogeneous iridium dimer. It was inferred that the formation of an Ir_2−H_2 fragment on the surface of γ-Al_2O_3 existed as a key intermediate in the TH.[702]

Scheme 92. TH of Ketones Catalyzed by Ir_2/γ-Al_2O_3[a]



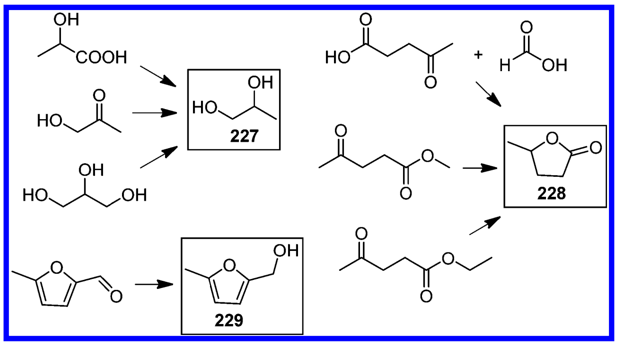
[a]Reprinted with permission from ref 702. Copyright 2012 Owner Societies.

Aluminum oxyhydroxide, AlO(OH), formed by condensation of aluminum *sec*-butoxide, was used to encapsulate ruthenium. Detailed characterization revealed that the entrapped ruthenium containing a mixture of ruthenium(0) and ruthenium(III) has an average diameter of 1.5−1.8 nm with narrow distribution. The aqueous TH of aldehydes and ketones with formate was efficiently conducted in the presence of the AlO(OH)−ruthenium composite.[703] Both aromatic and aliphatic aldehydes were quantitatively converted to the desired primary alcohols within 2−14 h, whereas ketones were less reactive in the process, providing moderate to excellent yields after a longer reaction time. AlO(OH)−ruthenium is removed from the reaction media and repeatedly used for at least five runs with no obvious activity decline.[703]

2.2.7. Zirconium-Immobilized Catalysts.

Zirconium materials-immobilized catalysts were shown to be applicable in the synthesis of bioderived platform molecules via TH.[707] An Ag−Ni/ZrO_2 catalyst catalyzes the transformation from levulinic acid and formic acid to γ-valerolactone **228**, and 99% conversion and 99% selectivity were obtained when the reaction was carried out at 220 °C for 7 h.[708] This catalytic strategy was successfully extended to the synthesis of the bioderived C_3−C_6 platform molecules **227**, **228**, and **229**, based on the use of various starting materials (Scheme 93). The synergism between Ag and Ni in TH remarkably improved the catalytic efficiency and eliminated the need for external hydrogen, making the process safer. In the case of the reaction between levulinic acid and formic acid, after the completion of the first cycle, the catalyst Ag−Ni/ZrO_2 was magnetically separated using an external magnet and retained the same activity and selectivity in at least five runs.[708]

Scheme 93. TH of the Bioderived C_3−C_6 Platform Molecules Catalyzed by Ag−Ni/ZrO_2



A new, safe, economical, and environmentally benign route has been reported for the synthesis of 1,6-hexanediol (HDO) from 5-hydroxymethylfurfural (HMF) through heterogeneous Pd/zirconium phosphate (ZrP)-catalyzed hydrogenolytic ring-opening reaction under atmospheric pressure, utilizing formic acid as hydrogen donor.[709] A 43% yield was achieved over this supported catalyst at 140 °C; such a high yield of this transformation was published for the first time without the use of high-pressure H_2 gas. The high catalytic efficiency was mainly attributed to the specific Brønsted acidity on ZrP support that accelerated the cleavage of the C−O bond in a furan ring. The efficient formic acid dissociation resulting from the presence of palladium was also a key factor for the excellent catalytic results.[709] Moreover, the solid catalyst was easily collected by centrifugation and successfully recycled at least five times.

Lin's and Sun's groups[710] found that a low-cost ZrO_2 that was prepared by the precipitation way was also active to catalyze the TH of biomass-derived ethyl levulinate producing γ-valerolactone with the assistance of supercritical ethanol as both solvent and hydrogen source. In 3 h, 95.5% conversion and 81.5% yield were observed over the amorphous and recyclable ZrO_2 catalyst with a high specific surface area and a large number of acid−base sites. A reaction mechanism involving a six-membered ring transition state was proposed.[710]

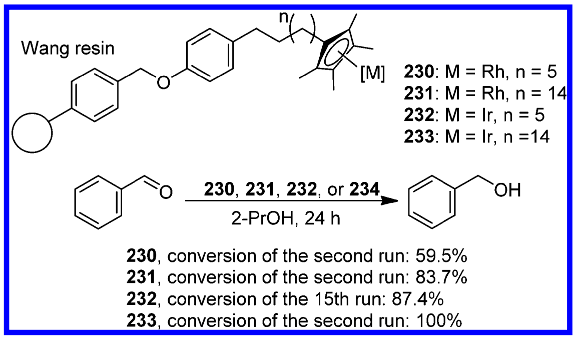
2.2.8. Other Material-Immobilized Catalysts. Other recent advances in heterogeneous TH catalysts focused on the uses of hydrotalcite,[711] zeolitic,[712] cerium dioxide,[197,713,714] resin,[715−718] Montmorillonite clay,[719,720] glass,[721] aluminosilicate,[722] metal−organic framework (MOF),[723] etc.

As a widely used immobilized support, cerium dioxide has been shown to be efficient for the synthesis of heterogeneous TH catalysts involving iridium oxide, nickel, and gold(0) nanoparticles. An iridium species supported on CeO_2 that was made by the reduction of $H_2Ir^{IV}Cl_6$ at 400 °C exhibited good catalytic performances in TH of cyclohexanone with 2-butanol.[713] It was suggested that the real active species was Ir_2O_3 nanoparticulate. The activity of this catalyst was influenced by the properties of the support and the iridium oxide center. A β-hydride elimination mechanism was proposed for the reaction, and the ability of the catalyst to form metal hydroxide was a key issue for the success of TH.[717] Shimizu's group[714] showed that a Ni-loaded CeO_2 composite serves as an effective catalyst in the reduction of ketones under TH conditions involving the use of 2-PrOH, and in this process several alcohols were isolated in 70−98% yields. In addition, this Ni−CeO_2 catalyst was reused in four successive catalytic cycles, and no detectable catalyst deactivation was observed.[714] Mesoporous CeO_2-immobilized gold nanoparticles were also found to be an effective and recyclable catalyst for the aqueous TH of aldehydes at ambient temperature.[197] This gold catalyst displayed a remarkable tolerance to functional groups including halogens, ketones, and olefins.

Das and co-workers[715] showed that rhodium(0) supported on a resin was a highly active and chemoselective catalyst for TH of nitroarenes to anilines using hydrazine hydrate as a reducing source with the assistance of microwave irradiation. It is of significant practical importance that the catalyst tolerated a wide variety of synthetically useful functional groups. Furthermore, this catalyst can be simply removed from reaction media and maintained a consistent activity in 13 cycles.[715]

The four Wang resin-supported Ir/Rh Cp*-based catalysts **230**, **231**, **232**, and **233** have been applied to mediate TH of benzaldehyde to benzyl alcohol using 2-PrOH as reductant source.[716] The catalytic results indicated that all of these catalysts presented excellent conversion. Lengthening the tether (C14 vs C5) between the catalyst and the resin support increased both the activity and the recyclability of these immobilized catalysts. In general, iridium-based catalysts revealed better catalytic performances than their rhodium counterpart. A 79.8% conversion was observed in the 26th cycle with the iridium catalyst **232** bearing a long tether (Scheme 94).[716] This reproducible and robust methodology shown here for the immobilization of metal catalysts represents a powerful way of building great heterogeneous organometallic catalysts.

Scheme 94. Wang Resin-Anchored Ir/RhCp*-Based Catalysts in TH of Benzaldehyde

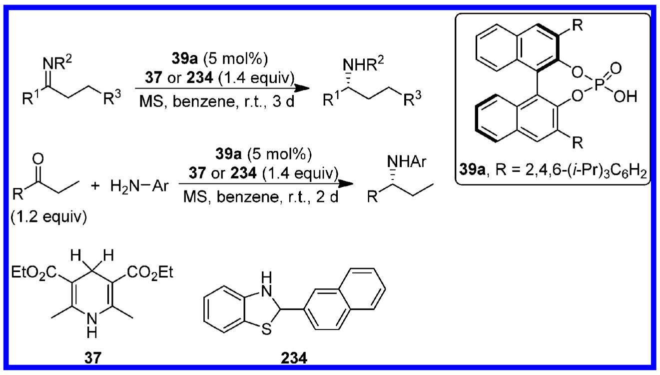


3. ORGANOCATALYSTS IN TH

As a well-studied alternative to transition-metal catalysts, organocatalysts for TH are nowadays undergoing an explosive development, and the main trends are focused on the exploration of more effective catalysts, catalyst diversity, practical applications in the synthesis of functional chemicals, and cascade reactions involving multiple reductions and rearrangements.[724−726] Very recently, plenty of organocatalysts including various types of Brønsted acids, activated carbon, fluorine/phenyl chelated boron complexes, diazaphospholene, ammonium salts, 1,3-diarylimidazolium salts, amines, thiourea hydrogen-bonded compounds, and other organic molecules were extensively used in TH,[727−731] especially in the ATH process.[732,733]

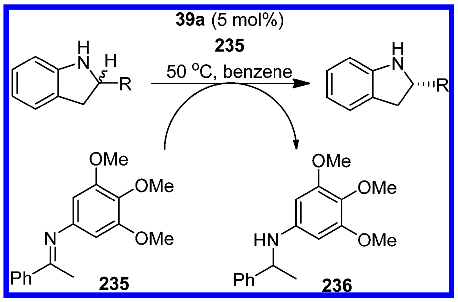
To date, chiral phosphoric acids are the most-used organocatalysts for TH.[734] ATH of ketimines derived from propiophenone derivatives and reductive amination of alkyl ethyl ketone derivatives were smoothly achieved by the use of a chiral phosphoric acid catalyst (**39a**) with the aid of Hantzsch ester (**37**) or benzothiazoline[735] having a 2-naphthyl group (**234**) as hydrogen donor (Scheme 95).[736] With both processes, a series of secondary products were synthesized in good to excellent yields. More importantly, the presence of benzothiazoline **234** provided excellent and much higher enantioselectivity than Hantzsch ester **37**.

Scheme 95. Chiral Phosphoric-Acid-Catalyzed TH of Aromatic Ketimines



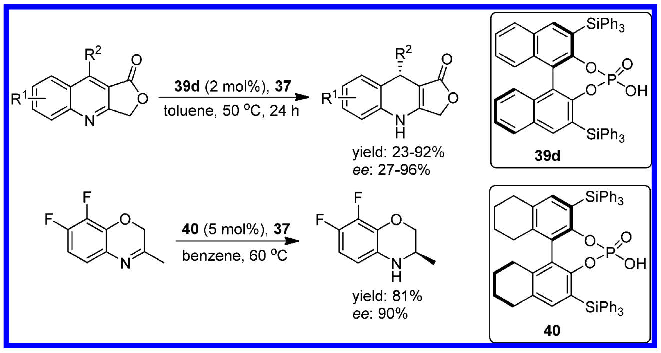
An astute strategy for the oxidative kinetic resolution of substituted indoline derivatives over the chiral phosphoric acid organocatalyst **39a** has been reported. This transformation was realized by TH to imines such as **235** leading to the formation of the amine product **236** (Scheme 96).[737] This new method was successfully applied to the syntheses of various racemic alkyl- or aryl-substituted indolines, giving around 50% yields and >99% enantioselectivities.

Scheme 96. Chiral Phosphoric Acid-Catalyzed Oxidative Kinetic Resolution of Indolines Based on TH of Imines



Pélinski and Rueping et al.[726,739] reported that the chiral phosphoric acids **39d** and **40** connected to $SiPh_3$ groups acted as catalysts in the enantioselective syntheses of 4-azapodophyllotoxin derivatives and fluoroquinolone via TH of lactone-fused quinolines and benzoxazine, respectively. In these two procedures, the Hantzsch ester **37** was employed as a reducing reagent (Scheme 97). Numerous 4-azapodophyllotoxin derivatives that are biologically active with a broad range of substituents were obtained in 23−92% yields and up to 96% ee values.[738] When the TH of 7,8-difluoro-3-methyl-2*H*-benzo[*b*][1,4]oxazine was carried out in benzene at 60 °C in the presence of 5 mol % catalyst **40**, the desired antibiotic molecule 7,8-difluoro-3-methyl-benzoxazine was obtained in 81% yield with 90% ee.[739]

Scheme 97. Chiral Phosphoric Acid-Catalyzed ATH of Quinoline and Benzoxazine



1,1-Diarylalkanes, in particular unsymmetrically substituted 1,1-diarylethanes, are very important fragments in plenty of biologically active natural products and notable synthetic pharmaceuticals. In 2015, the groups of Sun and Zhu[740] reported a new organocatalytic TH strategy for the asymmetric synthesis of 1,1-diarylethanes. In the initial study, a series of chiral phosphoric acids were tested as catalysts in the ATH of aromatic olefins to 1,1-diarylethanes in various solvents under mild conditions with various Hantzsch esters. It was found that the best conditions for this transformation were 5 mol % of the phosphoric acid **39d**, 2 equiv of the Hantzsch ester **37**, and DCM as solvent. This catalytic system tolerates various functional groups such as alkenes, alkynes, silyl ethers, thioethers, etc. A range of 1,1-diarylethanes substituted with an *o*-hydroxyphenyl or indole unit were obtained with excellent efficiency, chemoselectivity, and enantioselectivity (Scheme 98).[740] Encouraged by the importance of chiral 1,1-diarylalkanes and the outstanding catalytic performance of phosphoric acid catalysts, the scope of the TH was extended to substrates without an *o*-hydroxyl directing group (Scheme 99). Because of the loss of *o*-position anchoring group for the effective stereocontrol, the above-mentioned conditions did not provide good enantioselectivity. Further investigation revealed that the switch of catalyst and solvent to **237** and DME led to good enantioselectivity in the synthesis of 1,1-diarylalkanes with a *p*-hydroxyl or methoxyl group at the *p*-position.[740]

A styryl-functionalized chiral phosphoric acid **238** was synthesized, and then the PS-immobilized chiral phosphoric acid **239** was formed via cross-linking of **238**.[741] The catalytic applications of both **238** and **239** were explored in organocatalytic asymmetric TH of benzoxazine with the Hantzsch ester **37** (Scheme 100), showing that both of them exhibited excellent catalytic performance in terms of activity and enantioselectivity. Indeed, the catalytic activity of **239** is comparatively even higher than that of **238**. Notably, the supported catalyst **239** displayed its heterogeneous nature in the catalytic system and allowed multiple consecutive catalysis cycles, retaining almost the same activity and enantioselectivity in 12 reaction cycles.[741]

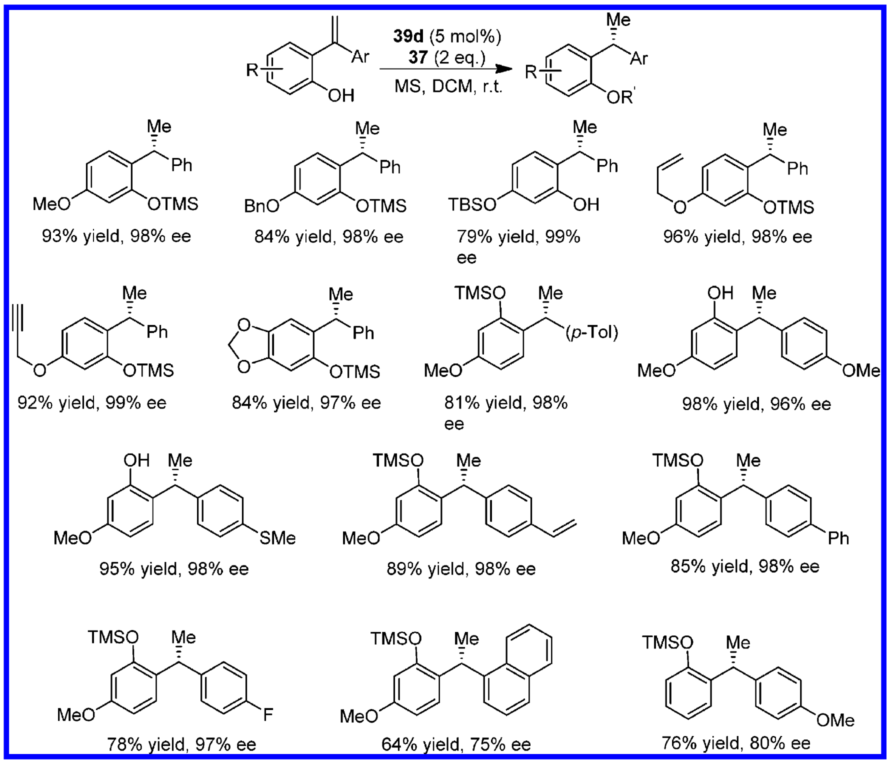
Recently, some examples of cascade reactions involving the use chiral phosphoric acid catalysts have appeared for the synthesis of complicated compounds from the easy-to-get starting materials, and chiral phosphoric acid catalysts displayed good compatibility with metal catalysts.[742,743] Akiyama's group[743] conducted the asymmetric synthesis of chrial isochromenes **242** via a cascade of intramolecular cyclization/ATH reaction of *o*-alkynylacetophenone **241** catalyzed by the $Cu(OTf)_2$-**40** catalyst, utilizing Hantzsch ester **240** as reducing donor. Under these conditions, a series of polysubstituted isochromenes were isolated in 75−90% yields and more than 90% enantioselectivities. It was proposed that the generation of copper carbonyl ylides containing ion pair intermediates **243** is a key step in this catalytic cycle (Scheme 101).[743]

Tosylic acid (TsOH) is a frequently used Brønsted acid. TsOH was found active in the organocatalytic TH of 3-indolemethanols with the assistance of Hantzsch ester **37**, delivering C-3 alkyl-substituted indoles that are useful pharmacophores in medicinal chemistry, especially in the neuroscience arena.[744] Investigation of the substrate scope revealed that a number of desired C-3 alkyl-substituted indoles were smoothly obtained in 84−99% yields. Remarkably, the catalytic protocol tolerated various functional groups that are sensitive to the conditions of conventional hydrogenations (Scheme 102).[744]

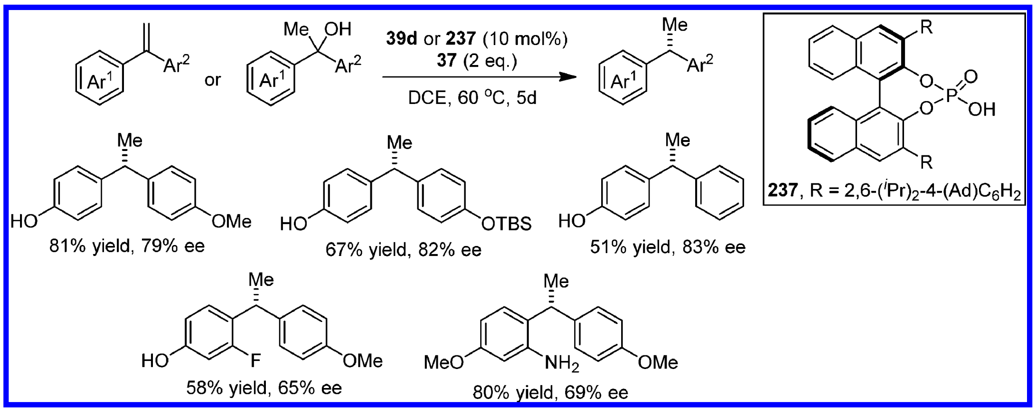
Kilic and co-workers[745,746] synthesized the six fluorine/phenyl chelated boron complexes **244**−**249** (Scheme 103) from the reactions of the boron reagent BPh_3 or $BF_3{\cdot}Et_2O$ with the corresponding ligands. These air-stable complexes were applied as catalysts in TH of acetophenone with various substituents in the presence of 2-PrOH and KOH, and several alcohols were quantitatively produced.

Recently, the NH-containing organocatalysts **250**−**255** have emerged in the catalytic symmetric TH and ATH of nitroolefin (C=C bond),[747,748] *α*,*β*-unsaturated aldehydes,[749] and conjugated olefins of steroids.[750] For example, Paradies' group[747,748] found that the chiral thiourea-type hydrogen-

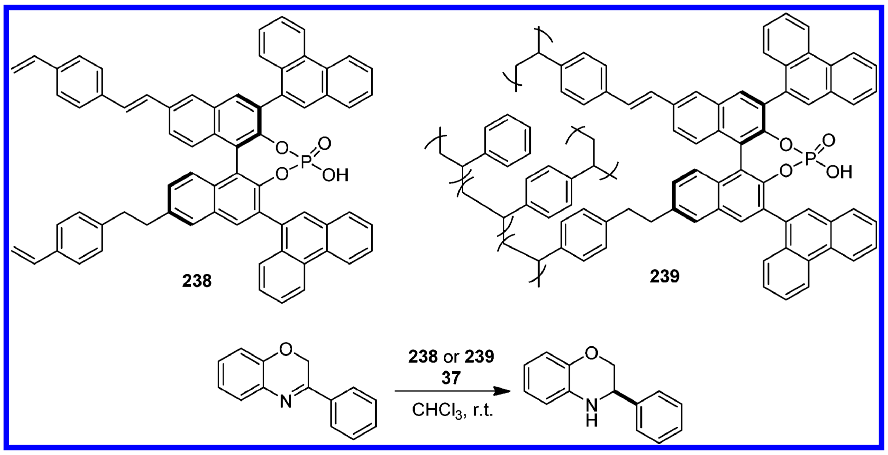
Scheme 98. Organocatalytic ATH of Aromatic Olefins Bearing an *o*-Hydroxy Group



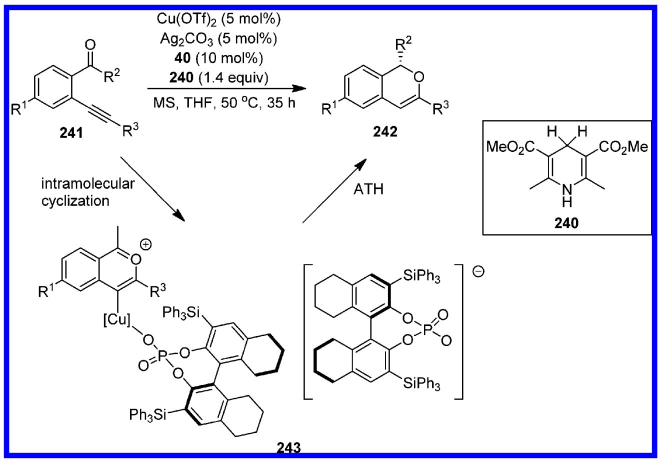
Scheme 99. Organocatalytic ATH of Aromatic Olefins without an *o*-Hydroxy Group



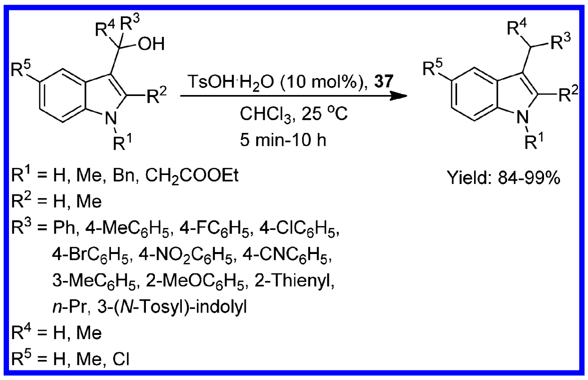
Scheme 100. TH of Benzoxazine Applying Unsupported Catalyst 238 and Polymer-Supported Chiral Phosphoric Acid Catalyst 239



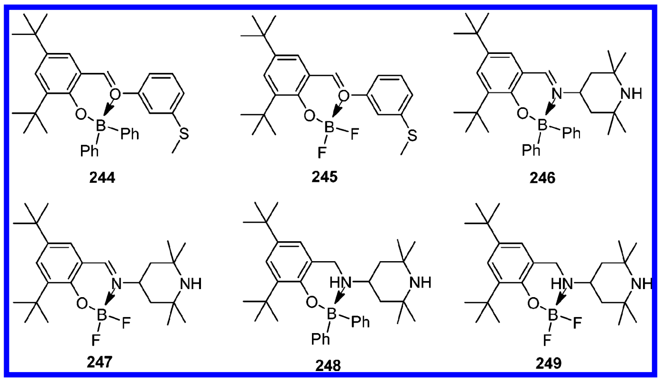
Scheme 101. Enantioselective Synthesis of Isochromene Derivatives by Sequential Intramolecular Cyclization and ATH of *o*-Alkynylacetophenones



Scheme 102. Synthesis of C-3 Alkyl-Substituted Indoles via Brønsted Acid-Catalyzed TH



Scheme 103. Boron Complexes for Organocatalytic TH of Acetophenone Derivatives



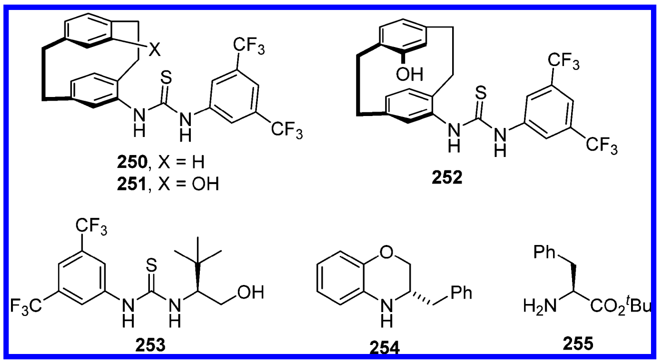
bonded catalysts **250**–**252** presented activity in the ATH of nitroolefins to chiral saturated nitro products (Scheme 104). With compound **252** as catalyst, up to 99% yield and 87% ee value were obtained.[748]

4. OTHER CATALYSTS OR PROTOCOLS FOR TH

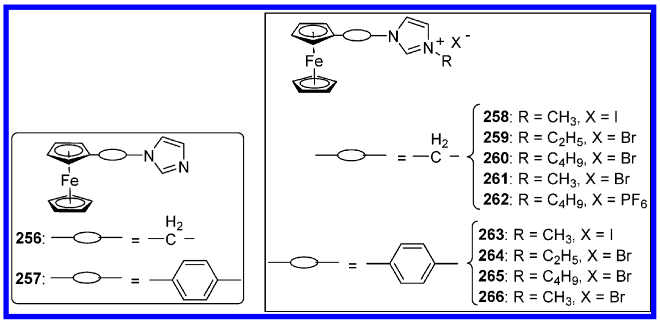
Reports on catalytic TH involving Lewis acids,[751] ferrocenylimidazolium salts,[752] and bases[249,250] have also recently appeared.

The series of ferrocenylimidazolium salts **256**–**266** with methylene and phenyl groups as bridges between the ferrocenyl and alkylimidazolium moieties were synthesized (Scheme 105), and their catalytic property was evaluated in the reduction of ketones under TH conditions with 2-PrOH/KOH.[752] Compounds **260** and **265** presented the best catalytic activity, reaching as high as 1880 TON. The reactions of α,β-unsaturated ketones (3-penten-2-one and 4-hexen-3-one) chemoselectively generated the corresponding saturated ketones. On the contrary, the use of unconjugated 5-hexen-2-one yielded an unsaturated alcohol.[752]

Scheme 104. Amine-Containing Organocatalysts



Scheme 105. Ferrocenylimidazolium Salts

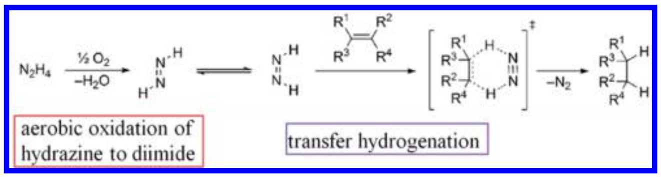


Base-catalyzed TH have also emerged recently and received considerable attention. The groups of Polshettiwar and Varma et al.[249,250] illustrated for the first time the importance of the hydroxide bases for the TH of carbonyls using 2-PrOH as hydrogen sources, without the use of any transition metal. Chuah and co-workers[753] discovered that potassium triphosphate that was preactivated at 600 °C was a surprisingly active catalyst for the TH of aromatic aldehydes to the corresponding primary alcohols with the use of 2-PrOH. In this catalytic system, the reactivities of ketones were lower than those of aldehydes. In the catalytic process, the formation of new, weaker basic sites by high temperature pretreatment was essential for high catalytic activity.[753] Later, Astruc's group[754] reported that the abundant and cheap NaOH efficiently promoted TH of carbonyls including ketones and aldehydes yielding primary and secondary alcohols with renewable and cheap EtOH as both hydrogen source and solvent. The combination of NaOH and 2-PrOH also mediated the reduction of nitroarenes to the corresponding anilines and azobenzenes by TH means.[754] For the based-catalyzed TH protocol, these authors suggested that the possibility of catalysis of the reaction by subppm traces of transition metal in commercial bases cannot be retained, because only transition metals with remarkably higher quantities or with strongly activating ligands are effective for these reactions.

As mentioned in the Introduction, TH eventually also proceeds under uncatalytic condition. The group of Berke[755] very recently reported that metal-free TH of imines with ammonia—borane was achieved under mild conditions. On the basis of deuterium kinetic isotope effects (DKIE) determinations, ab initio calculations, Hammett correlations, and the significantly polar nature of ammonia—borane, a direct reaction of ammonia—borane with imines via a double H transfer process was proposed for the transformation.[755] Subsequently, the same group[756] extended this method to TH of polarized olefins bearing strongly electron-withdrawing groups such as nitriles or esters on one side of the double bond, producing several alkanes in more than 92% yields. It was suggested that a direct double-H transfer occurred stepwise with a unique hydroboration intermediate and hydride transfer before proton transfer.[756]

A catalyst-free process containing in situ generation of diimide from hydrazine hydrate and molecular oxygen for the subsequent TH of olefins with the aid of diimide was discovered (Scheme 106).[757] To achieve this process, a gas—liquid continuous-flow system was designed and used (Figure 7). This system included several components including a pump (P), a mass-flow controller (MFC), a glass static mixer (GSM) to generate segments of the liquid phase and O_2, a heat exchanger (HE), a residence time unit (RT), and a static (BPR1) and adjustable back pressure regulator (BPR2). The use of a gas—liquid continuous flow system did not only avoid the potential problems caused by high oxygen pressure, but also enabled the production in large scale. Through this strategy, a series of internal and terminal olefins were smoothly converted to the desired alkanes, affording >99% conversions, excellent yields, and >99% selectivities in most cases.[757]

Scheme 106. Aerobic Oxidation of Hydrazine to Diimide and Subsequent Uncatalytic TH



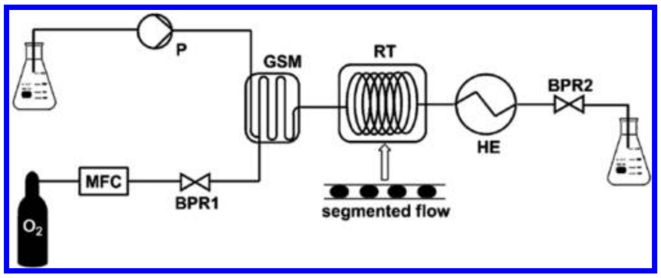


Figure 7. Continuous-flow setup for the in situ generation of diimide and subsequent olefin reduction by TH.[757] Reprinted with permission from ref 757. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

5. CONCLUSIONS AND PERSPECTIVES

As an attractive alternative to direct hydrogenation with a pressure of H_2 gas, TH involving non-H_2 hydrogen sources is a rapidly growing field in the context of the high demand for the development of sustainable and green chemistry including economy consideration. To date, plenty of catalysts, ligands, bases, solvents, and hydrogen sources have been explored in the syntheses of a variety of compounds,[758,759] in particular fine chemicals, bioactive molecules, pharmaceuticals, agricultural chemicals, and complicated products bearing functional groups.

Significant breakthroughs and developments of TH have been achieved in the past few years. This great progress was witnessed in several aspects of the published studies, such as exploration of catalyst diversity, design of more efficient ligands or stabilizers to improve precious metal catalysts, use of abundant biometal catalysts involving Fe, Co, and Ni, development of recyclable catalysts, exploration of "green" hydrogen donors, generalization of aqueous reaction medium, improvement in asymmetric synthesis, expansion of substrate diversity, and investigations of reaction mechanisms. Building on previous studies, plenty of broader, greener, more efficient, more economic, and more practical catalytic systems for TH were recently exploited. Notably, Sadler's group[760] disclosed TH catalysis in cell in the presence of Noyori-type ruthenium complexes using nontoxic concentrations of formate as a hydride donor, a new anticancer strategy. All of the information indicates that the field of TH is now in its golden age.

Although remarkable progress in TH has been made, many unsolved problems and challenges remain in many reported results. For instance, most of the known catalytic reactions with abundant metal catalysts are either limited in scope or do not qualify for practical applications. In general, the catalytic results of ATH are not as good as those of direct asymmetric hydrogenations. The efficiency of TH of imines, olefins, and nitroarenes is still lower than that of ketones. The use of metal nanoparticle catalysts in this area is so far underdeveloped.

Further work is also required to seek artificial enzymes for the extremely efficient catalytic TH, to use the TH process in convenient cascade reaction by combination with other transformations, and to push these TH catalysts, especially supported heterogeneous catalysts, to their use in multikilogram scale synthesis toward industrial production. Nowadays, new discoveries are propelling the field by addressing these challenges. Thus, it is believed that TH has a bright future.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wangdong0377@163.com.
*E-mail: d.astruc@ism.u-bordeaux1.fr.

Notes

The authors declare no competing financial interest.

Biographies

Dong Wang studied organic chemistry with Prof. Baohua Chen at the University of Lanzhou. He received a doctoral degree there in 2013 and a second doctorate with Prof. Didier Astruc at the University of Bordeaux in 2014 on catalytic reactions including transfer hydrogenation. He is presently carrying out postdoc studies with Prof. Datong Song in Toronto.

Didier Astruc is Professor of Chemistry at the University of Bordeaux and Member of the Institut Universitaire de France and various Academies. He did his Ph.D. in Rennes with Prof. René Dabard and his postdoc at MIT with Prof. Richard R. Schrock. His present interests are in nanosciences and applications to catalysis, sensing, and nanomedicine.

ACKNOWLEDGMENTS

Financial support from the Chinese Research Council (Ph.D. grant to D.W.), the Université de Bordeaux, the Centre National de la Recherche Scientifique (CNRS), and L'Oréal R&D France is gratefully acknowledged.

ABBREVIATIONS

acac	acetylacetonate
AH	asymmetric hydrogenation
ampy	2-aminomethylpyridine
aNHC	abnormal *N*-heterocyclic carbenes
ATH	asymmetric transfer hydrogenation
BIN	1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)-imidazol-2-ylidene
CF_3TsEN	*N*-[*p*-(trifluoromethyl)benzenesulfonyl]-1,2-ethylenediamine)
CHD	cyclohexadiene
CNF	carbon nanofibers
CNTs	carbon nanotubes
Cp	pentahapto cyclopentadienyl (η^5-C_5H_5)
Cp*	pentahapto 1,2,3,4,5-pentamethylcyclopentadienyl (η^5-C_5Me_5)
CPB	cetylpyridine bromide
CsDPEN	*N*-(camphorsulfonyl)-1,2-diphenylethylenediamine
CTAB	cetyltrimethylammonium bromide
CuAAC	Cu^I-catalyzed azide alkyne cycloaddition
dhtp	6,6′-dihydroxy terpyridine
dmpe	1,2-(bis)dimethylphosphinoethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
DPEN	1,2-diphenylethylenediamine
EDX	energy-dispersive X-ray spectroscopy
GNPs	graphene nanoplatelets
GNSs	graphene nanosheets
HDO	1,6-hexanediol
HMF	5-hydroxymethylfurfural
hPG	hyperbranched polyglycerol
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
KHMDS	potassium hexamethylsilazan
MNPs	magnetic nanoparticles
MOF	metal–organic framework
MPV	Meerwein–Ponndorf–Verley
MWCNTs	multiwall carbon nanotubes
NHC	*N*-heterocyclic carbenes
NP	naphthyridine
NSHC	*N,S*-heterocyclic carbene
PANI	polyaniline
PMA	poly(methyl acrylate)
PMO	periodic mesoporous organosilica
PPY	olypyrrole
PS	polystyrene
PTA	1,3,5-triaza-7-phosphaadamantane
PVI	poly(1-vinylimidazole)
PVP	poly(4-vinylpyridine)
Pyme	1-(pyridine-2-yl)methanamine
rt	room temperature
SEM	scanning electron microscopy
SQUID	superconducting quantum interference device
(*S,S*)-^{i}Pr pybox	2,6-bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
TOF	turnover frequency
TON	turnover number
TOPO	trioctylphosphine oxide
TH	transfer hydrogenation
TsDPEN	*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine)
XPS	X-ray photoelectron spectroscopy

REFERENCES

(1) Cerveny, L., Ed. *Catalytic Hydrogenation*; Elsevier: Amsterdam, 1986.

(2) de Vries, J. G., Elsevier, C. J., Eds. *The Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, 2007.

(3) Andersson, P. G., Munslow, I. J., Eds. *Modern Reduction Methods*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2008.

(4) Brieger, G.; Nestrick, T. J. Catalytic Transfer Hydrogenation. *Chem. Rev.* **1974**, *74*, 567–580.

(5) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. Heterogeneous Catalytic Transfer Hydrogenation and its Relation to Other Methods for Reduction of Organic Compounds. *Chem. Rev.* **1985**, *85*, 129–170.

(6) Zassinovich, G.; Mestroni, G.; Gladiali, S. Asymmetric Hydrogen Transfer Reactions Promoted by Homogeneous Transition Metal Catalysts. *Chem. Rev.* **1992**, *92*, 1051−1069.

(7) Noyori, R.; Hashiguchi, S. Asymmetric Transfer Hydrogenation Catalyzed by Chiral Ruthenium Complexes. *Acc. Chem. Res.* **1997**, *30*, 97−102.

(8) Palmer, M. J.; Wills, M. Asymmetric Transfer Hydrogenation of C═O and C═N Bonds. *Tetrahedron: Asymmetry* **1999**, *10*, 2045−2061.

(9) Everaere, K.; Mortreux, A.; Carpentier, J.-F. Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Carbonyl Compounds with 2-Propanol and Ephedrine-Type Ligands. *Adv. Synth. Catal.* **2003**, *345*, 67−77.

(10) Gladiali, S.; Alberico, E. Asymmetric Transfer Hydrogenation: Chiral Ligands and Applications. *Chem. Soc. Rev.* **2006**, *35*, 226−236.

(11) Ikariya, T.; Blacker, A. J. Asymmetric Transfer Hydrogenation of Ketones with Bifunctional Transition Metal-Based Molecular Catalysts. *Acc. Chem. Res.* **2007**, *40*, 1300−1308.

(12) Wang, C.; Wu, X.; Xiao, J. Broader, Greener, and More Efficient: Recent Advances in Asymmetric Transfer Hydrogenation. *Chem.—Asian. J.* **2008**, *3*, 1750−1770.

(13) Wu, X.; Xiao, J. Aqueous-Phase Asymmetric Transfer Hydrogenation of Ketones – A Greener Approach to Chiral Alcohols. *Chem. Commun.* **2007**, 2449−2466.

(14) Clapham, S. E.; Hadzovic, A.; Morris, R. H. Mechanisms of The H_2-Hydrogenation and Transfer Hydrogenation of Polar Bonds Catalyzed by Ruthenium Hydride Complexes. *Coord. Chem. Rev.* **2004**, *248*, 2201−2237.

(15) Knoevenagel, E.; Bergdolt, B. Ueber das Verhalten Des $\Delta_{2.5}$-Dihydroterephtalsäuredimethylesters bei höheren Temperaturen und in Gegenwart von Palladiummohr. *Chem. Ber.* **1903**, *36*, 2857−2860.

(16) Wieland, H. Über hydrierung and dehydrierung. *Chem. Ber.* **1912**, *45*, 484−493.

(17) Braude, E. A.; Linstead, R. P. Hydrogen Transfer. Part I. Introductory Survey. *J. Chem. Soc.* **1954**, 3544−3547.

(18) Verley, A. Sur l'échange de groupements fonctionnels entre deux molécules. Passage de la fonction alcool à la fonction aldéhyde et inversement. *Bull. Soc. Chim. Fr.* **1925**, *37*, 537−542.

(19) Meerwein, H.; Schmidt, R. Ein neues Verfahren zur Reduktion von Aldehyden und Ketonen. *Liebigs Ann. Chem.* **1925**, *444*, 221−238.

(20) Chuah, G. K.; Jaenicke, S.; Zhu, Y. Z.; Liu, S. H. Meerwein-Ponndorf-Verley Reduction over Heterogeneous Catalysts. *Curr. Org. Chem.* **2006**, *10*, 1639−1654.

(21) de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. Meerwein-Ponndorf-Verley Reductions and Oppenauer Oxidations: An Integrated Approach. *Synthesis* **1994**, *10*, 1007−1017.

(22) Ashby, E. C. Single-Electron Transfer, A Major Reaction Pathway in Organic Chemistry. An Answer to Recent Criticisms. *Acc. Chem. Res.* **1988**, *21*, 414−421.

(23) Cohen, R.; Graves, C. R.; Nguyen, S. T.; Martin, J. M. L.; Ratner, M. A. The Mechanism of Aluminum-Catalyzed Meerwein-Schmidt-Ponndorf-Verley Reduction of Carbonyls to Alcohols. *J. Am. Chem. Soc.* **2004**, *126*, 14796−14803.

(24) Oppenauer, R. V. Eine Methode der Dehydrierung von Sekundären Alkoholen zu Ketonen. I. Zur Herstellung von Sterinketonen und Sexualhormonen. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 137−144.

(25) Figueras, F. Base Catalysis in The Synthesis of Fine Chemicals. *Top. Catal.* **2004**, *29*, 189−196.

(26) Campbell, E. J.; Zhou, H.; Nguyen, S. T. Catalytic Meerwein−Pondorf−Verley Reduction by Simple Aluminum Complexes. *Org. Lett.* **2001**, *3*, 2391−2393.

(27) Haddad, Y. M. Y.; Henbest, H. B.; Husbands, J.; Mitchell, T. R. B. Reduction of Cyclohexanones to Axial Alcohols via Iridium Containing Catalysts. *Proc. Chem. Soc. London* **1964**, 361−365.

(28) Trochagr, J.; Henbest, H. B. Catalysis of the Transfer of Hydrogen from Propan-2-ol to *α,β*-Unsaturated Ketones by Organo-iridium Compounds. A Carbon-Iridium Compound Containing a Chelate Keto-group. *Chem. Commun.* **1967**, 544−544.

(29) McPartli, M.; Mason, R. The Structure of a Bis(dimethy1 sulfoxide)iridium(III) Complex Containing a Metal-Carbon *σ*-Bond. *Chem. Commun.* **1967**, 545−546.

(30) Sasson, Y.; Blum, J. Homogeneous Catalytic Transfer-Hydrogenation of *α,β*-Unsaturated Carbonyl Compounds by Dichlorotris-(triphenylphosphine)ruthenium(II). *Tetrahedron Lett.* **1971**, *12*, 2167−2170.

(31) Blum, J.; Sasson, Y.; Iflah, S. Hydrogen Transfer from Formyl Compounds to *α,β*-Unsaturated Ketones Catalyzed by Ru, Rh and Ir Complexes. *Tetrahedron Lett.* **1972**, *13*, 1015−1018.

(32) Sasson, Y.; Blum, J. Dichlorotris(triphenylphosphine)-ruthenium-Catalyzed Hydrogen Transfer from Alcohols to Saturated and *α,β*-Unsaturated Ketones. *J. Org. Chem.* **1975**, *40*, 1887−1896.

(33) Chowdhury, R. L.; Bäckvall, J.-E. Efficient Ruthenium-catalysed Transfer Hydrogenation of Ketones by Propan-2-ol. *J. Chem. Soc., Chem. Commun.* **1991**, 1063−1064.

(34) Bianchi, M.; Matteol, U.; Menchi, G.; Frediani, P.; Pratesi, U.; Piacenti, F.; Botteghi, C. Asymmetric Synthesis by Chiral Ruthenium Complexes: V. Homogeneous Reduction of Ketones: Transfer and Pressure Hydrogenation in The Presence of $H_4Ru_4(CO)_8[(-)\text{-}DIOP]_2$. *J. Organomet. Chem.* **1980**, *198*, 73−80.

(35) Matteoli, U.; Frediani, P.; Bianchi, M.; Botteghi, C.; Gladiali, S. Asymmetric Homogeneous Catalysis by Ruthenium Complexes. *J. Mol. Catal.* **1981**, *12*, 265−319.

(36) Pugin, B.; Blaser, H.-U. Immobilized Complexes for Enantioselective Catalysis: When Will They Be Used in Industry? *Top. Catal.* **2010**, *53*, 953−962.

(37) Václavík, J.; Šot, P.; Vilhanová, B.; Pecháček, J.; Kuzma, M.; Kačer, P. Practical Aspects and Mechanism of Asymmetric Hydrogenation with Chiral Half-Sandwich Complexes. *Molecules* **2013**, *18*, 6804−6828.

(38) Kitamura, M.; Tokunaga, M.; Noyori, R. Asymmetric Hydrogenation of.beta.-Keto Phosphonates: A Practical Way to Fosfomycin. *J. Am. Chem. Soc.* **1995**, *117*, 2931−2932.

(39) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Ketones Using a Formic Acid−Triethylamine Mixture. *J. Am. Chem. Soc.* **1996**, *118*, 2521−2522.

(40) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. Asymmetric Transfer Hydrogenation of Imines. *J. Am. Chem. Soc.* **1996**, *118*, 4916−4917.

(41) Noyori, R. Asymmetric Catalysis: Science and Opportunities (Nobel Lecture). *Angew. Chem., Int. Ed.* **2002**, *41*, 2008−2022.

(42) Samec, J. S. M.; Backvall, J.-E.; Andersson, P. G.; Brandt, P. Mechanistic Aspects of Transition Metal-Catalyzed Hydrogen Transfer Reactions. *Chem. Soc. Rev.* **2006**, *35*, 237−248.

(43) Ward, T. R. Artificial Metalloenzymes Based on the Biotin−Avidin Technology: Enantioselective Catalysis and Beyond. *Acc. Chem. Res.* **2011**, *44*, 47−57.

(44) Bartók, M. Unexpected Inversions in Asymmetric Reactions: Reactions with Chiral Metal Complexes, Chiral Organocatalysts, and Heterogeneous Chiral Catalysts. *Chem. Rev.* **2010**, *110*, 1663−1705.

(45) Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments. *Adv. Synth. Catal.* **2003**, *345*, 103−151.

(46) César, V.; Gade, L. H.; Bellemin-Laponnaz, S. In *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; RSC Catalysis Series No. 6; Royal Society of Chemistry: Cambridge, 2011.

(47) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612−3676.

(48) Dupont, J.; Consorti, C. S.; Spencer, J. The Potential of Palladacycles: More Than Just Precatalysts. *Chem. Rev.* **2005**, *105*, 2527−2572.

(49) van der Boom, M. E.; Milstein, D. Cyclometalated Phosphine-Based Pincer Complexes: Mechanistic Insight in Catalysis, Coordination, and Bond Activation. *Chem. Rev.* **2003**, *103*, 1759−1792.

(50) Albrecht, M.; van Koten, G. Platinum Group Organometallics Based on "Pincer" Complexes: Sensors, Switches, and Catalysts. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781.

(51) Arduengo, A. J.; Harlow, L. R.; Kline, M. A stable crystalline carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(52) Peris, E.; Crabtree, R. H. Recent homogeneous catalytic applications of chelate and pincer *N*-heterocyclic carbenes. *Coord. Chem. Rev.* **2004**, *248*, 2239−2246.

(53) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. Cationic Iridium Complexes Bearing Imidazol-2-ylidene Ligands as Transfer Hydrogenation Catalysts. *Organometallics* **2001**, *20*, 4246−4252.

(54) Saidi, O.; Williams, J. M. J. Iridium-Catalyzed Hydrogen Transfer Reactions. *Top. Organomet. Chem.* **2011**, *34*, 77−106.

(55) Zinner, S. C.; Rentzsch, C. F.; Herdtweck, E.; Herrmann, W. A.; Kühn, F. E. *N*-heterocyclic Carbenes of Iridium(I): Ligand Effects on The Catalytic Activity in Transfer Hydrogenation. *Dalton Trans.* **2009**, 7055−7062.

(56) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. Chelated Iridium(III) Bis-carbene Complexes as Air-Stable Catalysts for Transfer Hydrogenation. *Organometallics* **2002**, *21*, 3596−3604.

(57) da Costa, A. P.; Viciano, M.; Sanaú, M.; Merino, S.; Tejeda, J.; Peris, E.; Royo, B. First Cp*-Functionalized N-Heterocyclic Carbene and Its Coordination to Iridium. Study of the Catalytic Properties. *Organometallics* **2008**, *27*, 1305−1309.

(58) Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. Iridium Complexes with *N*-Allyl-Substituted Benzimidazol-2-ylidene Ligands and Their Application in Catalytic Transfer Hydrogenation. *Organometallics* **2005**, *24*, 2203−2209.

(59) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. Efficient Transfer Hydrogenation Using Iridium and Rhodium Complexes of Benzannulated N-Heterocyclic Carbenes. *Eur. J. Inorg. Chem.* **2008**, 5418−5423.

(60) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. Annulated N-Heterocyclic Carbene Ligands Derived from 2-Methylaminopiperidine: Their Complexes and Catalytic Applications. *Organometallics* **2008**, *27*, 571−575.

(61) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. H. Transfer Hydrogenation of Imines and Alkenes and Direct Reductive Amination of Aldehydes Catalyzed by Triazole-Derived Iridium(I) Carbene Complexes. *Organometallics* **2007**, *26*, 1226−1230.

(62) Sinha, A.; Rahaman, S. M. W.; Sarkar, M.; Saha, B.; Daw, P.; Bera, J. K. Multifaceted Coordination of Naphthyridine−Functionalized N-Heterocyclic Carbene: A Novel "$\mathrm{Ir^{III}}$(C^N)(C^C)" Compound and Its Evaluation as Transfer Hydrogenation Catalyst. *Inorg. Chem.* **2009**, *48*, 11114−11122.

(63) Dragutan, V.; Dragutan, I.; Delaude, L.; Demonceau, A. NHC−Ru Complexes—Friendly Catalytic Tools for Manifold Chemical Transformations. *Coord. Chem. Rev.* **2007**, *251*, 765−794.

(64) Enthaler, S.; Jackstell, R.; Hagemann, B.; Junge, K.; Erre, G.; Beller, M. Efficient Transfer Hydrogenation of Ketones in The Presence of Ruthenium *N*-Heterocyclic Carbene Catalysts. *J. Organomet. Chem.* **2006**, *691*, 4652−4659.

(65) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. Stable N-Functionalised 'Pincer' Bis Carbene Ligands and Their Ruthenium Complexes; Synthesis and Catalytic Studies. *Chem. Commun.* **2002**, 1376−1377.

(66) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. New Ruthenium(II) CNC-Pincer Bis(carbene) Complexes: Synthesis and Catalytic Activity. *Organometallics* **2003**, *22*, 1110−1114.

(67) Zeng, F.; Yu, Z. Ruthenium(II) Complexes Bearing a Pyridyl-Supported Pyrazolyl−N-Heterocyclic Carbene (NNC) Ligand and Their Catalytic Activity in the Transfer Hydrogenation of Ketones. *Organometallics* **2008**, *27*, 6025−6028.

(68) Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P. Fast Transfer Hydrogenation Using A Highly Active Orthometalated Heterocyclic Carbene Ruthenium Catalyst. *J. Organomet. Chem.* **2005**, *690*, 5570−5575.

(69) Poyatos, M.; Maisse-François, A.; Bellemin-Laponnaz, S.; Peris, E.; Gade, L. H. Synthesis and Structural Chemistry of Arene-Ruthenium Half-Sandwich Complexes Bearing an Oxazolinyl−Carbene Ligand. *J. Organomet. Chem.* **2006**, *691*, 2713−2720.

(70) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. Chelating Bis-Carbene Rhodium(III) Complexes in Transfer Hydrogenationof Ketones and Imines. *Chem. Commun.* **2002**, 32−33.

(71) Jokić, N. B.; Zhang-Presse, M.; Goh, S. L. M.; Straubinger, C. S.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E. Symmetrically Bridged Bis-N-Heterocyclic Carbene Rhodium(I) Complexes and Their Catalytic Application for Transfer Hydrogenation Reaction. *J. Organomet. Chem.* **2011**, *696*, 3900−3905.

(72) Cross, W. B.; Daly, C. G.; Boutadla, Y.; Singh, K. Variable Coordination of Amine Functionalised *N*-Heterocyclic Carbeneligands to Ru, Rh and Ir: C−H and N−H Activation and Catalytic Transfer Hydrogenation. *Dalton Trans.* **2011**, *40*, 9722−9730.

(73) Gülcemal, S.; Daran, J.-C.; Çetinkaya, B. Diether Functionalized Rhodium(I)−*N*-Heterocyclic Carbene Complexes and Their Catalytic Application for Transfer Hydrogenation Reactions. *Inorg. Chim. Acta* **2011**, *365*, 264−268.

(74) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by Chiral Ruthenium(II) Complexes. *J. Am. Chem. Soc.* **1995**, *117*, 7562−7563.

(75) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. The Hydrogenation/Transfer Hydrogenation Network: Asymmetric Hydrogenation of Ketones with Chiral η^6-Arene/*N*-Tosylethylenediamine−Ruthenium(II) Catalysts. *J. Am. Chem. Soc.* **2006**, *128*, 8724−8725.

(76) Takamura, H.; Ando, J.; Abe, T.; Murata, T.; Kadota, I.; Uemura, D. Stereocontrolled synthesis of the C79−C96 fragment of symbiodinolide. *Tetrahedron Lett.* **2008**, *49*, 4626−4629.

(77) Fu, R.; Chen, J.; Guo, L.-C.; Ye, J.-L.; Ruan, Y.-P.; Huang, P.-Q. Asymmetric Total Synthesis of (−)-Awajanomycin. *Org. Lett.* **2009**, *11*, 5242−5245.

(78) Kumaraswamy, G.; Ramakrishna, G.; Naresh, P.; Jagadeesh, B.; Sridhar, B. A Flexible Enantioselective Total Synthesis of Diospongins A and B and Their Enantiomers Using Catalytic Hetero-Diels−Alder/Rh-Catalyzed 1,4-Addition and Asymmetric Transfer Hydrogenation Reactions as Key Steps. *J. Org. Chem.* **2009**, *74*, 8468−8471.

(79) Mogi, M.; Fuji, K.; Node, M. Asymmetric Reduction of Methoxy Substituted *β*-Tetralones Using Transfer Hydrogenation. *Tetrahedron: Asymmetry* **2004**, *15*, 3715−3717.

(80) Hennig, M.; Püntener, K.; Scalone, M. Synthesis of (*R*)- and (*S*)-4-Hydroxyisophorone by Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Ketoisophorone. *Tetrahedron: Asymmetry* **2000**, *11*, 1849−1858.

(81) Ding, Z.; Yang, J.; Wang, T.; Shen, Z.; Zhang, Y. Dynamic Kinetic Resolution of *β*-Keto Sulfones *via* Asymmetric Transfer Hydrogenation. *Chem. Commun.* **2009**, 571−573.

(82) Zhang, B.; Xu, M.-H.; Lin, G.-Q. Catalytic Enantioselective Synthesis of Chiral Phthalides by Efficient Reductive Cyclization of 2-Acylarylcarboxylates under Aqueous Transfer Hydrogenation Conditions. *Org. Lett.* **2009**, *11*, 4712−4715.

(83) Leijondahl, K.; Fransson, A.-B. L.; Bäckvall, J.-E. Efficient Ruthenium-Catalyzed Transfer Hydrogenation/Hydrogenation of 1,3-Cycloalkanediones to 1,3-Cycloalkanediols Using Microwave Heating. *J. Org. Chem.* **2006**, *71*, 8622−8625.

(84) Kioke, T.; Murata, K.; Ikariya, T. Stereoselective Synthesis of Optically Active *α*-Hydroxy Ketones and *anti*-1,2-Diols via Asymmetric Transfer Hydrogenation of Unsymmetrically Substituted 1,2-Diketones. *Org. Lett.* **2000**, *2*, 3833−3836.

(85) Evanno, L.; Ormala, J.; Pihko, P. M. A Highly Enantioselective Access to Tetrahydroisoquinoline and *β*-Carboline Alkaloids with Simple Noyori-Type Catalysts in Aqueous Media. *Chem.—Eur. J.* **2009**, *15*, 12963−12967.

(86) Martins, J. E. D.; Clarkson, G. J.; Wills, M. Ru(II) Complexes of N-Alkylated TsDPEN Ligands in Asymmetric Transfer Hydrogenation of Ketones and Imines. *Org. Lett.* **2009**, *11*, 847−850.

(87) Zhang, J.; Blazecka, P. G.; Bruendl, M. M.; Huang, Y. Ru-TsDPEN with Formic Acid/Hünig's Base for Asymmetric Transfer Hydrogenation, a Practical Synthesis of Optically Enriched *N*-Propyl Pantolactam. *J. Org. Chem.* **2009**, *74*, 1411−1414.

(88) Václavík, J.; Šot, P.; Pecháček, J.; Vilhanová, B.; Matuška, O.; Kuzma, M.; Kačer, P. Experimental and Theoretical Perspectives of the Noyori-Ikariya Asymmetric Transfer Hydrogenation of Imines. *Molecules* **2014**, *19*, 6987−7007.

(89) Murata, K.; Okano, K.; Miyagi, M.; Iwane, H.; Noyori, R.; Ikariya, T. A Practical Stereoselective Synthesis of Chiral Hydrobenzoins via Asymmetric Transfer Hydrogenation of Benzils. *Org. Lett.* **1999**, *1*, 1119−1121.

(90) Watanabe, M.; Murata, K.; Ikariya, T. Practical Synthesis of Optically Active Amino Alcohols via Asymmetric Transfer Hydrogenation of Functionalized Aromatic Ketones. *J. Org. Chem.* **2002**, *67*, 1712−1715.

(91) Canivet, J.; Labat, G.; Stoeckli-Evans, H.; Süss-Fink, G. Water-Soluble Arene Ruthenium Complexes Containing a *trans*-1,2-Diaminocyclohexane Ligand as Enantioselective Transfer Hydrogenation Catalysts in Aqueous Solution. *Eur. J. Inorg. Chem.* **2005**, 4493−4500.

(92) Canivet, J.; Süss-Fink, G. Water-Soluble Arene Ruthenium Catalysts Containing Sulfonated Diamine Ligands for Asymmetric Transfer Hydrogenation of α-Aryl Ketones and Imines in Aqueous Solution. *Green Chem.* **2007**, *9*, 391−397.

(93) Ma, Y. P.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J. Asymmetric Transfer Hydrogenation of Prochiral Ketones in Aqueous Media with New Water-Soluble Chiral Vicinal Diamine as Ligand. *Org. Lett.* **2003**, *5*, 2103−2106.

(94) Wu, J.; Wang, F.; Ma, Y.; Cun, X.; Zhu, J.; Deng, J.; Yu, B. Asymmetric Transfer Hydrogenation of Imines and Iminiums Catalyzed by A Water-Soluble Catalyst in Water. *Chem. Commun.* **2006**, 1766−1768.

(95) Hannedouche, J.; Clarkson, G. J.; Wills, M. A New Class of "Tethered" Ruthenium(II) Catalyst for Asymmetric Transfer Hydrogenation Reactions. *J. Am. Chem. Soc.* **2004**, *126*, 986−987.

(96) Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M. A Class of Ruthenium(II) Catalyst for Asymmetric Transfer Hydrogenations of Ketones. *J. Am. Chem. Soc.* **2005**, *127*, 7318−7319.

(97) Cheung, F. K.; Lin, C.; Minissi, F.; Lorente Crivillé, A.; Graham, M. A.; Fox, D. J.; Wills, M. An Investigation into the Tether Length and Substitution Pattern of Arene-Substituted Complexes for Asymmetric Transfer Hydrogenation of Ketones. *Org. Lett.* **2007**, *9*, 4659−4662.

(98) Morris, D. J.; Hayes, A. M.; Wills, M. The "Reverse-Tethered" Ruthenium (II) Catalyst for Asymmetric Transfer Hydrogenation: Further Applications. *J. Org. Chem.* **2006**, *71*, 7035−7044.

(99) Martins, J. E. D.; Morris, D. J.; Tripathi, B.; Wills, M. Further 'Tethered' Ru(II) Catalysts for Asymmetric Transfer Hydrogenation (ATH) of Ketones; The Use of A Benzylic Linker and A Cyclohexyldiamine Ligand. *J. Organomet. Chem.* **2008**, *693*, 3527−3532.

(100) Cheung, F. K.; Hayes, A. M.; Hannedouche, J.; Yim, A. S. Y.; Wills, M. Tethered" Ru(II) Catalysts for Asymmetric Transfer Hydrogenation of Ketones. *J. Org. Chem.* **2005**, *70*, 3188−3197.

(101) Takehara, J.; Hashiguchi, S.; Fujii, A.; Shin-ichi, I.; Ikariya, T.; Noyori, R. Amino alcohol effects on the ruthenium(II)-catalysed asymmetric transfer hydrogenation of ketones in propan-2-ol. *Chem. Commun.* **1996**, 233−234.

(102) Cortez, N. A.; Aguirre, G.; Parra-Hake, M.; Somanathan, R. Ruthenium(II) and Rhodium(III) Catalyzed Asymmetric Transfer Hydrogenation (ATH) of Acetophenone in Isopropanol and in Aqueous Sodium Formate Using New Chiral Substituted Aromatic Monosulfonamide Ligands Derived from (1*R*,2*R*)-Diaminocyclohexane. *Tetrahedron: Asymmetry* **2008**, *19*, 1304−1309.

(103) Wu, X.; Li, X.; McConville, M.; Saidi, O.; Xiao, J. β-Amino Alcohols as Ligands for Asymmetric Transfer Hydrogenation of Ketones in Water. *J. Mol. Catal. A: Chem.* **2006**, *247*, 153−158.

(104) Mao, J.; Wan, B.; Wu, F.; Lu, S. First Example of Asymmetric Transfer Hydrogenation in Water Induced by A Chiral Amino Alcohol Hydrochloride. *Tetrahedron Lett.* **2005**, *46*, 7341−7344.

(105) Schlatter, A.; Kundu, M. K.; Woggon, W.-D. Enantioselective Reduction of Aromatic and Aliphatic Ketones Catalyzed by Ruthenium Complexes Attached to β-Cyclodextrin. *Angew. Chem., Int. Ed.* **2004**, *43*, 6731−6734.

(106) Petra, D. G. I.; Reek, J. N. H.; Handgraaf, J.-W.; Meijer, E. J.; Dierkes, P.; Kamer, P. C. J.; Brussee, J.; Schoemaker, H. E.; van Leeuwen, P. W. N. M. Chiral Induction Effects in Ruthenium(II) Amino Alcohol Catalysed Asymmetric Transfer Hydrogenation of Ketones: An Experimental and Theoretical Approach. *Chem.—Eur. J.* **2000**, *6*, 2818−2829.

(107) Alonso, D. A.; Nordin, S. J. M.; Roth, P.; Tarnai, T.; Andersson, P. G. 2-Azanorbornyl Alcohols: Very Efficient Ligands for Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones. *J. Org. Chem.* **2000**, *65*, 3116−3122.

(108) Newkome, G. R. Pyridylphosphines. *Chem. Rev.* **1993**, *93*, 2067−2089.

(109) Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. A Cationic 1-(2-Methylpyridine)Phosphole Cymene Ruthenium Chloride Complex as an Efficient Catalyst in the Transfer Hydrogenation of Ketones. *Organometallics* **2003**, *22*, 1580−1581.

(110) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. A Formally Zwitterionic Ruthenium Catalyst Precursor for the Transfer Hydrogenation of Ketones that Does Not Feature an Ancillary Ligand N-H Functionality. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732−4735.

(111) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. The Catalyst Precursor, Catalyst, and Intermediate in the Ru^{II}-Promoted Asymmetric Hydrogen Transfer between Alcohols and Ketones. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285−288.

(112) Ogo, S.; Abura, T.; Watanabe, Y. pH-Dependent Transfer Hydrogenation of Ketones with HCOONa as a Hydrogen Donor Promoted by (η^6-C_6Me_6)Ru Complexes. *Organometallics* **2002**, *21*, 2964−2969.

(113) Türkmen, H.; Kani, İ.; Çetinkaya, B. Transfer Hydrogenation of Aryl Ketones with Half-Sandwich Ru^{II}Complexes That Contain Chelating Diamines. *Eur. J. Inorg. Chem.* **2012**, 4494−4499.

(114) Murata, K.; Ikariya, T.; Noyori, R. New Chiral Rhodium and Iridium Complexes with Chiral Diamine Ligands for Asymmetric Transfer Hydrogenation of Aromatic Ketones. *J. Org. Chem.* **1999**, *64*, 2186−2187.

(115) Hanasaka, F.; Fujita, K.; Yamaguchi, R. Cp*Ir Complexes Bearing N-Heterocyclic Carbene Ligands as Effective Catalysts for Oppenauer-Type Oxidation of Alcohols. *Organometallics* **2004**, *23*, 1490−1492.

(116) Han, S. B.; Kim, I. S.; Krische, M. J. Enantioselective Iridium-Catalyzed Carbonyl Allylation from The Alcohol Oxidation Level *via* Transfer Hydrogenation: Minimizing Pre-Activation for Synthetic Efficiency. *Chem. Commun.* **2009**, 7278−7287.

(117) Ahlford, K.; Ekström, J.; Zaitsev, A. B.; Ryberg, P.; Eriksson, L.; Adolfsson, H. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Amino Acid Derived Rhodium Complexes: On the Origin of Enantioselectivity and Enantioswitchability. *Chem.—Eur. J.* **2009**, *15*, 11197−11209.

(118) Soltani, O.; Ariger, M. A.; Carreira, E. M. Transfer Hydrogenation in Water: Enantioselective, Catalytic Reduction of (*E*)-β,β-Disubstituted Nitroalkenes. *Org. Lett.* **2009**, *11*, 4196−4198.

(119) Ahlford, K.; Lind, J.; Mäler, L.; Adolfsson, H. Rhodium-Catalyzed Asymmetric Transfer Hydrogenation of Alkyl and Aryl Ketones in Aqueous Media. *Green Chem.* **2008**, *10*, 832−835.

(120) Wu, X.; Li, X.; Zanotti-Gerosa, A.; Pettman, A.; Liu, J.; Mills, A. J.; Xia, J. Rh^{III}- and Ir^{III}-Catalyzed Asymmetric Transfer Hydrogenation of Ketones in Water. *Chem.—Eur. J.* **2008**, *14*, 2209−2222.

(121) Heiden, Z. M.; Rauchfuss, T. B. Homogeneous Catalytic Reduction of Dioxygen Using Transfer Hydrogenation Catalysts. *J. Am. Chem. Soc.* **2007**, *129*, 14303−14310.

(122) Wettergren, J.; Zaitsev, A. B.; Adolfsson, H. Rhodium-Catalyzed Asymmetric Transfer Hydrogenation of Aryl Alkyl Ketones Employing Ligands Derived from Amino Acids. *Adv. Synth. Catal.* **2007**, *349*, 2556−2562.

(123) Matharu, D. S.; Morris, D. J.; Clarkson, G. J.; Wills, M. An Outstanding Catalyst for Asymmetric Transfer Hydrogenation in Aqueous Solution and Formic Acid/Triethylamine. *Chem. Commun.* **2006**, 3232−3234.

(124) Wang, F.; Liu, H.; Cun, L.; Zhu, J.; Deng, J.; Jiang, Y. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Hydrophobic Metal−Amido Complexes in Aqueous Micelles and Vesicles. *J. Org. Chem.* **2005**, *70*, 9424−9429.

(125) Hamada, T.; Torii, T.; Onishi, T.; Izawa, K.; Ikariya, T. Asymmetric Transfer Hydrogenation of α-Aminoalkyl α'-Chloromethyl Ketones with Chiral Rh Complexes. *J. Org. Chem.* **2004**, *69*, 7391−7394.

(126) Fujita, K.; Kitatsuji, C.; Furukawa, S.; Yamaguchi, R. Regio- and Chemoselective Transfer Hydrogenation of Quinolines Catalyzed by A Cp*Ir Complex. *Tetrahedron Lett.* **2004**, *45*, 3215−3217.

(127) Ogo, S.; Makihara, N.; Kaneko, Y.; Watanabe, Y. pH-Dependent Transfer Hydrogenation, Reductive Amination, and Dehalogenation of Water-Soluble Carbonyl Compounds and Alkyl Halides Promoted by Cp*Ir Complexes. *Organometallics* **2001**, *20*, 4903−4910.

(128) Ogo, S.; Makihara, N.; Watanabe, Y. pH-Dependent Transfer Hydrogenation of Water-Soluble Carbonyl Compounds with $[\mathrm{Cp^*Ir^{III}(H_2O)_3}]^{2+}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) as a Catalyst Precursor and HCOONa as a Hydrogen Donor in Water. *Organometallics* **1999**, *18*, 5470−5474.

(129) Liu, Z.; Sadler, P. J. Organoiridium Complexes: Anticancer Agents and Catalysts. *Acc. Chem. Res.* **2014**, *47*, 1174−1185.

(130) Himeda, Y.; Onozawa-Komatsuzaki, N.; Miyazawa, S.; Sugihara, H.; Hirose, T.; Kasuga, K. pH-Dependent Catalytic Activity and Chemoselectivity in Transfer Hydrogenation Catalyzed by Iridium Complex with 4,4′-Dihydroxy-2,2′-bipyridine. *Chem.—Eur. J.* **2008**, *14*, 11076−11081.

(131) Li, L.; Wu, J.; Wang, F.; Liao, J.; Zhang, H.; Lian, C.; Zhu, J.; Deng, J. Asymmetric Transfer Hydrogenation of Ketones and Imines with Novel Water-Soluble Chiral Diamine as Ligand in Neat Water. *Green Chem.* **2007**, *9*, 23−25.

(132) Reetz, M. T.; Li, X. An Efficient Catalyst System for the Asymmetric Transfer Hydrogenation of Ketones: Remarkably Broad Substrate Scope. *J. Am. Chem. Soc.* **2006**, *128*, 1044−1045.

(133) Hamada, T.; Torii, T.; Izawa, K.; Noyori, R.; Ikariya, T. Practical Synthesis of Optically Active Styrene Oxides via Reductive Transformation of 2-Chloroacetophenones with Chiral Rhodium Catalysts. *Org. Lett.* **2002**, *4*, 4373−4376.

(134) Lundgren, R. J.; Stradiotto, M. Rapid Ketone Transfer Hydrogenation by Employing Simple, In Situ Prepared Iridium(I) Precatalysts Supported by "Non-N-H" P,N Ligands. *Chem.—Eur. J.* **2008**, *14*, 10388−10395.

(135) Braunstein, P.; Naud, F.; Pfaltz, A.; Rettig, S. J. Ruthenium Complexes with Novel Tridentate N,P,N Ligands Containing a Phosphonite Bridge between Two Chiral Oxazolines. Catalytic Activity in Cyclopropanation of Olefins and Transfer Hydrogenation of Acetophenone. *Organometallics* **2000**, *19*, 2676−2683.

(136) Díaz-Valenzuela, M.; Phillips, S. D.; France, M. B.; Gunn, M. E.; Clarke, M. L. Enantioselective Hydrogenation and Transfer Hydrogenation of Bulky Ketones Catalysed by a Ruthenium Complex of a Chiral Tridentate Ligand. *Chem.—Eur. J.* **2009**, *15*, 1227−1232.

(137) Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. Ruthenium(II) Complexes Containing Optically Active Hemilabile P,N,O-Tridentate Ligands. Synthesis and Evaluation in Catalytic Asymmetric Transfer Hydrogenation of Acetophenone by Propan-2-ol. *Organometallics* **1997**, *16*, 1401−1409.

(138) Dai, H.; Hu, X.; Chen, H.; Bai, C.; Zheng, Z. New Efficient *P,N,O*-Tridentate Ligands for Ru-Catalyzed Asymmetric Transfer Hydrogenation. *Tetrahedron: Asymmetry* **2003**, *14*, 1467−1472.

(139) Ito, J.; Ujiie, S.; Nishiyama, H. New Bis(oxazolinyl)phenyl−Ruthenium(II) Complexes and Their Catalytic Activity for Enantioselective Hydrogenation and Transfer Hydrogenation of Ketones. *Organometallics* **2009**, *28*, 630−638.

(140) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. Ruthenium(II) Complex Catalysts Bearing a Pyridyl-Supported Pyrazolyl-Imine Ligand for Transfer Hydrogenation of Ketones. *J. Organomet. Chem.* **2009**, *694*, 3068−3075.

(141) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. Room-temperature Ru(II)-Catalyzed Transfer Hydrogenation of Ketones and Aldehydes in Air. *Tetrahedron Lett.* **2009**, *50*, 4624−4628.

(142) Cuervo, D.; Gamasa, M. P.; Gimeno, J. New Chiral Ruthenium(II) Catalysts Containing 2,6-Bis(4′-(*R*)-phenyloxazolin-2′-yl)pyridine (Ph-pybox) Ligands for Highly Enantioselective Transfer Hydrogenation of Ketones. *Chem.—Eur. J.* **2004**, *10*, 425−432.

(143) Jiang, Y.; Jiang, Q.; Zhang, X. A New Chiral Bis(oxazolinylmethyl)amine Ligand for Ru-Catalyzed Asymmetric Transfer Hydrogenation of Ketones. *J. Am. Chem. Soc.* **1998**, *120*, 3817−3818.

(144) Paredes, P.; Díez, J.; Gamasa, M. P. Synthesis of Enantiopure Iridium(I) and Iridium(III) Pybox Complexes and Their Application in the Asymmetric Transfer Hydrogenation of Ketones. *Organometallics* **2008**, *27*, 2597−2607.

(145) Zeng, F.; Yu, Z. Exceptionally Efficient Unsymmetrical Ruthenium(II) NNN Complex Catalysts Bearing a Pyridyl-Based Pyrazolyl−Imidazolyl Ligand for Transfer Hydrogenation of Ketones. *Organometallics* **2008**, *27*, 2898−2901.

(146) Enthaler, S.; Hagemann, B.; Bhor, S.; Anilkumar, G.; Tse, M. K.; Bitterlich, B.; Junge, K.; Erre, G.; Beller, M. New Ruthenium Catalysts for Asymmetric Transfer Hydrogenation of Prochiral Ketones. *Adv. Synth. Catal.* **2007**, *349*, 853−860.

(147) Jiang, Q.; Van Plew, D.; Murtuza, S.; Zhang, X. Synthesis of (1R,1R′)-2,6-Bis[1-(diphenylphosphino)ethyl]pyridine and Its Application in Asymmetric Transfer Hydrogenation. *Tetrahedron Lett.* **1996**, *37*, 797−800.

(148) Mothes, E.; Sentets, S.; Luquin, M. A.; Mathieu, R.; Lugan, N.; Lavigne, G. New Insight into the Reactivity of Pyridine-Functionalized Phosphine Complexes of Ruthenium(II) with Respect to Olefin Metathesis and Transfer Hydrogenation. *Organometallics* **2008**, *27*, 1193−1206.

(149) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. A Family of Active Iridium Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2006**, *25*, 4113−4117.

(150) Crochet, P.; Gimeno, J.; García-Granda, S.; Borge, J. Five- and Six-Coordinate Ruthenium(II) Complexes Containing 2-$\mathrm{Ph_2PC_6H_4CH{=}N^tBu}$ and 2-$\mathrm{Ph_2PC_6H_4CH_2NH^tBu}$ as Chelate Ligands: Synthesis, Characterization, and Catalytic Activity in Transfer Hydrogenation of Ketones. *Organometallics* **2001**, *20*, 4369−4377.

(151) Baratta, W.; Ros, P. D.; Zotto, A. D.; Sechi, A.; Zangrando, E.; Rigo, P. Cyclometalated Ruthenium(II) Complexes as Highly Active Transfer Hydrogenation Catalysts. *Angew. Chem., Int. Ed.* **2004**, *43*, 3584−3588.

(152) Göttker-Schnetmann, I.; White, P.; Brookhart, M. Iridium Bis(phosphinite) *p*-XPCP Pincer Complexes: Highly Active Catalysts for the Transfer Dehydrogenation of Alkanes. *J. Am. Chem. Soc.* **2004**, *126*, 1804−1811.

(153) Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P. Role of the $\mathrm{NH_2}$ Functionality and Solvent in Terdentate CNN Alkoxide Ruthenium Complexes for the Fast Transfer Hydrogenation of Ketones in 2-Propanol. *Chem.—Eur. J.* **2008**, *14*, 5588−5595.

(154) Baratta, W.; Siega, K.; Rigo, P. Catalytic Transfer Hydrogenation with Terdentate CNN Ruthenium Complexes: The Influence of the Base. *Chem.—Eur. J.* **2007**, *13*, 7479−7486.

(155) Baratta, W.; Bosco, M.; Chelucci, G.; Zotto, A. D.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. Terdentate RuX(CNN)(PP) (X = Cl, H, OR) Complexes: Synthesis, Properties, and Catalytic Activity in Fast Transfer Hydrogenation. *Organometallics* **2006**, *25*, 4611−4620.

(156) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. Ruthenium(II) Terdentate CNN Complexes: Superlative Catalysts for the Hydrogen-Transfer Reduction of Ketones by Reversible Insertion of a Carbonyl Group into the Ru-H Bond. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214−6219.

(157) Deng, H.; Yu, Z.; Dong, J.; Wu, S. 2,6-Bis(3,5-dimethylpyrazol-1-yl)pyridine: A Useful Pseudo-N_3 Ligand in Efficient Ruthenium(II)-Catalyzed Transfer Hydrogenation of Ketones. *Organometallics* **2005**, *24*, 4110−4112.

(158) Gao, J. X.; Ikariya, T.; Noyori, R. A Ruthenium(II) Complex with a C_2-Symmetric Diphosphine/Diamine Tetradentate Ligand for Asymmetric Transfer Hydrogenation of Aromatic Ketones. *Organometallics* **1996**, *15*, 1087−1089.

(159) Laue, S.; Greiner, L.; Wöltinger, J.; Liese, A. Continuous Application of Chemzymes in a Membrane Reactor: Asymmetric Transfer Hydrogenation of Acetophenone. *Adv. Synth. Catal.* **2001**, *343*, 711−720.

(160) Baratta, W.; Chelucci, G.; Herdtweck, E.; Magnolia, S.; Siega, K.; Rigo, P. Highly Diastereoselective Formation of Ruthenium Complexes for Efficient Catalytic Asymmetric Transfer Hydrogenation. *Angew. Chem., Int. Ed.* **2007**, *46*, 7651−7654.

(161) Li, T.; Bergner, I.; Haque, F. N.; Zimmer-De Iuliis, M.; Song, D.; Morris, R. H. Hydrogenation of Benzonitrile to Benzylamine Catalyzed by Ruthenium Hydride Complexes with P−NH−NH−P Tetradentate Ligands: Evidence for a Hydridic−Protonic Outer Sphere Mechanism. *Organometallics* **2007**, *26*, 5940−5949.

(162) Li, B. Z.; Chen, J. S.; Dong, A. R.; Li, Y. Y.; Li, Q. B.; Gao, J. X. The Novel Water-Soluble Chiral PNNP-Type Ligand for The Enantioselective Reduction of Ketones in Aqueous Media. *J. Mol. Catal. A: Chem.* **2006**, *258*, 113−117.

(163) Xing, Y.; Chen, J. S.; Dong, Z. R.; Li, Y. Y.; Gao, J. X. Highly Efficient Chiral PNNP Ligand for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water. *Tetrahedron Lett.* **2006**, *47*, 4501−4503.

(164) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. 2-(Aminomethyl)pyridine−Phosphine Ruthenium(II) Complexes: Novel Highly Active Transfer Hydrogenation Catalysts. *Organometallics* **2005**, *24*, 1660−1669.

(165) Chen, J. S.; Li, Y. Y.; Dong, Z. R.; Li, B. Z.; Gao, J. X. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by The Iridium Hydride Complex Under Ambient Conditions. *Tetrahedron Lett.* **2004**, *45*, 8415−8418.

(166) Zhang, X.; Li, Y.; Dong, Z.; Shen, W.; Cheng, Z.; Gao, J. Asymmetric Transfer Hydrogenation of Aromatic Ketones with Chiral Diamino-Thiophene/Iridium Catalyst Systems. *J. Mol. Catal. A: Chem.* **2009**, *307*, 149−153.

(167) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. Hydrogen-Transfer Catalysis with Pincer-Aryl Ruthenium(II) Complexes. *Angew. Chem., Int. Ed.* **2000**, *39*, 743−745.

(168) Chen, G.; Xing, Y.; Zhang, H.; Gao, J. X. Synthesis of Novel Chiral Macrocyclic ONNO-Type Ligands and Use in Asymmetric Transfer Hydrogenation. *J. Mol. Catal. A: Chem.* **2007**, *273*, 284−288.

(169) Ito, J.; Nishiyama, H. Recent Topics of Transfer Hydrogenation. *Tetrahedron Lett.* **2014**, *55*, 3133−3146.

(170) Sues, P. E.; Demmans, K. Z.; Morris, R. H. Rational Development of Iron Catalysts for Asymmetric Transfer Hydrogenation. *Dalton Trans.* **2014**, *43*, 7650−7667.

(171) Quintard, A.; Rodriguez, J. Iron Cyclopentadienone Complexes: Discovery, Properties, and Catalytic Reactivity. *Angew. Chem., Int. Ed.* **2014**, *53*, 4044−4055.

(172) Bullock, R. M. Abundant Metals Give Precious Hydrogenation Performance. *Science* **2013**, *342*, 1054−1055.

(173) Enthaler, S.; Hagemann, B.; Erre, G.; Junge, K.; Beller, M. An Environmentally Benign Process for the Hydrogenation of Ketones with Homogeneous Iron Catalysts. *Chem.—Asian J.* **2006**, *1*, 598−604.

(174) Darwish, M.; Wills, M. Asymmetric catalysis using iron complexes – 'Ruthenium Lite'? *Catal. Sci. Technol.* **2012**, *2*, 243−255.

(175) Bailly, B. A. F. L.; Thomas, S. P. Iron-catalysed reduction of carbonyls and olefins. *RSC Adv.* **2011**, *1*, 1435−1445.

(176) Gaillard, S.; Renaud, J.-L. Iron-Catalyzed Hydrogenation, Hydride Transfer, and Hydrosilylation: An Alternative to Precious-Metal Complexes? *ChemSusChem* **2008**, *1*, 505−509.

(177) Meyer, N.; Lough, A. J.; Morris, R. H. Iron(II) Complexes for the Efficient Catalytic Asymmetric Transfer Hydrogenation of Ketones. *Chem.—Eur. J.* **2009**, *15*, 5605−5610.

(178) Sui-Seng, C.; Freutel, F.; Lough, A. J.; Morris, R. H. Highly Efficient Catalyst Systems Using Iron Complexes with a Tetradentate PNNP Ligand for the Asymmetric Hydrogenation of Polar Bonds. *Angew. Chem., Int. Ed.* **2008**, *47*, 940−943.

(179) Mikhailine, A.; Lough, A. J.; Morris, R. H. Efficient Asymmetric Transfer Hydrogenation of Ketones Catalyzed by an Iron Complex Containing a P−N−N−P Tetradentate Ligand Formed by Template Synthesis. *J. Am. Chem. Soc.* **2009**, *131*, 1394−1395.

(180) Sonavane, S. U.; Gawande, M. B.; Deshpande, S. S.; Venkataraman, A.; Jayaram, R. V. Chemoselective transfer hydrogenation reactions over nanosized γ-Fe_2O_3 catalyst prepared by novel combustion route. *Catal. Commun.* **2007**, *8*, 1803−1806.

(181) Enthaler, S.; Erre, G.; Tse, M. K.; Junge, K.; Beller, M. Biomimetic Transfer Hydrogenation of Ketones with Iron Porphyrin Catalysts. *Tetrahedron Lett.* **2006**, *47*, 8095−8099.

(182) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. Heterogeneous Catalytic Transfer Hydrogenation of Aromatic Nitro and Carbonyl Compounds Over Cobalt(II) Substituted Hexagonal Mesoporous Aluminophosphate Molecular Sieves. *Tetrahedron Lett.* **2002**, *43*, 8527−8529.

(183) Polshettiwar, V.; Baruwati, B.; Varma, R. S. Nanoparticle-Supported and Magnetically Recoverable Nickel Catalyst: A Robust and Economic Hydrogenation and Transfer Hydrogenation Protocol. *Green Chem.* **2009**, *11*, 127−131.

(184) Kuhl, S.; Schneider, R.; Fort, Y. Transfer Hydrogenation of Imines Catalyzed by a Nickel(0)/NHC Complex. *Organometallics* **2003**, *22*, 4184−4186.

(185) Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V.; Selvam, P. Regio- and Chemoselective Catalytic Transfer Hydrogenation of Aromatic Nitro and Carbonyl as Well as Reductive Cleavage of Azo Compounds over Novel Mesoporous NiMCM-41 Molecular Sieves. *Org. Lett.* **2002**, *4*, 4297−4300.

(186) Cadierno, V.; Crochet, P.; Francos, J.; García-Garrido, S. E.; Gimeno, J.; Nebra, N. Ruthenium-Catalyzed Redox Isomerization/Transfer Hydrogenation in Organic and Aqueous Media: A One-Pot Tandem Process for The Reduction of Allylic Alcohols. *Green Chem.* **2009**, *11*, 1992−2000.

(187) Zanardi, A.; Mata, J. A.; Peris, E. Well-Defined Ir/Pd Complexes with a Triazolyl-diylidene Bridge as Catalysts for Multiple Tandem Reactions. *J. Am. Chem. Soc.* **2009**, *131*, 14531−14537.

(188) Hauwert, P.; Maestri, G.; Sprengers, J. W.; Catellani, M.; Elsevier, C. J. Transfer Semihydrogenation of Alkynes Catalyzed by a Zero-Valent Palladium N-Heterocyclic Carbene Complex. *Angew. Chem., Int. Ed.* **2008**, *47*, 3223−3226.

(189) Brunel, J. M. Pd/P(t-Bu)$_3$: A Mild Catalyst for Selective Reduction of Alkenes under Transfer-Hydrogenation Conditions. *Synlett* **2007**, *2*, 330−332.

(190) Yu, J. Q.; Wu, H. C.; Ramarao, C.; Spencer, J. B.; Ley, S. V. Transfer Hydrogenation Using Recyclable Polyurea-Encapsulatedpalladium: Efficient and Chemoselective Reduction of Aryl Ketones. *Chem. Commun.* **2003**, 678−679.

(191) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. Development of Rhenium Catalysts for Amine Borane Dehydrocoupling and Transfer Hydrogenation of Olefins. *Organometallics* **2009**, *28*, 5493−5504.

(192) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. New Benzo[*h*]quinoline-Based Ligands and their Pincer Ru and Os Complexes for Efficient Catalytic Transfer Hydrogenation of Carbonyl Compounds. *Chem.—Eur. J.* **2008**, *14*, 9148−9160.

(193) Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P. Osmium(II) CNN Pincer Complexes as Efficient Catalysts for Both

Asymmetric Transfer and H_2 Hydrogenation of Ketones. *Angew. Chem., Int. Ed.* **2008**, *47*, 4362−4365.

(194) Baratta, W.; Ballico, M.; Zotto, A. D.; Siega, K.; Magnolia, S.; Rigo, P. Osmium Pyme Complexes for Fast Hydrogenation and Asymmetric Transfer Hydrogenation of Ketones. *Chem.—Eur. J.* **2008**, *14*, 2557−2563.

(195) Chelucci, G.; Baldino, S.; Baratta, W. Recent Advances in Osmium-Catalyzed Hydrogenation and Dehydrogenation Reactions. *Acc. Chem. Res.* **2015**, *48*, 363−379.

(196) Alonso, F.; Riente, P.; Rodriguez-Reinoso, F.; Ruiz-Martínez, J.; Sepúlveda-Escribano, A.; Yus, M. Platinum Nanoparticles Supported on Titania as An Efficient Hydrogen-Transfer Catalyst. *J. Catal.* **2008**, *260*, 113−118.

(197) He, L.; Ni, J.; Wang, L.-C.; Yu, F.-J.; Cao, Y.; He, H.-Y.; Fan, K.-N. Aqueous Room-Temperature Gold-Catalyzed Chemoselective Transfer Hydrogenation of Aldehydes. *Chem.—Eur. J.* **2009**, *15*, 11833−11836.

(198) Su, F.-Z.; He, L.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. Efficient and Chemoselective Reduction of Carbonyl Compounds with Supported Gold Catalysts under Transfer Hydrogenation Conditions. *Chem. Commun.* **2008**, 3531−3533.

(199) Bart, S. C.; Hawrelak, E. J.; Lobkovsky, E.; Chirik, P. J. Low-Valent α-Diimine Iron Complexes for Catalytic Olefin Hydrogenation. *Organometallics* **2005**, *24*, 5518−5527.

(200) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation. *J. Am. Chem. Soc.* **2004**, *126*, 13794−13807.

(201) Archer, A. M.; Bouwkamp, M. W.; Cortez, M. P.; Lobkovsky, E.; Chirik, P. J. Arene Coordination in Bis(imino)pyridine Iron Complexes: Identification of Catalyst Deactivation Pathways in Iron-Catalyzed Hydrogenation and Hydrosilation. *Organometallics* **2006**, *25*, 4269−4278.

(202) Abdur-Rashid, K.; Faatz, M.; Lough, A. J.; Morris, R. H. Catalytic Cycle for the Asymmetric Hydrogenation of Prochiral Ketones to Chiral Alcohols: Direct Hydride and Proton Transfer from Chiral Catalysts *trans*-Ru(H)$_2$(diphosphine)(diamine) to Ketones and Direct Addition of Dihydrogen to the Resulting Hydridoamido Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 7473−7474.

(203) Zheng, C.; You, S. L. Transfer Hydrogenation with Hantzsch Esters and Related Organic Hydridedonors. *Chem. Soc. Rev.* **2012**, *41*, 2498−2518.

(204) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. Iridium Complexes in Alkane Dehydrogenation. *J. Am. Chem. Soc.* **1979**, *101*, 7738−7740.

(205) Burk, M. J.; Crabtree, R. H. Selective Catalytic Dehydrogenation of Alkanes to Alkenes. *J. Am. Chem. Soc.* **1987**, *109*, 8025−8032.

(206) Baudry, D.; Ephritikhine, M.; Felkin, H. The Activation of C-H Bonds in Cyclopentane by Bis(phosphine)rhenium Heptahydrides. *J. Chem. SOC., Chem. Commun.* **1980**, 1243−1244.

(207) Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. Mechanism of Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex. *J. Am. Chem. Soc.* **2003**, *125*, 7770−7771.

(208) Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. Novel Synthesis of Enamines by Iridium-Catalyzed Dehydrogenation of Tertiary Amines. *Chem. Commun.* **2003**, 2060−2061.

(209) Geldbach, T. J.; Dyson, P. J. A Versatile Ruthenium Precursor for Biphasic Catalysis and Its Application in Ionic Liquid Biphasic Transfer Hydrogenation: Conventional vs Task-Specific Catalysts. *J. Am. Chem. Soc.* **2004**, *126*, 8114−8115.

(210) Baán, Z.; Finta, Z.; Keglevich, G.; Hermecz, I. Unexpected Chemoselectivity in The Rhodium-Catalyzed Transferhydrogenation of α,β-Unsaturated Ketones in Ionic Liquids. *Green Chem.* **2009**, *11*, 1937−1940.

(211) Vasiloiu, M.; Gaertner, P.; Zirbs, R.; Bica, K. Coordinating Chiral Ionic Liquids: Design, Synthesis, and Application in Asymmetric Transfer Hydrogenation under Aqueous Conditions. *Eur. J. Org. Chem.* **2015**, *11*, 2374−2381.

(212) Uchimoto, H.; Tsuji, T.; Kawasaki, I.; Arimitsu, K.; Yasui, H.; Yamashita, M.; Ohta, S.; Nishide, K. Preparation of Chiral Ligands Connected with Quaternary Ammonium Group for Recyclable Catalytic Asymmetric Transfer Hydrogenation in Ionic Liquid. *Chem. Pharm. Bull.* **2015**, *63*, 200−209.

(213) Denizaltı, S.; Mercan, D.; Şen, B.; Gökçe, A. G.; Çetinkaya, B. Asymmetric Transfer Hydrogenation Reaction in Water: Comparison of Chiral Proline Amide/Amine Ruthenium(II) Complexes. *J. Organomet. Chem.* **2015**, *779*, 62−66.

(214) Rhyoo, H. Y.; Park, H. J.; Chung, Y. K. The First Ru(II)-Catalysed Asymmetric Hydrogen Transfer Reduction of Aromatic Ketones in Aqueous Media. *Chem. Commun.* **2001**, 2064−2065.

(215) Wei, Y.; Wu, X.; Wang, C.; Xiao, J. Transfer Hydrogenation in Aqueous Media. *Catal. Today* **2015**, *247*, 104−116.

(216) Akagawa, K.; Akabane, H.; Sakamoto, S.; Kudo, K. Asymmetric Transfer Hydrogenation in Aqueous Media Catalyzed by Resin-Supported Peptide Having A Polyleucine Tether. *Tetrahedron: Asymmetry* **2009**, *20*, 461−466.

(217) Robertson, A.; Matsumoto, T.; Ogo, S. The Development of Aqueous Transfer Hydrogenation Catalysts. *Dalton Trans.* **2011**, *40*, 10304−10310.

(218) Dwars, T.; Oehme, G. Complex-Catalyzed Hydrogenation Reactions in Aqueous Media. *Adv. Synth. Catal.* **2002**, *344*, 239−260.

(219) Zhou, Z.; Sun, Y. Water-Soluble Chiral Aminosulfonamides as Ligands for Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation. *Catal. Commun.* **2009**, *10*, 1685−1688.

(220) Liu, J.; Zhou, Y.; Wu, Y.; Lia, X.; Chan, A. S. C. Asymmetric Transfer Hydrogenation of Ketones with A Polyethylene Glycol Bound Ru Catalyst in Water. *Tetrahedron: Asymmetry* **2008**, *19*, 832−837.

(221) Thorpe, T.; Blacker, J.; Brown, S. M.; Bubert, C.; Crosby, J.; Fitzjohn, S.; Muxworthy, J. P.; Williams, J. M. J. Efficient Rhodium and Iridium-Catalysed Asymmetric Transfer Hydrogenation Using Water-Soluble Aminosulfonamide Ligands. *Tetrahedron Lett.* **2001**, *42*, 4041−4043.

(222) Abura, T.; Ogo, S.; Watanabe, Y.; Fukuzumi, S. Isolation and Crystal Structure of a Water-Soluble Iridium Hydride: A Robust and Highly Active Catalyst for Acid-Catalyzed Transfer Hydrogenations of Carbonyl Compounds in Acidic Media. *J. Am. Chem. Soc.* **2003**, *125*, 4149−4154.

(223) Wu, X.; Li, X.; King, F.; Xiao, J. Insight into and Practical Application of pH-Controlled Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water. *Angew. Chem., Int. Ed.* **2005**, *44*, 3407−3411.

(224) Butler, R. N.; Coyne, A. G. Water: Nature's Reaction Enforcer—Comparative Effects for Organic Synthesis "In-Water" and "On-Water. *Chem. Rev.* **2010**, *110*, 6302−6337.

(225) Szatmári, I.; Papp, G.; Joó, F.; Kathó, Á. Unexpectedly Fast Catalytic Transfer Hydrogenation of Aldehydes by Formate in 2-Propanol−Water Mixtures under Mild Conditions. *Catal. Today* **2015**, *247*, 14−19.

(226) Chen, S.-J.; Lu, G.-P.; Cai, C. A Base-Controlled Chemoselective Transfer Hydrogenation of Alpha, Beta-Unsaturated Ketones Catalyzed by [IrCp*Cl-2](2) with 2-Propanol. *RSC Adv.* **2015**, *5*, 13208−13211.

(227) Landwehr, A.; Dudle, B.; Fox, T.; Blacque, O.; Berke, H. Bifunctional Rhenium Complexes for the Catalytic Transfer-Hydrogenation Reactions of Ketones and Imines. *Chem.—Eur. J.* **2012**, *18*, 5701−5714.

(228) Corberán, R.; Peris, E. An Unusual Example of Base-Free Catalyzed Reduction of C═O and C═NR Bonds by Transfer Hydrogenation and Some Useful Implications. *Organometallics* **2008**, *27*, 1954−1958.

(229) Burling, S.; Whittlesey, M. K.; Williams, J. M. J. Direct and Transfer Hydrogenation of Ketones and Imines with a Ruthenium N-Heterocyclic Carbene Complex. *Adv. Synth. Catal.* **2005**, *347*, 591−594.

(230) Long, J.; Zhou, Y.; Li, Y. Transfer Hydrogenation of Unsaturated Bonds in the Absence of Base Additives Catalyzed by a

Cobalt-Based Heterogeneous Catalyst. *Chem. Commun.* **2015**, *51*, 2331−2334.

(231) Blaser, H.-U., Federsel, H.-J., Eds. *Asymmetric Catalysis on Industrial Scale*; Wiley-VCH: Weinheim, 2010.

(232) Dalkó, P. I.; Moisan, L. In the Golden Age of Organocatalysis. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138−5175.

(233) de Vries, J. G.; Mršic, N. Organocatalytic Asymmetric Transfer Hydrogenation of Imines. *Catal. Sci. Technol.* **2011**, *1*, 727−735.

(234) Singh, S.; Batra, U. K. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1989**, *28*, 1.

(235) Yang, J. W.; Fonseca, M. T. H.; List, B. A Metal-Free Transfer Hydrogenation: Organocatalytic Conjugate Reduction of *α*,*β*-Unsaturated Aldehydes. *Angew. Chem., Int. Ed.* **2004**, *43*, 6660−6662.

(236) Gutierrez, O.; Iafe, R. G.; Houk, K. N. Origin of Stereoselectivity in the Imidazolidinone-Catalyzed Reductions of Cyclic *α*,*β*-Unsaturated Ketones. *Org. Lett.* **2009**, *11*, 4298−4301.

(237) Tuttle, J. B.; Ouellet, S. G.; MacMillan, D. W. C. Organocatalytic Transfer Hydrogenation of Cyclic Enones. *J. Am. Chem. Soc.* **2006**, *128*, 12662−12663.

(238) Schreiner, P. R. Metal-Free Organocatalysis through Explicit Hydrogen Bonding Interactions. *Chem. Soc. Rev.* **2003**, *32*, 289−296.

(239) Pihko, P. M. Activation of Carbonyl Compounds by Double Hydrogen Bonding: An Emerging Tool in Asymmetric Catalysis. *Angew. Chem., Int. Ed.* **2004**, *43*, 2062−2064.

(240) Rueping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. Enantioselective Brønsted Acid Catalyzed Transfer Hydrogenation: Organocatalytic Reduction of Imines. *Org. Lett.* **2005**, *7*, 3781−3783.

(241) Hoffmann, S.; Seayad, A. M.; List, B. A Powerful Brønsted Acid Catalyst for the Organocatalytic Asymmetric Transfer Hydrogenation of Imines. *Angew. Chem., Int. Ed.* **2005**, *44*, 7424−7427.

(242) Rueping, M.; Antonchick, A. P.; Theissmann, T. A Highly Enantioselective Brønsted Acid Catalyzed Cascade Reaction: Organocatalytic Transfer Hydrogenation of Quinolines and their Application in the Synthesis of Alkaloids. *Angew. Chem., Int. Ed.* **2006**, *45*, 3683−3686.

(243) Rueping, M.; Antonchick, A. P.; Theissmann, T. Remarkably Low Catalyst Loading in Brønsted Acid Catalyzed Transfer Hydrogenations: Enantioselective Reduction of Benzoxazines, Benzothiazines, and Benzoxazinones. *Angew. Chem., Int. Ed.* **2006**, *45*, 6751−6755.

(244) Guo, Q.-S.; Du, D.-M.; Xu, J. The Development of Double Axially Chiral Phosphoric Acids and Their Catalytic Transfer Hydrogenation of Quinolines. *Angew. Chem., Int. Ed.* **2008**, *47*, 759−762.

(245) Marcelli, T.; Hammar, P.; Himo, F. Phosphoric Acid Catalyzed Enantioselective Transfer Hydrogenation of Imines: A Density Functional Theory Study of Reaction Mechanism and the Origins of Enantioselectivity. *Chem.—Eur. J.* **2008**, *14*, 8562−8571.

(246) Kamitanaka, T.; Matsudab, T.; Haradaa, T. Mechanism for the Reduction of Ketones to the Corresponding Alcohols Using Supercritical 2-Propanol. *Tetrahedron* **2007**, *63*, 1429−1434.

(247) Bagnell, L.; Strauss, C. R. Uncatalysed Hydrogen-Transfer Reductions of Aldehydes and Ketones. *Chem. Commun.* **1999**, 287−288.

(248) Choi, C. Y.; Stock, L. M. Aspects of the Chemistry of Donor Solvent Coal Dissolution Reactions. The Reduction of Benzophenone and the Disproportionation of Benzhydrol in Hydrocarbon Solvents at High Temperature. *J. Org. Chem.* **1984**, *49*, 2871−2875.

(249) Polshettiwar, V.; Varma, R. S. Revisiting the Meerwein−Ponndorf−Verley Reduction: A Sustainable Protocol for Transfer Hydrogenation of Aldehydes and Ketones. *Green Chem.* **2009**, *11*, 1313−1316.

(250) Ouali, A.; Majoral, J.-P.; Caminade, A.-M.; Taillefer, M. NaOH-Promoted Hydrogen Transfer: Does NaOH or Traces of Transition Metals Catalyze the Reaction? *ChemCatChem* **2009**, *1*, 504−509.

(251) Haraguchi, N.; Tsuru, K.; Arakawa, Y.; Itsuno, S. Asymmetric Transfer Hydrogenation of Imines Catalyzed by A Polymer-Immobilized Chiral Catalyst. *Org. Biomol. Chem.* **2009**, *7*, 69−75.

(252) Arakawa, Y.; Chiba, A.; Haraguchi, N.; Itsuno, S. Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water using a Polymer-Supported Chiral Catalyst Containing a Hydrophilic Pendant Group. *Adv. Synth. Catal.* **2008**, *350*, 2295−2304.

(253) Mennecke, K.; Cecilia, R.; Glasnov, T. N.; Gruhl, S.; Vogt, C.; Feldhoff, A.; Vargas, M. A. L.; Kappe, C. O.; Kunz, U.; Kirschning, A. Palladium(0) Nanoparticles on Glass-Polymer Composite Materials as Recyclable Catalysts: A Comparison Study on their Use in Batch and Continuous Flow Processes. *Adv. Synth. Catal.* **2008**, *350*, 717−730.

(254) Li, X.; Wu, X.; Chen, W.; Hancock, F. E.; King, F.; Xiao, J. Asymmetric Transfer Hydrogenation in Water with a Supported Noyori−Ikariya Catalyst. *Org. Lett.* **2004**, *6*, 3321−3324.

(255) Li, X.; Chen, W.; Hems, W.; King, F.; Xiao, J. Asymmetric Transfer Hydrogenation of Ketones with A Polymer-Supported Chiral Diamine. *Tetrahedron Lett.* **2004**, *45*, 951−953.

(256) Chen, Y.-C.; Wu, T.-F.; Deng, J.-G.; Liu, H.; Cui, X.; Zhu, J.; Jiang, Y.-Z.; Choi, M. C. K.; Chan, A. S. C. Multiple Dendritic Catalysts for Asymmetric Transfer Hydrogenation. *J. Org. Chem.* **2002**, *67*, 5301−5306.

(257) Chen, Y.-C.; Wu, T.-F.; Deng, J.-G.; Liu, H.; Jiang, Y.-Z.; Choi, M. C. K.; Chan, A. S. C. Dendritic Catalysts for Asymmetric Transfer Hydrogenation. *Chem. Commun.* **2001**, 1488−1489.

(258) Erathodiyil, N.; Ooi, S.; Seayad, A. M.; Han, Y.; Lee, S. S.; Ying, J. Y. Palladium Nanoclusters Supported on Propylurea-Modified Siliceous Mesocellular Foam for Coupling and Hydrogenation Reactions. *Chem.—Eur. J.* **2008**, *14*, 3118−3125.

(259) Liu, G.; Yao, M.; Zhang, F.; Gao, Y.; Li, H. Facile Synthesis of A Mesoporous Silica-Supported Catalyst for Ru-Catalyzed Transfer Hydrogenation of Ketones. *Chem. Commun.* **2008**, 347−349.

(260) Huang, X.; Ying, J. Y. Asymmetric Transfer Hydrogenation over Ru−TsDPEN Catalysts Supported on Siliceous Mesocellular Foam. *Chem. Commun.* **2007**, 1825−1827.

(261) Liu, P.; Gu, P.; Deng, J.; Tu, Y.; Ma, Y. Efficient Heterogeneous Asymmetric Transfer Hydrogenation Catalyzed by Recyclable Silica-Supported Ruthenium Complexes. *Eur. J. Org. Chem.* **2005**, 3221−3227.

(262) Liu, P.; Gu, P.; Wang, F.; Tu, Y. Efficient Heterogeneous Asymmetric Transfer Hydrogenation of Ketones Using Highly Recyclable and Accessible Silica-Immobilized Ru-TsDPEN Catalysts. *Org. Lett.* **2004**, *6*, 169−172.

(263) Bartoszewicz, A.; Ahlsten, N.; Martín-Matute, B. Enantioselective Synthesis of Alcohols and Amines by Iridium-Catalyzed Hydrogenation, Transfer Hydrogenation, and Related Processes. *Chem.—Eur. J.* **2013**, *19*, 7274−7302.

(264) Alonso, F.; Riente, P.; Yus, M. Nickel Nanoparticles in Hydrogen Transfer Reactions. *Acc. Chem. Res.* **2011**, *44*, 379−391.

(265) Malacea, R.; Poli, R.; Manoury, E. Asymmetric Hydrosilylation, Transfer Hydrogenation and Hydrogenation of Ketones Catalyzed by Iridium Complexes. *Coord. Chem. Rev.* **2010**, *254*, 729−752.

(266) Morris, R. H. Asymmetric Hydrogenation, Transfer Hydrogenation and Hydrosilylation of Ketones Catalyzed by Iron Complexes. *Chem. Soc. Rev.* **2009**, *38*, 2282−2291.

(267) Robertson, A.; Matsumoto, T.; Ogo, S. The Development of Aqueous Transfer Hydrogenation Catalysts. *Dalton Trans.* **2011**, *40*, 10304−10310.

(268) Bullock, R. M. Catalytic Ionic Hydrogenations. *Chem.—Eur. J.* **2004**, *10*, 2366−2374.

(269) Wills, M.; Palmer, M.; Smith, A.; Kenny, J.; Walsgrove, T. Recent Developments in the Area of Asymmetric Transfer Hydrogenation. *Molecules* **2000**, *5*, 4−18.

(270) Wang, C.; Villa-Marcos, B.; Xiao, J. Hydrogenation of Imino Bonds with Half-Sandwich Metal Catalysts. *Chem. Commun.* **2011**, *47*, 9773−9785.

(271) Enthaler, S.; Junge, K.; Beller, M. Sustainable Metal Catalysis with Iron: From Rust to a Rising Star? *Angew. Chem., Int. Ed.* **2008**, *47*, 3317−3321.

(272) Bullock, R. M., Ed. *Catalysis Without Precious Metals*; Wiley-VCH: Weinheim, Germany, 2010.

(273) Bolm, C. A New Iron Age. *Nat. Chem.* **2009**, *1*, 420−420.

(274) Mazza, S.; Scopelliti, R.; Hu, X. Chemoselective Hydrogenation and Transfer Hydrogenation of Aldehydes Catalyzed by Iron(II) PONOP Pincer Complexes. *Organometallics* **2015**, *34*, 1538−1545.
(275) Bata, P.; Notheisz, F.; Kluson, P.; Zsigmond, Á. Iron Phthalocyanine as New Efficient Catalyst for Catalytic Transfer Hydrogenation of Simple Aldehydes and Ketones. *Appl. Organomet. Chem.* **2015**, *29*, 45−49.
(276) Mikhailine, A. A.; Morris, R. H. Effect of the Structure of the Diamine Backbone of P−N−N−P ligands in Iron(II) Complexes on Catalytic Activity in the Transfer Hydrogenation of Acetophenone. *Inorg. Chem.* **2010**, *49*, 11039−11044.
(277) Zuo, W.; Morris, R. H. Synthesis and Use of an Asymmetric Transfer Hydrogenation Catalyst Based on Iron(II) for the Synthesis of Enantioenriched Alcohols and Amines. *Nat. Protoc.* **2015**, *10*, 241−257.
(278) Sues, P. E.; Lough, A. J.; Morris, R. H. Stereoelectronic Factors in Iron Catalysis: Synthesis and Characterization of Aryl-Substituted Iron(II) Carbonyl P−N−N−P Complexes and Their Use in the Asymmetric Transfer Hydrogenation of Ketones. *Organometallics* **2011**, *30*, 4418−4431.
(279) Lagaditis, P. O.; Lough, A. J.; Morris, R. H. Low-Valent Ene−Amido Iron Complexes for the Asymmetric Transfer Hydrogenation of Acetophenone without Base. *J. Am. Chem. Soc.* **2011**, *133*, 9662−9665.
(280) Prokopchuk, D. E.; Sonnenberg, J. F.; Meyer, N.; Zimmer-De Iuliis, M.; Lough, A. J.; Morris, R. H. Spectroscopic and DFT Study of Ferraaziridine Complexes Formed in the Transfer Hydrogenation of Acetophenone Catalyzed Using *trans*-[Fe(CO)(NCMe)($PPh_2C_6H_4CH{=}NCH_2{-}$)$_2$-κ^4*P,N,N,P*]$(BF_4)_2$. *Organometallics* **2012**, *31*, 3056−3064.
(281) Prokopchuk, D. E.; Morris, R. H. Inner-Sphere Activation, Outer-Sphere Catalysis: Theoretical Study on the Mechanism of Transfer Hydrogenation of Ketones Using Iron(II) PNNP Eneamido Complexes. *Organometallics* **2012**, *31*, 7375−7385.
(282) Mikhailine, A. A.; Maishan, M. I.; Lough, A. J.; Morris, R. H. The Mechanism of Efficient Asymmetric Transfer Hydrogenation of Acetophenone Using an Iron(II) Complex Containing an (*S,S*)-$Ph_2PCH_2CH{=}NCHPhCHPhN{=}CHCH_2PPh_2$ Ligand: Partial Ligand Reduction Is the Key. *J. Am. Chem. Soc.* **2012**, *134*, 12266−12280.
(283) Zuo, W.; Tauer, S.; Prokopchuk, D. E.; Morris, R. H. Iron Catalysts Containing Amine(imine)diphosphine P-NH-N-P Ligands Catalyze both the Asymmetric Hydrogenation and Asymmetric Transfer Hydrogenation of Ketones. *Organometallics* **2014**, *33*, 5791−5801.
(284) Zuo, W.; Lough, A. J.; Li, Y. F.; Morris, R. H. Amine(imine)-diphosphine Iron Catalysts for Asymmetric Transfer Hydrogenation of Ketones and Imines. *Science* **2013**, *342*, 1080−1083.
(285) Sonnenberg, J. F.; Coombs, N.; Dube, P. A.; Morris, R. H. Iron Nanoparticles Catalyzing the Asymmetric Transfer Hydrogenation of Ketones. *J. Am. Chem. Soc.* **2012**, *134*, 5893−5899.
(286) Zhou, S.; Fleischer, S.; Junge, K.; Das, S.; Addis, D.; Beller, M. Enantioselective Synthesis of Amines: General, Efficient Iron-Catalyzed Asymmetric Transfer Hydrogenation of Imines. *Angew. Chem., Int. Ed.* **2010**, *49*, 8121−8125.
(287) Bigler, R.; Mezzetti, A. Isonitrile Iron(II) Complexes with Chiral N_2P_2 Macrocycles in the Enantioselective Transfer Hydrogenation of Ketones. *Org. Lett.* **2014**, *16*, 6460−6463.
(288) Bigler, R.; Huber, R.; Mezzetti, A. Highly Enantioselective Transfer Hydrogenation of Ketones with Chiral (NH)2P2Macrocyclic Iron(II) Complexes. *Angew. Chem., Int. Ed.* **2015**, *54*, 5171−5174.
(289) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B. Iron(II) Complexes Bearing Chelating Cyclopentadienyl-N-Heterocyclic Carbene Ligands as Catalysts for Hydrosilylation and Hydrogen Transfer Reactions. *Organometallics* **2010**, *29*, 2777−2782.
(290) Hashimoto, T.; Urban, S.; Hoshino, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. Synthesis of Bis(N-heterocyclic carbene) Complexes of Iron(II) and Their Application in Hydrosilylation and Transfer Hydrogenation. *Organometallics* **2012**, *31*, 4474−4479.
(291) Bala, M. D.; Ikhile, M. I. Application of Three-Legged Piano-Stool Cyclopentadienyl-N-Heterocyclic Carbene Iron(II) Complexes as *in situ* Catalysts for the Transfer Hydrogenation of Ketones. *J. Mol. Catal. A: Chem.* **2014**, *385*, 98−105.
(292) Naik, A.; Maji, T.; Reiser, O. Iron(II)−Bis(isonitrile) Complexes: Novel Catalysts in Asymmetric Transferhydrogenations of Aromatic and Heteroaromatic Ketones. *Chem. Commun.* **2010**, *46*, 4475−4477.
(293) Hopewell, J. P.; Martins, J. E. D.; Johnson, T. C.; Godfrey, J.; Wills, M. Developing Asymmetric Iron and Ruthenium-Based Cyclone Complexes; Complex Factors Influence the Asymmetric Induction in the Transfer Hydrogenation of Ketones. *Org. Biomol. Chem.* **2012**, *10*, 134−145.
(294) Kamitani, M.; Nishiguchi, Y.; Tada, R.; Itazaki, M.; Nakazawa, H. Synthesis of Fe−H/Si−H and Fe−H/Ge−H Bifunctional Complexes and Their Catalytic Hydrogenation Reactions toward Nonpolar Unsaturated Organic Molecules. *Organometallics* **2014**, *33*, 1532−1535.
(295) Wienhöfer, G.; Westerhaus, F. A.; Jagadeesh, R. V.; Junge, K.; Junge, H.; Beller, M. Selective Iron-Catalyzed Transfer Hydrogenation of Terminal Alkynes. *Chem. Commun.* **2012**, *48*, 4827−4829.
(296) Wienhöfer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F. A.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base. *J. Am. Chem. Soc.* **2011**, *133*, 12875−12879.
(297) Wienhöfer, G.; Westerhaus, F. A.; Junge, K.; Beller, M. Fast and Selective Iron-Catalyzed Transfer Hydrogenations of Aldehydes. *J. Organomet. Chem.* **2013**, *744*, 156−159.
(298) Liu, Y.; Tüysüz, H.; Jia, C.-J.; Schwickardi, M.; Rinaldi, R.; Lu, A.-H.; Schmidt, W.; Schüth, F. From Glycerol to Allyl alcohol: Iron Oxide Catalyzed Dehydration and Consecutive Hydrogen Transfer. *Chem. Commun.* **2010**, *46*, 1238−1240.
(299) Strassberger, Z.; Mooijman, M.; Ruijter, E.; Alberts, A. H.; de Graaff, C.; Orru, R. V. A.; Rothenberg, G. A Facile Route to Ruthenium−Carbene Complexes and Their Application in Furfural Hydrogenation. *Appl. Organometal. Chem.* **2010**, *24*, 142−146.
(300) Monney, A.; Venkatachalam, G.; Albrecht, M. Synthesis and Catalytic Activity of Histidine-Based NHC Ruthenium Complexes. *Dalton Trans.* **2011**, *40*, 2716−2719.
(301) Akta, A.; Gök, Y. 4-Vinylbenzyl-Substituted Silver(I) *N*-Heterocyclic Carbene Complexes and Ruthenium(II) *N*-Heterocyclic Carbene Complexes: Synthesis and Transfer Hydrogenation of Ketones. *Transition Met. Chem.* **2014**, *39*, 925−931.
(302) Yasar, S.; Çekirdek, S.; Özdemir, I. Synthesis, characterization, and transfer hydrogenation of Ru(II)-*N*-heterocyclic carbene complexes. *J. Coord. Chem.* **2014**, *67*, 1236−1248.
(303) DePasquale, J.; White, N. J.; Ennis, E. J.; Zeller, M.; Foley, J. P.; Papish, E. T. Synthesis of chiral *N*-heterocyclic carbene (NHC) ligand precursors and formation of ruthenium(II) complexes for transfer hydrogenation catalysts. *Polyhedron* **2013**, *58*, 162−170.
(304) Wdowik, T.; Samojłowicz, C.; Jawiczuk, M.; Malińska, M.; Woźniak, K.; Grela, K. Ruthenium Nitronate Complexes as Tunable Catalysts for Olefin Metathesisand Other Transformations. *Chem. Commun.* **2013**, *49*, 674−676.
(305) Yigit, B.; Yigit, M.; Özdemir, I.; Çetinkaya, E. Synthesis of Ruthenium(II) N-Heterocyclic Carbene Complexes and Their Catalytic Activities in Transfer Hydrogenation of Ketones. *Transition Met. Chem.* **2012**, *37*, 297−302.
(306) Witt, J.; Pöthig, A.; Kühn, F. E.; Baratta, W. Abnormal N-Heterocyclic Carbene-Phosphine Ruthenium(II) Complexes as Active Catalysts for Transfer Hydrogenation. *Organometallics* **2013**, *32*, 4042−4045.
(307) Aktas, A.; Gok, Y. *N*-Propylphthalimide-Substituted Silver(I) *N*-Heterocyclic Carbene Complexes and Ruthenium(II) N-Heterocyclic Carbene Complexes: Synthesis and Transfer Hydrogenation of Ketones. *Catal. Lett.* **2015**, *145*, 631−639.

(308) Zielinski, G. K.; Samojlowicz, C.; Wdowik, T.; Grela, K. In Tandem or Alone: A Remarkably Selective Transfer Hydrogenation of Alkenes Catalyzed by Ruthenium Olefin Metathesis Catalysts. *Org. Biomol. Chem.* **2015**, *13*, 2684−2688.

(309) Li, X.-W.; Wang, G.-F.; Chen, F.; Li, Y.-Z.; Chen, X.-T.; Xue, Z.-L. Ruthenium(II) Carbonyl Chloride Complexes Containing Pyridine-Functionalised Bidentate N-Heterocyclic Carbenes: Synthesis, Structures, and Impact of the Carbene Ligands on Catalytic Activities. *Inorg. Chim. Acta* **2011**, *378*, 280−287.

(310) Fernández, F. E.; Puerta, M. C.; Valerga, P. Half-Sandwich Ruthenium(II) Picolyl-NHC Complexes: Synthesis, Characterization, and Catalytic Activity in Transfer Hydrogenation Reactions. *Organometallics* **2011**, *30*, 5793−5802.

(311) Fernández, F. E.; Puerta, M. C.; Valerga, P. Ruthenium(II) Picolyl-NHC Complexes: Synthesis, Characterization, and Catalytic Activity in Amine N-alkylation and Transfer Hydrogenation Reactions. *Organometallics* **2012**, *31*, 6868−6879.

(312) Horn, S.; Albrecht, M. Transfer Hydrogenation of Unfunctionalised Alkenes Using *N*-Heterocyclic Carbeneruthenium Catalyst Precursors. *Chem. Commun.* **2011**, *47*, 8802−8804.

(313) Horn, S.; Gandolfi, C.; Albrecht, M. Transfer Hydrogenation of Ketones and Activated Olefins Using Chelating NHC Ruthenium Complexes. *Eur. J. Inorg. Chem.* **2011**, 2863−2868.

(314) Wylie, W. N. O.; Lough, A. J.; Morris, R. H. Mechanistic Investigation of the Hydrogenation of Ketones Catalyzed by a Ruthenium(II) Complex Featuring an N-Heterocyclic Carbene with a Tethered Primary Amine Donor: Evidence for an Inner Sphere Mechanism. *Organometallics* **2011**, *30*, 1236−1252.

(315) Ohara, H.; Wylie, W. N. O.; Lough, A. J.; Morris, R. H. Effect of Chelating Ring Size in Catalytic Ketone Hydrogenation: Facile Synthesis of Ruthenium(II) Precatalysts Containing an *N*-Heterocyclic Carbene with A Primary Amine Donor for Ketone Hydrogenation and A DFT Study of Mechanisms. *Dalton Trans.* **2012**, *41*, 8797−8808.

(316) Humphries, M. E.; Pecak, W. H.; Hohenboken, S. A.; Alvarado, S. R.; Swenson, D. C.; Domski, G. J. Ruthenium(II) Supported by Phosphine-Functionalized *N*-Heterocyclic Carbene Ligands as Catalysts for the Transfer Hydrogenation of Ketones. *Inorg. Chem. Commun.* **2013**, *37*, 138−143.

(317) Mangalum, A.; McMillen, C. D.; Tennyson, A. G. Synthesis, coordination chemistry and reactivity of transition metal complexes supported by a chelating benzimidazolylidene carboxylate ligand. *Inorg. Chim. Acta* **2015**, *426*, 29−38.

(318) Gürbüz, N.; Özcan, E. Ö.; Özdemir, I.; Çetinkaya, B.; Sahin, O.; Büyükgüngör, O. Preparation of A Series of Ru(II) Complexes with *N*-Heterocyclic Carbeneligands for the Catalytic Transfer Hydrogenation of Aromatic Ketones. *Dalton Trans.* **2012**, *41*, 2330−2339.

(319) Cheng, Y.; Lu, X.-Y.; Xu, H.-J.; Li, Y.-Z.; Chen, X.-T.; Xue, Z.-L. Bis-N-heterocyclic carbene ruthenium(II) carbonyl complexes: Synthesis, structural characterization and catalytic activities in transfer hydrogenation of ketones. *Inorg. Chim. Acta* **2010**, *363*, 430−437.

(320) Sanz, S.; Azua, A.; Peris, E. '(η^6-arene)Ru(bis-NHC)' Complexes for the Reduction of CO_2 to Formatewith Hydrogen and by Transfer Hydrogenation with *i*PrOH. *Dalton Trans.* **2010**, *39*, 6339−6343.

(321) Lai, Y.-B.; Lee, C.-S.; Lin, W.-J.; Naziruddin, A. R.; Hwang, W.-S. Bis-Chelate *N*-Heterocyclic Tetracarbene Ru(II) Complexes: Synthesis, Structure, and Catalytic Activity toward Transfer Hydrogenation of Ketones. *Polyhedron* **2013**, *53*, 243−248.

(322) Ding, N.; Hor, T. S. A. Ruthenium(II) N,S-Heterocyclic Carbene Complexes and Transfer Hydrogenation of Ketones. *Dalton Trans.* **2010**, *39*, 10179−10185.

(323) Manzini, S.; Fernández-Salas, J. A.; Nolan, S. P. From a Decomposition Product to an Efficient and Versatile Catalyst: The [Ru(η^5-indenyl)(PPh_3)$_2$Cl] Story. *Acc. Chem. Res.* **2014**, *47*, 3089−3101.

(324) Carrión, M. C.; Ruiz-Castañeda, M.; Espino, G.; Aliende, C.; Santos, L.; Rodríguez, A. M.; Manzano, B. R.; Jalón, F. A.; Lledós, A. Selective Catalytic Deuterium Labeling of Alcohols during a Transfer Hydrogenation Process of Ketones Using D_2O as the Only Deuterium Source. Theoretical and Experimental Demonstration of a Ru−H/D^+Exchange as the Key Step. *ACS Catal.* **2014**, *4*, 1040−1053.

(325) Roszkowski, P.; Maurin, J. K.; Czarnocki, Z. Synthesis of New Mono-*N*-tosylated Diamine Ligands Based on (*R*)-(+)-Limonene and Their Application in Asymmetric Transfer Hydrogenation of Ketones and Imines. *Tetrahedron: Asymmetry* **2013**, *24*, 643−650.

(326) Mercan, D.; Çetinkaya, E.; Sahin, E. Ru(II)−Arene Complexes with N-Substituted 3,4-Dihydroquinazoline Ligands and Catalytic Activity for Transfer Hydrogenation Reaction. *Inorg. Chim. Acta* **2013**, *400*, 74−81.

(327) Lundberg, H.; Adolfsson, H. Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Ketones in Ethanol. *Tetrahedron Lett.* **2011**, *52*, 2754−2758.

(328) Han, M.-L.; Hu, X.-P.; Huang, J.-D.; Chen, L.-J.; Zheng, Z. New Chiral Amino Alcohol Ligands Derived from 1-Phenylethylamine for Efficient Ru-Catalyzed Asymmetric Transfer Hydrogenation. *Tetrahedron: Asymmetry* **2011**, *22*, 222−225.

(329) Aydemir, M.; Baysal, A.; Ozkar, S.; Yıldırım, L. T. Ruthenium Complexes of Aminophosphine Ligands and Their Use as Pre-Catalysts in the Transfer Hydrogenation of Aromatic Ketones: X-ray Crystal Structure of Thiophene-2-(*N*-diphenylthiophosphino)-methylamine. *Polyhedron* **2011**, *30*, 796−804.

(330) Dayan, S.; Kayacı, N.; Kalaycioglu, N. O.; Dayan, O.; Öztürk, E. C. Synthesis of Ruthenium(II) Complexes Derived from Reduced Imine Ligands: As Catalysts for Transfer Hydrogenation of Ketones. *Inorg. Chim. Acta* **2013**, *401*, 107−113.

(331) Hounjet, L. J.; Bierenstiel, M.; Ferguson, M. J.; McDonald, R.; Cowie, M. Coordinatively Diverse *ortho*-Phosphinoaniline Complexes of Ruthenium and Isolation of a Putative Intermediate in Ketone Transfer Hydrogenation Catalysis. *Inorg. Chem.* **2010**, *49*, 4288−4300.

(332) Wang, L.; Yang, Q.; Fu, H.-Y.; Chen, H.; Yuan, M.-L.; Li, R.-X. Ru−η^6-Benzene−Phosphine Complex-Catalyzed Transfer Hydrogenation of Ketones. *Appl. Organomet. Chem.* **2011**, *25*, 626−631.

(333) Gök, L.; Türkmen, H. Half-Sandwich η^6-Arene−Ruthenium-(II) Complexes Bearing 1-Alkyl(benzyl)-Imidazo[4,5-*f*][1,10]-Phenanthroline (IP) Derivatives: the Effect of Alkyl Chain Length of Ligands to Catalytic Activity. *Tetrahedron* **2013**, *69*, 10669−10674.

(334) Volbeda, J.; Jones, P. G.; Tamm, M. Preparation of Chiral Imidazolin-2-Imine Ligands and Their Application in Ruthenium-Catalyzed Transfer Hydrogenation. *Inorg. Chim. Acta* **2014**, *422*, 158−166.

(335) Deshpande, S. H.; Kelkar, A. A.; Gonnade, R. G.; Shingote, S. K.; Chaudhari, R. V. Catalytic Asymmetric Transfer Hydrogenation of Ketones Using [Ru(*p*-cymene)Cl_2]$_2$ with Chiral Amino Alcohol Ligands. *Catal. Lett.* **2010**, *138*, 231−238.

(336) Václavík, J.; Kuzma, M.; Prech, J.; Kacer, P. Asymmetric Transfer Hydrogenation of Imines and Ketones Using Chiral Ru^{II}Cl(η^6-*p*-cymene)[(*S,S*)-*N*-TsDPEN] as a Catalyst: A Computational Study. *Organometallics* **2011**, *30*, 4822−4829.

(337) Zhang, B.; Wang, H.; Lin, G.-Q.; Xu, M.-H. Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation Using Unsymmetrical Vicinal Diamine-Based Ligands: Dramatic Substituent Effect on Catalyst Efficiency. *Eur. J. Org. Chem.* **2011**, 4205−4211.

(338) Soni, R.; Cheung, F. K.; Clarkson, G. C.; Martins, J. E. D.; Graham, M. A.; Wills, M. The Importance of the N−H Bond in Ru/TsDPEN Complexes for Asymmetric Transfer Hydrogenation of Ketones and Imines. *Org. Biomol. Chem.* **2011**, *9*, 3290−3294.

(339) Lu, C.; Luo, Z.; Huang, L.; Li, X. The Ru-Catalyzed Enantioselective Preparation of Chiral Halohydrins and their Application in the Synthesis of (*R*)-Clorprenaline and (*S*)-Sotalol. *Tetrahedron: Asymmetry* **2011**, *22*, 722−727.

(340) Zhou, X.; Wu, X.; YanG, B.; Xiao, J. Varying the Ratio of Formic Acid to Triethylamine Impacts on Asymmetric Transfer Hydrogenation of Ketones. *J. Mol. Catal. A: Chem.* **2012**, *357*, 133−140.

(341) Dayan, S.; Kalaycioglu, N. O.; Daran, J. C.; Labande, A.; Poli, R. Synthesis and Characterization of Half-Sandwich Ruthenium Complexes Containing Aromatic Sulfonamides Bearing Pyridinyl

Rings: Catalysts for Transfer Hydrogenation of Acetophenone Derivatives. *Eur. J. Inorg. Chem.* **2013**, 3224−3232.

(342) Kayan, C.; Meriç, N.; Aydemir, M.; Ocak, Y. S.; Baysal, A.; Temel, H. Novel Cyclohexyl-Based Aminophosphine Ligands and Use of their Ru(II) Complexes in Transfer Hydrogenation of Ketones. *Appl. Organomet. Chem.* **2014**, *28*, 127−133.

(343) Aydemir, M.; Meric, N.; Baysal, A.; Kayan, C.; Togrul, M.; Gümgüm, B. New Chiral Phosphinite Ligands with C_2-Symmetric Axis and their Possible Applications in Ru-Catalyzed Asymmetric Transfer Hydrogenation. *Appl. Organomet. Chem.* **2010**, *24*, 215−221.

(344) Aydemir, M.; Meriç, N.; Durap, F.; Baysal, A.; Togrul, M. Asymmetric Transfer Hydrogenation of Aromatic Ketones with the Ruthenium(II) Catalyst Derived from C_2 Symmetric *N,N′*-bis[(1*S*)-1-benzyl-2-*O*-(diphenylphosphinite)ethyl]ethanediamide. *J. Organomet. Chem.* **2010**, *695*, 1392−1398.

(345) Aydemir, M.; Meric, N.; Baysal, A.; Gümgüm, B.; Togrul, M.; Turgut, Y. A Modular Design of Ruthenium(II) Catalysts with Chiral C_2-Symmetric Phosphinite Ligands for Effective Asymmetric Transfer Hydrogenation of Aromatic Ketones. *Tetrahedron: Asymmetry* **2010**, *21*, 703−710.

(346) Aydemir, M.; Rafikova, K.; Kystaubayeva, N.; Paşa, S.; Meric, N.; Ocak, Y. S.; Zazybin, A.; Temel, H.; Gurbuz, N.; Ozdemir, I. Ionic Liquid Based Ru(II)−Phosphinite Compounds and their Catalytic Use in Transfer Hydrogenation: X-ray Structure of an Ionic Compound 1-Chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol. *Polyhedron* **2014**, *81*, 245−255.

(347) Aydemir, M.; Meric, N.; Baysal, A.; Turgut, Y.; Kayan, C.; Şeker, S.; Togrul, M.; Gümgüm, B. Asymmetric Transfer Hydrogenation of Acetophenone Derivatives with Novel Chiral Phosphinite Based η^6-*p*-Cymene/Ruthenium(II) Catalysts. *J. Organomet. Chem.* **2011**, *696*, 1541−1546.

(348) Zirakzadeh, A.; Schuecker, R.; Gorgas, N.; Mereiter, K.; Spindler, F.; Weissensteiner, W. Ruthenium Complexes of Phosphino-Substituted Ferrocenyloxazolines in the Asymmetric Hydrogenation and Transfer Hydrogenation of Ketones: A Comparison. *Organometallics* **2012**, *31*, 4241−4250.

(349) Ak, B.; Aydemir, M.; Ocak, Y. S.; Durap, F.; Kayan, C.; Baysal, A.; Temel, H. Readily Available Ferrocenyl-Phosphinite Ligands for Ru(II)-Catalyzed Enantioselective Transfer Hydrogenation of Ketones and Fabrication of Hybrid Heterojunctions. *Inorg. Chim. Acta* **2014**, *409*, 244−253.

(350) Ak, B.; Elma, D.; Meric, N.; Kayan, C.; Işık, U.; Aydemir, M.; Durap, F.; Baysal, A. New Chiral Ruthenium(II)−Phosphinite Complexes Containing a Ferrocenyl Group in Enantioselective Transfer Hydrogenations of Aromatic Ketones. *Tetrahedron: Asymmetry* **2013**, *24*, 1257−1264.

(351) Işıka, U.; Aydemira, M.; Meric, N.; Durap, F.; Kayan, C.; Temel, H.; Baysal, A. Tunable Ferrocenyl-Phosphinite Ligands for the Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Ketones. *J. Mol. Catal. A: Chem.* **2013**, *379*, 225−233.

(352) Facchetti, G.; Gandolfi, R.; Fusè, M.; Zerla, D.; Cesarotti, E.; Pellizzoni, M. Irimoldi. Simple 1,3-diamines and their application as ligands in ruthenium(II) catalysts for asymmetric transfer hydrogenation of aryl ketones. *New J. Chem.* **2015**, *39*, 3792−3800.

(353) Aliende, C.; Pérez-Manrique, M.; Jalón, F. A.; Manzano, B. R.; Rodrıguez, A. M.; Espino, G. Arene Ruthenium Complexes as Versatile Catalysts in Water in both Transfer Hydrogenation of Ketones and Oxidation of Alcohols. Selective Deuterium Labeling of *rac*-1-Phenylethanol. *Organometallics* **2012**, *31*, 6106−6123.

(354) Nieto, I.; aaLivings, M. S.; Sacci, J. B.; Reuther, L. E.; Zeller, M.; Papish, E. T. Transfer Hydrogenation in Water via a Ruthenium Catalyst with OH Groups near the Metal Center on a Bipy Scaffold. *Organometallics* **2011**, *30*, 6339−6342.

(355) Alami, M. S. I.; Amrani, M. A. E.; Dahdouh, A.; Roussel, P.; Suisse, I.; Mortreux, A. α-Amino-Oximes Based on Optically Pure Limonene: A New Ligands Family for Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation. *Chirality* **2012**, *24*, 675−682.

(356) Pablo, Ó.; Guijarro, D.; Kovács, G.; Lledós, A.; Ujaque, G.; Yus, M. A Versatile Ru Catalyst for the Asymmetric Transfer Hydrogenation of Both Aromatic and Aliphatic Sulfinylimines. *Chem.—Eur. J.* **2012**, *18*, 1969−1983.

(357) Dayan, S.; Ozpozan, N. K.; Özdemir, N.; Dayan, O. Synthesis of Some Ruthenium(II)−Schiff Base Complexes Bearing Sulfonamide Fragment: New Catalysts for Transfer Hydrogenation of Ketones. *J. Organomet. Chem.* **2014**, *770*, 21−28.

(358) Sheeba, M. M.; Tamizh, M. M.; Farrugia, L. J.; Endo, A.; Karvembu, R. Chiral (η^6-*p*-Cymene)ruthenium(II) Complexes Containing Monodentate Acylthiourea Ligands for Efficient Asymmetric Transfer Hydrogenation of Ketones. *Organometallics* **2014**, *33*, 540−550.

(359) Pandiarajan, D.; Ramesh, R. Ruthenium(II) Half-Sandwich Complexes Containing Thioamides: Synthesis, Structures and Catalytic Transfer Hydrogenation of Ketones. *J. Organomet. Chem.* **2013**, *723*, 26−35.

(360) Singh, P.; Singh, A. K. Transfer Hydrogenation of Ketones and Catalytic Oxidation of Alcohols with Half-Sandwich Complexes of Ruthenium(II) Designed Using Benzene and Tridentate (S, N, E) Type Ligands (E = S, Se, Te). *Organometallics* **2010**, *29*, 6433−6442.

(361) Prakash, O.; Sharma, K. N.; Joshi, H.; Gupta, P. L.; Singh, A. K. Half Sandwich Complexes of Chalcogenated Pyridine Based Bi-(N, S/Se) and Terdentate (N, S/Se, N) Ligands with (η^6-Benzene)-ruthenium(II): Synthesis, Structure and Catalysis of Transfer Hydrogenation of Ketonesand Oxidation of Alcohols. *Dalton Trans.* **2013**, *42*, 8736−8747.

(362) Cheung, F. K.; Clarke, A. J.; Clarkson, G. J.; Fox, D. J.; Graham, M. A.; Lin, C.; Crivillé, A. L.; Wills, M. Kinetic and Structural Studies on ‘Tethered’ Ru(II) Arene Ketone Reduction Catalysts. *Dalton Trans.* **2010**, *39*, 1395−1402.

(363) Ji, Y.; Xue, P.; Ma, D. D.; Li, X. Q.; Gu, P.; Li, R. Asymmetric Transfer Hydrogenation of Alpha-Azido Acrylates. *Tetrahedron Lett.* **2015**, *56*, 192−194.

(364) Soni, R.; Jolley, K. E.; Clarkson, G. J.; Wills, M. Direct Formation of Tethered Ru(II) Catalysts Using Arene Exchange. *Org. Lett.* **2013**, *15*, 5110−5113.

(365) Soni, R.; Collinson, J.-M.; Clarkson, G. C.; Wills, M. An Unexpected Directing Effect in the Asymmetric Transfer Hydrogenation of α,α-Disubstituted Ketones. *Org. Lett.* **2011**, *13*, 4304−4307.

(366) Su, Y.; Tu, Y.-Q.; Gu, P. Preparation of Enantioenriched γ-Substituted Lactones via Asymmetric Transfer Hydrogenation of β-Azidocyclopropane Carboxylates Using the Ru-TsDPEN Complex. *Org. Lett.* **2014**, *16*, 4204−4207.

(367) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. Oxo-Tethered Ruthenium(II) Complex as a Bifunctional Catalyst for Asymmetric Transfer Hydrogenation and H_2 Hydrogenation. *J. Am. Chem. Soc.* **2011**, *133*, 14960−14963.

(368) Parekh, V.; Ramsden, J. A.; Wills, M. Ether-Tethered Ru(II)/TsDPEN Complexes; Synthesis and Applications to Asymmetric Transfer Hydrogenation. *Catal. Sci. Technol.* **2012**, *2*, 406−414.

(369) Kišic, A.; Stephan, M.; Mohar, B. Asymmetric Transfer Hydrogenation of 1-Naphthyl Ketones by an *ansa*-Ru(II) Complex of a DPEN-$SO_2N(Me)$-$(CH_2)_2$(η^6-*p*-Tol) Combined Ligand. *Org. Lett.* **2013**, *15*, 1614−1617.

(370) Kırkar, B. T.; Türkmen, H.; Kani, İ.; Cetinkaya, B. Synthesis, Characterization, and Reactivity of Ruthenium(II) Complexes Containing η^6-Arene-η^1-Pyrazole Ligands. *Tetrahedron* **2012**, *68*, 8655−8662.

(371) Manzini, S.; Blanco, C. A. U.; Nolan, S. P. Ruthenium Phenylindenyl Complex as an Efficient Transfer Hydrogenation Catalyst. *Adv. Synth. Catal.* **2012**, *354*, 3036−3044.

(372) Moya, S. A.; Vidal, M.; Abarca, G.; Martinez, C.; Guerchais, V.; Le Bozec, H.; Garland, M. T.; Rodriguez, S.; Aguirre, P. Synthesis, Structure and Catalytic Activities for Hydrogen Transfer Reaction of the Carbonyl Ruthenium(II) Complex Containing Polypyridine and Phosphine Ligands. *Inorg. Chem. Commun.* **2010**, *13*, 1519−1521.

(373) Dyer, H.; Picot, A.; Vendier, L.; Auffrant, A.; Le Floch, P.; Sabo-Etienne, S. Tridentate and Tetradentate Iminophosphorane-

Based Ruthenium Complexes in Catalytic Transfer Hydrogenation of Ketones. *Organometallics* **2011**, *30*, 1478−1486.

(374) Cuervo, D.; Menéndez-Pedregal, E.; Díez, J.; Gamasa, M. P. Mononuclear Ruthenium(II) Complexes Bearing the (*S,S*)-*i*Pr-Pybox Ligand. *J. Organomet. Chem.* **2011**, *696*, 1861−1867.

(375) Ghoochany, L. T.; Farsadpour, S.; Sun, Y.; Thiel, W. T. New N,N,N-Donors Resulting in Highly Active Ruthenium Catalysts for Transfer Hydrogenation at Room Temperature. *Eur. J. Inorg. Chem.* **2011**, 3431−3437.

(376) Günnaz, S.; Özdemir, N.; Dayan, S.; Dayan, O.; Çetinkaya, B. Synthesis of Ruthenium(II) Complexes Containing Tridentate Triamine ('NNN') and Bidentate Diamine Ligands (NN'): as Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2011**, *30*, 4165−4173.

(377) Ren, P.; Vechorkin, O.; Csok, Z.; Salihu, I.; Scopelliti, R.; Hu, X. Pd, Pt, and Ru Complexes of a Pincer Bis(amino)amide Ligand. *Dalton Trans.* **2011**, *40*, 8906−8911.

(378) Basal, A.; Aydemir, M.; Durap, F.; Özkar, S.; Yildirim, L. T.; Ocak, Y. S. A Ruthenium(II) Bipyridine Complex Containing a 4,5-Diazafluorene Moiety: Synthesis, Characterization and its Applications in Transfer Hydrogenation of Ketones and Dye Sensitized Solar Cells. *Polyhedron* **2015**, *89*, 55−61.

(379) Liang, T.; Nguyen, K. D.; Zhang, W.; Krische, M. J. Enantioselective Ruthenium-Catalyzed Carbonyl Allylation via Alkyne−Alcohol C−C Bond-Forming Transfer Hydrogenation: Allene Hydrometalation vs Oxidative Coupling. *J. Am. Chem. Soc.* **2015**, *137*, 3161−3164.

(380) Cavarzan, D. A.; Pinheiro, C. B.; de Araujo, M. P. Neutral and Cationic Ruthenium Carbonyl Complexes [Ru(CO)(2,2′-dipyridylamine)(PR_3)Cl_2] and [Ru(CO)(N-N)(PPh_3)$_2$H]Cl: Synthesis, Structural Characterization and Transfer-Hydrogenation. *Transition Met. Chem.* **2015**, *40*, 117−123.

(381) Dayan, O.; Demirmen, S.; Ozdemir, N. Heteroleptic Ruthenium(II) Complexes of 2-(2-pyridyl)benzimidazoles: A Study of Catalytic Efficiency towards Transfer Hydrogenation of Acetophenone. *Polyhedron* **2015**, *85*, 926−932.

(382) Dayan, O.; Inan, M. Y. Synthesis and Characterization of Ruthenium(II) Complexes Bearing Benzimidazole Ligands: For Transfer Hydrogenation Catalysis. *Synth. React. Inorg. Met.-Org. Chem.* **2015**, *45*, 1018−1024.

(383) Karabuga, S.; Bars, S.; Karakaya, I.; Gumus, S. Efficient transfer hydrogenation reactions with quinazoline-based ruthenium complexes. *Tetrahedron Lett.* **2015**, *56*, 101−104.

(384) Hsu, S.-F.; Plietker, B. Selective Transfer Hydrogenation and Hydrogenation of Ketones Using a Defined Monofunctional (P̂N-(Bn)̂N(Bn)̂P)−Ru^{II} Complex. *Chem.—Eur. J.* **2014**, *20*, 4242−4245.

(385) Dub, P. A.; Henson, N. J.; Martin, R. L.; Gordon, J. C. Unravelling the Mechanism of the Asymmetric Hydrogenation of Acetophenone by [RuX_2(diphosphine)(1,2-diamine)] Catalysts. *J. Am. Chem. Soc.* **2014**, *136*, 3505−3521.

(386) Keleş, M.; Şahinoğlu, C.; Emir, D. M.; Mart, M. New Iminophosphine−Ru(II) Complexes and their Application in Hydrogenation and Transfer Hydrogenation. *Appl. Organomet. Chem.* **2014**, *28*, 768−772.

(387) Zhang, S.; Baldino, S.; Baratta, W. Synthesis of [RuX(CO)(dppp)(NN)]Cl (X = H, Cl; NN = en, ampy) Complexes and Their Use as Catalysts for Transfer Hydrogenation. *Organometallics* **2013**, *32*, 5299−5304.

(388) Türkmen, H. Synthesis of 2-Aminomethylpiperidine Ruthenium(II) Phosphine Complexes and their Applications in Transfer Hydrogenation of Aryl Ketones. *Appl. Organomet. Chem.* **2012**, *26*, 731−735.

(389) Rimoldi, I.; Facchetti, G.; Cesarotti, E.; Pellizzoni, M.; Fusè, M.; Zerla, D. Enantioselective Transfer Hydrogenation of Aryl Ketones: Synthesis and 2D-NMR Characterization of New 8-amino-5,6,7,8-tetrahydroquinoline Ru(II)-complexes. *Curr. Org. Chem.* **2012**, *16*, 2982−2988.

(390) Menéndez-Pedregal, E.; Vaquero, M.; Lastra, E.; Gamasa, P.; Pizzano, A. Highly Enantioselective Hydrogenation of *N*-Aryl Imines Derived from Acetophenones by Using Ru−Pybox Complexes under Hydrogenation or Transfer Hydrogenation Conditions in Isopropanol. *Chem.—Eur. J.* **2015**, *21*, 549−553.

(391) Du, W.; Wang, Q.; Wang, L.; Yu, Z. Ruthenium Complex Catalysts Supported by a Bis(trifluoromethyl)pyrazolyl−Pyridyl-Based NNN Ligand for Transfer Hydrogenation of Ketones. *Organometallics* **2014**, *33*, 974−982.

(392) Moore, C. M.; Szymczak, N. K. 6,6′-Dihydroxy Terpyridine: A Proton-Responsive Bifunctional Ligand and Its Application in Catalytic Transfer Hydrogenation of Ketones. *Chem. Commun.* **2013**, *49*, 400−402.

(393) Dayan, O.; Dayan, S.; Kani, İ.; Çetinkaya, B. Ruthenium(II) Complexes Bearing Pyridine-Based Tridentate and Bidentate Ligands: Catalytic Activity for Transfer Hydrogenation of Aryl Ketones. *Appl. Organomet. Chem.* **2012**, *26*, 663−670.

(394) Ye, W.; Zhao, M.; Yu, Z. Ruthenium(II) Pyrazolyl−Pyridyl−Oxazolinyl Complex Catalysts for the Asymmetric Transfer Hydrogenation of Ketones. *Chem.—Eur. J.* **2012**, *18*, 10843−10846.

(395) Jin, W.; Wang, L.; Yu, Z. A Highly Active Ruthenium(II) Pyrazolyl−Pyridyl−Pyrazole Complex Catalyst for Transfer Hydrogenation of Ketones. *Organometallics* **2012**, *31*, 5664−5667.

(396) Jagadeesh, R. V.; Wienhöfer, G.; Westerhaus, F. A.; Surkus, A. E.; Junge, H.; Junge, K.; Beller, M. A Convenient and General Ruthenium-Catalyzed Transfer Hydrogenation of Nitro- and Azobenzenes. *Chem.—Eur. J.* **2011**, *17*, 14375−14379.

(397) Baratta, W.; Baldino, S.; Calhorda, M. J.; Costa, P. J.; Esposito, G.; Herdtweck, E.; Magnolia, S.; Mealli, C.; Messaoudi, A.; Mason, S. A.; Veiros, L. F. CNN Pincer Ruthenium Catalysts for Hydrogenation and Transfer Hydrogenation of Ketones: Experimental and Computational Studies. *Chem.—Eur. J.* **2014**, *20*, 13603−13617.

(398) Du, W.; Wang, L.; Wu, P.; Yu, Z. A Versatile Ruthenium(II)−NNC Complex Catalyst for Transfer Hydrogenation of Ketones and Oppenauer-Type Oxidation of Alcohols. *Chem.—Eur. J.* **2012**, *18*, 11550−11554.

(399) Wang, T.; Hao, X.-Q.; Zhang, X.-X.; Gong, J.-F.; Song, M.-P. Synthesis, structure and catalytic properties of CNN pincer palladium(II) and ruthenium(II) complexes with *N*-substituted-2-aminomethyl-6-phenylpyridines. *Dalton Trans.* **2011**, *40*, 8964−8976.

(400) Suganthy, P. K.; Prabhu, R. N.; Sridevi, V. S. Synthesis, Structural Characterization and Catalytic Transfer Hydrogenation of Ruthenium(II) Carbonyl Complexes Bearing N,N,O Pincer Type Benzoylhydrazone Ligands. *Polyhedron* **2015**, *88*, 57−62.

(401) Cavarzan, D. A.; Fagundes, F. D.; Fuganti, O.; da Silva, C. W. P.; Pinheiro, C. B.; Back, D. F.; Barison, A.; Bogado, A. L.; de Araujo, M. P. Mixed Phosphine/Diimines and/or Amines Ruthenium Carbonyl Complexes: Synthesis, Characterization and Transfer-Hydrogenation. *Polyhedron* **2013**, *62*, 75−82.

(402) Allen, O. R.; Field, L. D.; Magill, A. M.; Vuong, K. Q.; Bhadbhade, M. M.; Dalgarno, S. J. Ruthenium Complexes of CP_3: A New Carbon-Centered Polydentate Podand Ligand. *Organometallics* **2011**, *30*, 6433−6440.

(403) Chevalley, A.; Cherrier, M. V.; Fontecilla-Camps, J. C.; Ghasemia, M.; Salmain, M. Artificial Metalloenzymes Derived from Bovine *β*-Lactoglobulin for the Asymmetric Transfer Hydrogenation of an Aryl Ketone - Synthesis, Characterization and Catalytic Activity. *Dalton Trans.* **2014**, *43*, 5482−5489.

(404) Ogweno, A. O.; Ojwach, S. O.; Akerman, M. P. Pyridyl)-benzoazole Ruthenium(II) and Ruthenium(III) Complexes: Role of Heteroatom and Ancillary Phosphine Ligand in the Transfer Hydrogenation of Ketones. *Dalton Trans.* **2014**, *43*, 1228−1237.

(405) Li, K.; Niu, J.-L.; Yang, M.-Z.; Li, Z.; Wu, L.-Y.; Hao, X.-Q.; Song, M.-P. New Type of 2,6-Bis(imidazo[1,2-a]pyridin-2-yl)pyridine-Based Ruthenium Complexes: Active Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2015**, *34*, 1170−1176.

(406) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. POP−Pincer Ruthenium Complexes: d^6 Counterparts of Osmium d^4 Species. *Inorg. Chem.* **2014**, *53*, 1195−1209.

(407) Manikandan, R.; Viswanathamurthi, P.; Muthukumar, M. Ruthenium(II) Hydrazone Schiff Base Complexes: Synthesis, Spectral

Study and Catalytic Applications. *Spectrochim. Acta, Part A* **2011**, *83*, 297−303.

(408) Li, X.-W.; Chen, F.; Xu, W.-F.; Li, Y.-Z.; Chen, X.-T.; Xue, Z.-L. Syntheses, structures and catalytic activities of ruthenium (II) carbonyl iodide complexes with CNC-pincer bis (carbene) ligand. *Inorg. Chem. Commun.* **2011**, *14*, 1673−1676.

(409) Walker, J. M.; Cox, A. M.; Wang, R.; Spivak, G. J. Synthesis and Reactivity of $[(PhB(CH_2PPh_2)_3\text{-}\kappa^3P)Ru(NCMe)_3]PF_6$ and Its Potential as a Transfer Hydrogenation Catalyst. *Organometallics* **2010**, *29*, 6121−6124.

(410) Belger, C.; Neisius, N. M.; Plietker, B. A Selective Ru-Catalyzed Semireduction of Alkynes to Z Olefins under Transfer-Hydrogenation Conditions. *Chem.—Eur. J.* **2010**, *16*, 12214−12220.

(411) Page, M. J.; Wagler, J.; Messerle, B. A. Pyridine-2,6-bis(thioether) (SNS) Complexes of Ruthenium as Catalysts for Transfer Hydrogenation. *Organometallics* **2010**, *29*, 3790−3798.

(412) Kharat, A. N.; Bakhoda, A.; Jahromi, B. T. Ru(II) Xantphos Complex as an Efficient Catalyst in Transfer Hydrogenation of Carbonyl Compounds. *Inorg. Chem. Commun.* **2011**, *14*, 1161−1164.

(413) He, L.-P.; Chen, T.; Xue, D.-X.; Eddaoudi, M.; Huang, K.-W. Efficient Transfer Hydrogenation Reaction Catalyzed by a Dearomatized PN^3P Ruthenium Pincer Complex under Base-Free Conditions. *J. Organomet. Chem.* **2012**, *700*, 202−206.

(414) Prabhu, R. N.; Ramesh, R. Synthesis, Structural Characterization, Electrochemistry and Catalytic Transfer Hydrogenation of Ruthenium(II) Carbonyl Complexes Containing Tridentate Benzoylhydrazone Ligands. *J. Organomet. Chem.* **2012**, *718*, 43−51.

(415) Mathew, P.; Neels, A.; Albrecht, M. 1,2,3-Triazolylidenes as Versatile Abnormal Carbene Ligands for Late Transition Metals. *J. Am. Chem. Soc.* **2008**, *130*, 13534−13535.

(416) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. Crystalline 1*H*-1,2,3-Triazol-5-ylidenes: New Stable Mesoionic Carbenes (MICs). *Angew. Chem., Int. Ed.* **2010**, *49*, 4759−4762.

(417) Donnelly, K. F.; Petronilho, A.; Albrecht, M. Application of 1,2,3-Triazolylidenes as Versatile NHC-Type Ligands: Synthesis, Properties, and Application in Catalysis and Beyond. *Chem. Commun.* **2013**, *49*, 1145−1159.

(418) Timmis, F.; Adolfsson, H. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Rhodium Complexes Containing Amino Acid Triazole Ligands. *Org. Biomol. Chem.* **2010**, *8*, 4536−4539.

(419) Cambreiro, X. C.; Pericas, M. A. Proline-Derived Aminotriazole Ligands: Preparation and Use in the Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation. *Adv. Synth. Catal.* **2011**, *353*, 113−124.

(420) Johnson, T. C.; Totty, W. G.; Wills, M. Application of Ruthenium Complexes of Triazole-Containing Tridentate Ligands to Asymmetric Transfer Hydrogenation of Ketones. *Org. Lett.* **2012**, *14*, 5230−5233.

(421) Du, W.; Wu, P.; Wang, Q.; Yu, Z. Ruthenium(II) Complex Catalysts Bearing a Pyridyl-Based Benzimidazolyl−Benzotriazolyl Ligand for Transfer Hydrogenation of Ketones. *Organometallics* **2013**, *32*, 3083−3090.

(422) Delgado-Rebollo, M.; Canseco-Gonzalez, D.; Hollering, M.; Mueller-Bunz, H.; Albrecht, M. Synthesis and Catalytic Alcohol Oxidation and Ketone Transfer Hydrogenation Activity of Donor-Functionalized Mesoionic Triazolylidene Ruthenium(II) Complexes. *Dalton Trans.* **2014**, *43*, 4462−4473.

(423) Kumar, M.; DePasquale, J.; White, N. J.; Zeller, M.; Papish, E. T. Ruthenium Complexes of Triazole-Based Scorpionate Ligands Transfer Hydrogen to Substrates under Base-Free Conditions. *Organometallics* **2013**, *32*, 2135−2144.

(424) Fu, Q.; Zhang, L.; Yi, T.; Zou, M.; Wang, X.; Fu, H.; Li, R.; Chen, H. Synthesis of ruthenium (II) complexes containing a dihydroperimidine-derived phosphine ligand and their application in transfer hydrogenation of ketones. *Inorg. Chem. Commun.* **2013**, *38*, 28−32.

(425) Aydemir, M.; Durap, F.; Baysal, A.; Meric, N.; Buldağ; Gumgum, B.; Ozkar, S.; Yıldırım, L. T. Novel Neutral Phosphinite Bridged Dinuclear Ruthenium(II) Arene Complexes and their Catalytic Use in Transfer Hydrogenation of Aromatic Ketones: X-ray Structure of a New Schiff Base, N3,N3′-Di-2-Hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-Diamine. *J. Mol. Catal. A: Chem.* **2010**, *326*, 75−81.

(426) Raja, N.; Ramesh, R. Binuclear Ruthenium(II) Pyridazine Complex Catalyzed Transfer Hydrogenation of Ketones. *Tetrahedron Lett.* **2012**, *53*, 4770−4774.

(427) Meriç, N.; Durap, F.; Aydemir, M.; Baysal, A. The Application of Tunable Tridentate P-Based Ligands for the Ru(II)-Catalysed Transfer Hydrogenation of Various Ketones. *Appl. Organomet. Chem.* **2014**, *28*, 803−808.

(428) Benyei, A.; Joo, F. Organometallic Catalysis in Aqueous Solutions: the Biphasic Transfer Hydrogenation of Aldehydes Catalyzed by Water-Soluble Phosphine Complexes of Ruthenium, Rhodium and Iridium. *J. Mol. Catal.* **1990**, *58*, 151−163.

(429) Zhou, Z.; Sun, Y. Synthesis of Polyethylene Glycol Supported Chiral Monosulfonamide and its Application in Asymmetric Transfer Hydrogenation of Prochiral Ketones. *React. Kinet. Mech. Catal.* **2010**, *99*, 391−396.

(430) Shan, W.; Meng, F.; Wu, Y.; Mao, F.; Li, X. The Synthesis of a New Nitrogen Joined N-PEG-TsDPEN Ligand and its Application in Asymmetric Transfer Hydrogenation of Ketones in Neat Water. *J. Organomet. Chem.* **2011**, *696*, 1687−1690.

(431) Virboul, M. A. N.; Gebbink, R. J. M. K. Incorporation of an *n*-Butylsulfonate Functionality To Induce Aqueous Solubility on Ruthenium(II) η^6-Arene Complexes. *Organometallics* **2012**, *31*, 85−91.

(432) Zammit, C. M.; Wills, M. Use of Triazole-Ring Formation to Attach a Ru/TsDPEN Complex for Asymmetric Transfer Hydrogenation to a Soluble Polymer. *Tetrahedron: Asymmetry* **2013**, *24*, 844−852.

(433) Jonas, D.; Uwe, S.; Juliane, K.; Rainer, H.; Reinhard, S. New Polymer-Supported Catalysts for the Asymmetric Transfer Hydrogenation of Acetophenone in Water − Kinetic and Mechanistic Investigations. *Adv. Synth. Catal.* **2011**, *353*, 1335−1344.

(434) Babin, M.; Clement, R.; Gagnon, J.; Fontaine, F.-G. Homogeneous Asymmetric Transfer Hydrogenation of Ketones Using a Ruthenium Catalyst Anchored on Chitosan: Natural Chirality at Work. *New J. Chem.* **2012**, *36*, 1548−1551.

(435) Kalsin, A. M.; Peganova, T. A.; Novikov, V. V.; Zhamoytina, A. I.; Gonsalvi, L.; Peruzzini, M. Transfer Hydrogenation of Ketones Catalyzed by Surface-Active Ruthenium and Rhodium Complexes in Water. *Chem.—Eur. J.* **2014**, *20*, 846−854.

(436) Zhou, Z.; Ma, Q.; Sun, Y.; Zhang, A.; Li, L. Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water Using Novel Water-Soluble Chiral Monosulfonamide Ligands. *Heteroat. Chem.* **2010**, *21*, 505−514.

(437) Zhu, M. Integration of Phase Transfer Catalysis into Aqueous Transfer Hydrogenation. *Appl. Catal., A* **2014**, *479*, 45−48.

(438) Wang, L.; Ma, H.; Song, L.; Li, L.; Wang, Y.; Wang, H. Transfer Hydrogenation of Acetophenone in an Organic-Aqueous Biphasic System Containing Double Long-Chain Surfactants. *RSC Adv.* **2014**, *4*, 1567−1569.

(439) Li, J.; Li, X.; Ma, Y.; Wu, J.; Wang, F.; Xiang, J.; Zhu, J.; Wang, Q.; Deng, J. Surfactant-Accelerated Asymmetric Transfer Hydrogenation with Recyclable Water-Soluble Catalyst in Aqueous Media. *RSC Adv.* **2013**, *3*, 1825−1834.

(440) Lee, S.-H.; Nikonov, G. I. Transfer Hydrogenation of Ketones, Nitriles, and Esters Catalyzed by a Half-Sandwich Complex of Ruthenium. *ChemCatChem* **2015**, *7*, 107−113.

(441) Nixon, T. D.; Whittlesey, M. K.; Williams, J. M. J. Ruthenium-Catalysed Transfer Hydrogenation Reactions with Dimethylamine Borane. *Tetrahedron Lett.* **2011**, *52*, 6652−6654.

(442) Guijarro, D.; Pablo, Ó.; Yus, M. Achiral *β*-Amino Alcohols as Efficient Ligands for the Ruthenium-Catalysed Asymmetric Transfer Hydrogenation of Sulfinylimines. *Tetrahedron Lett.* **2011**, *52*, 789−791.

(443) Werkmeister, S.; Bornschein, C.; Junge, K.; Beller, M. Selective Ruthenium-Catalyzed Transfer Hydrogenations of Nitriles to Amines with 2-Butanol. *Chem.—Eur. J.* **2013**, *19*, 4437−4440.

(444) Zhang, D.; Cheng, T.; Zhao, Q.; Xu, J.; Liu, G. Highly Enantioselective One-Pot Synthesis of Chiral *β*-Hydroxy Sulfones via Asymmetric Transfer Hydrogenation in an Aqueous Medium. *Org. Lett.* **2014**, *16*, 5764−5767.

(445) Fang, Z.; Clarkson, G. J.; Wills, M. Asymmetric Reduction of 2,2-Dimethyl-6-(2-oxoalkyl/oxoaryl)-1,3-dioxin-4-ones and application to the synthesis of (+)-yashabushitriol. *Tetrahedron Lett.* **2013**, *54*, 6834−6837.

(446) Yamamoto, Y.; Mori, S.; Shibuya, M. Ruthenium-Catalyzed Transfer-Hydrogenative Cyclization of 1,6-Diynes with Hantzsch 1,4-Dihydropyridine as a H_2 Surrogate. *Chem.—Eur. J.* **2013**, *19*, 12034−12041.

(447) Steward, K. M.; Gentry, E. C.; Johnson, J. S. Dynamic Kinetic Resolution of *α*-Keto Esters via Asymmetric Transfer Hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 7329−7332.

(448) Dai, X.; Cahard, D. Enantioselective Synthesis of *α*-Trifluoromethyl Arylmethylamines by Ruthenium-Catalyzed Transfer Hydrogenation Reaction. *Adv. Synth. Catal.* **2014**, *356*, 1317−1328.

(449) Wu, M.; Cheng, T.; Ji, M.; Liu, G. Ru-Catalyzed Asymmetric Transfer Hydrogenation of *α*-Trifluoromethylimines. *J. Org. Chem.* **2015**, *80*, 3708−3713.

(450) Son, S.-M.; Lee, H.-K. Dynamic Kinetic Resolution Based Asymmetric Transfer Hydrogenation of *α*-Alkoxy-*β*-Ketophosphonates. Diastereo- and Enantioselective Synthesis of Monoprotected 1,2-Dihydroxyphosphonates. *J. Org. Chem.* **2014**, *79*, 2666−2681.

(451) Zhang, H.; Feng, D.; Sheng, H.; Ma, X.; Wan, J.; Tang, Q. Asymmetric Transfer Hydrogenation of Unsymmetrical Benzyls. *RSC Adv.* **2014**, *4*, 6417−6423.

(452) Fábos, V.; Mika, L. T.; Horváth, I. T. Selective Conversion of Levulinic and Formic Acids to *γ*-Valerolactone with the Shvo Catalyst. *Organometallics* **2014**, *33*, 181−187.

(453) Verzijl, G. K. M.; et al. Catalytic Asymmetric Reduction of a 3,4-Dihydroisoquinoline for the Large-Scale Production of Almorexant: Hydrogenation or Transfer Hydrogenation? *Org. Process Res. Dev.* **2013**, *17*, 1531−1539.

(454) Villacrez, M.; Somfai, L. Enantioselective Synthesis of *anti-β*-Amido-*α*-hydroxy Esters via Asymmetric Transfer Hydrogenation Coupled with Dynamic Kinetic Resolution. *Tetrahedron Lett.* **2013**, *54*, 5266−5268.

(455) Wang, X.; Yan, Y.; Gong, B.; Tang, X.; Li, Q.; Meng, Y.; Xu, H. E.; Yi, W. Efficient Synthesis of Functionalized 1-oxo-1-phenyl-2-acetic Acids through Ru(II)-catalyzed Transfer Hydrogenation. *Bull. Korean Chem. Soc.* **2013**, *34*, 3143−3146.

(456) Fang, Z.; Wills, M. Asymmetric Transfer Hydrogenation of Functionalized Acetylenic Ketones. *J. Org. Chem.* **2013**, *78*, 8594−8605.

(457) Bisset, A. A.; Shiibashi, A.; Desmond, J. L.; Dishington, A.; Jones, T.; Clarkson, G. J.; Ikariya, T.; Wills, M. Synthesis and Asymmetric Hydrogenation of (3*E*)-1-Benzyl-3-[(2-oxopyridin-1(2*H*)-yl)methylidene]piperidine-2,6-Dione. *Chem. Commun.* **2012**, *48*, 11978−11980.

(458) Seashore-Ludlow, B.; Saint-Dizier, F.; Somfai, P. Asymmetric Transfer Hydrogenation Coupled with Dynamic Kinetic Resolution in Water: Synthesis of *anti-β*-Hydroxy-*α*-amino Acid Derivatives. *Org. Lett.* **2012**, *14*, 6334−6337.

(459) Mirabal-Gallardo, Y.; Piérola, J.; Shankaraiah, N.; Santos, L. S. Enantioselective Total Synthesis of (*S*)-(+)-Lennoxamine through Asymmetric Hydrogenation Mediated by L-Proline-Tetrazole Ruthenium Catalyst. *Tetrahedron Lett.* **2012**, *53*, 3672−3675.

(460) Seashore-Ludlow, B.; Villo, P.; Somfai, P. Enantioselective Synthesis of *anti-β*-Hydroxy-*α*-Amido Esters by Asymmetric Transfer Hydrogenation in Emulsion. *Chem.—Eur. J.* **2012**, *18*, 7219−7223.

(461) Seashore-Ludlow, B.; Villo, P.; Häcker, C.; Somfai, P. Enantioselective Synthesis of *anti-β*-Hydroxy-*α*-amido Esters via Transfer Hydrogenation. *Org. Lett.* **2010**, *12*, 5274−5277.

(462) Clay, D. R.; McIntosh, M. C. Anomalies in the Asymmetric Transfer Hydrogenation of Several Polycyclic *meso* Compounds. *Tetrahedron Lett.* **2012**, *53*, 1691−1694.

(463) Luo, Z.; Qin, F.; Yan, S.; Li, X. An efficient and Promising Method to Prepare Ladostigil (TV3326) via Asymmetric Transfer Hydrogenation Catalyzed by Ru−Cs-DPEN in an HCOONa−H_2O−Surfactant System. *Tetrahedron: Asymmetry* **2012**, *23*, 333−338.

(464) Yin, L.; Zheng, Y.; Jia, X.; Li, X.; Chan, A. S. C. Efficient and promising asymmetric preparation of enantiopure tolvaptan via transfer hydrogenation with robust catalysts. *Tetrahedron: Asymmetry* **2010**, *21*, 2390−2393.

(465) Limanto, J.; Krska, S. W.; Dorner, B. T.; Vazquez, E.; Yoshikawa, N.; Tan, L. Dynamic Kinetic Resolution: Asymmetric Transfer Hydrogenation of *α*-Alkyl-Substituted *β*-Ketoamides. *Org. Lett.* **2010**, *12*, 512−515.

(466) Baratta, W.; Benedetti, F.; Zotto, A. D.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. Chiral Pincer Ruthenium and Osmium Complexes for the Fast and Efficient Hydrogen Transfer Reduction of Ketones. *Organometallics* **2010**, *29*, 3563−3570.

(467) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W. MCl_2(ampy)(dppf) (M = Ru, Os): Multitasking Catalysts for Carbonyl Compound/Alcohol Interconversion Reactions. *Organometallics* **2012**, *31*, 1133−1142.

(468) Carmona, D.; Lahoz, F. J.; García-Orduña, P.; Oro, L. A. Half-Sandwich Complexes of Osmium(II) with L-*α*-Amino Carboxylate Ligands as Asymmetric Transfer Hydrogenation Catalysts. On the Origin of the Enantioselectivity. *Organometallics* **2012**, *31*, 3333−3345.

(469) Vega, E.; Lastra, E.; Gamasa, M. P. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Enantiopure Osmium(II) Pybox Complexes. *Inorg. Chem.* **2013**, *52*, 6193−6198.

(470) Friedfeld, M. R. Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013**, *342*, 1076−1080.

(471) Dombray, T.; Helleu, C.; Darcel, C.; Sortais, J.-B. Cobalt Carbonyl-Based Catalyst for Hydrosilylation of Carboxamides. *Adv. Synth. Catal.* **2013**, *355*, 3358−3362.

(472) Jagadeesh, R. V.; Banerjee, D.; Arockiam, P. B.; Junge, H.; Junge, K.; Pohl, M. M.; Radnik, J.; Brückner, A.; Beller, M. Highly Selective Transfer Hydrogenation of Functionalised Nitroarenes Using Cobalt-Based Nanocatalysts. *Green Chem.* **2015**, *17*, 898−902.

(473) Zhang, G.; Hanson, S. K. Cobalt-Catalyzed Transfer Hydrogenation of C=O and C=N Bonds. *Chem. Commun.* **2013**, *49*, 10151−10153.

(474) King, S. M.; Ma, X.; Herzon, S. B. A Method for the Selective Hydrogenation of Alkenyl Halides to Alkyl Halides. *J. Am. Chem. Soc.* **2014**, *136*, 6884−6887.

(475) Akıncı, P. A.; Gülcemal, S.; Kazheva, O. N.; Alexandrov, G. G.; Dyachenko, O. A.; Çetinkaya, E.; Çetinkaya, B. Perimidin-2-ylidene Rhodium(I) Complexes; Unexpected Halogen Exchange and Catalytic Activities in Transfer Hydrogenation Reaction. *J. Organomet. Chem.* **2014**, *765*, 23−30.

(476) Gülcemal, S. Symmetric and Dissymmetric *N*-Heterocyclic Carbene Rhodium(I) Complexes: A Comparative Study of their Catalytic Activities in Transfer Hydrogenation Reaction. *Appl. Organometal. Chem.* **2012**, *26*, 246−251.

(477) Gierz, V.; Urbanaite, A.; Seyboldt, A.; Kunz, D. Rhodium Complexes Bearing 1,10-Phenanthroline Analogue Bis-NHC Ligands Are Active Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2012**, *31*, 7532−7538.

(478) Sluijter, S. N.; Elsevier, C. J. Synthesis and Reactivity of Heteroditopic Dicarbene Rhodium(I) and Iridium(I) Complexes Bearing Chelating 1,2,3-Triazolylidene−Imidazolylidene Ligands. *Organometallics* **2014**, *33*, 6389−6397.

(479) Saleem, F.; Rao, G. K.; Kumar, A.; Mukherjee, G.; Singh, A. K. Catalyst Activation with Cp*Rh^{III}/Ir^{III}−1,2,3-Triazole-Based Organochalcogen Ligand Complexes: Transfer Hydrogenation via Loss of Cp* and *N*-Methylmorpholine *N*-Oxide Based vs Oppenauer-Type Oxidation. *Organometallics* **2014**, *33*, 2341−2351.

(480) Aydemir, M.; Baysal, A.; Meric, N.; Kayan, C.; Gümgüm, B.; Özkar, S.; Şahin, E. Organometallic Ruthenium, Rhodium and Iridium Complexes Containing a P-Bound Thiophene-2-(*N*-diphenylphosphino)methylamine Ligand: Synthesis, Molecular Struc-

ture and Catalytic Activity. *J. Organomet. Chem.* **2011**, *696*, 2584–2588.

(481) Pannetier, N.; Sortais, J.-B.; Issenhuth, J.-T.; Barloy, L.; Sirlin, C.; Holuigue, A.; Lefort, L.; Panella, L.; de Vries, J. G.; Pfeffer, M. Cyclometalated Complexes of Ruthenium, Rhodium and Iridium as Catalysts for Transfer Hydrogenation of Ketones and Imines. *Adv. Synth. Catal.* **2011**, *353*, 2844–2852.

(482) Nordin, M.; Liao, R.-Z.; Ahlford, K.; Adolfsson, H.; Himo, F. Theoretical Study of Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Amino Acid-Derived Rhodium Complexes. *ChemCatChem* **2012**, *4*, 1095–1104.

(483) Satyanarayana, P.; Reddy, G. M.; Maheswaran, H.; Kantam, M. L. Tris(acetylacetonato)rhodium(III)-Catalyzed α-Alkylation of Ketones, β-Alkylation of Secondary Alcohols and Alkylation of Amines with Primary Alcohols. *Adv. Synth. Catal.* **2013**, *355*, 1859–1867.

(484) Nova, A.; Taylor, D. J.; Blacker, A. J.; Duckett, S. B.; Perutz, R. N.; Eisenstein, O. Computational Studies Explain the Importance of Two Different Substituents on the Chelating Bis(amido) Ligand for Transfer Hydrogenation by Bifunctional Cp*Rh(III) Catalysts. *Organometallics* **2014**, *33*, 3433–3442.

(485) McSkimming, A.; Chan, B.; Bhadbhade, M. M.; Ball, G. E.; Colbran, S. B. Bio-Inspired Transition Metal-Organic Hydride Conjugates for Catalysis of Transfer Hydrogenation: Experiment and Theory. *Chem.—Eur. J.* **2015**, *21*, 2821–2834.

(486) Ok, F.; Aydemir, M.; Durap, F.; Baysal, A. Novel Half-Sandwich η^5-Cp*–Rhodium(III) and η^5-Cp*–Ruthenium(II) Complexes Bearing Bis(phosphino)amine Ligands and their Use in the Transfer Hydrogenation of Aromatic Ketones. *Appl. Organomet. Chem.* **2014**, *28*, 38–43.

(487) Prakash, O.; Sharma, K. N.; Joshi, H.; Gupta, P. L.; Singh, A. K. Half-Sandwich Rhodium/Iridium(III) Complexes Designed with Cp* and 1,2-Bis(phenylchalcogenomethyl)benzene as Catalysts for Transfer Hydrogenation in Glycerol. *Organometallics* **2014**, *33*, 2535–2543.

(488) McSkimming, A.; Bhadbhade, M. M.; Colbran, S. B. Bio-Inspired Catalytic Imine Reduction by Rhodium Complexes with Tethered Hantzsch Pyridinium Groups: Evidence for Direct Hydride Transfer from Dihydropyridine to Metal-Activated Substrate. *Angew. Chem., Int. Ed.* **2013**, *52*, 3411–3416.

(489) Coll, M.; Pàmies, O.; Adolfsson, H.; Diéguez, M. Second-Generation Amino Acid Furanoside Based Ligands from D-Glucose for the Asymmetric Transfer Hydrogenation of Ketones. *ChemCatChem* **2013**, *5*, 3821–3828.

(490) Kang, S.; Han, J.; Lee, E. S.; Choi, E. B.; Lee, H.-K. Enantioselective Synthesis of Cyclic Sulfamidates by Using Chiral Rhodium-Catalyzed Asymmetric Transfer Hydrogenation. *Org. Lett.* **2010**, *12*, 4184–4187.

(491) Echeverria, P.-G.; Férard, C.; Phansavath, P.; Ratovelomanana-Vidal, V. Synthesis, Characterization and Use of a New Tethered Rh(III) Complex in Asymmetric Transfer Hydrogenation of Ketones. *Catal. Commun.* **2015**, *62*, 95–99.

(492) Rafikova, K.; Kystaubayeva, N.; Aydemir, M.; Kayan, C.; Ocak, Y. S.; Temel, H.; Zazybin, A.; Gürbüz, N.; Özdemir, İ. Transfer Hydrogenation of Ketones Catalyzed by New Rhodium and Iridium Complexes of Aminophosphine Containing Cyclohexyl Moiety and Photosensing Behaviors of Rhodium and Iridium Based Devices. *J. Organomet. Chem.* **2014**, *758*, 1–8.

(493) Aydemir, M.; Ocak, Y. S.; Rafikova, K.; Kystaubayeva, N.; Kayan, C.; Zazybin, A.; Ok, F.; Baysal, A.; Temel, H. Rhodium-Catalyzed Transfer Hydrogenation with Aminophosphines and Analysis of Electrical Characteristics of Rhodium(I) Complex/n-Si Heterojunctions. *Appl. Organomet. Chem.* **2014**, *28*, 396–404.

(494) Nikishkin, N. I.; Huskens, J.; Verboom, W. Hydrophilic Pyrazine-Based Phosphane Ligands: Synthesis and Application in Asymmetric Hydride Transfer and H_2-Hydrogenation of Acetophenone. *Tetrahedron Lett.* **2013**, *54*, 1857–1861.

(495) Buchard, A.; Payet, E.; Auffrant, A.; Le Goff, X.; Le Floch, P. Iminophosphorane-Based [P_2N_2] Rhodium Complexes: Synthesis, Reactivity, and Application in Catalysed Transfer Hydrogenation of Polar Bonds. *New J. Chem.* **2010**, *34*, 2943–2949.

(496) Kang, G.; Lin, S.; Shiwakoti, A.; Ni, B. Imidazolium Ion Tethered TsDPENs as Efficient Water-Soluble Ligands for Rhodium Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones. *Catal. Commun.* **2014**, *57*, 111–114.

(497) Ajjou, A. N. Aqueous-Phase Catalytic Oxidation, Transfer Hydrogenation, Reductive Amination and Hydration Reactions. *Catal. Today* **2015**, *247*, 177–181.

(498) Li, J.; Tang, Y.; Wang, Q.; Li, X.; Cun, L.; Zhang, X.; Zhu, J.; Li, L.; Deng, J. Chiral Surfactant-Type Catalyst for Asymmetric Reduction of Aliphatic Ketones in Water. *J. Am. Chem. Soc.* **2012**, *134*, 18522–18525.

(499) Wei, Y.; Wu, J.; Xue, D.; Wang, C.; Liu, Z.; Zhang, Z.; Chen, G.; Xiao, J. Highly Efficient Rhodium-Catalyzed Transfer Hydrogenation of Nitroarenes into Amines and Formanilides. *Synlett* **2014**, *25*, 1295–1298.

(500) Wu, J.; Tang, W.; Pettman, A.; Xiao, J. Efficient and Chemoselective Reduction of Pyridines to Tetrahydropyridines and Piperidines *via* Rhodium-Catalyzed Transfer Hydrogenation. *Adv. Synth. Catal.* **2013**, *355*, 35–40.

(501) Tang, L.; Lin, Z.; Wang, Q.; Wang, X.; Cun, L.; Yuan, W.; Zhu, J.; Deng, J. Rh(II)-Cp*–TsDPEN Catalyzed Aqueous Asymmetric Transfer Hydrogenation of Chromenones into Saturated Alcohol: C=C and C=O Reduction in One Step. *Tetrahedron Lett.* **2012**, *53*, 3828–3830.

(502) Wu, J.; Jiang, H. Rh-Catalyzed One-Pot Reductive Alkylation of Malononitrile Under Transfer Hydrogenation Conditions. *Synth. Commun.* **2011**, *41*, 1218–1226.

(503) Parekh, V.; Ramsden, J. A.; Wills, M. Asymmetric Transfer Hydrogenation of Quinolines Using Tethered Ru(II) Catalysts. *Tetrahedron Asym.* **2010**, *21*, 1549–1556.

(504) Wang, D.; Zhao, K.; Yang, S.; Ding, Y. Synthesis, Structure, and Photophysical Properties of Tributyl Phosphine Bisbenzothienyl Iridium(III) Complex and its Application on Transfer Hydrogenation of Acetophenone. *Z. Anorg. Allg. Chem.* **2015**, *641*, 400–404.

(505) Mestroni, G.; Zassinovich, G.; Camus, A. Complexes of Rhodium(I) and Iridium(I) with 2,2′-Bipyridine and Similar Ligands as Hydrogenation Catalysts. *J. Organomet. Chem.* **1977**, *140*, 63–72.

(506) Mestroni, G.; Zassinovich, G.; Camus, A.; Martinelli, F. Transfer of Hydrogen from Alcohols to Ketones Catalyzed by Iridium Complexes with 2,2′-Bipyridine, 1,10-Phenanthroline, and their Derivatives. *J. Organomet. Chem.* **1980**, *198*, 87–96.

(507) Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Modrego, F. J.; García-Orduna, P.; Oro, L. A. Mechanistic Insights into Transfer Hydrogenation Catalysis by $[Ir(cod)(NHC)_2]^+$ Complexes with Functionalized N-Heterocyclic Carbene Ligands. *Organometallics* **2015**, *34*, 926–940.

(508) Gülcemal, D.; Gökçe, A. G.; Gülcemal, S.; Çetinkaya, B. Hydroxyl and Ester Functionalized *N*-Heterocyclic Carbene Complexes of Iridium(I): Efficient Catalysts for Transfer Hydrogenation Reactions. *RSC Adv.* **2014**, *4*, 26222–26230.

(509) Gülcemal, S.; Gökçeb, A. G.; Çetinkaya, B. Iridium(I) *N*-Heterocyclic Carbene Complexes of Benzimidazol-2-ylidene: Effect of Electron Donating Groups on the Catalytic Transfer Hydrogenation Reaction. *Dalton Trans.* **2013**, *42*, 7305–7311.

(510) Gülcemal, S.; Gökçe, A. G.; Çetinkaya, B. N-Benzyl Substituted N-Heterocyclic Carbene Complexes of Iridium(I): Assessment in Transfer Hydrogenation Catalyst. *Inorg. Chem.* **2013**, *52*, 10601–10609.

(511) Furfari, S. K.; Gyton, M. R.; Twycross, D.; Cole, M. L. Air Stable NHCs: A Study of Stereoelectronics and Metallorganic Catalytic Activity. *Chem. Commun.* **2015**, *51*, 74–76.

(512) Azua, A.; Mata, J. A.; Peris, E.; Lamaty, F.; Martinez, J.; Colacino, E. Alternative Energy Input for Transfer Hydrogenation using Iridium NHC Based Catalysts in Glycerol as Hydrogen Donor and Solvent. *Organometallics* **2012**, *31*, 3911–3919.

(513) Gong, X.; Zhang, H.; Li, X. Iridium Phosphine Abnormal N-Heterocyclic Carbene Complexes in Catalytic Hydrogen Transfer Reactions. *Tetrahedron Lett.* **2011**, *52*, 5596–5600.

(514) Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Modrego, F. J.; Winterle, S.; Cunchillos, C.; Lahoz, F. J.; Oro, L. A. Iridium(I) Complexes with Hemilabile N-Heterocyclic Carbenes: Efficient and Versatile Transfer Hydrogenation Catalysts. *Organometallics* **2011**, *30*, 5493−5508.

(515) Binobaid, A.; Iglesias, M.; Beetstra, D.; Dervisi, A.; Fallis, I.; Cavell, K. J. Donor-Functionalised Expanded Ring N-Heterocyclic Carbenes: Highly Effective Ligands in Ir-Catalysed Transfer Hydrogenation. *Eur. J. Inorg. Chem.* **2010**, 5426−5431.

(516) Ashley, J. M.; Farnaby, J. H.; Hazari, N.; Kim, K. E., Jr.; E, D. L.; Meehan, R. E.; Meyer, E. B.; Schley, N. D.; Schmeier, T. J.; Tailor, A. N. Axially Chiral Dimeric Ir and Rh Complexes Bridged by Flexible NHC Ligands. *Inorg. Chim. Acta* **2012**, *380*, 399−410.

(517) Yasar, S.; Cavell, K. J.; Ward, B. D.; Kariuki, B. Novel *quasi*-Scorpionate Ligand Structures Based on a Bis-*N*-Heterocyclic Carbene Chelate Core: Synthesis, Complexation and Catalysis. *Appl. Organomet. Chem.* **2011**, *25*, 374−382.

(518) Azua, A.; Sanz, S.; Peris, E. Water-Soluble Ir^{III} N-Heterocyclic Carbene Based Catalysts for the Reduction of CO_2 to Formate by Transfer Hydrogenation and the Deuteration of Aryl Amines in Water. *Chem.—Eur. J.* **2011**, *17*, 3963−3967.

(519) Sanz, S.; Benítez, M.; Peris, E. A New Approach to the Reduction of Carbon Dioxide: CO_2 Reduction to Formate by Transfer Hydrogenation in *i*PrOH. *Organometallics* **2010**, *29*, 275−277.

(520) Azua, A.; Mata, J. A.; Peris, E. Iridium NHC Based Catalysts for Transfer Hydrogenation Processes Using Glycerol as Solvent and Hydrogen Donor. *Organometallics* **2011**, *30*, 5532−5536.

(521) Aydemir, M.; Baysal, A.; Turgut, Y. Applications of Transition Metal Complexes Containing Aminophosphine Ligand to Transfer Hydrogenation of Ketones. *Appl. Organomet. Chem.* **2011**, *25*, 270−275.

(522) Watanabe, M.; Kashiwame, Y.; Kuwata, S.; Ikariya, T. Synthesis, Structures, and Transfer Hydrogenation Catalysis of Bifunctional Iridium Complexes Bearing a C−N Chelate Oxime Ligand. *Eur. J. Inorg. Chem.* **2012**, 504−511.

(523) Aydemir, M.; Baysal, A.; Gümgüm, B. A Modular Design of Metal Catalysts for the Transfer Hydrogenation of Aromatic Ketones. *Appl. Organomet. Chem.* **2012**, *26*, 1−8.

(524) Kayan, C.; Meric, N.; Aydemir, M.; Baysal, A.; Elma, D.; Ak, B.; Şahin, E.; Gurbuz, N.; Özdemir, İ. Ruthenium, Rhodium and Iridium Complexes of the Furfuryl-2-(*N*-diphenylphosphino)methylamine Ligand: Molecular Structure and Catalytic Activity. *Polyhedron* **2012**, *42*, 142−148.

(525) Betanzos-Lara, S.; Liu, Z.; Habtemariam, A.; Pizarro, A. M.; Qamar, B.; Sadler, P. J. Organometallic Ruthenium and Iridium Transfer-Hydrogenation Catalysts Using Coenzyme NADH as a Cofactor. *Angew. Chem., Int. Ed.* **2012**, *51*, 3897−3900.

(526) Talwar, D.; Li, H. Y.; Durham, E.; Xiao, J. A Simple Iridicycle Catalyst for Efficient Transfer Hydrogenation of N-Heterocycles in Water. *Chem.—Eur. J.* **2015**, *21*, 5370−5379.

(527) Chiyojima, H.; Sakaguchi, S. Iridium Complex Bearing a Chiral Hydroxy-Amide Functionalized N-Heterocyclic Carbene: A Catalyst Precursor for Asymmetric Transfer Hydrogenation. *Tetrahedron Lett.* **2011**, *52*, 6788−6791.

(528) Zhu, X.-H.; Cai, L.-H.; Wang, C.-X.; Wang, Y.-N.; Guo, X.-Q.; Hou, X.-F. Efficient and Versatile Transfer Hydrogenation Catalysts: Iridium (III) and Ruthenium (II) Complexes with 4-Acetylbenzyl-*N*-Heterocyclic Carbenes. *J. Mol. Catal. A: Chem.* **2014**, *393*, 134−141.

(529) Hintermair, U.; Campos, J.; Brewster, T. P.; Pratt, L. M.; Schley, N. D.; Crabtree, R. H. Hydrogen-Transfer Catalysis with Cp^*Ir^{III} Complexes: The Influence of the Ancillary Ligands. *ACS Catal.* **2014**, *4*, 99−108.

(530) Campos, J.; Hintermair, U.; Brewster, T. P.; Takase, M. K.; Crabtree, R. H. Catalyst Activation by Loss of Cyclopentadienyl Ligands in Hydrogen Transfer Catalysis with Cp^*Ir^{III} Complexes. *ACS Catal.* **2014**, *4*, 973−985.

(531) Toubiana, J.; Sasson, Y. The True Catalyst in Hydrogen Transfer Reactions with Alcohol Donors in the Presence of $RuCl_2(PPh_3)_3$ is Ruthenium(0) Nanoparticles. *Catal. Sci. Technol.* **2012**, *2*, 1644−1653.

(532) Fonseca, G. S.; Scholten, J. D.; Dupont, J. Iridium Nanoparticles Prepared in Ionic Liquids: An Efficient Catalytic System for the Hydrogenation of Ketones. *Synlett* **2004**, 1525−1528.

(533) Hohloch, S.; Suntrup, L.; Sarkar, B. Arene−Ruthenium(II) and −Iridium(III) Complexes with "Click"-Based Pyridyl-triazoles, Bis-triazoles, and Chelating Abnormal Carbenes: Applications in Catalytic Transfer Hydrogenation of Nitrobenzene. *Organometallics* **2013**, *32*, 7376−7385.

(534) Maity, R.; Hohloch, S.; Su, C.-Y.; van der Meer, M.; Sarkar, B. Cyclometalated Mono- and Dinuclear Ir^{III} Complexes with "Click"-Derived Triazoles and Mesoionic Carbenes. *Chem.—Eur. J.* **2014**, *20*, 9952−9961.

(535) Wang, C.; Pettman, A.; Bacsa, J.; Xiao, J. A Versatile Catalyst for Reductive Amination by Transfer Hydrogenation. *Angew. Chem., Int. Ed.* **2010**, *49*, 7548−7552.

(536) Wei, Y.; Xue, D.; Lei, Q.; Wang, C.; Xiao, J. Cyclometalated Iridium Complexes for Transfer Hydrogenation of Carbonyl Groups in Water. *Green Chem.* **2013**, *15*, 629−634.

(537) Talwar, D.; Wu, X.; Saidi, O.; Salguero, N. P.; Xiao, J. Versatile Iridicycle Catalysts for Highly Efficient and Chemoselective Transfer Hydrogenation of Carbonyl Compounds in Water. *Chem.—Eur. J.* **2014**, *20*, 12835−12842.

(538) Lei, Q.; Wei, Y.; Talwar, D.; Wang, C.; Xue, D.; Xiao, J. Fast Reductive Amination by Transfer Hydrogenation "on Water. *Chem.—Eur. J.* **2013**, *19*, 4021−4029.

(539) Talwar, D.; Salguero, N. P.; Robertson, C. M.; Xiao, J. Primary Amines by Transfer Hydrogenative Reductive Amination of Ketones by Using Cyclometalated Ir^{III} Catalysts. *Chem.—Eur. J.* **2014**, *20*, 245−252.

(540) He, Y.-M.; Fan, Q.-H. Advances in Transfer Hydrogenation of Carbonyl Compounds in Water. *ChemCatChem* **2015**, *7*, 398−400.

(541) Vázquez-Villa, H.; Reber, S.; Ariger, M. A.; Carreira, E. M. Iridium Diamine Catalyst for the Asymmetric Transfer Hydrogenation of Ketones. *Angew. Chem., Int. Ed.* **2011**, *50*, 8979−8981.

(542) Kuo, Y.-Y.; Haddow, M.-F.; Pérez-Redondo, A.; Owen, G. R. Rhodium and Iridium Complexes Containing Diphenyl-2-(3-methyl)-indolylphosphine: Synthesis, Structure and Application in the Catalytic Transfer Hydrogenation of Ketones. *Dalton Trans.* **2010**, *39*, 6239−6248.

(543) Ahlford, K.; Adolfsson, H. Amino Acid Derived Amides and Hydroxamic Acids as Ligands for Asymmetric Transfer Hydrogenation in Aqueous Media. *Catal. Commun.* **2011**, *12*, 1118−1121.

(544) Tang, L.; Wang, Q.; Wang, J.; Lin, Z.; Wang, X.; Cun, L.; Yuan, W.; Zhu, J.; Liao, J.; Deng, J. A New Chiral Sulfinyl−NH−Pyridine Ligand for Ir-Catalyzed Asymmetric Transfer Hydrogenation Reaction. *Tetrahedron Lett.* **2012**, *53*, 3839−3842.

(545) Mena, I.; Jaseer, E. A.; Casado, M. A.; García-Orduña, P.; Lahoz, F. J.; Oro, L. A. Terminal and Bridging Parent Amido 1,5-Cyclooctadiene Complexes of Rhodium and Iridium. *Chem.—Eur. J.* **2013**, *19*, 5665−5675.

(546) Fuentes, J. A.; Carpenter, I.; Kann, N.; Clarke, M. L. Highly Enantioselective Hydrogenation and Transfer Hydrogenation of Cycloalkyl and Heterocyclic Ketones Catalysed by an Iridium Complex of a Tridentate Phosphine-Diamine Ligand. *Chem. Commun.* **2013**, *49*, 10245−10247.

(547) Liu, W. P.; Yuan, M. L.; Yang, X. H.; Li, K.; Xie, J. H.; Zhou, Q. L. Efficient Asymmetric Transfer Hydrogenation of Ketones in Ethanol with Chiral Iridium Complexes of Apiro PAP Ligands as Catalysts. *Chem. Commun.* **2015**, *51*, 6123−6125.

(548) Chen, L.-A.; Xu, W.; Huang, B.; Ma, J.; Wang, L.; Xi, J.; Harms, K.; Gong, L.; Meggers, E. Asymmetric Catalysis with an Inert Chiral-at-Metal Iridium Complex. *J. Am. Chem. Soc.* **2013**, *135*, 10598−10601.

(549) Tan, J.; Tang, W.; Sun, Y.; Jiang, Z.; Chen, F.; Xu, L.; Fan, Q.; Xiao, J. pH-Regulated Transfer Hydrogenation of Quinoxalines with a Cp*Ir−Diamine Catalyst in Aqueous Media. *Tetrahedron* **2011**, *67*, 6206−6013.

(550) Wu, J.; Wang, C.; Tang, W.; Pettman, A.; Xiao, J. The Remarkable Effect of a Simple Ion: Iodide-Promoted Transfer Hydrogenation of Heteroaromatics. *Chem.—Eur. J.* **2012**, *18*, 9525−9529.

(551) Wilson, Y. M.; Dürrenberger, M.; Nogueira, E. S.; Ward, T. R. Neutralizing the Detrimental Effect of Glutathione on Precious Metal Catalysts. *J. Am. Chem. Soc.* **2014**, *136*, 8928−8932.

(552) Montgomery, T. P.; Hassan, A.; Park, B. Y.; Krische, M. J. Enantioselective Conversion of Primary Alcohols to α-*exo*-Methylene γ-Butyrolactones via Iridium-Catalyzed C−C Bond-Forming Transfer Hydrogenation: 2-(Alkoxycarbonyl)allylation. *J. Am. Chem. Soc.* **2012**, *134*, 11100−11103.

(553) Wei, Y.; Wang, C.; Jiang, X.; Xue, D.; Li, J.; Xiao, J. Highly Efficient Transformation of Levulinic Acid into Pyrrolidinones by Iridium Catalysed Transfer Hydrogenation. *Chem. Commun.* **2013**, *49*, 5408−5410.

(554) Han, S. B.; Han, H.; Krische, M. J. Diastereo- and Enantioselective *anti*-Alkoxyallylation Employing Allylicgem-Dicarboxylates as Allyl Donors via Iridium-Catalyzed Transfer Hydrogenation. *J. Am. Chem. Soc.* **2010**, *132*, 1760−1761.

(555) Bechem, B.; Patman, R. L.; Hashmi, A. S. K.; Krische, M. J. Enantioselective Carbonyl Allylation, Crotylation, and *tert*-Prenylation of Furan Methanols and Furfurals via Iridium-Catalyzed Transfer Hydrogenation. *J. Org. Chem.* **2010**, *75*, 1795−1798.

(556) Tavor, D.; Gefen, I.; Dlugy, C.; Wolfson, A. Transfer Hydrogenations of Nitrobenzene Using Glycerol as Solvent and Hydrogen Donor. *Synth. Commun.* **2011**, *41*, 3409−3416.

(557) Geboers, J.; Wang, X.; de Carvalho, A. B.; Rinaldi, R. Densification of Biorefinery Schemes by H-Transfer with Raney Ni and 2-Propanol: A Case Study of a Potential Avenue for Valorization of Alkyl Levulinates to Alkyl γ-Hydroxypentanoates and γ-Valerolactone. *J. Mol. Catal. A: Chem.* **2014**, *388*−*389*, 106−115.

(558) Xu, H.; Yang, P.; Chuanprasit, P.; Hirao, H.; Zhou, J. Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Hydrazones and Other Ketimines. *Angew. Chem., Int. Ed.* **2015**, *54*, 5112−5116.

(559) Chen, Z.; Zeng, M.; Zhang, Y.; Zhang, Z.; Liang, F. Preparation and Structures of a Series of Phosphorus-Free Nickel(II) Diamine Complexes and their Applications in Hydrogenation of Acetophenone. *Appl. Organomet. Chem.* **2010**, *24*, 625−630.

(560) Zhong, R.; Wang, Y.-N.; Guo, X.-Q.; Chen, Z.-X.; Hou, X.-F. Preparation of Mononuclear, Homodinuclear, and Heterotrinuclear Complexes by Salicylaldiminato-Functionalized Imidazolium Salt: Approach to Multifunctional Catalysts. *Chem.—Eur. J.* **2011**, *17*, 11041−11051.

(561) Yang, P.; Xu, H.; Zhou, J. Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Olefins for the Synthesis of α- and β-Amino Acids. *Angew. Chem., Int. Ed.* **2014**, *53*, 12210−12213.

(562) Alonso, F.; Riente, P.; Yus, M. Transfer Hydrogenation of Olefins Catalysed by Nickel Nanoparticles. *Tetrahedron* **2009**, *65*, 10637−10643.

(563) Alonso, F.; Riente, P.; Sirvent, J. A.; Yus, M. Nickel Nanoparticles in Hydrogen-Transfer Reductions: Characterisation and Nature of the Catalyst. *Appl. Catal., A: Gen* **2010**, *378*, 42−51.

(564) Alonso, F.; Riente, P.; Yus, M. Hydrogen-Transfer Reductive Amination of Aldehydes Catalysed by Nickel Nanoparticles. *Synlett* **2008**, 1289−1292.

(565) Burwell, J.; Robert, L. Sterochemistry and Heterogeneous Catalysis. *Chem. Rev.* **1957**, *57*, 895−934.

(566) Oger, C.; Balas, L.; Durand, T.; Galano, J. Are Alkyne Reductions Chemo-, Regio-, and Stereoselective Enough To Provide Pure (*Z*)-Olefins in Polyfunctionalized Bioactive Molecules? *Chem. Rev.* **2013**, *113*, 1313−1350.

(567) Warsink, S.; Chang, I.-H.; Weigand, J. J.; Hauwert, P.; Chen, J.-T.; Elsevier, C. J. NHC Ligands with a Secondary Pyrimidyl Donor for Electron-Rich Palladium(0) Complexes. *Organometallics* **2010**, *29*, 4555−4561.

(568) Hauwert, P.; Boerleider, R.; Warsink, S.; Weigand, J. J.; Elsevier, C. J. Mechanism of Pd(NHC)-Catalyzed Transfer Hydrogenation of Alkynes. *J. Am. Chem. Soc.* **2010**, *132*, 16900−16910.

(569) Hauwert, P.; Dunsford, J. J.; Tromp, D. S.; Weigand, J. J.; Lutz, M.; Cavell, K. J.; Elsevier, C. J. Zerovalent $[\mathrm{Pd(NHC)(Alkene)}_{1,2}]$ Complexes Bearing Expanded-Ring N-Heterocyclic Carbene Ligands in Transfer Hydrogenation of Alkynes. *Organometallics* **2013**, *32*, 131−140.

(570) Drost, R. M.; Bouwens, T.; van Leest, N. P.; de Bruin, B.; Elsevier, C. J. Convenient Transfer Semihydrogenation Methodology for Alkynes Using a $\mathrm{Pd^{II}}$-NHC Precatalyst. *ACS Catal.* **2014**, *4*, 1349−1357.

(571) Drost, R. M.; Broere, D. L. J.; Hoogenboom, J.; de Baan, S. N.; Lutz, M.; de Bruin, B.; Elsevier, C. J. Allylpalladium(II) Histidylidene Complexes and Their Application in *Z*-Selective Transfer Semihydrogenation of Alkynes. *Eur. J. Inorg. Chem.* **2015**, 982−996.

(572) Li, J.; Hua, R.; Liu, T. Highly Chemo- and Stereoselective Palladium-Catalyzed Transfer Semihydrogenation of Internal Alkynes Affording *cis*-Alkenes. *J. Org. Chem.* **2010**, *75*, 2966−2970.

(573) Wang, X.; Wang, J.; Qi, F.; Hu, L.; Li, X.; Cao, X.; Gu, H. Synthesis of in-situ Surfactant-Free Pd Nanoparticle Catalysts for the Synthesis of Aromatic Azo Compounds and for Unsaturated Bond Hydrogenation by Hydrogen Transfer. *Chin. J. Catal.* **2013**, *34*, 2084−2088.

(574) Gorin, D. J.; Toste, F. D. Relativistic Effects in Homogeneous Gold Catalysis. *Nature* **2007**, *446*, 395−403.

(575) Zhang, M.; Yang, H.; Zhang, Y.; Zhu, C.; Li, W.; Cheng, Y.; Hu, H. Direct Reductive Amination of Aromatic Aldehydes Catalyzed by Gold(I) Complex under Transfer Hydrogenation Conditions. *Chem. Commun.* **2011**, *47*, 6605−6607.

(576) Fujita, T.; Guan, P. F.; McKenna, K.; Lang, X. Y.; Hirata, A.; Zhang, L.; Tokunaga, T.; Arai, S.; Yamamoto, Y.; Tanaka, N.; Ishikawa, Y.; Asao, N.; Yamamoto, Y.; Chen, M. W. Atomic Origins of the High Catalytic Activity of Nanoporous Gold. *Nat. Mater.* **2012**, *11*, 775−780.

(577) Yan, M.; Jin, T.; Ishikawa, Y.; Minato, T.; Fujita, T.; Chen, L.-Y.; Bao, M.; Asao, N.; Chen, M.-W.; Yamamoto, Y. Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives. *J. Am. Chem. Soc.* **2012**, *134*, 17536−17542.

(578) Wagh, Y. S.; Asao, N. Selective Transfer Semihydrogenation of Alkynes with Nanoporous Gold Catalysts. *J. Org. Chem.* **2015**, *80*, 847−851.

(579) Daniel, M.-C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2004**, *104*, 293−346.

(580) Zhao, P.; Feng, X.; Huang, D.; Yang, G.; Astruc, D. Basic Concepts and Recent Advances in Nitrophenol Reduction by Gold- and Other Transition Metal Nanoparticles. *Coord. Chem. Rev.* **2015**, *287*, 114−136.

(581) Mauriello, F.; Ariga, H.; Musolino, M. G.; Pietropaolo, R.; Takakusagi, S.; Asakura, K. Exploring the Catalytic Properties of Supported Palladium Catalysts in the Transfer Hydrogenolysis of Glycerol. *Appl. Catal., B* **2015**, *166*−*167*, 121−131.

(582) Villaverde, M. M.; Garetto, T. F.; Marchi, A. J. Liquid-Phase Transfer Hydrogenation of Furfural to Furfuryl Alcohol on Cu-Mg-Al Catalysts. *Catal. Commun.* **2015**, *58*, 6−10.

(583) Dehury, N.; Tripathy, S. K.; Sahoo, A.; Maity, N.; Patra, S. Facile Tandem Suzuki Coupling/Transfer Hydrogenation Reaction with a Bis-Heteroscorpionate Pd−Ru Complex. *Dalton Trans.* **2014**, *43*, 16597−16600.

(584) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. Y-Shaped Tris-N-Heterocyclic-Carbene Ligand for the Preparation of Multifunctional Catalysts of Iridium, Rhodium, and Palladium. *Organometallics* **2012**, *31*, 5606−5614.

(585) Sabater, S.; Mata, J. A.; Peris, E. Dual Catalysis with an $\mathrm{Ir^{III}}$−$\mathrm{Au^{I}}$ Heterodimetallic Complex: Reduction of Nitroarenes by Transfer Hydrogenation using Primary Alcohols. *Chem.—Eur. J.* **2012**, *18*, 6380−6385.

(586) Petkar, D. R.; Kadu, B. S.; Chikate, R. C. Highly Efficient and Chemoselective Transfer Hydrogenation of Nitroarenes at Room

Temperature over Magnetically Separable Fe−Ni Bimetallic Nanoparticles. *RSC Adv.* **2014**, *4*, 8004−8010.

(587) Ito, Y.; Ohta, H.; Yamada, Y. M. A.; Enoki, T.; Uozumi, Y. Transfer Hydrogenation of Alkenes Using Ni/Ru/Pt/Au Heteroquatermetallic Nanoparticle Catalysts: Sequential Cooperation of Multiple Nano-Metal Species. *Chem. Commun.* **2014**, *50*, 12123−12126.

(588) Yoshida, K.; Gonzalez-Arellano, C.; Luque, R.; Gai, P. L. Efficient Hydrogenation of Carbonyl Compounds Using Low-Loaded Supported Copper Nanoparticles under Microwave Irradiation. *Appl. Catal., A: Gen.* **2010**, *379*, 38−44.

(589) Zhang, J.; Geng, J.; Zheng, G.; Dai, J.; Fu, Z. Highly Stable Photoresponsive Complex Framework Formation Involves Unusual Selective Hydrogenation of a Pyridine Derivative. *Chem. Commun.* **2014**, *50*, 7326−7328.

(590) Ringwald, M.; Stürmer, R.; Brintzinger, H. H. Asymmetric Thermal Transformation, a New Way to Enantiopure Biphenyl-Bridged Titanocene and Zirconocene Complexes: Efficient Catalysts for Asymmetric Imine Hydrogenation. *J. Am. Chem. Soc.* **1999**, *121*, 1524−1527.

(591) Tang, X.; Chen, H.; Hu, L.; Hao, W.; Sun, Y.; Zeng, X.; Lin, L.; Liu, S. Conversion of Biomass to γ-Valerolactone by Catalytic Transfer Hydrogenation of Ethyl Levulinate over Metal Hydroxides. *Appl. Catal., B* **2014**, *147*, 827−834.

(592) Assary, R. S.; Curtiss, L. A.; Dumesic, J. A. Exploring Meerwein−Ponndorf−Verley Reduction Chemistry for Biomass Catalysis Using a First-Principles Approach. *ACS Catal.* **2013**, *3*, 2694−2704.

(593) Song, J.; Wu, L.; Zhou, B.; Zhou, H.; Fan, H.; Yang, Y.; Meng, Q.; Han, B. A New Porous Zr-Containing Catalyst with a Phenate Group: an Efficient Catalyst for the Catalytic Transfer Hydrogenation of Ethyl Levulinate to Gamma-Valerolactone. *Green Chem.* **2015**, *17*, 1626−1632.

(594) Sorribes, I.; Wienhöfer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. Chemoselective Transfer Hydrogenation to Nitroarenes Mediated by Cubane-Type Mo_3S_4 Cluster Catalysts. *Angew. Chem., Int. Ed.* **2012**, *51*, 7794−7798.

(595) Neary, M. C.; Parkin, G. Dehydrogenation, Disproportionation and Transfer Hydrogenation Reactions of Formic Acid Catalyzed by Molybdenum Hydride Compounds. *Chem. Sci.* **2015**, *6*, 1859−1865.

(596) Breno, K. L.; Ahmed, T. J.; Pluth, M. D.; Balzarek, C.; Tyler, D. R. Organometallic Chemistry in Aqueous Solution: Reactions Catalyzed by Water-Soluble Molybdocenes. *Coord. Chem. Rev.* **2006**, *250*, 1141−1151.

(597) Mejía, E.; Aardoom, R.; Togni, A. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Rhenium Complexes with Chiral Ferrocenylphosphane Ligands. *Eur. J. Inorg. Chem.* **2012**, 5021−5032.

(598) Dong, H.; Berke, H. A Mild and Efficient Rhenium-Catalyzed Transfer Hydrogenation of Terminal Olefins Using Alcoholysis of Amine−Borane Adducts as a Reducing System. *J. Organomet. Chem.* **2011**, *696*, 1803−1808.

(599) Kuninobu, Y.; Nakahara, T.; Yu, P.; Takai, K. Rhenium-Catalyzed Insertion of Terminal Alkenes into a $C(sp^2)$−H Bond and Successive Transfer Hydrogenation. *J. Organomet. Chem.* **2011**, *696*, 348−351.

(600) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; DuBois, M. R. Homogeneous Reductions of Nitrogen-Containing Substrates Catalyzed by Molybdenum(IV) Complexes with.mu.-Sulfido Ligands. *Organometallics* **1986**, *5*, 951−955.

(601) Fernandes, A. C.; Romao, C. C. Silane/MoO_2Cl_2 as an Efficient System for the Reduction of Esters. *J. Mol. Catal. A* **2006**, *253*, 96−98.

(602) Nolin, K. A.; Ahn, R. W.; Toste, F. D. Enantioselective Reduction of Imines Catalyzed by a Rhenium(V)−Oxo Complex. *J. Am. Chem. Soc.* **2005**, *127*, 12462−12463.

(603) Yeung, C.-T.; Teng, P.-F.; Yeung, H.-L.; Wong, W.-T.; Kwong, H.-L. Catalytic and Asymmetric Cyclopropanation of Alkenes Catalysed by Rhenium(I) Bipyridine and Terpyridine Tricarbonyl Complexes. *Org. Biomol. Chem.* **2007**, *5*, 3859−3864.

(604) Wright, W. R. H.; Palkovits, R. Development of Heterogeneous Catalysts for the Conversion of Levulinic Acid to γ-Valerolactone. *ChemSusChem* **2012**, *5*, 1657−1667.

(605) Basset, J.-M., Psaro, R., Roberto, D., Ugo, R., Eds. *Modern Surface Organometallic Chemistry*; Wiley-VCH: Weinheim, 2009.

(606) Lu, A. H.; Salabas, E. L.; Schüth, F. Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application. *Angew. Chem., Int. Ed.* **2007**, *46*, 1222−1244.

(607) Shylesh, S.; Schünemann, V.; Thiel, W. R. Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 3428−3459.

(608) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J. M. Magnetically Recoverable Nanocatalysts. *Chem. Rev.* **2011**, *111*, 3036−3075.

(609) Kainz, Q. M.; Reiser, O. Polymer- and Dendrimer-Coated Magnetic Nanoparticles as Versatile Supports for Catalysts, Scavengers, and Reagents. *Acc. Chem. Res.* **2014**, *47*, 667−677.

(610) Wang, D.; Astruc, D. Magnetically Recoverable Ruthenium Catalysts in Organic Synthesis. *Molecules* **2014**, *19*, 4635−4653.

(611) Wang, D.; Astruc, D. Fast-Growing Field of Magnetically Recyclable Nanocatalysts. *Chem. Rev.* **2014**, *114*, 6949−6985.

(612) Yuzik-Klimova, E. Y.; Kuchkna, N. V.; Sorokina, S. A.; Bronstein, L. M. Magnetically Recoverable Catalysts Based on Polyphenylenepyridyl Dendrons and Dendrimers. *RSC Adv.* **2014**, *4*, 23271−23280.

(613) Xu, H.-J.; Wan, X.; Geng, Y.; Xu, X.-L. The Catalytic Application of Recoverable Magnetic Nanoparticles-Supported Organic Compounds. *Curr. Org. Chem.* **2013**, *17*, 1034−1050.

(614) Shoola, C. O.; DelMastro, T.; Wu, R.; et al. Nitrogen-Doped Graphene-Activated Iron-Oxide-Based Nanocatalysts for Selective Transfer Hydrogenation of Nitroarenes Asymmetric Transfer Hydrogenation of Secondary Allylic Alcohols. *Eur. J. Org. Chem.* **2015**, 1670−1673.

(615) Baig, R. B. N.; Varma, R. S. Magnetic Silica-Supported Ruthenium Nanoparticles: An Efficient Catalyst for Transfer Hydrogenation of Carbonyl Compounds. *ACS Sustainable Chem. Eng.* **2013**, *1*, 805−809.

(616) Dayan, S.; Arslan, F.; Ozpozan, N. K. Ru(II) Impregnated Al_2O_3, Fe_3O_4, SiO_2 and *N*-Coordinate Ruthenium(II) Arene Complexes: Multifunctional Catalysts in the Hydrogenation of Nitroarenes and the Transfer Hydrogenation of Aryl Ketones. *Appl. Catal., B* **2015**, *164*, 305−315.

(617) Liu, G.; Gu, H.; Sun, Y.; Long, J.; Xu, Y.; Li, H. Magnetically Recoverable Nanoparticles: Highly Efficient Catalysts for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium. *Adv. Synth. Catal.* **2011**, *353*, 1317−1324.

(618) Sun, Y.; Liu, G.; Gu, H.; Huang, T.; Zhang, Y.; Li, H. Magnetically Recoverable SiO_2-Coated Fe_3O_4 Nanoparticles: A New Platform for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium. *Chem. Commun.* **2011**, *47*, 2583−2585.

(619) Gao, X.; Liu, R.; Zhang, D.; Wu, M.; Cheng, T.; Liu, G. Phenylene-Coated Magnetic Nanoparticles that Boost Aqueous Asymmetric Transfer Hydrogenation Reactions. *Chem.—Eur. J.* **2014**, *20*, 1515−1519.

(620) Serpell, C. J.; Cookson, J.; Ozkaya, D.; Beer, P. D. Core@Shell Bimetallic Nanoparticle Synthesis via Anion Coordination. *Nat. Chem.* **2011**, *3*, 478−483.

(621) Tao, F.; Grass, M. E.; Zhang, Y.; Butcher, D. R.; Renzas, J. M.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles. *Science* **2008**, *322*, 932−934.

(622) Gawande, M. B.; Guo, H.; Rathi, A. K.; Branco, P. S.; Chen, Y.; Varmad, R. S.; Peng, D.-L. First Application of Core-Shell Ag@Ni Magnetic Nanocatalyst for Transfer Hydrogenation Reactions of Aromatic Nitro and Carbonyl Compounds. *RSC Adv.* **2013**, *3*, 1050−1054.

(623) Yang, S.; Cao, C.; Sun, Y.; Huang, P.; Wei, F.; Song, W. Nanoscale Magnetic Stirring Bars for Heterogeneous Catalysis in Microscopic Systems. *Angew. Chem., Int. Ed.* **2015**, *54*, 2661−2664.

(624) Scholz, D.; Aellig, C.; Hermans, I. Catalytic Transfer Hydrogenation/Hydrogenolysis for Reductive Upgrading of Furfural and 5-(Hydroxymethyl)furfural. *ChemSusChem* **2014**, *7*, 268−275.

(625) Guino, M.; Hii, K. K. M. Applications of Phosphine-Functionalised Polymers in Organic Synthesis. *Chem. Soc. Rev.* **2007**, *36*, 608−617.

(626) Bergbreiter, D. E.; Tian, J. H.; Hongfa, C. Using Soluble Polymer Supports To Facilitate Homogeneous Catalysis. *Chem. Rev.* **2009**, *109*, 530−582.

(627) McNamara, C. A.; Dixon, M. J.; Bradley, M. Recoverable Catalysts and Reagents Using Recyclable Polystyrene-Based Supports. *Chem. Rev.* **2002**, *102*, 3275−3300.

(628) Leadbeater, N. E.; Marco, M. Preparation of Polymer-Supported Ligands and Metal Complexes for Use in Catalysis. *Chem. Rev.* **2002**, *102*, 3217−3274.

(629) Zhang, X.; Zhao, Y.; Peng, J.; Yang, Q. Polymer@silica Composites with Tunable Outer and Inner Surface Properties: A Platform for Aqueous Asymmetric Transfer Hydrogenation. *Green Chem.* **2015**, *17*, 1899−1906.

(630) Modak, A.; Mondal, J.; Sasidharan, M.; Bhaumik, A. Triazine Functionalized Ordered Mesoporous Polymer: A Novel Solid Support for Pd-Mediated C−C Cross-Coupling Reactions in Water. *Green Chem.* **2011**, *13*, 1317−1331.

(631) Salam, N.; Kundu, S. K.; Roy, A. S.; Mondal, P.; Ghosh, K.; Bhaumik, A.; Islam, S. M. A Ruthenium-Grafted Triazine Functionalized Mesoporous Polymer: a Highly Efficient and Multifunctional Catalyst for Transfer Hydrogenation and the Suzuki−Miyaura Cross-Coupling Reactions. *Dalton Trans.* **2014**, *43*, 7057−7068.

(632) Salam, N.; Banerjee, B.; Roy, A. S.; Mondal, P.; Roy, S.; Bhaumik, A.; Islam, S. M. Silver nanoparticles embedded over mesoporous organic polymer as highly efficient and reusable nanocatalyst for the reduction of nitroarenes and aerobic oxidative esterification of alcohols. *Appl. Catal., A* **2014**, *477*, 184−194.

(633) Sun, Q.; Jin, Y.; Zhu, L.; Wang, L.; Meng, X.; Xiao, F. Superhydrophobic, Chiral, and Mesoporous TsDPEN Copolymer Coordinated to Ruthenium Species as an Efficient Catalyst for Asymmetric Transfer Hydrogenation. *Nano Today* **2013**, *8*, 342−350.

(634) Xu, X.; Wang, R.; Wan, J.; Ma, X.; Peng, J. Phosphonate-Containing Polystyrene Copolymer-Supported Ru Catalystfor Asymmetric Transfer Hydrogenation in Water. *RSC Adv.* **2013**, *3*, 6747−6751.

(635) Wang, R.; Wan, J.; Ma, X.; Xu, X.; Liu, L. Anchored [$RuCl_2$(*p*-cymene)]$_2$ in Hybrid Zirconium Phosphate−Phosphonate Coated and Pillared with Double-Stranded Hydrophobic Linear Polystyrene as Heterogeneous Catalyst Suitable for Aqueous Asymmetric Transfer Hydrogenation. *Dalton Trans.* **2013**, *42*, 6513−6522.

(636) Molla, R. A.; Roy, A. S.; Ghosh, K.; Salam, N.; Iqubal, M. A.; Tuhina, K.; Islam, S. M. Polymer Anchored Ruthenium Complex: A Highly Active and Recyclable Catalyst for One-Pot Azide−Alkyne Cycloaddition and Transfer-Hydrogenation of Ketones under Mild Conditions. *J. Organomet. Chem.* **2015**, *776*, 170−179.

(637) Marcos, R.; Jimeno, C.; Pericàs, M. A. Polystyrene-Supported Enantiopure 1,2-Diamines: Development of a Most Practical Catalyst for the Asymmetric Transfer Hydrogenation of Ketones. *Adv. Synth. Catal.* **2011**, *353*, 1345−1352.

(638) Sugie, H.; Hashimoto, Y.; Haraguchi, N.; Itsuno, S. Synthesis of Polymer-Immobilized TsDPEN Ligand and Its Application in Asymmetric Transfer Hydrogenation of Cyclic Sulfonimine. *J. Organomet. Chem.* **2014**, *751*, 711−716.

(639) Zhou, Z.; Ma, Q. Polyethylene Glycol-Bound Ru Catalyst for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Water. *Appl. Organomet. Chem.* **2011**, *25*, 233−237.

(640) Haraguchi, N.; Nishiyama, A.; Itsuno, S. Synthesis of Polymer Microspheres Functionalized with Chiral Ligand by Precipitation Polymerization and their Application to Asymmetric Transfer Hydrogenation. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3340−3349.

(641) Indra, A.; Maity, P.; Bhaduri, S.; Lahiri, G. K. Chemoselective Hydrogenation and Transfer Hydrogenation of Olefins and Carbonyls with the Cluster-Derived Ruthenium Nanocatalyst in Water. *ChemCatChem* **2013**, *5*, 322−330.

(642) Wei, J.; Zhang, X.; Zhang, X.; Zhao, Y.; Li, R.; Yang, Q. Facile Synthesis of Hybrid Core−Shell Nanospheres for the Asymmetric Transfer Hydrogenation of Aromatic Ketones. *ChemCatChem* **2014**, *6*, 1368−1374.

(643) Itsuno, S.; Hashimoto, Y.; Haraguchi, N. Synthesis of Chiral Iridium Complexes Immobilized on Amphiphilic Polymers and Their Application to Asymmetric Catalysis. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3037−3044.

(644) Mahato, S. K.; Islam, R. U.; Acharya, C.; Witcomb, M. J.; Mallick, K. Polymer-Stabilized Palladium Nanoparticles for the Chemoselective Transfer Hydrogenation of *α,β*-Unsaturated Carbonyls: Single-Step Bottom-Up Approach. *ChemCatChem* **2014**, *6*, 1419−1426.

(645) Newkome, G. R.; He, E.; Moorefield, C. N. Suprasupermolecules with Novel Properties: Metallodendrimers. *Chem. Rev.* **1999**, *99*, 1689−1746.

(646) Astruc, D.; Chardac, F. Dendritic Catalysts and Dendrimers in Catalysis. *Chem. Rev.* **2001**, *101*, 2991−3024.

(647) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. Dendrimers as Support for Recoverable Catalysts and Reagents. *Chem. Rev.* **2002**, *102*, 3717−3756.

(648) Astruc, D.; Boisselier, E.; Ornelas, C. Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, Photonics, and Nanomedicine. *Chem. Rev.* **2010**, *110*, 1857−1959.

(649) Wang, D.; Astruc, D. Dendritic Catalysis—Basic Concepts and Recent Trends. *Coord. Chem. Rev.* **2013**, *257*, 2317−2334.

(650) Wang, W.-W.; Wang, Q.-R. A Fluorinated Dendritic TsDPEN-Ru(II) Catalyst for Asymmetric Transfer Hydrogenation of Prochiral Ketones in Aqueous Media. *Chem. Commun.* **2010**, *46*, 4616−4618.

(651) Wang, W.-W.; Li, Z.-M.; Su, L.; Wang, Q.-R.; Wu, Y.-L. Insight into the Role of Fluorinated Dendrimers in Ruthenium(II) Catalyst for Asymmetric Transfer Hydrogenation: The Stabilizing Effects from Experimental and DFT Approach. *J. Mol. Catal. A: Chem.* **2014**, *387*, 92−102.

(652) Dimroth, J.; Keilitz, J.; Schedler, U.; Schomäcker, R.; Haag, R. Immobilization of a Modified Tethered Rhodium(III)-*p*-Toluenesulfonyl-1,2-diphenylethylenediamine Catalyst on Soluble and Solid Polymeric Supports and Successful Application to Asymmetric Transfer Hydrogenation of Ketones. *Adv. Synth. Catal.* **2010**, *352*, 2497−2506.

(653) Shen, Y.; Chen, Q.; Lou, L.-L.; Yu, K.; Ding, F.; Liu, S. Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by SBA-15 Supported Ir(I) Complex Under Mild Conditions. *Catal. Lett.* **2010**, *137*, 104−109.

(654) Sarkar, S. M.; Yusoff, M. M.; Rahman, M. L. Asymmetric Transfer Hydrogenation Catalyzed by Mesoporous MCM-41-Supported Chiral Ru-Complex. *J. Chin. Chem. Soc.* **2015**, *62*, 177−181.

(655) Chen, S.-J.; You, H.-X.; Vo-Thanh, G.; Liu, Y. Heterogeneous Transfer Hydrogenation over Mesoporous SBA-15 Co-Modified by Anionic Sulfonate and Cationic Ru(III) Complex. *Monatsh. Chem.* **2013**, *144*, 851−858.

(656) Lou, L.-L.; Du, H.; Shen, Y.; Yu, K.; Yu, W.; Chen, Q.; Liu, S. Chiral Ir(I) Complex Supported on External Surface Passivated SBA-15 as Heterogeneous Catalyst for Asymmetric Transfer Hydrogenation of Aromatic Ketones. *Microporous Mesoporous Mater.* **2014**, *187*, 94−99.

(657) Cheng, T.; Long, J.; Liang, X.; Liu, R.; Liu, G. Exploiting Mesoporous Silica Matrixes for Aqueous Asymmetric Transfer Hydrogenation: Morphology and Surface Chemistry Dominate Catalytic Performance. *Mater. Res. Bull.* **2014**, *53*, 1−6.

(658) Xu, Y.; Cheng, T.; Long, J.; Liu, K.; Qian, Q.; Gao, F.; Liu, G.; Li, H. An Ion-Pair Immobilization Strategy in Rhodium-Catalyzed

Asymmetric Transfer Hydrogenation of Aromatic Ketones. *Adv. Synth. Catal.* **2012**, *354*, 3250−3258.

(659) Long, J.; Liu, G.; Cheng, T.; Yao, H.; Qian, Q.; Zhuang, J.; Gao, F.; Li, H. Immobilization of Rhodium-Based Transfer Hydrogenation Catalysts on Mesoporous Silica Materials. *J. Catal.* **2013**, *298*, 41−50.

(660) Gao, F.; Jin, R.; Zhang, D.; Liang, Q.; Ye, Q.; Liu, G. Flower-Like Mesoporous Silica: A Bifunctionalized Catalyst for Rhodium-Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium. *Green Chem.* **2013**, *15*, 2208−2214.

(661) Liu, R.; Cheng, T.; Kong, L.; Chen, C.; Liu, G.; Li, H. Highly Recoverable Organoruthenium-Functionalized Mesoporous Silica Boosts Aqueous Asymmetric Transfer Hydrogenation Reaction. *J. Catal.* **2013**, *307*, 55−61.

(662) Zhang, H.; Jin, R.; Yao, H.; Tang, S.; Zhuang, J.; Liu, G.; Li, H. Core−Shell Structured Mesoporous Silica: A New Immobilized Strategy for Rhodium Catalyzed Asymmetric Transfer Hydrogenation. *Chem. Commun.* **2012**, *48*, 7874−7876.

(663) Liu, R.; Jin, R.; Kong, L.; Wang, J.; Chen, C.; Cheng, T.; Liu, G. Organorhodium-Functionalized Periodic Mesoporous Organosilica: High Hydrophobicity Promotes Asymmetric Transfer Hydrogenation in Aqueous Medium. *Chem.—Asian J.* **2013**, *8*, 3108−3115.

(664) Zhang, D.; Xu, J.; Zhao, Q.; Cheng, T.; Liu, G. A Site-Isolated Organoruthenium-/Organopalladium-Bifunctionalized Periodic Mesoporous Organosilica Catalyzes Cascade Asymmetric Transfer Hydrogenation and Suzuki Cross-Coupling. *ChemCatChem* **2014**, *6*, 2998−3003.

(665) Verho, O.; Nagendiran, A.; Johnston, E. V.; Tai, C.-W.; Bäckvall, J.-E. Nanopalladium on Amino-Functionalized Mesocellular Foam: An Efficient Catalyst for Suzuki Reactions and Transfer Hydrogenations. *ChemCatChem* **2013**, *5*, 612−618.

(666) Verho, O.; Nagendiran, A.; Tai, C.-W.; Johnston, E.-V.; Bäckvall, J.-E. Nanopalladium on Amino-Functionalized Mesocellular Foam as an Efficient and Recyclable Catalyst for the Selective Transfer Hydrogenation of Nitroarenes to Anilines. *ChemCatChem* **2014**, *6*, 205−211.

(667) Bouhrara, M.; Ranga, C.; Fihri, A.; Shaikh, R. R.; Sarawade, P.; Emwas, A. H.; Hedhili, M. N.; Polshettiwar, V. Nitridated Fibrous Silica (KCC-1) as a Sustainable Solid Base Nanocatalyst. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1192−1199.

(668) Polshettiwar, V.; Thivolle-Cazat, J.; Taoufik, M.; Stoffelbach, F.; Norsic, S.; Basset, J. M. Hydro-metathesis" of Olefins: A Catalytic Reaction Using a Bifunctional Single-Site Tantalum Hydride Catalyst Supported on Fibrous Silica (KCC-1) Nanospheres. *Angew. Chem., Int. Ed.* **2011**, *50*, 2747−2751.

(669) Peng, H. G.; Xu, L.; Wu, H.; Zhang, K.; Wu, P. One-Pot Synthesis of Benzamide over a Robust Tandem Catalyst Based on Center Radially Fibrous Silica Encapsulated TS-1. *Chem. Commun.* **2013**, *49*, 2709−2711.

(670) Qureshi, Z. S.; Sarawade, P. B.; Albert, M.; D'Elia, V.; Hedhili, M. N.; Kçhler, K.; Basset, J.-M. Palladium Nanoparticles Supported on Fibrous-Structured Silica Nanospheres (KCC-1): An Efficient and Selective Catalyst for the Transfer Hydrogenation of Alkenes. *ChemCatChem* **2015**, *7*, 635−642.

(671) Modugno, G.; Monney, A.; Bonchio, M.; Albrecht, M.; Carraro, M. Transfer Hydrogenation Catalysis by a N-Heterocyclic Carbene Iridium Complex on a Polyoxometalate Platform. *Eur. J. Inorg. Chem.* **2014**, 2356−2360.

(672) Xiao, W.; Jin, R.; Cheng, T.; Xia, D.; Yao, H.; Gao, F.; Deng, B.; Liu, G. A Bifunctionalized Organic−Inorganic Hybrid Silica: Synergistic Effect Enhances Enantioselectivity. *Chem. Commun.* **2012**, *48*, 11898−11900.

(673) Tang, S.; Jin, R.; Zhang, H.; Yao, H.; Zhuang, J.; Liu, G.; Li, H. Recoverable Organorhodium-Functionalized Polyhedral Oligomeric Silsesquioxane: A Bifunctional Heterogeneous Catalyst for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium. *Chem. Commun.* **2012**, *48*, 6286−6288.

(674) Ganesamoorthy, S.; Jerome, P.; Shanmugasundaram, K.; Karvembu, R. Highly Efficient Homogeneous and Heterogenized Ruthenium Catalysts for Transfer Hydrogenation of Carbonyl Compounds. *RSC Adv.* **2014**, *4*, 27955−27962.

(675) Dayan, S.; Kalaycıoğlu, N. Ö.; Dayan, O.; Özdemir, N.; Dinçer, M.; Büyükgüngör, O. Synthesis and Characterization of SiO_2-Supported Ruthenium Complexes Containing Aromatic Sulfonamides: as Catalysts for Transfer Hydrogenation of Acetophenone. *Dalton Trans.* **2013**, *42*, 4957−4969.

(676) Yang, Y.; Weng, Z.; Muratsugu, S.; Ishiguro, N.; Ohkoshi, S.; Tada, M. Preparation and Catalytic Performances of a Molecularly Imprinted Ru-Complex Catalyst with an NH_2 Binding Site on a SiO_2 Surface. *Chem.—Eur. J.* **2012**, *18*, 1142−1153.

(677) Weng, Z.; Muratsugu, S.; Ishiguro, N.; Ohkoshi, S.; Tada, M. Preparation of Surface Molecularly Imprinted Ru-Complex Catalysts for Asymmetric Transfer Hydrogenation in Water Media. *Dalton Trans.* **2011**, *40*, 2338−2347.

(678) Furukawa, S.; Yoshida, Y.; Komatsu, T. Chemoselective Hydrogenation of Nitrostyrene to Aminostyrene over Pd- and Rh-Based Intermetallic Compounds. *ACS Catal.* **2014**, *4*, 1441−1450.

(679) Wang, Z.; Huang, L.; Geng, L.; Chen, R.; Xing, W.; Wang, Y.; Huang, J. Chemoselective Transfer Hydrogenation of Aldehydes and Ketones with a Heterogeneous Iridium Catalyst in Water. *Catal. Lett.* **2015**, *145*, 1008−1013.

(680) Panagiotopoulou, P.; Vlachos, D. G. Liquid Phase Catalytic Transfer Hydrogenation of Furfural over a Ru/C Catalyst. *Appl. Catal., A* **2014**, *480*, 17−24.

(681) Panagiotopoulou, P.; Martin, N.; Vlachos, D. G. Effect of Hydrogen Donor on Liquid Phase Catalytic Transfer Hydrogenation of Furfural over a Ru/RuO_2/C Catalyst. *J. Mol. Catal. A: Chem.* **2014**, *392*, 223−228.

(682) Jae, J.; Zheng, W.; Lobo, R. F.; Vlachos, D. G. Production of Dimethylfuran from Hydroxymethylfurfural through Catalytic Transfer Hydrogenation with Ruthenium Supported on Carbon. *ChemSusChem* **2013**, *6*, 1158−1162.

(683) Jae, J.; Zheng, W.; Karim, A. M.; Guo, W.; Lobo, R. F.; Vlachos, D. G. The Role of Ru and RuO_2 in the Catalytic Transfer Hydrogenation of 5-Hydroxymethylfurfural for the Production of 2,5-Dimethylfuran. *ChemCatChem* **2014**, *6*, 848−856.

(684) Perdriau, S.; Harder, S.; Heeres, H. J.; de Vries, J. G. Selective Conversion of Polyenes to Monoenes by $RuCl_3$-Catalyzed Transfer Hydrogenation: The Case of Cashew Nutshell Liquid. *ChemSusChem* **2012**, *5*, 2427−2434.

(685) Shrotri, A.; Kobayashi, H.; Tanksale, A.; Fukuoka, A.; Beltramini, J. Transfer Hydrogenation of Cellulose-based Oligomers over Carbon-supported Ruthenium Catalyst in a Fixed-bed Reactor. *ChemCatChem* **2014**, *6*, 1349−1356.

(686) Liu, R.; Wang, Y.; Cheng, H.; Yu, Y.; Zhao, F.; Arai, M. Reduction of Citral in Water under Typical Transfer Hydrogenation Conditions—Reaction Mechanisms with Evolution of and Hydrogenation by Molecular Hydrogen. *J. Mol. Catal. A: Chem.* **2013**, *366*, 315−320.

(687) Quinn, J. F.; Bryant, C. E.; Golden, K. C.; Gregg, B. T. Rapid Reduction of Heteroaromatic Nitro Groups Using Catalytic Transfer Hydrogenation with Microwave Heating. *Tetrahedron Lett.* **2010**, *51*, 786−789.

(688) Zhu, K.; Hao, J.-H.; Zhang, C.-P.; Zhang, J.; Feng, Y.; Qin, H.-L. Diversified Facile Synthesis of Benzimidazoles, Quinazolin-4(3*H*)-ones and 1,4-Benzodiazepine-2,5-diones *via* Palladium-Catalyzed Transfer Hydrogenation/Condensation Cascade of Nitro Arenes under Microwave Irradiation. *RSC Adv.* **2015**, *5*, 11132−11135.

(689) Li, F.; Frett, B.; Li, H.-Y. Selective Reduction of Halogenated Nitroarenes with Hydrazine Hydrate in the Presence of Pd/C. *Synlett* **2014**, *25*, 1403−1408.

(690) Gopiraman, M.; Babu, S. G.; Khatri, Z.; Kai, W.; Kim, Y. A.; Endo, M.; Karvembu, R.; Kim, I. S. Dry Synthesis of Easily Tunable Nano Ruthenium Supported on Graphene: Novel Nanocatalysts for Aerial Oxidation of Alcohols and Transfer Hydrogenation of Ketones. *J. Phys. Chem. C* **2013**, *117*, 23582−23596.

(691) Gopiraman, M.; Babu, S. G.; Khatri, Z.; Wei, K.; Endo, M.; Karvembu, R.; Kim, I. S. Facile and Homogeneous Decoration of

RuO_2 Nanorods on Graphenenanoplatelets for Transfer Hydrogenation of Carbonyl Compounds. *Catal. Sci. Technol.* **2013**, *3*, 1485−1489.

(692) Barati, B.; Moghadam, M.; Rahmati, A.; Mirkhani, V.; Tangestaninejad, S.; Mohammadpoor-Baltork, I. Ruthenium Hydride Complex Supported on Multi-Wall Carbon Nanotubes for Catalytic C−C Bond Formation *via* Transfer Hydrogenation. *J. Organomet. Chem.* **2013**, *724*, 32−39.

(693) Gopiraman, M.; Babu, S. G.; Karvembu, R.; Kim, I. S. Nanostructured RuO_2 on MWCNTs: Efficient Catalyst for Transfer Hydrogenation of Carbonyl Compounds and Aerial Oxidation of Alcohols. *Appl. Catal., A* **2014**, *484*, 84−96.

(694) Blanco, M.; Álvarez, P.; Blanco, C.; Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Oro, L. A.; Menéndez, R. Enhanced Hydrogen-Transfer Catalytic Activity of Iridium N-Heterocyclic Carbenes by Covalent Attachment on Carbon Nanotubes. *ACS Catal.* **2013**, *3*, 1307−1317.

(695) Lu, Y.-M.; Zhu, H.-Z.; Li, W.-G.; Hu, B.; Yu, S.-H. Size-Controllable Palladium Nanoparticles Immobilized on Carbon Nanospheres for Nitroaromatic Hydrogenation. *J. Mater. Chem. A* **2013**, *1*, 3783−3788.

(696) Chen, A.; Li, Y.; Chen, J.; Zhao, G.; Ma, L.; Yu, Y. Selective Hydrogenation of Phenol and Derivatives over Polymer-Functionalized Carbon-Nanofiber-Supported Palladium Using Sodium Formate as the Hydrogen Source. *ChemPlusChem* **2013**, *78*, 1370−1378.

(697) Zhao, Y.; Pan, F.; Li, H.; Xu, G. Q.; Chen, W. Titania-Photocatalyzed Transfer Hydrogenation Reactions with Methanol as a Hydrogen Source: Enhanced Catalytic Performance by Pd−Pt Alloy at Ambient Temperature. *ChemCatChem* **2014**, *6*, 454−458.

(698) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, *112*, 4469−4506.

(699) Fountoulaki, S.; Daikopoulou, V.; Gkizis, P. L.; Tamiolakis, I.; Armatas, G. S.; Lykakis, I. N. Mechanistic Studies of the Reduction of Nitroarenes by $NaBH_4$ or Hydrosilanes Catalyzed by Supported Gold Nanoparticles. *ACS Catal.* **2014**, *4*, 3504−3511.

(700) Aellig, C.; Jenny, F.; Scholz, D.; Wolf, P.; Giovinazzo, I.; Kollhoff, F.; Hermans, I. Combined 1,4-Butanediol Lactonization and Transfer Hydrogenation/Hydrogenolysis of Furfural-Derivatives under Continuous Flow Conditions. *Catal. Sci. Technol.* **2014**, *4*, 2326−2331.

(701) Pupovac, K.; Palkovits, R. Cu/$MgAl_2O_4$ as Bifunctional Catalyst for Aldol Condensation of 5-Hydroxymethylfurfural and Selective Transfer Hydrogenation. *ChemSusChem* **2013**, *6*, 2103−2110.

(702) Muratsugu, S.; Weng, Z.; Nakai, H.; Isobe, K.; Kushida, Y.; Sasaki, T.; Tada, M. Surface-Assisted Transfer Hydrogenation Catalysis on a γ-Al_2O_3-Supported Ir Dimer. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16023−16031.

(703) Gao, Y.; Jaenicke, S.; Chuah, G.-K. Highly Efficient Transfer Hydrogenation of Aldehydes and Ketones Using Potassium Formate over AlO(OH)-Entrapped Ruthenium Catalysts. *Appl. Catal., A* **2014**, *484*, 51−58.

(704) Kar, P.; Mishra, B. G. Hydrodehalogenation of Halogenated Organic Contaminants from Aqueous Sources by Pd Nanoparticles Dispersed in the Micropores of Pillared Clays Under Transfer Hydrogenation Condition. *J. Cluster Sci.* **2014**, *25*, 1463−1478.

(705) Gandarias, I.; Arias, P. L.; Fernandez, S. G.; Requies, J.; Doukkali, M. E.; Guemez, M. B. Hydrogenolysis through Catalytic Transfer Hydrogenation: Glycerol Conversion to 1,2-Propanediol. *Catal. Today* **2012**, *195*, 22−31.

(706) Gandarias, I.; Arias, P. L.; Requies, J.; Doukkali, M. E.; Güemez, M. B. Liquid-Phase Glycerol Hydrogenolysis to 1,2-Propanediol under Nitrogen Pressure Using 2-Propanol as Hydrogen Source. *J. Catal.* **2011**, *282*, 237−247.

(707) Du, Y.; Feng, D.; Wan, J.; Ma, X. The Enhanced Asymmetric Hydrogenation of Unsymmetrical Benzils to Hydrobenzoin Catalyzed by Organosoluble Zirconium Phosphonate-Immobilized Ruthenium Catalyst. *Appl. Catal., A* **2014**, *479*, 49−58.

(708) Hengne, A. M.; Malawadkar, A. V.; Biradar, N. S.; Rode, C. V. Surface Synergism of an Ag−Ni/ZrO_2 Nanocomposite for the Catalytic Transfer Hydrogenation of Bio-Derived Platform Molecules. *RSC Adv.* **2014**, *4*, 9730−9736.

(709) Tuteja, J.; Choudhary, H.; Nishimura, S.; Ebitani, K. Direct Synthesis of 1,6-Hexanediol from HMF over a Heterogeneous Pd/ZrP Catalyst using Formic Acid as Hydrogen Source. *ChemSusChem* **2014**, *7*, 96−100.

(710) Tang, X.; Hu, L.; Sun, Y.; Zhao, G.; Hao, W.; Lin, L. Conversion of Biomass-Derived Ethyl Levulinate into γ-Valerolactone *via* Hydrogen Transfer from Supercritical Ethanol over a ZrO_2 Catalyst. *RSC Adv.* **2013**, *3*, 10277−10284.

(711) Tao, R.; Xie, Y.; An, G.; Ding, K.; Zhang, H.; Sun, Z.; Liu, Z. Arginine-Mediated Synthesis of Highly Efficient Catalysts for Transfer Hydrogenations of Ketones. *J. Colloid Interface Sci.* **2010**, *351*, 501−506.

(712) Yurderi, M.; Bulut, A.; Zahmakiran, M.; Gülcan, M.; Özkar, S. Ruthenium(0) Nanoparticles Stabilized by Metal-Organic Framework (ZIF-8): Highly Efficient Catalyst for the Dehydrogenation of Dimethylamine-Borane and Transfer Hydrogenation of Unsaturated Hydrocarbons Using Dimethylamine-Borane as Hydrogen Source. *Appl. Catal., B* **2014**, *160*−*161*, 534−541.

(713) Hammond, C.; Schümperli, M. T.; Conrad, S.; Hermans, I. Hydrogen Transfer Processes Mediated by Supported Iridium Oxide Nanoparticles. *ChemCatChem* **2013**, *5*, 2983−2990.

(714) Shimura, K.; Shimizu, K. Transfer Hydrogenation of Ketones by Ceria-Supported Ni Catalysts. *Green Chem.* **2012**, *14*, 2983−2985.

(715) Guha, N. R.; Bhattacherjee, D.; Das, P. Solid Supported Rhodium(0) Nanoparticles: An Efficient Catalyst for Chemo- and Regio-Selective Transfer Hydrogenation of Nitroarenes to Anilines under Microwave Irradiation. *Tetrahedron Lett.* **2014**, *55*, 2912−2916.

(716) Lucas, S. J.; Crossley, B. D.; Pettman, A. J.; Vassileiou, A. D.; Screen, T. E. O.; Blackera, A. J.; McGowan, P. C. A Robust Method to Heterogenise and Recycle Group 9 Catalysts. *Chem. Commun.* **2013**, *49*, 5562−5564.

(717) Fürniss, D.; Schepers, U.; Bräse, S. Killing Double Bonds Softly: the Reduction of Polymer-Bound Alkenes. *RSC Adv.* **2012**, *2*, 11273−11278.

(718) Sherborne, G. J.; Chapman, M. R.; Blacker, A. J.; et al. Activation and Deactivation of a Robust Immobilized Cp*Ir-Transfer Hydrogenation Catalyst: A Multielement *in Situ* X-ray Absorption Spectroscopy Study. *J. Am. Chem. Soc.* **2015**, *137*, 4151−4157.

(719) Sarmah, P. P.; Dutta, D. K. Stabilized Rh^0-Nanoparticles-Montmorillonite Clay Composite: Synthesis and Catalytic Transfer Hydrogenation Reaction. *Appl. Catal., A* **2014**, *470*, 355−360.

(720) Sarmah, P. P.; Dutta, D. K. Chemoselective Reduction of a Nitro Group through Transfer Hydrogenation Catalysed by Ru^0-Nanoparticles Stabilized on Modified Montmorillonite Clay. *Green Chem.* **2012**, *14*, 1086−1093.

(721) Cheng, T.-Y.; Zhuang, J.-L.; Yao, H.; Zhang, H.-S.; Liu, G.-H. Immobilization of Chiral Rh Catalyst on Glass and Application to Asymmetric Transfer Hydrogenation of Aryl Ketones in Aqueous Media. *Chin. Chem. Lett.* **2014**, *25*, 613−616.

(722) Neelakandeswari, N.; Sangami, G.; Emayavaramban, P.; Babu, S. G.; Karvembub, R.; Dharmaraj, N. Preparation and Characterization of Nickel Aluminosilicate Nanocomposites for Transfer Hydrogenation of Carbonyl Compounds. *J. Mol. Catal. A: Chem.* **2012**, *356*, 90−99.

(723) Long, J.; Zhou, Y.; Li, Y. Transfer Hydrogenation of Unsaturated Bonds in the Absence of Base Additives Catalyzed by a Cobalt-Based Heterogeneous Catalyst. *Chem. Commun.* **2015**, *51*, 2331−2334.

(724) List, B. Introduction: Organocatalysis. *Chem. Rev.* **2007**, *107*, 5413−5415.

(725) Gaunt, M. J.; Johansson, C. C. C. Recent Developments in the Use of Catalytic Asymmetric Ammonium Enolates in Chemical Synthesis. *Chem. Rev.* **2007**, *107*, 5596−5605.

(726) Bertelsen, S.; Jorgensen, K. A. Organocatalysis—after the Gold Rush. *Chem. Soc. Rev.* **2009**, *38*, 2178−2189.

(727) Zeng, G.; Maeda, S.; Taketsugu, T.; Sakaki, S. Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or $\mathrm{P^{III}}/\mathrm{P^{V}}$ Redox Pathway? *Angew. Chem., Int. Ed.* **2014**, *53*, 4633−4637.

(728) Chong, C. C.; Hirao, H.; Kinjo, R. A Concerted Transfer Hydrogenolysis: 1,3,2-Diazaphospholene-Catalyzed Hydrogenation of N═N Bond with Ammonia−Borane. *Angew. Chem., Int. Ed.* **2014**, *53*, 3342−3346.

(729) Fujita, S.; Watanabe, H.; Katagiri, A.; Yoshida, H.; Arai, M. Nitrogen and Oxygen-Doped Metal-Free Carbon Catalysts for Chemoselective Transfer Hydrogenation of Nitrobenzene, Styrene, and 3-Nitrostyrene with Hydrazine. *J. Mol. Catal. A: Chem.* **2014**, *393*, 257−262.

(730) Ikhile, M. I.; Nyamori, V. O.; Bala, M. D. Transition Metal Free Transfer Hydrogenation of Ketones Promoted by 1,3-Diarylimidazolium Salts and KOH. *Tetrahedron Lett.* **2012**, *53*, 4925−4928.

(731) Chatterjee, I.; Oestreich, M. $B(C_6F_5)_3$-Catalyzed Transfer Hydrogenation of Imines and Related Heteroarenes Using Cyclohexa-1,4-dienes as a Dihydrogen Source. *Angew. Chem., Int. Ed.* **2015**, *54*, 1965−1968.

(732) Ferry, A.; Stemper, J.; Marinetti, A.; Voituriez, A.; Guinchard, X. Thiophostone-Derived Brønsted Acids in the Organocatalyzed Transfer Hydrogenation of Quinolines: Influence of the P-Stereogenicity. *Eur. J. Org. Chem.* **2014**, 188−193.

(733) Martinelli, E.; Vicini, A. C.; Mancinelli, M.; Mazzanti, A.; Zani, P.; Bernardi, L.; Fochi, M. Catalytic Highly Enantioselective Transfer Hydrogenation of Beta-Trifluoromethyl Nitroalkenes. An Easy and General Entry to Optically Active Beta-Trifluoromethyl Amines. *Chem. Commun.* **2015**, *51*, 658−660.

(734) Shibata, Y.; Yamanaka, M. DFT Study of the Mechanism and Origin of Enantioselectivity in Chiral BINOL-Phosphoric Acid Catalyzed Transfer Hydrogenation of Ketimine and α-Imino Ester Using Benzothiazoline. *J. Org. Chem.* **2013**, *78*, 3731−3736.

(735) Zhu, C.; Saito, K.; Yamanaka, M.; Akiyama, T. Benzothiazoline: Versatile Hydrogen Donor for Organocatalytic Transfer Hydrogenation. *Acc. Chem. Res.* **2015**, *48*, 388−398.

(736) Saito, K.; Horiguchi, K.; Shibata, Y.; Yamanaka, M.; Akiyama, T. Chiral Phosphoric-Acid-Catalyzed Transfer Hydrogenation of Ethyl Ketimine Derivatives by Using Benzothiazoline. *Chem.—Eur. J.* **2014**, *20*, 7616−7620.

(737) Saito, K.; Shibata, Y.; Yamanaka, M.; Akiyama, T. Chiral Phosphoric Acid-Catalyzed Oxidative Kinetic Resolution of Indolines Based on Transfer Hydrogenation to Imines. *J. Am. Chem. Soc.* **2013**, *135*, 11740−11743.

(738) Aillerie, A.; de Talancé, V. L.; Moncomble, A.; Bousquet, T.; Pélinski, L. Enantioselective Organocatalytic Partial Transfer Hydrogenation of Lactone-Fused Quinolines. *Org. Lett.* **2014**, *16*, 2982−2985.

(739) Rueping, M.; Stoeckel, M.; Sugiono, E.; Theissmann, T. Asymmetric Metal-Free Synthesis of Fluoroquinolones by Organocatalytic Hydrogenation. *Tetrahedron* **2010**, *66*, 6565−6568.

(740) Wang, Z.; Ai, F.; Wang, Z.; Zhao, W.; Zhu, G.; Lin, Z.; Sun, J. Organocatalytic Asymmetric Synthesis of 1,1-Diarylethanes by Transfer Hydrogenation. *J. Am. Chem. Soc.* **2015**, *137*, 383−389.

(741) Rueping, M.; Sugiono, E.; Steck, A.; Theissmann, T. Synthesis and Application of Polymer-Supported Chiral Brønsted Acid Organocatalysts. *Adv. Synth. Catal.* **2010**, *352*, 281−287.

(742) Patil, N. T.; Raut, V. S.; Tella, R. B. Enantioselective Cooperative Triple Catalysis: Unique Roles of Au(I)/amine/chiral Brønsted Acid Catalysts in the Addition/Cycloisomerization/Transfer Hydrogenation Cascade. *Chem. Commun.* **2013**, *49*, 570−572.

(743) Saito, K.; Kajiwara, Y.; Akiyama, T. Chiral Copper(II) Phosphate Catalyzed Enantioselective Synthesis of Isochromene Derivatives by Sequential Intramolecular Cyclization and Asymmetric Transfer Hydrogenation of *o*-Alkynylacetophenones. *Angew. Chem., Int. Ed.* **2013**, *52*, 13284−13288.

(744) Chen, C.; Feng, H.-X.; Li, Z.-L.; Cai, P.-W.; Liu, Y.-K.; Shan, L.-H.; Zhou, X.-L. A Highly Efficient Route to C-3 Alkyl-Substituted Indoles via a Metal-Free Transfer Hydrogenation. *Tetrahedron Lett.* **2014**, *55*, 3774−3776.

(745) Kilica, A.; Kayan, C.; Aydemir, M.; Durap, F.; Durgun, M.; Baysal, A.; Tas, E.; Gümgüm, B. Synthesis of New Boron Complexes: Application to Transfer Hydrogenation of Acetophenone Derivatives. *Appl. Organomet. Chem.* **2011**, *25*, 390−394.

(746) Kilic, A.; Aydemir, M.; Durgun, M.; Meriç, N.; Ocak, Y. S.; Keles, A.; Temel, H. Fluorine/Phenyl Chelated Boron Complexes: Synthesis, Fluorescence Properties and Catalyst for Transfer Hydrogenation of Aromatic ketones. *J. Fluorine Chem.* **2014**, *162*, 9−16.

(747) Schneider, J. F.; Falk, F. C.; Fröhlich, R.; Paradies, J. Planar-Chiral Thioureas as Hydrogen-Bond Catalysts. *Eur. J. Org. Chem.* **2010**, 2265−2269.

(748) Schneider, J. F.; Lauber, M. B.; Muhr, V.; Kratzer, D.; Paradies, J. Readily Available Hydrogen Bond Catalysts for the Asymmetric Transfer Hydrogenation of Nitroolefins. *Org. Biomol. Chem.* **2011**, *9*, 4323−4327.

(749) Ebner, C.; Pfaltz, A. Chiral Dihydrobenzo[1,4]oxazines as Catalysts for the Asymmetric Transfer-Hydrogenation of α,β-Unsaturated Aldehydes. *Tetrahedron* **2011**, *67*, 10287−10290.

(750) Ramachary, D. B.; Sakthidevi, R.; Reddy, P. S. Direct Organocatalytic Stereoselective Transfer Hydrogenation of Conjugated Olefins of Steroids. *RSC Adv.* **2013**, *3*, 13497−13506.

(751) Eddy, N. A.; Richardson, J. J.; Fenteany, G. The Effect of Lewis Acids on the Cycloaddition of 3,3,6-Trimethylcyclohex-5-ene-1,2,4-trione: Hydrogen Transfer versus Cycloaddition with Cyclopentadiene. *Eur. J. Org. Chem.* **2013**, 5041−5044.

(752) Ikhile, M. I.; Bala, M. D.; Nyamori, V. O.; Ngila, J. C. Application of Ferrocenylimidazolium Salts as Catalysts for the Transfer Hydrogenation of Ketones. *Appl. Organomet. Chem.* **2013**, *27*, 98−108.

(753) Radhakrishan, R.; Do, D. M.; Jaenicke, S.; Sasson, Y.; Chuah, G.-K. Potassium Phosphate as a Solid Base Catalyst for the Catalytic Transfer Hydrogenation of Aldehydes and Ketones. *ACS Catal.* **2011**, *1*, 1631−1636.

(754) Wang, D.; Deraedt, C.; Ruiz, J.; Astruc, D. Sodium Hydroxide-Catalyzed Transfer Hydrogenation of Carbonyl Compounds and Nitroarenes Using Ethanol or Isopropanol as Both Solvent and Hydrogen Donor. *J. Mol. Catal. A: Chem.* **2015**, *400*, 14−21.

(755) Yang, X.; Zhao, L.; Fox, T.; Wang, Z.-X.; Berke, H. Transfer Hydrogenation of Imines with Ammonia−Borane: A Concerted Double-Hydrogen-Transfer Reaction. *Angew. Chem., Int. Ed.* **2010**, *49*, 2058−2062.

(756) Yang, X.; Fox, T.; Berke, H. Facile Metal Free Regioselective Transfer Hydrogenation of Polarized Olefins with Ammonia Borane. *Chem. Commun.* **2011**, *47*, 2053−2055.

(757) Pieber, B.; Martinez, S. T.; Cantillo, D.; Kappe, C. O. In Situ Generation of Diimide from Hydrazine and Oxygen: Continuous-Flow Transfer Hydrogenation of Olefins. *Angew. Chem., Int. Ed.* **2013**, *52*, 10241−10244.

(758) Chen, T. Y.; Tsutsumi, R.; Montgomery, T. P.; Volchkov, I.; Krische, M. J. Ruthenium-Catalyzed C−C Coupling of Amino Alcohols with Dienes via Transfer Hydrogenation: Redox-Triggered Imine Addition and Related Hydroaminoalkylations. *J. Am. Chem. Soc.* **2015**, *137*, 1798−1801.

(759) Stone, S. D.; Lajkiewicz, N. J.; Whitesell, L.; Hilmy, A.; Porco, J. A. Biomimetic Kinetic Resolution: Highly Enantio- and Diastereoselective Transfer Hydrogenation of Aglain Ketones To Access Flavagline Natural Products. *J. Am. Chem. Soc.* **2015**, *137*, 525−530.

(760) Soldevila-Barreda, J. J.; Romero-Canelon, I.; Habtemariam, A.; Sadler, P. J. Transfer Hydrogenation Catalysis in Cells as a New Approach to Anticancer Drug Design. *Nat. Commun.* **2015**, DOI: 10.1038/ncomms7582.

(761) Bolje, A.; Hohloch, S.; van der Meer, M.; Kosmrlj, J.; Sarkar, B. $\mathrm{Ru^{II}}$, $\mathrm{Os^{II}}$, and $\mathrm{Ir^{III}}$ Complexes with Chelating Pyridyl−Mesoionic Carbene Ligands: Structural Characterization and Applications in Transfer Hydrogenation Catalysis. *Chem. Eur. J.* **2015**, *21*, 6756−6764.

(762) Scholz, D.; Aellig, C.; Mondelli, C.; Pérez-Ramírez, J. Continuous Transfer Hydrogenation of Sugars to Alditols with

Bioderived Donors over Cu–Ni–Al Catalysts. *ChemCatChem* **2015**, *7*, 1551–1558.

(763) Hou, R.; Lan, X.; Wang, T. Selective Hydrogenation of Acetylene on Pd/SiO_2 in Bulk Liquid Phase: A Comparison with Solid Catalyst with Ionic Liquid Layer (SCILL). *Catal. Today* **2015**, *251*, 47–52.

(764) Jagadeesh, R. V.; Natte, K.; Junge, H.; Beller, M. Nitrogen-Doped Graphene-Activated Iron-Oxide-Based Nanocatalysts for Selective Transfer Hydrogenation of Nitroarenes. *ACS Catal.* **2015**, *5*, 1526–1529.

(765) Zhang, Y.; Zhao, R.; Bao, R. L.-Y.; Shi, L. Highly Enantioselective SPINOL-Derived Phosphoric Acid Catalyzed Transfer Hydrogenation of Diverse C=N-Containing Heterocycles. *Eur. J. Org. Chem.* **2015**, 3344–3351.

NOTE ADDED IN PROOF

Major contributions to the field of transfer hydrogenation have appeared since this paper was submitted concerning Ru, Os, and Ir complexes catalysts with chelating pyridyl–mesoionic carbene ligands,[761] Cu–Ni–Al catalysts,[762] SiO_2-immobilized Pd catalysts,[763] nitrogen-doped graphene-activated iron-oxide-based nanocatalysts,[764] and 1,1′-spirobiindane-7,7′-diol (SPINOL)-derived phosphoric acid catalysts.[765]

DOI: 10.1021/acs.chemrev.5b00203
Chem. Rev. XXXX, XXX, XXX–XXX