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A Ferrocene-Based NH-Free Phosphine-Oxazoline Ligand for Iridium-Catalyzed Asymmetric Hydrogenation of Ketones

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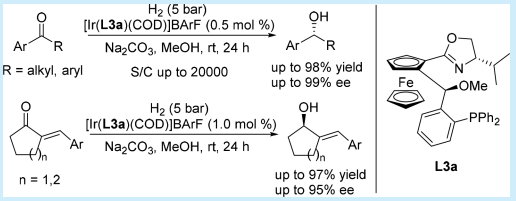
Supporting Information

ABSTRACT: A new type of ferrocene-based phosphine-oxazoline ligand has been prepared over a few simple steps. An iridium complex of this ligand is air stable and exhibits excellent performance for the asymmetric hydrogenation of simple ketones (up to 98% yield, up to 99% ee, and 20 000 S/C). *Exo*-α,β-unsaturated cyclic ketones could be regiospecifically hydrogenated to give chiral allylic alcohols with good results. This study indicates that P,N-ligands can also efficiently promote Ir-catalyzed asymmetric hydrogenation without NH-hydrogen-bonding assistance.



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Asymmetric hydrogenation employing chiral metal complexes is an efficient, economical, and environmentally benign methodology for the preparation of chiral compounds.[1] Chiral alcohols, being a class of versatile building block and important skeletons for pharmaceutical compounds, have attracted much attention from chemists.[2] The asymmetric hydrogenation of ketones is one of the most efficient methods for the preparation of chiral alcohols.[3] Since the pioneering work of Noyori's [$RuCl_2$(diphosphine)-(diamine)] catalytic system,[4] many chiral Ru-catalysts have been developed.[5] Over the past two decades, asymmetric hydrogenation using iridium catalysts has received much attention due to its high efficiency for the asymmetric hydrogenation of imines and unfunctionalized and weakly functionalized olefins.[6] However, iridium catalysis has not been widely employed in the asymmetric hydrogenation of ketones. In 2011, Kempe developed a phosphine-free amido-iridium complex for the asymmetric hydrogenation of ketones.[7] In the same year, the Zhou group divulged a SpiroPNP-Ir catalyst for such reactions, showing excellent enantioselectivities (up to 99.9% ee) and an extremely high TON for the hydrogenation of simple ketones.[8] Recently, several groups have developed ferrocene-based tridentate amino-phosphine ligands (such as f-Ampha) which exhibited excellent performance in the Ir-catalyzed asymmetric hydrogenation of simple ketones, affording chiral alcohols (full conversions, up to >99% ee) (Figure 1).[9] The high efficiency of these Ir catalysts relies on the assistance of the amino NH group of the chiral ligands (possibly via hydrogen bonding).

Chiral iridium complexes with phosphine-oxazoline ligands are commonly used for the asymmetric hydrogenation of olefins and imines,[6] but rarely for the asymmetric hydrogenation of ketones.[5g] We were interested in determining if phosphine-oxazoline is capable of promoting the asymmetric hydrogenation of simple ketones without the assistance of an amino group; thus, we tested several well-known phosphine-oxazoline ligands **L1** and related ligands **L2** that have been developed by our group. The results show that these

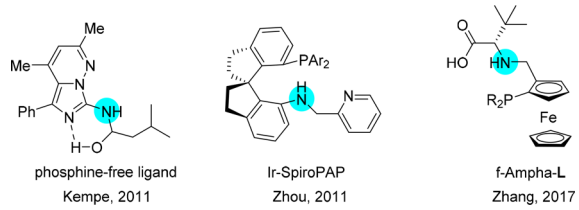

Figure 1. Examples of efficient and practical chiral ligands.

complexes are able to catalyze the asymmetric hydrogenation of ketones smoothly, albeit with somewhat low enantioselectivity (Figure 2, up to 60% ee, see below). We therefore

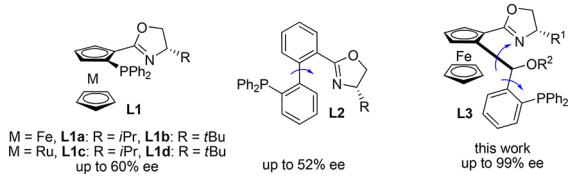

Figure 2. Examples of our group's phosphine-oxazoline ligands.

decided to design new phosphine-oxazoline ligands to enable this reaction. Since the ferrocene-based phosphine-oxazoline ligands showed the best catalytic activity, we chose ferrocene as the backbone to design our new ligand. Taking into account the design concept of axially unfixed ligands,[10] ease of preparation, and different coordinating ring size, we designed ligand **L3**. This ligand bears two flexible axes and, thus, possesses several potential configurations, allowing it to coordinate with a transition metal to form different complexes with different configurations. We propose that one of the possible Ir-complexes of **L3** can be formed predominantly as a

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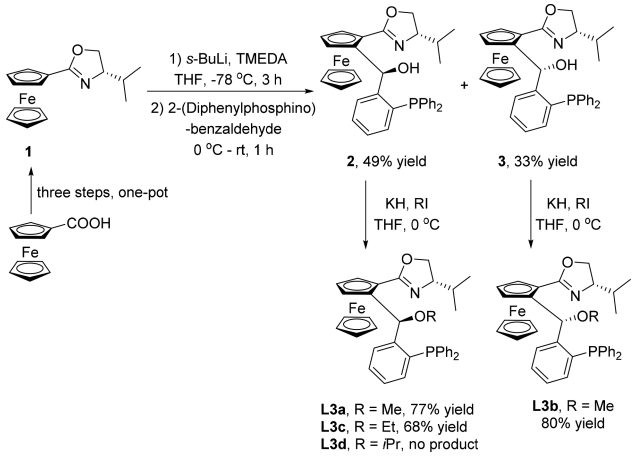
result of the chiral-inducing effect from the already present chiral elements. Herein, we report the design and preparation of a ferrocene-based phosphine-oxazoline ligand and its application in the iridium-catalyzed asymmetric hydrogenation of ketones.

Phosphine-oxazoline ligands **L3** were easily prepared via a simple synthetic route (Scheme 1). Starting from commercially

Scheme 1. Synthetic Route to the Phosphine-Oxazoline Ligands



available ferrocenecarboxylic acid, key intermediate **1** was obtained according to the reported literature.[11] After lithiation of **1** followed by treatment with 2-(diphenylphosphino)-benzaldehyde, **2** and **3** were obtained in more than 80% overall yields. The alternative diastereomers, corresponding to lithiation at the other *ortho* position of oxazoline group, were not observed. Finally, **2** and **3** were reacted with iodomethane or iodoethane to generate **L3**.

The coordination of ligands **L3a** to $[Ir(COD)Cl]_2$ was verified by analysis of the single crystal structure of the complex [Ir(COD)(**L3a**)]BArF (CCDC 1858033) (Figure 3)

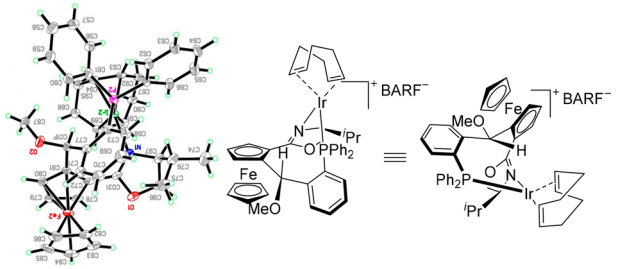


Figure 3. Single crystal structure of [Ir(COD)(**L3a**)]BArF.

obtained from the reaction of **L3a** with $[Ir(COD)Cl]_2$ and NaBArF in DCM under nitrogen. In the crystal structure, ligand **L3a** is coordinated to the iridium atom by means of one phosphorus atom and one nitrogen atom, forming a conformationally restricted nine-membered ring. It appears that the configuration of the MeO-linked carbon is essential for coordination because **L3b** cannot form its corresponding Ir-complex under the same conditions. The complex [Ir(COD)-(**L3a**)]BArF exhibits a stable conformation in which steric interactions between the MeO group and the groups around the Ir center are avoided.

With the new phosphine-oxazoline ligands in hand, we began our study by employing acetophenone **4a** as the model substrate with 0.5 mol % Ir-catalyst in MeOH under 5 bar of hydrogen for 24 h. Detailed hydrogenation conditions are listed in Table 1. First, different catalysts consisting of different

Table 1. Optimizing the Reaction Conditions for the Asymmetric Hydrogenation of Acetophenone[a]

entry	ligand	solvent	conv [%][b]	ee [%][c]
1	**L1a**	MeOH	91	−31
2	**L1b**	MeOH	67	5
3	**L1c**	MeOH	28	12
4	**L1d**	MeOH	57	60
5	**L2a**	MeOH	25	23
6	**L2b**	MeOH	64	52
7	**L3a**	MeOH	>99	99
8	**L3c**	MeOH	>99	97
9	**L4**	MeOH	67	45
10	**L3a**	EtOH	>99	95
11	**L3a**	iPrOH	>99	90
12	**L3a**	THF	trace	–
13	**L3a**	toluene	17	51
14	**L3a**	DCM	NR	–

[a]Reaction conditions: **4a** (0.40 mmol), ratio of substrate/catalyst (S/C) = 200, Na_2CO_3 (10 mol %), H_2 (5 bar), solvent (2.0 mL). [b]Determined by ^1H NMR spectroscopy. [c]Enantioselectivity was determined by HPLC using a chiral Daicel column.

chiral phosphine-oxazoline ligands were screened (entries 1−9).[12] The planar chiral Fe/Ru-metalocene-based phosphine-oxazoline ligands (**L1a−L1d**) were examined. However, most of them gave poor enantioselectivity and/or conversion (entries 1−4). The well-known center chiral ligand (s)-*t*Bu-PHOX (**L4**) and axially flexible ligands *i*Pr-BiphPHOX (**L2a**) and In-BiphPHOX (**L2b**) also gave poor conversion and enantioselectivity (entries 5, 6, and 9). Finally, our new phosphine-oxazoline ligands **L3** proved to be the best with regards to both conversion and enantioselectivity (>99% conv, up to 99% ee, entries 7 and 8). This reaction cannot proceed in the absence of base. The effect of solvent on the reaction was also examined. The hydrogenation is best conducted in protic solvents with MeOH, EtOH, and ^{i}PrOH all providing comparable conversions and selectivities (entries 7, 10, and 11, respectively). However, the reactivity and enantioselectivity decreased sharply when the solvent was changed to THF, toluene, or DCM (entries 12−14). Therefore, the optimal reaction conditions were found to include using [Ir(**L3a**)-(COD)]BArF as a catalyst and Na_2CO_3 as a base and carrying out the reaction under 5 bar of hydrogen in MeOH at room temperature for 24 h.

With the optimized conditions in hand, a variety of aryl alkyl ketones were examined, as shown in Scheme 2. It was found that electron-neutral, electron-deficient, and electron-rich, monosubstituted and dual substituted aryl groups gave the corresponding products with excellent yields and good to excellent enantioselectivities (up to 98% yield and 99% ee, **5a−5n**). However, increasing the electron-withdrawing ability of the substituents on the phenyl group led to a concomitant decrease in ee (**5j** vs **5n**, **5k** vs **5m**). An exception to these results was observed when the Me substituent was present at the *meta* position (**4c**), giving the corresponding product with relatively low ee; the reason for this is unclear. It is worth

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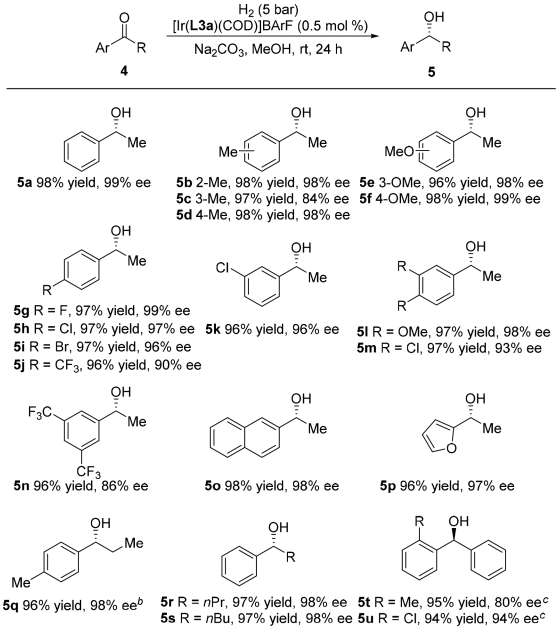
Scheme 2. Substrate Scope of Simples Ketones[a]



[a]Reaction conditions: substrate (0.40 mmol), ratio of substrate/catalyst (S/C) = 200, Na_2CO_3 (10 mol %), H_2 (5 bar), MeOH (2.0 mL), room temperature for 24 h. [b]H_2 (10 bar). [c]S/C = 100, 50 °C.

mentioning that fused-ring aryl and heterocyclic substrates (**4o** and **4p**) also gave their corresponding products with excellent yields and enantioselectivities (up to 98% yield and 98% ee). When R was changed from Me to Et, *n*Pr, and *n*Bu, they also could be successfully converted to the corresponding adducts with excellent yields and enantioselectivities (up to 97% yield and 98% ee, **5q**−**5s**) Finally, bisaryl ketones with different substituents at the *ortho* position of the benzene ring were also used for this hydrogenation; to our delight, the desired product was obtained with up to 94% ee.

Pleasingly, this catalytic asymmetric hydrogenation system is also amenable to *α*,*β*-unsaturated cyclic ketones **6**, of which the corresponding hydrogenation products are important skeletons present in numerous bioactive compounds. Zhou et al. reported the asymmetric hydrogenation of (*E*)-*α*-arylmethylene cyclohexanones to afford chiral allylic alcohols with excellent enantioselectivities.[13] With our catalytic system, this type of substrate can also be successfully converted to the corresponding adducts with full conversions and good to excellent enantioselectivities. As summarized in Table 2, a number of (*E*)-*α*-arylmethylene cyclopentanones **6** can be hydrogenated to the chiral *β*-arylmethylene cyclopentanols **7** in high yields and with good to excellent enantioselectivities (entries 1−6). Electron-donating and -withdrawing substituents on the phenyl ring of the substrate had a slight effect on both the reactivity and enantioselectivity of the reaction. Lower ee was also observed when the substituent Cl was present at the *ortho* or *meta* position of the phenyl ring (entries 3−4). It is worth mentioning that a naphthyl-substituted substrate gave its corresponding product **7f** with the best results (entry 6, 97% yield and 95% ee). When a substrate bearing a six-membered ring was subjected to the hydrogenation, the corresponding *β*-arylmethylene cyclic alcohol **7g** was obtained in 95% yield and with 87% enantioselectivity (entry 7).

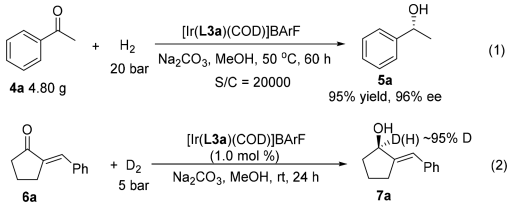
Table 2. Substrate Scope of *Exo*-*α*,*β*-Unsaturated Cyclic Ketones[a]

entry	Ar	*n*	product	yield [%][b]	ee [%][c]
1	Ph	1	**7a**	97	91
2	4-MeC_6H_4	1	**7b**	97	91
3	2-ClC_6H_4	1	**7c**	95	88
4	3-ClC_6H_4	1	**7d**	95	88
5	4-ClC_6H_4	1	**7e**	96	92
6	2-naphthyl	1	**7f**	97	95
7	Ph	2	**7g**	95	87

[a]Reaction conditions: substrate (0.30 mmol), ratio of substrate/catalyst (S/C) = 100, Na_2CO_3 (10 mol %), H_2 (5 bar), MeOH (2.0 mL). [b]Isolated yield. [c]Ee was determined by HPLC using a chiral column.

The Ir-**L3a** complex was very stable and exhibited high catalytic activity. When the catalyst loading was reduced to 0.005 mol % (S/C = 20 000), the asymmetric hydrogenation of acetophenone **4a** on a 4.80 g scale proceeded well providing product **5a** with 95% yield and 96% ee (Scheme 3, eq 1).

Scheme 3. Asymmetric Hydrogenation with High S/C and Deuteration Experiment



A deuteration experiment was performed to determine if transfer hydrogenation occurs in the reaction. Under a D_2 atomsphere, the hydrogenation gave the desired product with 95% D incorporation at the *α*-position. Based on these experiments and the fact that there was no reaction in the absence of hydrogen gas, a transfer hydrogenation pathway can be ruled out (Scheme 3, eq 2).

In conclusion, we have developed a novel planar chiral ferrocene phosphine-oxazoline ligand, which has been successfully applied to the iridium-catalyzed asymmetric hydrogenation of simple ketones and *exo*-*α*, *β*-unsaturated cyclic ketones. Under the optimal reaction conditions, the desired products can be obtained in up to 98% yield and 99% ee. The reaction can be conducted on a gram scale and with a low catalyst loading (S/C = 20 000) with little loss in enantioselectivity. Deuterium labeling experiments revealed that the reaction proceeds with hydrogen gas rather than via transfer hydrogenation with the alcohol solvent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02591.

Details on experimental procedures, characterization data, copies of ^{1}H NMR, ^{13}C NMR spectra and HPLC charts of new compounds (PDF)

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Accession Codes

CCDC 1858033 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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