Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 18 (2007) 629–634

Enantioselective hydrogenation of olefins with planar chiral iridium ferrocenyloxazolinylphosphine complexes

Xinsheng Li,[a,b,*] Qing Li,[b] Xiaohua Wu,[b] Yongguang Gao,[b] Dongcheng Xu[a,b] and Lichun Kong[b]

[a]*Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, PR China*

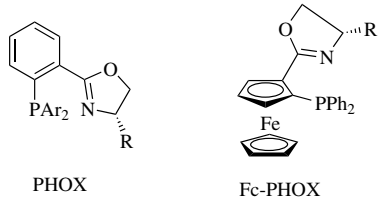
[b]*Department of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, PR China*

Received 18 December 2006; accepted 14 February 2007

Abstract—Chiral iridium Fc-PHOX complexes were readily prepared from Fc-PHOX, $[Ir(cod)Cl]_2$ and NaBArF (or $NaPF_6$) in high yields. They were applied as catalysts in the enantioselective hydrogenation of olefins to afford the corresponding products with high conversions and good enantioselectivities (up to 99% ee).

1. Introduction

The enantioselective hydrogenation of olefins is one of the more important methods in asymmetric synthesis.[1] Although Ru- and Rh-based systems with bidenate phosphine ligands have been developed since 1970s, the results of the hydrogenation of some olefins, especially unfunctionalized olefins, were unsatisfactory with these systems.[2] $[Ir(cod)(py)Pcy_3]PF_6$ was used for the first time in the hydrogenation of substituted olefins to provide good results by Crabtree et al.[3] However, Ir-based bidenate phosphine ligand catalysts have not been explored as extensively as Ru- and Rh-based systems.[4] Recently, Pfaltz et al. developed phosphino-oxazoline (PHOX) (Scheme 1) ligands to mimic a chiral Crabtree's catalyst and obtained excellent results for the enantioselective hydrogenation of both unfunctionalized and functionalized olefins.[5] After this discovery, a number of chiral Ir-based systems with N–P[6] C–P[7] and C–N[8] ligands were applied to improve the catalytic efficiency and expand the reaction scope. Since little was known about the mechanism and enantioselectivity-determining factors of the highly substrate dependent Ir-catalyzed hydrogenation, the development of new Ir-based catalytic systems still remains a challenge.



Scheme 1.

Planar chiral ferrocenyloxazolinylphosphines (Fc-PHOX) (Scheme 1) are versatile ligands and have a wide range of applications in asymmetric synthesis, such as the hydrogenations of quinolines[9] and ketones,[10] transfer hydrogenation[11] and α-alkylation of ketones,[12] oxidative kinetic resolution of racemic alcohols,[13] allylic substitutions,[14] Heck reactions[15] and 1,3-dipolar cycloadditions.[16] It is noteworthy that Fc-PHOX have not only a stereogenic centre in the oxazoline ring, but also a planar chirality in the ferrocene moiety. It is believed that the Fc-PHOX and some cations can form a rigid six-membered chelate ring, and the planar chirality forms a better chiral environment for chirality transfer during the asymmetric reaction, which has been demonstrated by Zhou et al. In their research, $[Ir(cod)Cl]_2$/(*S*,*S*)-Fc-PHOX was applied in the hydrogenation of quinolines and excellent enantiomeric excess values were obtained.[9] To the best of our knowledge, there have been no results reported on the successful

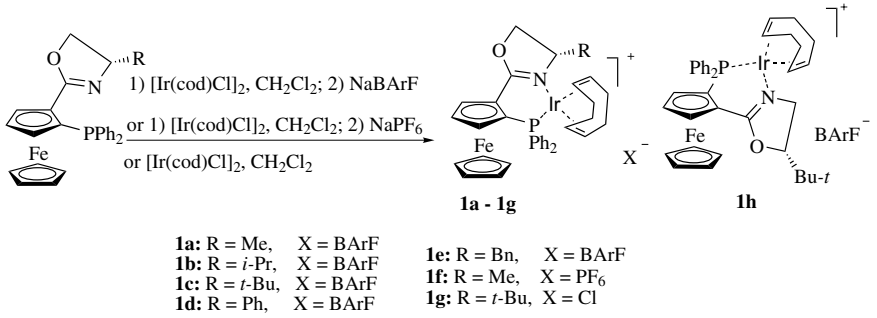
* Corresponding author. Tel.: +86 579 2283702; fax: +86 579 2282610; e-mail: sky33@zjnu.cn

0957-4166/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2007.02.018

use of [Ir(cod)Fc-PHOX]BArF complex (BArF: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in the enantioselective hydrogenation of unfunctionalized and functionalized olefins.[17,18] Herein, we report our recent study on the synthesis and application of these chiral iridium complexes in the enantioselective hydrogenation of olefins.

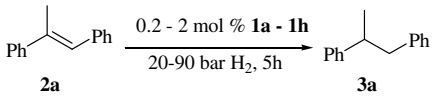
2. Results and discussion

All the iridium complexes were readily synthesized in good yields (Scheme 2). To investigate the influence of the relative configuration of the chirality in the oxazoline ring and the planar chirality of the ferrocene ring, two diastereomeric complexes **1c** and **1h** were synthesized. A series of complexes **1a**–**1h** were also synthesized to study the influence of the anion and the R group in the oxazoline ring. (*E*)-1,2-Diphenyl-1-propene as a typical substrate was hydrogenated to test the effectiveness of these complexes. The hydrogenation procedures were carried out in the presence of 0.2–2 mol % of iridium complexes under 20–90 bar of hydrogen pressure at room temperature (Table 1). The hydrogenation using **1f** with PF_6^- as an anion led to only 5.8% conversion (Table 1, entry 16). Complex **1g** with Cl^- as the anion resulted in a complete loss of catalytic activity (Table 1, entry 17). The results showed strongly coordinating anions deactivating the catalyst. Similar to the reported result of iridium catalysts,[3,6] good conversions were obtained in chlorinated solvents {Table 1, entries 1–6, CH_2Cl_2, 100%; $(CH_2Cl)_2$, 60.9%; CH_3Cl, 30.3%; Et_2O and THF, 0%; toluene, 4.9%}. Middle to complete conversion was obtained in the presence of 0.5 mol % **1a**–**1e** or **1h** as catalysts in CH_2Cl_2 (Table 1 entries 1, 7–15 and 18). Higher catalyst loading (2 mol %) did not increase the enantioselectivity (Table 1, entry 8). Lower catalyst loading (0.2 mol %) resulted in extremely low conversion



Scheme 2. Synthesis of catalysts.

Table 1. Asymmetric hydrogenation of (*E*)-1,2-diphenyl-1-propene in the presence of **1a**–**1h**



2a **3a**

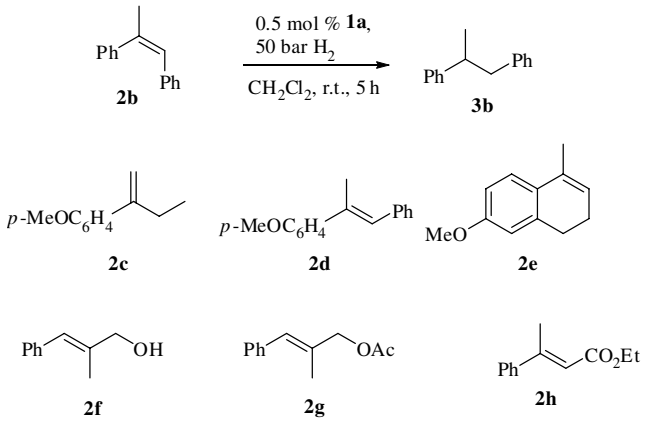
Entry	Cat.	mol % Cat.	Sol.	*P* (H_2) (bar)	Conversion[a] (%)	ee[b]
1	**1a**	0.5	CH_2Cl_2	50	100	87.4 (*R*)
2	**1a**	0.5	$(CH_2Cl)_2$	50	60.9	85.1
3	**1a**	0.5	CH_3Cl	50	30.3	Nd[c]
4	**1a**	0.5	Et_2O	50	0	
5	**1a**	0.5	THF	50	0	
6	**1a**	0.5	Toluene	50	4.9	Nd[c]
7	**1a**	0.2	CH_2Cl_2	50	51	86.1 (*R*)
8	**1a**	2	CH_2Cl_2	50	100	89.2 (*R*)
9	**1a**	0.5	CH_2Cl_2	90	100	82.5 (*R*)
10	**1a**	0.5	CH_2Cl_2	20	37	84.7 (*R*)
11	**1b**	0.5	CH_2Cl_2	50	66	71.6 (*R*)
12	**1c**	0.5	CH_2Cl_2	50	38	77.6 (*R*)
13	**1c**	0.5	CH_2Cl_2	90	98	79.7 (*R*)
14	**1d**	0.5	CH_2Cl_2	50	74	62.4 (*R*)
15	**1e**	0.5	CH_2Cl_2	50	100	74.3 (*R*)
16	**1f**	2	CH_2Cl_2	50	5.8	Nd[c]
17	**1g**	2	CH_2Cl_2	60	0	
18	**1h**	0.5	CH_2Cl_2	50	45	60.4 (*R*)

[a] Determined by GC.
[b] Determined by HPLC using a chiral Chiracel OJ-H column. The absolute configurations were assigned by comparison of the HPLC retention times with literature values.[5]
[c] Not determined.

(Table 1, entry 7). The steric bulk of the R group in the oxazoline ring controlled both the activation and the enantioselectivity of the catalysts. The Ir-complexes **1a** and **1e** with little steric bulk in the oxazoline ring gave complete conversion (Table 1, entries 1 and 15). The highest ee value was achieved with **1a** as the catalyst (87.4% ee). A decrease in activity was found upon the introduction of bulky R substituents. Conversions of 66%, 38% and 74% were obtained with catalysts **1b**, **1c** and **1d**, respectively (Table 1, entries 11, 12 and 14). Higher hydrogen pressure could enhance the conversion of substrates (Table 1, entries 12 and 13). The same configuration of product was found with **1c** and **1h** as catalysts, which indicated that the central chirality in the oxazoline ring of the catalyst determined the configuration of the product (Table 1, entries 12, 13 and 18). The lower ee induced by **1h** suggested the mismatched nature of the (*R*) planar chirality with the (*S*) central chirality of the oxazoline ring (77.6% ee vs 60.4% ee). Complexes **1a**–**1e** with (*S*,*S*) configuration are the matched case in terms of planar and central chiralities.

Other unfunctionalized olefins **2b**–**2e** could also be hydrogenated using complex **1a** as a catalyst to afford the products in high yields and moderate to high ee values. Asymmetric hydrogenation of a (*Z*)-1,2-diphenyl-1-propene led to a product with a different configuration, and a lower enantiomeric excess was obtained (Table 2, entry 1). Substrates **2c**, **2d** and **2e** were subjected to hydrogenation to provide 22.1%, 88.5% and 89% ee, respectively (Table 2, entries 3, 4 and 5). Reduction of the hydrogen pressure caused an increase in the enantioselectivity of the terminal olefin **2c** (Table 2, entries 2 and 3, 14.3% vs 22.1% ee). The functionalized 2-methyl-3-phenylpropenol **2f** and 3-acetoxy-2-methylphenylpropene **2g** were hydrogenated to afford the product with the highest ee (Table 2, entries 6 and 7). β-Methyl cinnamic ester **2h** could be hydrogenated in 100% conversion and 81.8% ee (Table 2, entry 8).

Table 2. The results of asymmetric hydrogenation in the presence of **1a** (0.5 mol %)



Entry	Substrate	Conversion[a] (%)	ee[b]
1	**2b**	100	67.0 (*S*)
2	**2c**	100	14.3 (*S*)
3	**2c**	100	22.1 (*S*)[c]
4	**2d**	100	88.5 (*R*)
5	**2e**	95	89.0 (*S*)
6	**2f**	100	98.8[d]
7	**2g**	100	99.0[d]
8	**2h**	100	81.8 (*R*)

[a] Determined by ^{1}H NMR.
[b] Determined by HPLC using a chiral Chiracel OJ-H, OD-H and OB-H column. The absolute configurations were assigned by comparison of the HPLC retention times with literature values.[5,6a]
[c] 20 bar pressure was used.
[d] The absolute configurations were not determined.

3. Conclusions

In conclusion, the work presented here serves to expand the scope of Ir-based catalysts. [Ir(cod)Fc-PHOX]BArF complexes are effective catalysts for the asymmetric hydrogenation of both unfunctionalized and functionalized olefins. High yields and moderate to good enantioselectivities were obtained when using the complexes as catalysts. Central chirality dominates the configuration of the product in the hydrogenation of (*E*)-1,2-diphenyl-1-propene. The facile synthesis of ligands and catalysts provides a useful method for the preparation of this type of chiral compounds.

4. Experimental

Melting points were determined on a Yanagimoto micro apparatus and are uncorrected. Optical rotations were measured with WZZ-2B digital polarimeter. The ee values were determined by HPLC using Chiralcel^{TM} OD-H, OB-H and OJ-H column with 2-propanol–hexane as the eluent. The conversion was determined on an Agilent 6820 or a Bruker AV-400 MHz spectrometer. The ^{1}H NMR (at 400 MHz), ^{13}C NMR (at 100 MHz) and ^{31}P NMR (at 160 MHz) spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal reference for ^{1}H NMR and ^{13}C NMR or 85% H_3PO_4 as external reference for ^{31}P NMR. IR spectra were determined on a Nicolet-670 FT spectrophotometer. Elemental analyses were performed on a Carlo Erba 1110 analyser. All reactions were carried out in dry glassware under nitrogen.

4.1. General procedure for the preparation of iridium complexes 1a–1h

Oxazolines (0.1 mmol), $[Ir(cod)Cl]_2$ (33.6 mg, 0.05 mmol) and CH_2Cl_2 (5 mL), were added to a flask under N_2. The solution was stirred at room temperature for about 2 h until TLC indicated that the ligand had been consumed. $NaPF_6$ or Na[BArF] (0.15 mmol) was added followed by H_2O (5 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (2×5 mL). The combined organic phase was washed with H_2O (5 mL) and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography with CH_2Cl_2 as the eluent to afford yellow or red complexes.

4.2. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-methyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*S*)-1a

Yield 86.4%, mp 193–196 °C. $[\alpha]_D^{20} = -336.7$ (*c* 0.28, CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) 1.26–1.31 (m, 1H, COD), 1.41 (d, 3H, $J = 6.5$ Hz, CH_3), 1.67–1.75 (m, 2H, COD), 2.09–2.20 (m, 2H, COD), 2.27–2.37 (m, 3H, COD), 2.42–2.48 (m, 1H, COD), 3.35–3.42 (m, 1H, COD), 3.67 (s, 5H, CpH), 4.16–4.22 (m, 1H, CHN), 4.29 (d, 2H, $J = 5.2$, CH_2O), 4.66–4.67 (m, 1H, CpH), 4.78–4.79 (m, 1H, COD), 4.83–4.85 (m, 1H, CpH), 4.91–4.98 (m, 1H, COD), 5.15–5.17 (m, 1H, CpH), 7.08–7.14 (m, 2H, PhH), 7.34–7.44 (m, 3H, PhH), 7.51 (s, 4H, BArF–H), 7.65–7.68 (m, 3H, PhH), 7.77 (br s, 8H, BArF–H), 8.13–8.17 (m, 2H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 23.3 (CH_3), 26.9 (COD), 28.5 (COD), 31.8 (COD), 35.4 (COD), 59.6 (COD), 60.4 (COD), 61.3 (CH_2O), 64.8 (d, CHN), 72.5, 72.6, 74.2, 74.3, 74.6, 77.9 (CpH), 91.7 (COD), 95.3 (COD), 117.7 (m, BArF), 123.2 (CF_3), 125.9, 128.5 (BArF), 128.6, 129.0, 129.1, 129.2, 132.4, 132.8, 134.8 (BArF), 135.8, 136.3, 136.8, 161.0 (ArB), 171.5 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 9.8 (PPh_2). IR (KBr): 1587. Anal. Calcd for $C_{66}H_{48}BF_{24}FeIrNOP$: C, 49.03; H, 2.99; N, 0.87. Found: C, 48.65; H, 2.87; N, 0.88.

4.3. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-isopropyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*S*)-1b

Yield, 81.3%, mp 135–137 °C, $[\alpha]_D^{20} = -471.2$ (*c* 0.29, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (d, 3H, $J = 6.8$ Hz, CH_3), 1.02 (d, 3H, $J = 7.2$ Hz, CH_3), 1.25–1.30 (m, 1H, COD), 1.52–1.55 (m, 1H, CH), 1.64–1.70 (m, 1H, COD), 2.01–2.08 (m, 2H, COD), 2.27–2.39 (m, 4H, COD), 2.43–2.48 (m, 1H, COD), 3.32–3.36 (m, 1H, COD), 4.33 (s, 5H, CpH), 4.00 (dd, 1H, $J = 4.0$, 8.0 Hz, CH_2O), 4.26 (t, 1H, $J = 9.2$, CHN), 4.51 (dd, 1H, $J = 4.0$, 8.0 Hz CH_2O), 4.70–4.72 (m, 1H, CpH), 4.78–4.81 (m, 1H, COD), 4.82–4.83 (m, 1H, CpH), 4.86–4.89 (m, 1H, COD), 5.12–5.13 (m, 1H, CpH), 7.14–7.19 (m, 2H, PhH), 7.38–7.40 (m, 3H, PhH), 7.53 (s, 4H, BArF–H), 7.65–7.68 (m, 3H, PhH), 7.72 (sbr, 8H, BArF–H), 8.13–8.15 (m, 2H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 14.9 (CH_3), 18.6 ((CH_3)$_3$), 22.6 (COD), 26.1 (COD), 27.8 ((CH_3)$_3$C), 32.8 (COD), 36.2 (COD), 61.4 (COD), 63.4 (COD), 68.8 (CHN), 71.6 (CH_2O), 72.6 (CpH), 73.5 (CpH), 73.6 (CpH), 74.5 (CpH), 74.6 (CpH), 77.9 (CpH), 90.6 (COD), 96.1 (COD), 117.5 (BArF), 123.2 (CF_3), 125.9, 128.4 (BArF), 129.0, 129.1, 131.3, 132.8 (BArF), 132.9, 134.8 (BArF), 136.2, 136.3, 136.8, 160.9 (ArB), 171.6 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 11.6 (PPh_2). IR (KBr): 1586. Anal. Calcd for $C_{68}H_{52}BF_{24}FeIrNOP$: C, 49.65; H, 3.19; N, 0.85. Found: C, 49.14; H, 3.11; N, 0.86.

4.4. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*S*)-1c

Yield, 85.0%, mp 172–175 °C, $[\alpha]_D^{20} = -641.1$ (*c* 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 1.18 (s, 9H, *t*-Bu), 1.26–1.33 (m, 1H, COD), 1.50–1.54 (m, 1H, COD), 1.56–1.64 (m, 1H, COD), 1.93–2.07 (m, 2H, COD), 2.20–2.37 (m, 3H, COD), 2.43–2.53 (m, 1H, COD), 3.43–3.47 (m, 1H, COD), 3.80 (s, 5H, CpH), 3.89 (dd, 1H, $J = 3.2$, 9.6 Hz, CH_2O), 4.22 (t, 1H, $J = 9.6$, CHN), 4.62 (dd, 1H, $J = 3.2$, 9.6 Hz, CH_2O), 4.73–4.74 (m, 1H, CpH), 4.82–4.84 (m, 1H, COD), 4.85–4.86 (m, 1H, CpH), 4.87–4.89 (m, 1H, COD), 5.13–5.15 (m, 1H, CpH), 7.08–7.10 (m, 2H, PhH), 7.36–7.40 (m, 3H, PhH), 7.53 (s, 4H, BArF–H), 7.66–7.68 (m, 3H, PhH), 7.71 (sbr, 8H, BArF–H), 8.10–8.15 (m, 2H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 25.2 ((CH_3)$_3$), 26.2 (COD), 27.4 (COD), 33.0 (COD), 34.3 (*t*-BuC), 36.9 (COD), 60.9 (COD), 63.0 (COD), 70.3 (CpH), 71.8 (CH_2O), 72.7 (CpH), 73.4 (CHN), 73.5 (CpH), 74.7 (CpH), 74.8 (CpH), 78.2 (CpH), 90.0 (COD), 96.5 (COD), 117.4 (BArF), 123.2 (CF_3), 125.9, 128.4, 128.6, 128.8 (BArF), 131.3, 132.8 (BArF), 132.9, 133.0, 134.8 (BArF), 136.2, 136.4, 160.9 (ArB), 171.6 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 13.1 (PPh_2). IR (KBr): 1856. Anal. Calcd for $C_{69}H_{54}BF_{24}FeIrNOP$: C, 49.95; H, 3.28; N, 0.84. Found: C, 49.58; H, 3.08; N, 0.83.

4.5. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-phenyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*S*)-1d

Yield, 73.1%, mp 190–192 °C, $[\alpha]_D^{20} = -578.0$ (*c* 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 1.27–1.34 (m, 1H, COD), 1.50–1.56 (m, 1H, COD), 1.74–1.81 (m, 2H, COD), 2.07–2.10 (m, 1H, COD), 2.14–2.18 (m, 2H, COD), 2.20–2.25 (m, 1H, COD), 2.31–2.39 (m, 1H, COD), 3.22–3.24 (m, 1H, COD), 3.73 (s, 5H, CpH), 4.50 (dd, 1H, $J = 3.2$, 9.2 Hz, CH_2O), 4.70 (t, 1H, $J = 8.8$, CHN), 4.73–4.76 (m, 1H, CpH), 4.78 (dd, 1H, $J = 3.2$, 9.2 Hz, CH_2O), 4.87–4.88 (m, 1H, CHCOD), 4.89–4.90 (m, 1H, CHCOD), 4.90–4.91 (m, 1H, CpH), 5.20–5.21 (m, 1H, CpH), 7.10–7.12 (m, 2H, PhH), 7.28–7.29 (m, 3H, PhH), 7.30–7.34 (m, 5H, PhH), 7.52 (s, 4H, BArF–H), 7.69–7.75 (m, 3H, PhH), 7.71 (br s, 8H, BArF–H), 8.14–8.18 (m, 2H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 27.4 (COD), 29.2 (COD), 31.2 (COD), 34.4 (COD), 60.6 (COD), 64.3 (COD), 66.7 (CH_2O), 71.6 (CHN), 72.8 (CpH), 72.9 (CpH), 74.6 (CpH), 74.7 (CpH), 74.8 (CpH), 78.4 (CpH), 93.0 (COD), 96.6 (COD), 117.4 (BArF), 123.2 (CF_3), 125.2, 125.9, 128.5 (BArF), 129.0, 129.1, 131.3, 132.4 (BArF), 132.8, 134.8, 136.3, 140.1, 160.9 (ArB), 173.9 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 9.47 (PPh_2). IR (KBr): 1856. Anal. Calcd for $C_{71}H_{50}BF_{24}FeIrNOP$: C, 50.79; H, 3.00; N, 0.83. Found: C, 50.31; H, 2.89; N, 0.84.

4.6. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-benzyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*S*)-1e

Yield, 69.6%, Mp 80–82 °C, $[\alpha]_D^{20} = -397.4$ (*c* 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 1.25–1.32 (m, 1H, COD), 1.52–1.65 (m, 2H, COD), 2.10–2.22 (m, 2H, COD), 2.30–2.39 (m, 3H, COD), 2.41–2.54 (m, 1H, COD), 2.51–2.57 (m, 2H, $PhCH_2$), 3.42–3.46 (m, 1H, COD), 3.78 (s, 5H, CpH), 4.22 (t, 1H, $J = 8.4$ Hz, CHN), 4.46–4.57 (m, 2H, CH_2O), 4.69–4.71 (m, 1H, CpH), 4.86–4.99 (m, 1H, CpH), 5.12–5.14 (m, 1H, COD), 5.18–5.19

(m, 1H, CpH), 7.10–7.13 (m, 2H, PhH), 7.21–7.24 (m, 3H, PhH), 7.35–7.43 (m, 5H, PhH), 7.51 (s, 4H, BArF–H), 7.70–7.76 (m, 3H, PhH), 7.71 (br s, 8H, BArF–H), 8.20–8.22 (m, 2H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 29.4 (COD), 29.6 (COD), 31.9 (COD), 34.1 (COD), 42.9 ($PhCH_2$), 61.6 (COD), 64.4 (COD), 65.2 (CpH), 71.8 (CH_2O), 72.6 (CHN), 72.7 (CpH), 74.5 (CpH), 75.3 (CpH), 76.6 (CpH), 78.3 (CpH), 92.3 (COD), 96.5 (COD), 117.4 (BArF), 123.2 (CF_3), 125.9, 128.5 (BArF), 128.6, 128.7, 128.9, 129.1, 129.4, 132.3, 134.1, 134.8 (BArF), 135.8, 136.0, 161.0 (ArB), 171.9 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 9.8 (PPh_2). IR (KBr): 1857. Anal Calcd for $C_{72}H_{52}BF_{24}FeIrNOP$: C, 51.08; H, 3.10; N, 0.83. Found: C, 50.62; H, 2.94; N, 0.82.

4.7. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-methyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) hexafluorophosphate (*S*,*S*)-1f

Yield 56.4%, mp 153–156 °C. $[\alpha]_D^{20} = -160.1$ (*c* 0.11, CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) 1.25–1.30 (m, 1H, COD), 1.40 (d, 3H, $J = 6.5$ Hz, CH_3), 1.65–1.71 (m, 2H, COD), 2.07–2.22 (m, 2H, COD), 2.24–2.33 (m, 3H, COD), 2.41–2.45 (m, 1H, COD), 3.34–3.42 (m, 1H, COD), 3.68 (s, 5H, CpH), 4.14–4.21 (m, 1H, CHN), 4.30 (d, 2H, $J = 5.2$, CH_2O), 4.65–4.67 (m, 1H, CpH), 4.75–4.78 (m, 1H, COD), 4.82–4.86 (m, 1H, CpH), 4.92–4.97 (m, 1H, COD), 5.13–5.16 (m, 1H, CpH), 7.11–7.45 (m, 5H, PhH), 7.65–8.13 (m, 5H, PhH). ^{13}C NMR (100 MHz, $CDCl_3$) 23.2 (CH_3), 27.1 (COD), 28.4 (COD), 31.8 (COD), 35.5 (COD), 59.4 (COD), 60.5 (COD), 61.2 (CH_2O), 65.2 (d, CHN), 72.5, 72.7, 74.2, 74.4, 74.5, 77.8 (CpH), 91.8 (COD), 95.5 (COD), 126.0, 128.5, 128.9, 129.0, 129.2, 132.5, 132.9, 135.8, 136.2, 136.7, 172.5 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 32 (PPh_2), −147.4 (q, $J = 728$Hz, PF_6). IR (KBr): 1610. Anal. Calcd for $C_{34}H_{36}F_6FeIrNOP_2$: C, 45.44; H, 4.04; N, 1.56. Found: C, 45.02; H, 3.57; N, 1.54.

4.8. (η^4-1,5-Cyclooctadiene) [(*S*,*S*)-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) chloride (*S*,*S*)-1g

The complex was prepared in situ according to the procedure.[9]

4.9. (η^4-1,5-Cyclooctadiene) [(*S*,*R*)-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)-2-diphenylphosphinoferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (*S*,*R*)-1h

Yield, 83.8%, mp 181–183 °C, $[\alpha]_D^{20} = +217.2$ (*c* 0.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 1.18 (s, 9H, *t*-Bu), 1.45–1.51 (m, 1H, COD), 2.00–2.06 (m, 1H, COD), 2.12–2.16 (m, 1H, COD), 2.37–2.50 (m, 2H, COD), 2.53–2.62 (m, 2H, COD), 2.99–3.00 (m, 1H, COD), 3.55–3.59 (m, 1H, COD), 3.74 (dd, 1H, $J = 2.4$, 8.8 Hz, CH_2O), 4.18 (t, 1H, $J = 9.2$ Hz, CHN), 4.46 (dd, 1H, $J = 2.4$, 8.8 Hz, CH_2O), 4.60–4.63 (m, 1H, CpH), 4.62 (s, 5H, CpH), 4.84–4.85 (m, 1H, COD), 4.88–4.90 (m, 1H, COD), 4.99–5.00 (m, 1H, CpH), 5.23–5.25 (m, 1H, CpH), 7.34–7.47 (m, 5H, PhH), 7.48–7.51 (m, 5H, PhH), 7.52 (s, 4H, BArF–H), 7.71 (br s, 8H, BArF–H). ^{13}C NMR (100 MHz, $CDCl_3$) 24.9 ($(CH_3)_3$), 25.4 (COD), 28.2 (COD), 29.7 (COD), 32.6 (COD), 34.3 (COD), 37.0 (*t*-BuC), 58.3 (COD), 60.2 (COD), 68.4 (CpH), 70.4 (CH_2O), 72.5 (CHN), 73.2 (CpH), 75.2 (CpH), 75.3 (CpH), 75.5 (CpH), 76.3 (CpH), 91.3 (COD), 93.8 (COD), 117.4 (BArF), 122.2, 123.2 (CF_3), 125.9, 128.4, 128.7 (BArF), 128.9, 129.0, 129.2, 132.0, 132.2, 133.4, 134.8 (BArF), 136.2, 160.9 (ArB), 172.9 (C=N). ^{31}P NMR (160 MHz, $CDCl_3$) 10.9 (PPh_2). IR (KBr): 1586. Anal. Calcd for $C_{69}H_{54}BF_{24}FeIrNOP$: C, 49.95; H, 3.28; N, 0.84. Found: C, 49.53; H, 3.01; N, 0.80.

4.10. General procedure for hydrogenation in the presence of iridium complexes 1a–1h (0.5 mol %)

Enantioselective hydrogenation of olefins: olefins **2a**–**2h** (0.5 mmol) and chiral Fc-PHOX (0.0025 mmol) in 2 mL dry degassed CH_2Cl_2 were added to the autoclave under inert atmosphere. The autoclave was sealed immediately and pressurized to 50 bar H_2. The mixture was then stirred for 5 h. The CH_2Cl_2 was removed and the crude product was passed through a short silica-gel column with hexane or 10% ethyl acetate in hexane as eluent. After evaporation of the solvent, **3a**–**3h** were obtained and analyzed for conversion (GC or ^{1}H NMR) and % ee (HPLC).

Acknowledgements

This paper was supported by the Natural Science Foundation of Zhejiang Province (Y405013). Dr. Xiaoxia Wang is thanked for the useful discussions.

References

1. Brown, J. M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. I, pp 121–182.
2. Forman, G. S.; Ohkuma, T.; Hems, W. P.; Noyori, R. *Tetrahedron Lett.* **2000**, *41*, 9471–9475.
3. (a) Crabtree, R. H.; Felkin, H.; Morris, G. E. *Chem. Commun.* **1976**, 716–717; (b) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331–337.
4. (a) Giernoth, R.; Krumm, M. S. *Adv. Synth. Catal.* **2004**, *346*, 989–992; (b) Xiao, D.; Zhang, X. *Angew. Chem., Int. Ed.* **2001**, *40*, 3425–3428; (c) Lu, S.-M.; Wang, Y.-Q.; Han, X.-W.; Zhou, Y.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2260–2263; (d) Guiu, E.; Munñoz, B.; Castillón, S.; Claver, C. *Adv. Synth. Catal.* **2003**, *345*, 169–171; (e) Dervisi, A.; Carcedo, C.; Ooi, L.-l. *Adv. Synth. Catal.* **2006**, *348*, 175–183; (f) Lam, K. H.; Xu, L.; Feng, L.; Fan, Q.-H.; Lam, F. L.; Lo, W.-h.; Chan, A. S. C. *Adv. Synth. Catal.* **2005**, *347*, 1755–1758; (g) Chi, Y.; Zhou, Y.-G.; Zhang, X. *J. Org. Chem.* **2003**, *68*, 4120–4122; (h) Dorta, R.; Broggini, D.; Stoop, R.; Rüegger, H.; Spindler, F.; Togni, A. *Chem. Eur. J.* **2004**, *10*, 267–278.
5. Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2897–2899.
6. (a) Blankenstein, J.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4445–4447; (b) Källström, K.; Hedberg, C.; Brandt, P.; Bayer, A.; Andersson, P. G. *J. Am. Chem. Soc.* **2004**, *126*, 14308–14309; (c) Bernardinelli, G. H.; Kundig, E. P.; Pfaltz, A.; Radkowski, K.; Zimmermann, N.; Neuburger-Zehnder, M. *Helv. Chim. Acta* **2001**, *84*, 3233–3246; (d) Blackmond,

D. G.; Lightfoot, A.; Pfaltz, A.; Rosner, T.; Schnider, P.; Zimmermann, N. *Chirality* **2000**, *12*, 442–449; (e) Liu, D.; Tang, W.; Zhang, X. *Org. Lett.* **2004**, *6*, 513–516; (f) Hedberg, C.; Källström, K.; Brandt, P.; Hansen, L. K.; Andersson, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 2995–3001; (g) Drury, W. J., III; Zimmermann, N.; Keenan, M.; Hayashi, M.; Kaiser, S.; Goddard, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 70–74; (h) Hilgraf, R.; Pfaltz, A. *Synlett* **1999**, 1814–1816; (i) Cozzi, P. G.; Zimmermann, N.; Hilgraf, R.; Schaffner, S.; Pfaltz, A. *Adv. Synth. Catal.* **2001**, *343*, 450–454; (j) Smidt, S. P.; Menges, F.; Pfaltz, A. *Org. Lett.* **2004**, *6*, 2023–2026; (k) Hou, D.-R.; Reibenspies, J.; Colacot, T. J.; Burgess, K. *Chem. Eur. J.* **2001**, *7*, 5391–5400; (l) Tang, W.; Wang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 943–946; (m) Bunlaksananusorn, T.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3941–3943; (n) Menges, F.; Neuburger, M.; Pfaltz, A. *Org. Lett.* **2002**, *4*, 4713–4716; (o) Menges, F.; Pfaltz, A. *Adv. Synth. Catal.* **2002**, *344*, 40–44; (p) Schenkel, L. B.; Ellman, J. A. *J. Org. Chem.* **2004**, *69*, 1800–1802; (q) Hilgraf, R.; Pfaltz, A. *Adv. Synth. Catal.* **2005**, *347*, 61–77; (r) Cozzi, P. G.; Menges, F.; Kaiser, S. *Synlett* **2003**, 833–836; (s) Xu, G.; Gilbertson, S. R. *Tetrahedron Lett.* **2003**, *44*, 953–955; (t) Trifonova, A.; Diesen, J. S.; Chapman, C. J.; Andersson, P. G. *Org. Lett.* **2004**, *6*, 3825–3827; (u) Blanc, C.; Agbossou-Niedercorn, F.; Nowogrocki, G. *Tetrahedron: Asymmetry* **2004**, *15*, 2159–2163; (v) Trifonova, A.; Diesen, J. S.; Andersson, P. G. *Chem. Eur. J.* **2006**, *12*, 2318–2328; (w) Källström, K.; Munslow, I.; Andersson, P. G. *Chem. Eur. J.* **2006**, *12*, 3194–3200; (x) McIntyre, S.; Hörmann, E.; Menges, F.; Smidt, S. P.; Pfaltz, A. *Adv. Synth. Catal.* **2005**, *347*, 282–288; (y) Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 14212–14213.

7. Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004**, *15*, 1693–1706.
8. (a) Bolm, C.; Focken, T.; Raabe, G. *Tetrahedron: Asymmetry* **2003**, *14*, 1733–1746; (b) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879; (c) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113–123; (d) Nanchen, S.; Pfaltz, A. *Chem. Eur. J.* **2006**, *12*, 4550–4558; (e) Cui, X.; Fan, Y.; Hall, M. B.; Burgess, K. *Chem. Eur. J.* **2005**, *11*, 6859–6868.
9. Lu, S.-M.; Han, X.-W.; Zhou, Y.-G. *Adv. Synth. Catal.* **2004**, *346*, 909–912.
10. Naud, F.; Malan, C.; Spindler, F.; Rüggeberg, C.; Schmidt, A. T.; Blaser, H.-U. *Adv. Synth. Catal.* **2006**, *348*, 47–50.
11. (a) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97–102; (b) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201–2237; (c) Sammakia, T.; Stangeland, E. L. *J. Org. Chem.* **1997**, *62*, 6104–6105.
12. (a) Taguchi, K.; Nakagawa, H.; Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2004**, *126*, 72–73; (b) Onodera, G.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3819–3822.
13. Nishibayashi, Y.; Yamauchi, A.; Onodera, G.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 5875–5880.
14. (a) Geisler, F. M.; Helmchen, G. *J. Org. Chem.* **2006**, *71*, 2486–2492; (b) You, S.-L.; Zhu, X.-Z.; Luo, Y.-M.; Hou, X.-L.; Dai, L.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7471–7472; (c) Zheng, W.-H.; Sun, N.; Hou, X.-L. *Org. Lett.* **2005**, *7*, 5151–5154; (d) Hou, X.-L.; Sun, N. *Org. Lett.* **2004**, *6*, 4399–4401.
15. (a) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Dong, X.-W. *Chem. Commun.* **2000**, 1483–1484; (b) Tu, T.; Deng, W.-P.; Hou, X.- L.; Dai, L.-X.; Dong, X.-C. *Chem. Eur. J.* **2003**, *9*, 3073–3081; (c) Tu, T.; Hou, X.-L.; Dai, L.-X. *Org. Lett.* **2003**, *5*, 3651–3653; (d) Kilroy, T. G.; Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Farrell, A.; Guiry, P. J. *J. Mol. Catal. A* **2003**, *196*, 65–81; (e) Kiely, D.; Guiry, P. J. *Tetrahedron Lett.* **2003**, *44*, 7377–7380; (f) Kiely, D.; Guiry, P. J. *J. Organomet. Chem.* **2003**, *687*, 545–561; (g) Loiseleur, O.; Meier, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1996**, *35*, 200–202.
16. (a) Gao, W.; Zhang, X.; Raghunath, M. *Org. Lett.* **2005**, *7*, 4241–4244; (b) Yan, X.-X.; Peng, Q.; Zhang, Y.; Zhang, K.; Hong, W.; Hou, X.-L.; Wu, Y.-D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1979–1983; (c) Zeng, W.; Zhou, Y.-G. *Org. Lett.* **2005**, *7*, 5055–5058.
17. For chiral iridium complexes in the hydrogenation of olefins see review references: (a) Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hörmann, E.; McIntyre, S.; Menges, F.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33–43; (b) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272–3296.
18. For chiral ferrocenes in asymmetric synthesis see the review references: (a) Arrayás, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674–7715; (b) Sutcliffe, O. B.; Bryce, M. R. *Tetrahedron: Asymmetry* **2003**, *14*, 2297–2325; (c) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377–2407.