Asymmetric Hydrogenation of Imines via Metal–Organo Cooperative Catalysis

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Received: 19.01.2014; Accepted after revision: 12.02.2014

Abstract: The combination of a chiral phosphoric acid with an iridium complex affords a catalyst that allows for highly enantioselective hydrogenation of imines. Mechanistic studies suggest that the hydrogenation proceeds through a ternary transition state at the hydride-transfer step, in which the organocatalyst interacts with both the hydride donor and acceptor.

Key words: asymmetric hydrogenation, Brønsted acids, iridium, cooperative catalysis, imines, amines

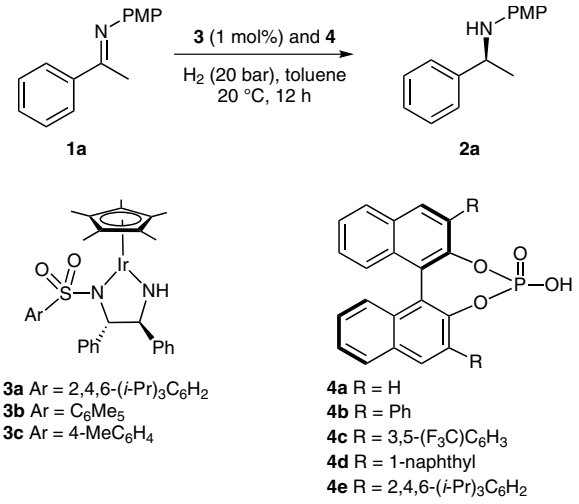
Weijun Tang completed his Ph.D. in 2008 at the Hong Kong Polytechnic University under the supervision of Professors Albert Chan and Qinghua Fan (ICCAS). After postdoctoral appointments with Professors Albert Chan, Jianliang Xiao and Guocheng Jia (HKUST), he was appointed Associate Professor at Shaanxi Normal University in 2013. His research interest is mainly in asymmetric catalysis.
Jianliang Xiao received his Ph.D. in organometallic chemistry under the supervision of Professor Martin Cowie. After a postdoctoral appointment with Professor Richard Puddephatt, he joined the ERATO Molecular Catalyst Project directed by Professor Noyori. In 1996 he took up a principal scientist position at the University of Liverpool, rising to professor of catalysis in 2005. He was awarded the UK Prize for Process Chemistry Research 2008 and the Chang-Jiang Chair Professor for Collaborative Research at Shaanxi Normal University. His research is concerned with the design, assembly and understanding of molecular architectures that act as catalysts for sustainable chemical synthesis.

Over the past few decades, the preparation of chiral amines has attracted a great deal of attention because of their importance in fine chemical, agrochemical and pharmaceutical products.[1] Among the approaches reported so far, the atom-economic, transition-metal-catalyzed asymmetric reduction with hydrogen gas is one of the most efficient and convenient methods.[2,3] However, in contrast to the great success enjoyed in the asymmetric hydrogenation of olefins and ketones,[4] imines are more challenging. This may be due to the poisoning effect of the substrate and product on the catalysts and/or the formation of *E*/*Z* isomeric mixtures of imines. Nonetheless, a variety of chiral transition-metal catalysts have been exploited for the asymmetric hydrogenation of imines, with well-known examples including chiral phosphine– and chiral diamine–metal complexes.[1–3] Apart from the transition-metal-catalytic systems, organo–Brønsted acids have been demonstrated to be highly enantioselective catalysts for transfer hydrogenation of imines with Hantzsch esters by the groups of List, Rueping and MacMillan.[5,6] In such an organocatalytic reduction, the imine is protonated by a chiral phosphoric acid, with the resulting chiral anion directing the facial attack of the hydride at the iminium cation. However, deriving the hydride from a Hantzsch ester and generating pyridine derivatives as a byproduct limit the application of these reactions. It is still highly desirable to have more economic and efficient catalytic systems capable of highly enantioselective reduction of imino bonds, particularly those attached to alkyl groups.

Recently, the combination of transition-metal complexes with organocatalysts has become one of the most active and exciting topics in catalysis.[7] Such combinations may allow for reactivity and selectivity patterns that are inaccessible within the individual field of homogeneous or organo catalysis. Many excellent examples have appeared in the literature, testifying to this assertion.[7] Over the past few years, part of our research has concentrated on developing better catalysts for imino reduction.[8] One of the strategies we pursued was to exploit metal–organo cooperative catalysis to benefit asymmetric imine hydrogenation. Herein, we provide a brief account of our recent work in this aspect.

In 2008, we found that a chiral rhodium(III) complex, [Cp*Rh(TsDPEN–H)(H_2O)][SbF_6], demonstrated excellent catalytic ability in asymmetric hydrogenation of cyclic imines.[9] It is, however, ineffective for the reduction of acyclic imines. For example, it only afforded 3% ee in the asymmetric hydrogenation of the model substrate 4-methoxy-*N*-(1-phenylethylidene)benzenamine (**1a**). Changing the metal from rhodium to iridium led to a higher ee of 22%.[10] Considering the ability of chiral phosphoric acids in inducing asymmetry in transfer hydrogenation of acyclic imines with organic hydride donors,[5,6] we then ex-

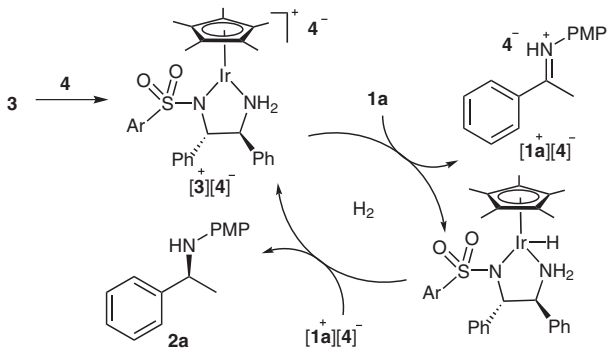
SYNTHESIS 2014, 46, 1297–1302
Advanced online publication: 14.03.2014
DOI: 10.1055/s-0033-1338603; Art ID: SS-2014-C0049-SR



Scheme 1 Asymmetric hydrogenation of imines by combining a chiral iridium catalyst with a chiral phosphoric acid

plored a variety of phosphoric acids in the iridium-catalyzed hydrogenation (Scheme 1).

Combination of **4** with **3** led to the protonation of the latter, turning it from an inactive neutral complex into a catalytically active cation. In particular, combining the 16e complex **3a** (1 mol%) with the chiral phosphoric acid **4e** (2 mol%) afforded **2a** in 94% yield and 97% ee under the hydrogenation conditions shown in Scheme 1.[11] The reduction was thought to proceed through an ionic pathway,[12] involving metal–organo cooperative catalysis as a key element in the catalytic cycle (Scheme 2). The iridium–phosphate complex activates H_2, resulting in the formation of the Ir(III)–H hydride and protonated **1a**. The phosphate anion pairs with the iminium cation, thereby influencing the face-selective addition of the hydride to the imino C=N bond. Indeed, dramatic changes in enantioselectivities (from 17% to 97% ee values) and reversal of the configuration of the amine product (**4a**, **4b**: *R*-product; **4c**–**e**: *S*-product) were observed on altering the steric bulk of the chiral phosphoric acids or the configuration of the diamine ligand (Scheme 1), showing the chirality of the metal catalyst needs to match that of its counteranion. On the basis of our more recent study, the hydride-transfer



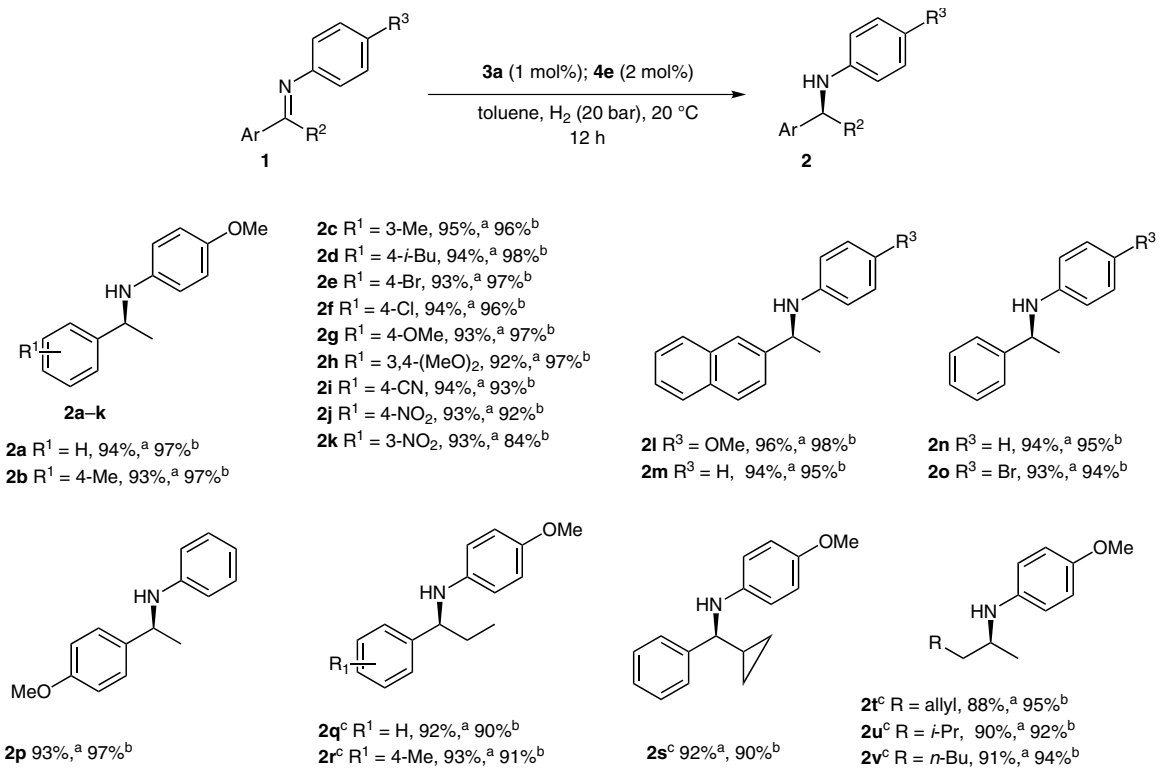
Scheme 2 Proposed mechanism for the asymmetric hydrogenation catalyzed by **3**–**4** (**4**$^-$ = **4** – H)

step in Scheme 2 is likely to involve complex interactions between the phosphate, the hydride and the iminium cation, with the former hydrogen-bonding with the latter two species.

Using the **3a**–**4e** combination as catalyst, a series of acyclic imines **1** were hydrogenated and the results are summarized in Scheme 3. As can be seen, the imines were successfully hydrogenated via this cooperative catalytic system, affording excellent yields and enantioselectivities. Of particular note are the aliphatic imines **1t**–**v**, which yielded the corresponding amines **2t**–**v** with up to 95% ee. It is also worth noting that the catalyst tolerates various functional groups.

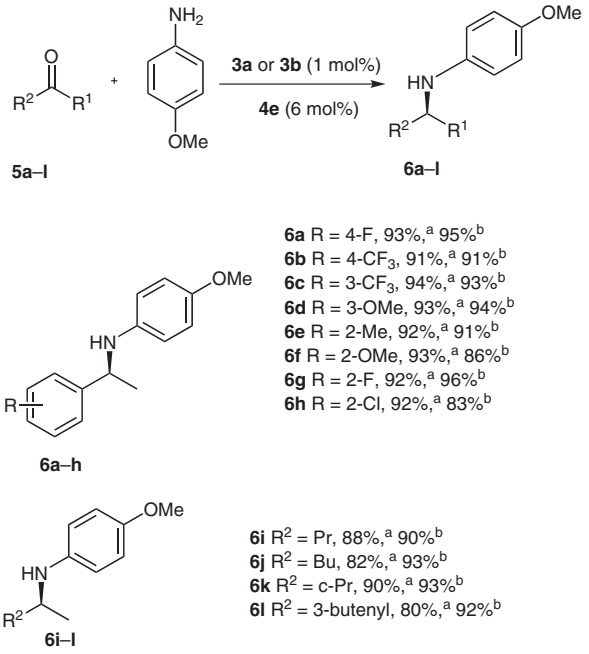
With the success in asymmetric hydrogenation of acyclic imines, we next turned our attention to direct asymmetric reductive amination (DARA) of prochiral ketones.[13] Since isolated imines are not always easy to synthesize due to their instability, it is more convenient and economical to prepare chiral amines by way of DARA. Delightfully, the iridium–phosphoric acid combination was also effective for DARA. Selected examples are given in Scheme 4. A great variety of ketones, including aryl ketones **5a**–**h** with electron-donating or electron-withdrawing groups and aliphatic ketones **5i**–**l**, were aminated via this reaction, affording >90% ee in general. This was the first report of a catalyst which is effective in the DARA of both aryl ketones and aliphatic ketones. The phosphoric acid plays multiple roles in the reaction, promoting the imine formation and its subsequent hydrogenation.[13a] The presence of the acid also suppresses the hydrogenation of ketones into alcohols, presumably due to its interaction with both the iminium cation and the catalyst, bringing the two into close proximity (see below). More recently, an excellent paper was reported by Zhao and co-workers,[14] who developed the first asymmetric amination of alcohols via cooperative catalysis coupled with hydrogen borrowing.

The success in the asymmetric hydrogenation of imines prompted us to search for a more efficient catalytic system. The importance of the chiral Brønsted acid and the chirality match between the metal catalyst and acid suggested to us that it might be possible to combine a *chiral* organocatalyst with an *achiral* metal catalyst, or vice versa, for highly enantioselective hydrogenation.[15] The chiral phosphate would be expected to form ion pairs with the protonated imine, and when approaching an achiral metal hydride, face discrimination could occur, leading to enantioselective hydride delivery. This appeared to be feasible, since chiral phosphoric acids had been demonstrated to be able to induce the enantioselective attack of an achiral organic hydride at an imine by hydrogen bonding.[16] We therefore set out in 2008 to examine the appropriate chiral–achiral combinations, initially focusing on asymmetric imine hydrogenation.[15a] While our research was in progress, Rueping[17] and Beller[3k] and their co-workers reported in 2011 on the combination of chiral organocatalysts with achiral metal catalysts for the asymmetric hydrogenation of quinolines and imines, respectively.



Scheme 3 Examples of hydrogenation with **3**–**4**. *Reagents and conditions*: **1** (0.5 mmol), **3a** (1 mol%), **4e** (2 mol%), toluene (2 mL), H_2 (20 bar), 20 °C, 12 h. [a] Isolated yield. [b] Enantioselectivity, determined by HPLC. [c] **3b** was used as the catalyst.

After a great deal of trial and error, we were able to identify a class of easily accessible achiral [Cp*Ir(diamine)] complexes **C** (Figure 1), which, when combined with chiral phosphoric acids **4**, give rise to high enantioselectivity in the asymmetric hydrogenation of acyclic imines.[18,19] Our endeavor revealed that the R^1 substituent on the ethylenediamine ligand plays a critical role in the asymmetric induction. For example, the combination of $\mathbf{C_1}$ (1 mol%) and **4e** (2 mol%) led to only 50% ee and 10% conversion in the hydrogenation of **1a**. In sharp contrast, full conversion and 97% ee were obtained by replacing $\mathbf{C_1}$ with $\mathbf{C_3}$ or $\mathbf{C_4}$.



Scheme 4 Examples of DARA. *Reagents and conditions*: **5** (0.6 mmol), *p*-anisidine (0.5 mmol), **3a** (1 mol%, for **5a**–**h**) or **3b** (1 mol%, for **5i**–**l**), **4e** (6 mol%), toluene (2 mL), 4 Å MS (200 mg), H_2 (5 bar), 35 °C, 15–24 h. [a] Isolated yield. [b] Enantioselectivity, determined by HPLC.

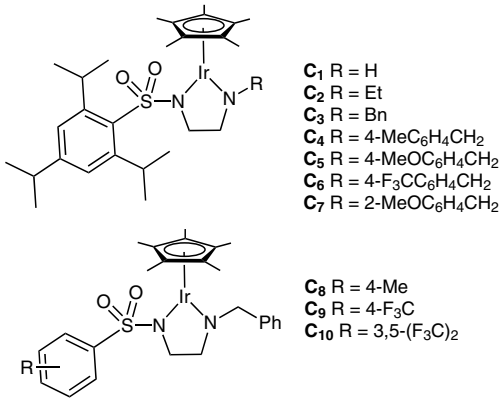
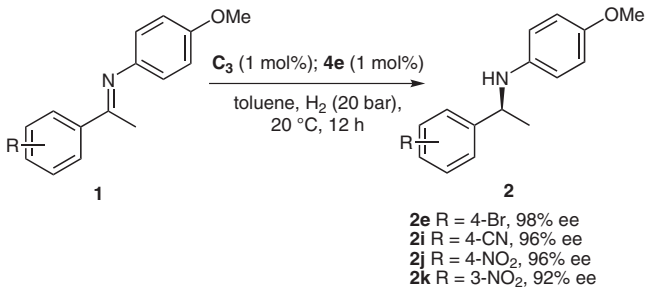


Figure 1 Achiral [Cp*Ir(diamine)] complexes examined for the achiral–chiral combinations

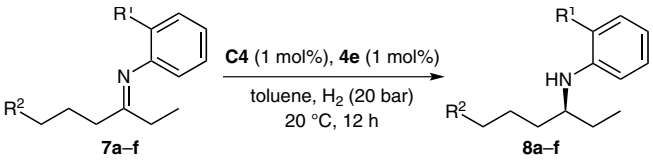
A wide range of imines were hydrogenated with $\mathbf{C_3}$–**4e** or $\mathbf{C_4}$–**4e**. The enantioselectivities obtained were similar to those achieved with the chiral combination (Scheme 3).

There are, however, examples where the achiral–chiral couple gave significantly higher ee values, particularly for some imines bearing electron-withdrawing substituents (Scheme 5).



Scheme 5 Selected examples of asymmetric hydrogenation with $\mathbf{C_3}$–**4e**

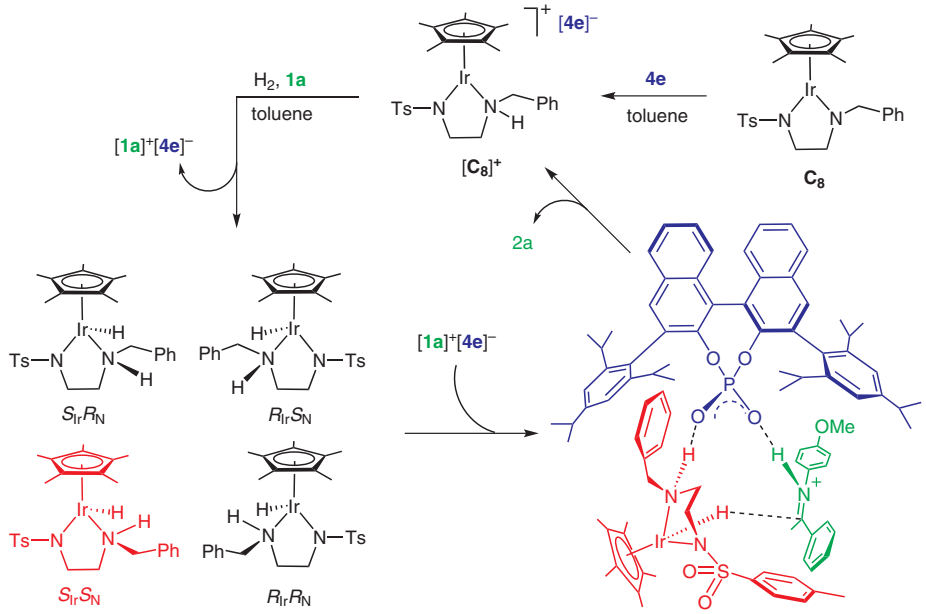
The advantage of the achiral–chiral combination is further illustrated in the asymmetric hydrogenation of more challenging aliphatic ketone-derived imines. Selected examples obtained with the $\mathbf{C_4}$–**4e** catalyst are found in Scheme 6. As can be seen, the catalyst is capable of discriminating an ethyl group from a butyl or a propyl group in a highly enantioselective manner. However, the enantioselectivity decreased progressively when the R^1 substituent in the imine **7** was moved from the *ortho* to the *meta* and then the *para* position.



Scheme 6 Examples of asymmetric hydrogenation of alkyl imines. *Reagents and conditions*: **7** (0.15 mmol), $\mathbf{C_4}$ (1 mol%), **4e** (1 mol%), toluene (0.7 mL), H_2 (20 bar), 20 °C, 12 h. [a] Isolated yield. [b] Enantioselectivity, determined by HPLC.

It should be mentioned that although this achiral–chiral catalytic system affords better results than those with the chiral–chiral combination, it is not efficient in the DARA of ketones under the conditions employed. The reason is not immediately clear; but, the turnover may be limited by the step of imine formation.

We expended a lot of effort in order to gain insight into the mechanism of this achiral–chiral catalytic system, aiming in particular to answer the question: how was the asymmetry induced by, or how did the chirality transfer from, the chiral organocatalyst? Detailed studies were carried out with the model hydrogenation of **1a** by $\mathbf{C_8}$ and **4e**. By using high-pressure 2D-NMR spectroscopy, diffusion measurements, and NOE-constrained computation, we were able to show that the reaction of H_2 with the iridium(III)–chiral phosphate complex is nonstereoselective, affording all four possible Ir–H hydrides, and it is the hydride-transfer step that determines the enantioselectivity observed (Scheme 7). We concluded that a ternary transition state is likely to be formed in the hydride-transfer step, which is responsible for the enantioselective hydride transfer, and that out of the four isomeric hydrides, it is the minor *cis*-$S_{Ir}S_N$-isomer that forms the productive ternary complex with the phosphate and an iminium cation, through which the imino bond is reduced. DFT/PM6 modeling indicates that the phosphate binds to both the *cis*-$S_{Ir}S_N$-isomer and the iminium cation $[\mathbf{1a}]^+$ through hydro-



Scheme 7 Mechanism showing how the chiral organocatalyst **4e** induces asymmetry in the hydrogenation of imine **1a** with the achiral iridium catalyst $\mathbf{C_8}$

gen bonding and CH π-interactions, allowing the hydride to add only to the *re*-face of the imino bond (Scheme 7).[19]

Whilst the chiral phosphate is highly effective in chirality relay, it is worth noting that its bulkiness retards the hydride transfer and hence the reaction rate. We also showed that in the absence of an imine substrate, the benzyl group in the cationic iridium catalyst undergoes cyclometalation with the iridium atom, forming a catalytically inactive complex.[18]

In summary, we have developed an efficient methodology for the asymmetric hydrogenation of imino bonds. The success of the strategy hinges on the cooperative catalysis between a hydrogen-activating iridium complex and asymmetry-inducing chiral phosphate. Exactly how the cooperative catalysis occurs has been mapped out, with the phosphate being shown to interact *selectively* with both the hydride donor and acceptor at the transition state of hydride transfer.

Acknowledgment

We are grateful to Drs Chaoqun Li, Steven Johnston, Barbara Villa-Marcos, Jon Iggo, Neil Berry, John Bacsa and Marie Phelan and to Prof. Luyun Lian for their contributions to our work. We also thank EPRSC for funding support on grant EP/G031444.

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