Iron Catalysis

DOI: 10.1002/anie.201002456

Enantioselective Synthesis of Amines: General, Efficient Iron-Catalyzed Asymmetric Transfer Hydrogenation of Imines**

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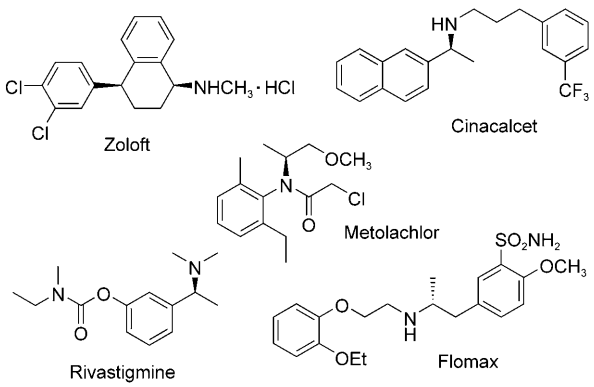
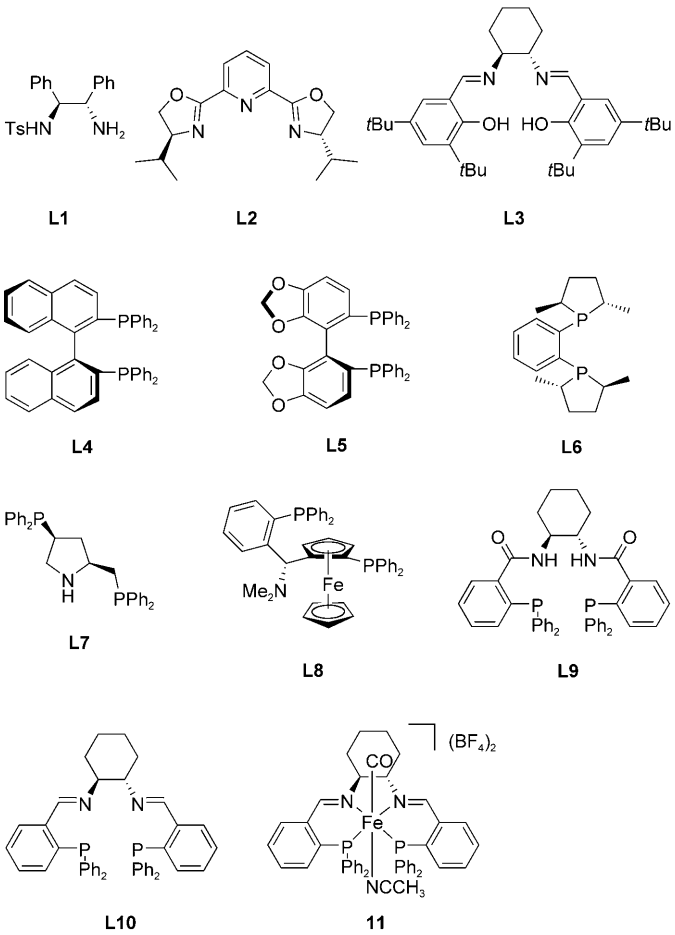
Chiral amines find numerous applications in the pharmaceutical and agrochemical industries. Notable examples of established drugs and their areas of application include Zoloft (depression), Cinacalcet (secondary hyperparathyroidism), Flomax (prostate), and Rivastigmine (Alzheimer's and Parkinson's disease) as well as the chiral herbicide Metolachlor (Scheme 1). The most direct and efficient synthesis of chiral amines is the asymmetric reduction of ketimines, an apparently simple but still challenging transformation.[1] Although in the last decades impressive advances have been made based on various transition-metal catalysts[2–9] and also organocatalysts,[10] the development of cost-efficient, environmentally benign catalysts for this transformation is still desirable. In this respect, iron-based catalysts are highly attractive candidates[11,12] owing to the abundant availability of the central metal and the relatively few investigations in the past.



Scheme 1. Selected chiral amines that are used as pharmaceuticals and agrochemicals.

Recently, significant progress has been achieved in iron-catalyzed enantioselective hydrosilylations[13] and transfer hydrogenations[14] of ketones to give the corresponding chiral alcohols. However, related asymmetric reductions of imines have remained an unexplored area so far. Herein, we report the first highly efficient iron-catalyzed asymmetric reduction of imines.

Morris and co-workers recently reported the synthesis of the well-defined catalyst [Fe(CO)(NCMe){(*S*,*S*)-cyP$_2$N$_2$}]-(BF$_4$)$_2$ (**11**; Scheme 2) and similar chiral iron complexes.[14c] Remarkably, these complexes give excellent results in the transfer hydrogenation of ketones and could be also successfully applied in the transfer hydrogenation of *N*-benzylideneaniline (Ph–CH=NPh). Unfortunately, no desired reaction occurred with prochiral *N*-(1-phenylethylidene)aniline (Ph–CMe=NPh).[14c] Inspired by this seminal work and based on our own experience in transfer hydrogenations, we started



Scheme 2. Structures of chiral ligands and iron complexes for asymmetric transfer hydrogenations.

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[**] This work was funded by the State of Mecklenburg-Western Pomerania, the BMBF, and the DFG (Leibniz prize). We thank Dr. W. Baumann, Dr. C. Fischer, S. Buchholz, S. Schareina, and A. Kammer, A. Koch, S. Rossmeisl, and K. Mevius for their excellent technical and analytical support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002456.

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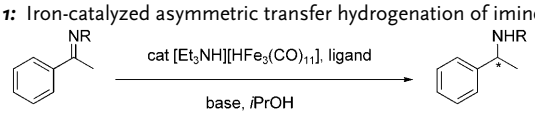
a program to develop iron catalysts for the enantioselective reduction of imines.

In exploratory studies different *N*-(1-phenylethylidene)-amines were tested with respect to their activity. Among the different substrates, (diphenylphosphinyl)(1-phenylethylidene)amine (**1a**) showed best reactivity. This class of imines is easily obtained as single isomers (*syn*/*anti*) from the corresponding oximes.[15] Advantageously, they are tolerant to air and moisture, and the removal of the phosphinyl group is conveniently achieved under acidic conditions. Selected experiments for the catalytic transfer hydrogenation of **1a** are outlined in Table 1. Here, several chiral ligands (Scheme 2) were tested with the iron carbonyl hydride cluster complex $[Et_3NH][HFe_3(CO)_{11}]$ as the catalyst precursor in the presence of KOH. Privileged chiral nitrogen and phosphorus ligands such as (*S*,*S*)-Ts-dpen (**L1**), (*R*)-pybox-*ip* (**L2**), (*S*,*S*)-Jacobsen ligand (**L3**), (*S*)-binap (**L4**), (*S*)-segphos (**L5**), (*S*,*S*)-Me-duphos (**L6**), (*2S*,*4S*)-ppm (**L7**), (*S*,*S*)-taniaphos (**L8**), and (*S*,*S*)-dach-phenyl Trost ligand (**L9**) did not show any appreciable activity. However, to our delight ligand **L10**, which was also used by Gao's group for the transfer hydrogenation of ketones,[16] showed excellent activity and enantioselectivity: 99% yield with 96% ee within 30 min (Table 1, entry 1)!

Next, the influence of critical reaction parameters, for example, temperature, base, and iron sources, was investigated. The reaction proceeded smoothly even at room temperature within 6 h giving the corresponding amine **2a** in 99% yield again with excellent enantioselectivity (96% *ee*) (Table 1, entry 2). In the absence of base, the reaction rate decreased and the *ee* value dropped to 42% (Table 1, entry 3). The type of base had no apparent effect on conversion or enantioselectivity (Table 1, entries 4 and 5). It is worth mentioning that even at lower catalyst loading (0.17 mol% Fe), excellent yield (95%), and enantioselectivity (96% *ee*) were obtained within 1 h (Table 1, entry 6). Control experiments confirmed that no amine **2a** was obtained in the absence of either iron source or ligand (Table 1, entries 7 and 8). Other iron complexes, for example $Fe_3(CO)_{12}$, led to only moderate enantioselectivities (55% *ee*; Table 1, entry 9). With respect to the active catalyst species, it is interesting to note that Morris' chiral iron complex **11** gave somewhat similar results. While the activity of this complex is somewhat higher, which can be explained by the faster preformation of the active species, the

Table 1: Iron-catalyzed asymmetric transfer hydrogenation of imines **1**.[a]



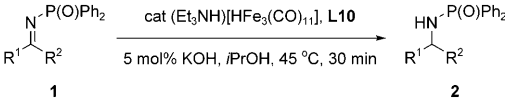
1 **2**

1a R = $P(O)Ph_2$; **1b** R = Ts; **1c** R = Ph

Entry	Imine	Ligand[b]	Base	Yield[c] [%]	*ee*[d] [%] (config.)[e]
1	**1a**	**L10**	KOH	99	96 (*R*)
2[f]	**1a**	**L10**	KOH	99	96 (*R*)
3[g]	**1a**	**L10**	–	90	42 (*R*)
4	**1a**	**L10**	NaO*t*Bu	99	96 (*R*)
5	**1a**	**L10**	NaO*i*Pr	99	96 (*R*)
6[h]	**1a**	**L10**	KOH	95	96 (*R*)
7[i]	**1a**	**L10**	KOH	n.r.	–
8	**1a**		KOH	n.r.	–
9[j]	**1a**	**L10**	KOH	93	55 (*R*)
10[k]	**1a**	**L11**	KOH	99	91 (*R*)
11	**1b**	**L10**	KOH	n.r.	–
12	**1c**	**L10**	KOH	n.r.	–

[a] Unless otherwise noted, the reaction was carried out with $[Et_3NH][HFe_3(CO)_{11}]$ (0.33 mol%), ligand (1 mol%), base (5 mol%), imine (0.5 mmol), *i*PrOH (10 mL) at 45 °C for 30 min. [b] For ligand structures see Scheme 2. [c] Determined by ^1H NMR analysis using dibromomethane as an internal standard. [d] Determined by HPLC on a chiral stationary phase. [e] Determined by comparison with reported data. [f] RT, 5.5 h. [g] 44 h. [h] 0.17 mol% catalyst. [i] No iron source. [j] 1 mol% $[Fe_3(CO)_{12}]$, 24 h. [k] 1 mol% **11**, 10 min. n.r. = no reaction.

Table 2: Scope of the iron-catalyzed asymmetric transfer hydrogenation of *N*-(diphenylphosphinyl)-imines.



1 **2**

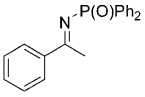
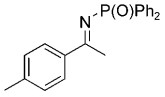
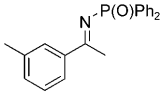
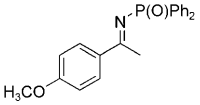
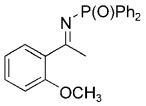
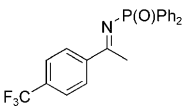
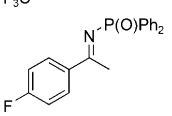
Entry	Imine		Catalyst [mol%]	Yield[a] [%]	*ee*[b] [%] (config.)[c]
1		**1a**	0.33	**2a** 87	96 (+)-(*R*)
2		**1d**	0.33	**2d** 87	96 (+)-(*R*)
3		**1e**	0.33	**2e** 95	97 (+)-(*R*)
4		**1f**	0.33	**2f** 94	96 (+)-(*R*)
5		**1g**	1.33	**2g** 94	96 (+)-(*R*)
6		**1h**	0.67	**2h** 85	95 (+)-(*R*)
7		**1i**	0.67	**2i** 94	96 (+)-(*R*)

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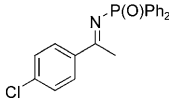
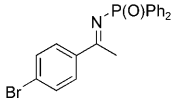
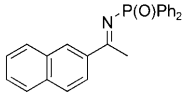
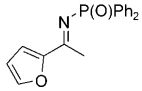
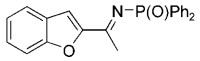
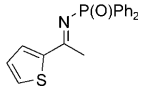
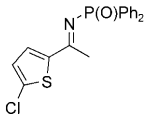
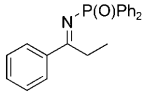
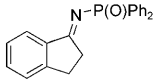
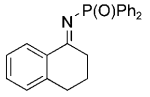
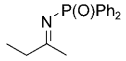
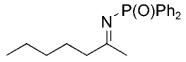
Table 2: (Continued)

Entry	Imine		Catalyst [mol%]	Yield[a] [%]	*ee*[b] [%] (config.)[c]
8		**1j**	0.67	**2j** 87	94 (+)-(*R*)
9		**1k**	0.67	**2k** 85	95 (+)-(*R*)
10		**1l**	0.33	**2l** 98	98 (+)-(*R*)
11		**1m**	1.0	**2m** 67	92 (+)-(*R*)
12		**1n**	0.67	**2n** 72	94 (+)-(*R*)
13		**1o**	1.0	**2o** 68	94 (+)-(*R*)
14		**1p**	0.67	**2p** 78	95 (+)-(*R*)
15		**1q**	0.67	**2q** 90	89 (+)-(*R*)
16		**1r**	1.33	**2r** 95	90 (+)-(*R*)
17		**1s**	1.33	**2s** 95	94 (+)-(*R*)
18[d]		**1t**	0.67	**2t** 62	39 (−)-(*R*)
19[d]		**1u**	0.67	**2u** 35	29 (−)-(*R*)

[a] Yield of isolated product. [b] Determined by HPLC on a chiral stationary phase. [c] Determined by comparison with reported data or by analogy. [d] Partial decomposition of imine to corresponding ketone and diphenylphosphinamide.

enantioselectivity was reproducibly lower (91% *ee*; Table 1, entry 10).

Once a suitable catalyst system was identified, the scope and limitations of our novel iron-catalyzed asymmetric transfer hydrogenation of *N*-(diphenylphosphinyl)ketimines were explored. A variety of ketimines, including aromatic, heteroaromatic, and cyclic imines were hydrogenated smoothly with high yields up to 98% and good to excellent enantioselectivities up to 98% *ee* (Table 2, entries 1–17). Both electron-donating and electron-withdrawing substituents on the aromatic ring at the *ortho*, *meta,* or *para* position had little impact on the enantioselectivity (94–97% *ee*; Table 2, entries 2–9). On the other hand, the steric hindrance of the substituent on the C=N bond had a significant effect on the activity, but only a little effect on the enantioselectivity (Table 2, entries 5, 15, and 16). For example, higher catalyst loading was needed for an effective conversion of **1g**, which bears a methoxy group at the *ortho* position, and no reduction was observed in the case of the corresponding isopropylphenylimine. In the latter case, decomposition to isobutyrophenone and diphenylphosphinamide was observed.

Gratifyingly, heteroaromatic imines were also reduced with excellent enantioselectivities (92–95% *ee*; Table 2, entries 11–14). Similarly, reduction of cyclic imines **1r** and **1s**, derived from 1-indanone and α-tetralone, was achieved with excellent enantioselectivities (90% and 94% *ee*) to afford α-aminoindane **2r** and α-aminotetralin **2s**, respectively (Table 2, entries 16 and 17). Both are important structural motifs in a number of biologically active compounds. Apart from acetophenone-type imines, also alkylidene(diphenylphosphinyl)amines can be reduced with our protocol, albeit lower activity and *ee* values were observed in preliminary studies (Table 2, entries 18 and 19).

In conclusion, we have developed the first iron-catalyzed asymmetric transfer hydrogenation of imines. Excellent enantioselectivities and high yields were observed for a variety of *N*-(diphenylphosphinyl)ketimines. Notable features of our protocol are the convenient formation of the active iron catalyst, the operational simplicity, and the safe and mild reaction conditions. This makes the new protocol attractive for various laboratory-scale applications. Further studies to improve the activity and enantioselectivity of aliphatic imines are in progress in our laboratory.

Experimental Section

General procedure for transfer hydrogenation imine **1a**: Ligand **L10** (3.3 mg, 0.005 mmol) and catalyst precursor $[Et_3NH][HFe_3(CO)_{11}]$ (0.96 mg, 0.0017 mmol) were dissolved in degassed 2-propanol in a 25 mL Schlenk tube under argon. After the solution had been stirred at room temperature for 20 min, KOH (0.5 mL, 0.05 M in *i*PrOH) was added and the solution was stirred for another 10 min. Then imine **1a** (160 mg, 0.5 mmol) was added to the catalyst solution and the reaction mixture was stirred at 45 °C for 30 min. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the

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corresponding amine **2a**, which was then analyzed by HPLC to determine the *ee* value.

Received: April 25, 2010
Published online: July 19, 2010

Keywords: asymmetric catalysis · enantioselectivity · imines · iron catalysis · transfer hydrogenation

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