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[17] This discrepancy can be attributed to either unsuccessful chemical reaction in one or more of the library steps and/or poor ionization by MS, and serves as a reminder that encoding records the sequence of chemical reactions to which a bead is subjected, not the structure of the compound.
[18] The structures assigned to the 108 samples can be found in the Supporting Information.
[19] Supporting Information available: Representative encoding and decoding protocols, ^1H NMR spectroscopy, LC, and GC data, and full details of the partial library decoding.

Highly Enantioselective Hydrogenation of Acyclic Imines Catalyzed by Ir – f-Binaphane Complexes**

Denming Xiao and Xumu Zhang*

Dedicated to Professor K. Barry Sharpless on the occasion of his 60th birthday

Although great accomplishments have been achieved in the highly enantioselective hydrogenation of prochiral alkenes and ketones in the last few decades,[1] limited progress has been made in the asymmetric hydrogenation of imines.[2] A number of efficient asymmetric catalysts for the reduction of alkenes and ketones are ineffective for the hydrogenation of related imine compounds. Since chiral amines are important functionalities in many biologically active molecules, the development of practical methods for the hydrogenation of imines is extremely important in organic synthesis.

Among some notable achievements in the field, Buchwald and co-workers[3] have developed a chiral titanocene catalyst for the reduction of imines, and the system is highly effective for the hydrogenation of cyclic imines. A number of group VIII transition metal catalysts that bear chiral chelating phosphanes have been explored for the hydrogenation of imines, and these systems generally have a very limited substrate scope.[4, 5] The highly enantioselective hydrogenation of *N*-(phenylethylidene)aniline (89 % *ee*) and related imines by using an Ir – phosphaneoxazoline complex as the catalyst have been reported by Pfaltz and co-workers.[6] A significant industrial process that uses the Ir-catalyzed asymmetric hydrogenation of an *N*-arylimine (10^6 turnovers and 80 % *ee*) has been developed.[7] Despite these impressive advances, the lack of highly enantioselective and reactive catalysts with broad substrate scopes for the hydrogenation of imines is still a major problem in asymmetric catalysis. Herein we report a highly enantioselective hydrogenation of *N*-arylimines catalyzed by Ir complexes with a novel chiral ferrocene phosphane group and an important additive effect for the Ir-catalyzed asymmetric hydrogenation of imines.

Recently we made a chiral phosphane ligand, binaphane, and used it for the Rh-catalyzed highly enantioselective hydrogenation of enamides.[8] However, Rh and Ir complexes of chiral binaphane are not effective for the hydrogenation of imines. To alter the steric and electronic properties of the binaphane ligand, we envisioned that the introduction of a ferrocene backbone would be helpful. The new air-stable, chiral 1,1′-bisphosphanoferrocene (**1**; abbreviated as f-binaphane) was then prepared by using a similar route used in the synthesis of binaphane (Scheme 1).

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[**] This work was supported by a NIH grant and a Dreyfus Teaching-Scholar Award. We acknowledge a generous loan of precious metals from Johnson Mathey Inc. and a gift of chiral GC columns from Supelco.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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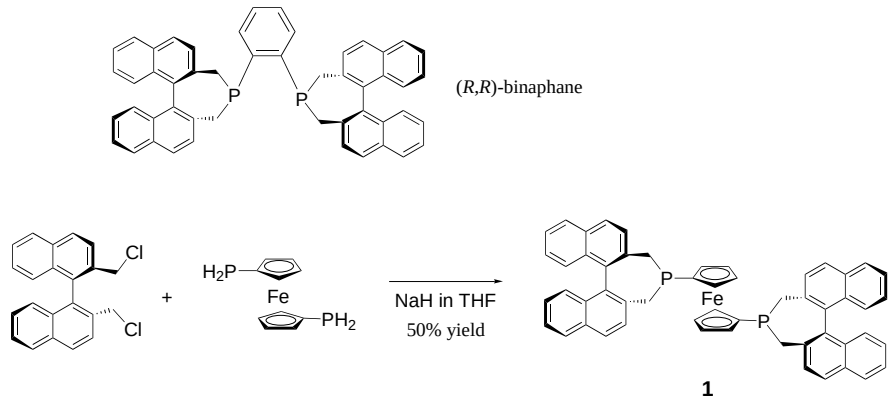


Scheme 1. (*R*,*R*)-Binaphane and (*R*,*R*)-f-binaphane (**1**).

Prior to our investigation, a number of effective chiral ligands with a ferrocene backbone were prepared and used for many asymmetric catalytic reactions.[9, 10] Based on these studies, we reason that there are many advantages of f-binaphane over the binaphane ligand: a) the low rotation barrier of the ferrocene backbone in f-binaphane offers flexibility, b) the bite angle of P-M-P is larger with the f-binaphane ligand than with the binaphane, c) the f-binaphane ligand is more electron donating than the binaphane ligand. We proposed that a strong electron back-donating ability from an Ir complex to an imine substrate is increased by the electron-donating f-binaphane ligand with a large P-Ir-P bite angle. The flexible ferrocene backbone of the f-binaphane can facilitate the binding of sterically demanding imines to the Ir center.

During the last two decades, several Ir–phosphane complexes were found to be active towards the hydrogenation of *N*-arylimines.[4, 6, 11] An advantage of many of these substrates is that the *E* isomers of the imines can be formed exclusively. If the *N*-aryl group can be removed at the end of reaction, it represents an attractive method for making chiral amines. The asymmetric hydrogenation of *N*-(1-phenylethylidene)aniline (**2a**) by using the Ir–f-binaphane complex as the catalyst showed promising results (Table 1, entry 1, 84% *ee*). Optimal conditions were found when **2a** was used as the substrate by screening catalyst precursors, solvents, and hydrogen pressures. The enantioselectivity with a neutral precursor $[\{Ir(cod)Cl\}_2]$ (cod = cycloocta-1,5-diene) was higher than that achieved with a cationic precursor $[Ir(cod)_2]PF_6$. The weak coordinating solvent CH_2Cl_2 was more desirable than other solvents such as THF, toluene, and methanol. A change in hydrogen pressure has no clear effect on the enantioselectivity, but the conversion was increased under high H_2 pressure. Interestingly, high enantioselectivity (>99% *ee*) was achieved when a new substrate **2b** with a 2,6-dimethyl-*N*-phenyl group was employed (Table 1, entry 2). With the sterically hindered 2,6-dimethyl-*N*-phenyl group, several *N*-arylimines were hydrogenated with high enantioselectivities (Table 1, entries 3 and 4). When the aryl group at the carbon terminal of the C=N bond was replaced with with an alkyl group, low enantioselectivities and reactivities were observed (Table 1, entries 5–7). Several other *N*-arylimines with a substituent at the *ortho* or *para* positions were hydrogenated with high conversions, albeit with low enantioselectivities (Table 1, entries 8 and 9).

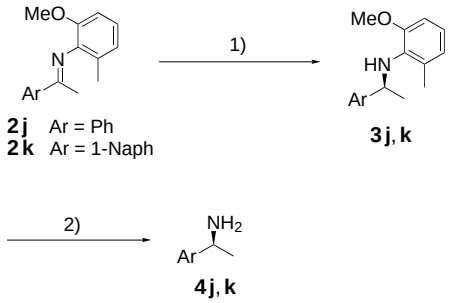
Table 1. Enantioselective hydrogenation of acyclic imines catalyzed by an Ir–f-binaphane complex.[a]

2a–j **3a–j**

Entry	Substrate	R	Ar′	*t* [h]	Conversion [%]	*ee* [%][b]
1	**2a**	Ph	Ph	40	100	84
2	**2b**	Ph	2,6-dimethyl-C_6H_3	44	77	>99
3	**2c**	4-MeO-C_6H_4	2,6-dimethyl-C_6H_3	44	77	98
4	**2d**	4-CF_3-C_6H_4	2,6-dimethyl-C_6H_3	44	80	99
5	**2e**	*t*Bu	2,6-dimethyl-C_6H_3	44	15	8
6	**2f**	*i*Pr	2,6-dimethyl-C_6H_3	44	29	23
7	**2g**	Cy	2,6-dimethyl-C_6H_3	44	24	31
8	**2h**	Ph	4-MeO-C_6H_4	12	100	77
9	**2i**	Ph	2-MeO-C_6H_4	14	100	81

[a] See Experimental Section for details. [b] Absolute configurations were not determined.

Although high enantioselectivities were achieved in the asymmetric hydrogenation of **2b**, the removal of the 2,6-dimethylphenyl group in the end product was difficult. Since the *ortho*-methoxy-substituted *N*-phenyl group can be cleaved with CAN (cerium ammonium nitrate), we selected *N*-arylimines with a 2-methyl-6-methoxyphenyl group as the preferred substrate for achieving high enantioselectivities and reactivities. Two substrates (**2j** and **2k**) were reduced smoothly and with high enantioselectivities to afford amines (Scheme 2). Based on this strategy, an efficient method of synthesizing chiral primary amines from *N*-arylimines has been realized.



Scheme 2. Synthesis of chiral amines. Reagents and conditions: 1) Ir–f-binaphane (1 mol%), CH_2Cl_2, RT, H_2 (1000 psi); 2) CAN, MeOH, H_2O; (*S*)-**4j** (72%, 98% *ee*), (*S*)-**4k** (75%, 96% *ee*).

The study of additive effects is important to achieve high reactivities and enantioselectivities in asymmetric catalysis. Inspired by the work of the Novartis group,[7] we investigated the additive effect in the asymmetric hydrogenation of acyclic imines (Table 2). Interestingly, different *N*-arylimines showed

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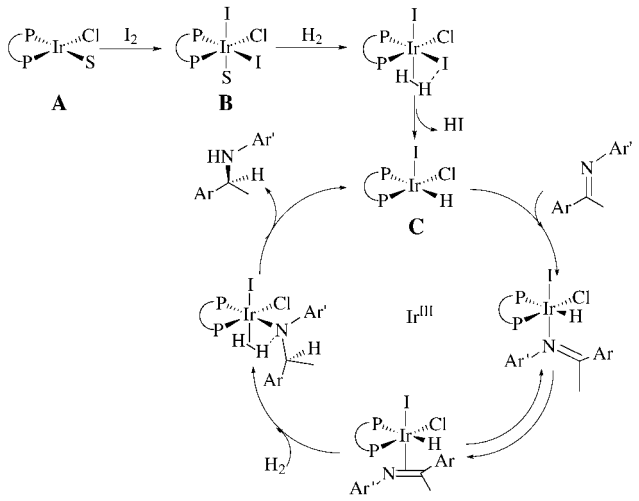
Table 2. Additive effect in Ir–f-binaphane-catalyzed hydrogenation of imines.[a]

Entry	Substrate	Additive	T [°C]	t [h]	Conversion [%]	*ee* [%][b]
1	**2a**	none	RT	40	100	84
2	**2a**	I_2 10%	RT	24	100	89
3	**2a**	I_2 10%	−5°C	24	100	94
4	**2h**	none	RT	24	100	77
5	**2h**	I_2 10%	RT	24	100	94
6	**2h**	I_2 10%	−5°C	24	100	95
7	**2b**	none	RT	24	64	98
8	**2b**	I_2 10%	RT	24	8	69

[a] See Experimental Section for details. [b] Absolute configurations were not determined.

different behaviors when I_2 was used as an additive. For *N*-(1-phenylethylidene)aniline (**2a**), the enantioselectivity increased from 84% *ee* (Table 2, entry 1) to 89% *ee* (Table 2, entry 2) when I_2 (10 mol%) was introduced as an additive, and an *ee* value of 94% was obtained at a lower temperature (Table 2, entry 3; −5°C). However, other common additives such as phthalimide, tetrabutylammonium iodide, and benzylamine have no effect on the enantioselectivity of the hydrogenation reaction of imines. A significant change in the enantioselectivity was observed in the hydrogenation of **2h** in the presence of I_2 (Table 2, entries 4 and 5; 77 to 94% *ee*). Since *p*-methoxyaniline is an inexpensive starting material for making *N*-*p*-methoxyphenyl-substituted aryl **2h**, and this group can be removed from the product by oxidation with CAN, the high yielding and enantioselective hydrogenation of **2h** is potentially a practical way of making chiral amines. Interestingly, the enantioselectivity of the hydrogenation reaction of a sterically hindered imine **2b** decreased from 98 to 69% *ee* and the conversion changed from 64 to 8% (Table 2, entries 7 and 8). Based on these observations, we conclude that the catalytic process with I_2 as an additive must differ from that without the additive.

Although the oxidative addition of H_2 to Ir^I to give Ir^{III} is a normal process for the hydrogenation of imines, Osborn and co-workers[11b] demonstrated that the Ir complex [{Ir^{III}(P–P)-HI_2}$_2$] facilitates the hydrogenation of *N*-arylimines, and that the Ir^{III} species remains in the same oxidation state in the catalytic cycle. They proposed that the heterolytic cleavage of H_2 by the Ir–N species can generate an amine and an Ir^{III}–H species. In the Novartis process for the synthesis of metolachlor, the addition of I_2 is critical in the hydrogenation of the imine. Through their mechanistic studies, investigators believe that the addition of I_2 leads to an Ir^{III}-catalyzed pathway.[7, 12] Although the situation is not exactly the same with our system, we speculate that the Ir^{III}-catalyzed hydrogenation of imines in the presence of I_2 as the additive is also possible (Scheme 3). The oxidative addition of I_2 to the Ir^I precursor **A** generates the Ir^{III} complex **B**. The heterolytic cleavage of H_2 can occur in the presence of an amine to form the Ir^{III}–H species **C**. An imine substrate can coordinate with **C** in a η^1 or η^2 fashion. Migratory insertion of the η^2-imine into the Ir^{III}–H bond forms an Ir^{III}–amide complex. The heterolytic cleavage of H_2 by the Ir^{III}–amide intermediate gives an amine and regenerates the Ir^{III}–H species **C**.[13]



Scheme 3. Proposed mechanism for the Ir–f-binaphane-catalyzed hydrogenation of imines. S = substrate or solvent.

In conclusion, a novel chiral ligand (f-binaphane) has been developed and high enantioselectivities (up to 99% *ee*) were achieved in the asymmetric hydrogenation of some acyclic *N*-arylimines. A mechanistic rationale was provided for the hydrogenation of imines with I_2 as the additive. Future work will focus on exploring the substrate scope of the imine hydrogenation with the Ir–f-binaphane complex and on the investigation of reaction mechanism.

Experimental Section

1: 1,1′-Bis(phosphano)ferrocene (1.32 g, 5.28 mmol) was added to a solution of (*R*)-2,2′-dichloromethyl-1,1′-binaphthyl[8] (3.71 g, 10.6 mmol) and NaH (2 g, 83 mmol) in THF (125 mL) at −78°C under nitrogen. The mixture was stirred at room temperature for 24 h, and then heated at reflux for 48 h. After the reaction was completed (monitored by ^{31}P NMR spectroscopy), the solvent was removed under vacuum, and the residue was washed with CH_2Cl_2 (3 × 25 mL). The organic phase was filtered through a silica-gel plug to give the crude product. Further purification by recrystallization from CH_2Cl_2/hexanes afforded **1** as an air-stable yellow solid (2.2 g, 50%). $[\alpha]_D^{20} = 160$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 360 MHz): $\delta =$ 8.07–7.99 (6H, m; Ar-H), 7.87–7.85 (2H, d, $J = 8.34$ Hz), 7.80–7.78 (2H, d, $J = 8.31$ Hz), 7.53–7.50 (4H, m; Ar-H), 7.31–7.28 (8H, m; Ar-H), 7.07–7.04 (2H, d, $J = 8.37$ Hz), 4.49 (2H, s; Cp-H), 4.45 (2H, s; Cp-H), 4.26 (2H, s; Cp-H), 3.56 (2H, s; Cp-H), 3.10–3.06 (2H, m; $ArCH_2$), 2.82–2.72 (4H, m; $ArCH_2$), 2.63–2.59 (2H, m; $ArCH_2$); ^{13}C NMR (CD_2Cl_2, 90 MHz): $\delta =$ 135.79, 135.18, 134.28, 133.57, 133.21, 133.05, 132.96, 132.67, 129.28, 129.00, 128.94, 128.10, 128.04, 127.29, 127.19, 126.58, 126.45, 125.73, 125.46, 76.22 (d, $J_{C,P} = 21.92$ Hz), 75.62 (d, $J_{C,P} = 32.00$ Hz), 72.43, 71.63, 71.14, 34.60 (d, $J_{C,P} = 20.90$ Hz), 31.36 (d, $J_{C,P} = 11.74$ Hz); ^{31}P NMR (CD_2Cl_2): $\delta = -1.26$; MS: m/z: 807 [M+H$^+$].

Hydrogenation of imines: The Ir–f-binaphane complex was made in situ by mixing [{Ir(cod)Cl}$_2$] (6.7 mg, 0.01 mmol) and **1** (17.7 mg, 0.022 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 30 min and then part of this solution (5 mL) was transferred into a 10-mL vial with an imine substrate (0.5 mmol). The hydrogenation was performed at room temperature under 1000 psi of hydrogen. After the reaction was finished, hydrogen was released carefully, and the reaction mixture was passed through a silica-gel plug with CH_2Cl_2 as eluent. Without further purification of the product, the enantiomeric excess was measured by using chiral GC with a Supelco chiral select 1000 column.

Received: February 19, 2001 [Z16641]

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Porous Polymer Films and Honeycomb Structures Made by the Self-Organization of Well-Defined Macromolecular Structures Created by Living Radical Polymerization Techniques**

Martina H. Stenzel-Rosenbaum, Thomas P. Davis,* Anthony G. Fane, and Vicki Chen

Macroporous polymers have become materials of high interest in recent years, because of their potential applications in diverse areas from membranes to medical devices.[1] Star and block polymers are known to template around water droplets to form isoporous arrays.[2–5] However, the utilization of this discovery has been severely restricted because the synthetic route used, anionic polymerization, is difficult and limited to a small number of (generally nonfunctional) monomers. A number of other synthetic routes to star polymers have become available in recent years,[6] and the development of living radical polymerization provides a great opportunity to significantly broaden the range of functional materials. We have adopted both metal-mediated radical polymerization and reversible addition–fragmentation transfer (RAFT) polymerization to synthesize star polymers for application in isoporous film and honeycomb-structure production. The porous structures are created from casting solutions of star polymers in an organic solvent onto a glass substrate under a humid atmosphere as described by Francois and co-workers.[4, 7, 8]

The star polymers were synthesized either by metal-mediated polymerization using a copper (atom-transfer radical polymerization, ATRP) or an iron catalyst system or by RAFT polymerization. Both types of polymerization require a multifunctional initiator, from which arm growth occurs. The preparation of 6-arm polystyrene stars by the RAFT process utilized hexakis(thiobenzoylthiomethyl) benzene (**1**) as an initiator.[9] The polymerization process is shown in Scheme 1.[10] The pseudo first-order reaction kinetics and molecular-weight development were both found to be consistent with a living radical polymerization process. This RAFT method yielded narrow polydispersity polystyrene stars with molecular weights of up to 400 000, and six arms, each with a thioester end group. One complication in this process is the parallel synthesis of a linear chain along with the star structure (Scheme 1).

ATRP/metal-mediated polymerization was also utilized to synthesize stars. Two different approaches were taken, both based on the application of sugar initiators. The first approach we took was based on the work of Haddleton and co-workers

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[**] We acknowledge a DAAD (German Academic Exchange Service) Scholarship (HSPIII) for Dr. M. H. Stenzel-Rosenbaum.

  1433-7851/01/4018-3428 $ 17.50+.50/0