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Iridium Catalysts with Chiral Bicyclic Pyridine-Phosphine Ligands for Asymmetric Hydrogenation of Olefins

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New bicyclic pyridine-phosphine ligands were prepared and their iridium complexes were evaluated in asymmetric hydrogenation of tri-substituted olefins with non-coordinating and weak-coordinating

substituents. The iridium catalysts showed high activity and enantioselectivity for both types of olefins.

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Introduction

Asymmetric hydrogenation of olefins with chiral iridium N,P-complexes is one of the most efficient and simple methods to create a chiral center.^[1] It overcomes the major problem that P,P-ligated rhodium and ruthenium catalysts have in asymmetric hydrogenation, in that these catalyst normally require the substrates to have a good coordinating group next to C=C double bond. Since Pfaltz and co-workers first introduced chiral N,P-complexes based on Crabtree's catalyst,^[2] [(Cy₃P)(pyridine)Ir (COD)]PF₆ (Cy=cyclohexyl, COD=cyclooctadiene), to hydrogenate non-functionalized olefins,^[3] there has been a number of N,P-ligands reported for use in iridium-catalyzed asymmetric hydrogenation of alkenes with non-coordinating and weakly-coordinating groups.^[4,5] The chiral N,P-ligands have also been successfully used in several other chemical transformations, such as the allylic substitution, C-C coupling reaction.^[6]

During the last several years, chiral iridium bicyclic N,P-complexes based on various heterocyclic moieties (Figure 1, A-C) has been developed by our group^[7,8] and have been successfully applied in reactions like asymmetric hydrogenation, Heck coupling^[9] and isomerization of allylic alcohol.^[10]

Figure 1. Examples of chiral N,P-ligands used in our group

The nitrogen part of the N,P-ligands consist of a heterocycle such as a thiazole and imidazole and are bounded to the iridium metal as the N-donor. Due to the different electronic properties of the N-donors used, the heterocyclic scaffolds play an important role in tuning the reactivities of the catalysts. In some cases, the linker between the backbone and phosphorus can also result in significant differences in hydrogenation, as was observed with the thiazole iridium complex with the N-linker (Figure 1, A) which hydrogenated fluorinated olefins with higher reactivity and lower C-F bond cleavage.^[7e] Pyridine is one of the most common heterocycles, and can be envisioned as an N-donor. In an early report, Pfaltz and co-workers prepared a series of iridium catalysts having pyridine-derived ligands with the oxygen linker.^[11] Their iridium complexes were highly active and enantioselective for hydrogenation of olefins. However, in most cases N,P-ligands having an oxygen linker (O-P) are normally less stable and this limits their range of practicability. Comparably, N,P-ligands with the carbon phosphorous bond (C-P) are more stable, making them more widely applicable. So, we envisioned to introduce the pyridine derived N,P-ligands having a carbon linker, while still maintaining the structure motif of the backbone we developed earlier. Here, we report the preparation of new pyridine-bicyclic N,P-ligands and the evaluation of their iridium complexes in asymmetric hydrogenation of trisubstituted olefins.

Results and Discussion

As shown in Scheme 1, iridium complexes **7a-d** were prepared from the corresponding bicyclic pyridine derivatives **1a** and **1b**. The compounds **1a-b** were lithiated and treated with dimethyl carbonate to obtain racemic esters **2a-b** which were resolved by preparative HPLC (Chiralcel OD-column, 20×250mm). Optically pure pyridine esters were further reduced to alcohols **3a-b** by DIBAL-H and the phenyl groups were introduced by Suzuki coupling reaction. Alcohols **4a-b** were converted to the corresponding iodinated compounds **5a-b** by treatment with iodine, triphenylphosphine and a catalytic amount of imidazole. The borane protected N,P-ligands **6a-d** were obtained by substitution with *in situ* prepared Ar₂P(BH₃)Li. Chiral HPLC confirmed that no racemization occurred during all the manipulations with the chiral compounds. After removing the protecting group by diethyl amine, the free N,P-ligands were subsequently treated with [Ir(COD)Cl]₂

to form the iridium complexes and anion exchange was done by addition of $\text{NaBARF} \cdot 3\text{H}_2\text{O}$ to give iridium N,P-complexes **7a-d**.

The newly prepared iridium complexes **7a-7d** were evaluated in the asymmetric hydrogenation of tri-substituted olefins. As shown in Table 1, complexes **7a** and **7b** having a five-membered ring generally possess better reactivity and selectivity. For the unfunctionalized substrates (Table 1, entry 1-3) complex **7a** and **7b** gave higher conversions and better enantioselectivities while complex **7c** and **7d**, although having similar ligand structures but six membered rings, differ significantly either in reactivity or selectivity.

Scheme 1. Preparation of iridium complexes **7a-7d**, reaction conditions: a) diisopropylamine, BuLi, $(\text{MeO})_2\text{CO}$, Et_2O , -30°C then r.t.; b) preparative HPLC (Chiralcel OD-column, $20 \times 250\text{mm}$, hexane : isopropanol=99:1, 3ml/min); c) DIBAL-H, Et_2O , -78°C ; d) $\text{PhB}(\text{OH})_2$, DPPF, PdCl_2 , K_2CO_3 , Toluene, H_2O , reflux; e) I_2 , PPh_3 , imidazole, DCM, r.t.; f) $\text{Ar}_2\text{P}(\text{BH}_3)\text{H}$, BuLi, THF, -78°C ; g) Diethylamine, r.t.; h) $[\text{Ir}(\text{COD})\text{Cl}]_2$, DCM, r.t.; i) $\text{NaBARF} \cdot 3\text{H}_2\text{O}$, H_2O .

Trans- α -methylstilbene (entry 1) gave full conversion and 99% *ee* using **7b**, substrates **9** and **10** (entry 2 and 3) were fully converted by **7a** with 93% and 91% *ee* respectively. In the case of functionalized olefins, **7a** and **7b** performed better than **7c** and **7d**. Complex **7a** generated the best results for substituted functionalized olefins in **11** and **13** (entry 4 and 6) as well. The β -substituted allylic alcohol **12** (entry 5) was the only exception and was hydrogenated by **7c** with full conversion and 99 % *ee*. The difference in reactivity between the five- and six-membered-ring catalysts was obvious for α -methylcinnamic ester **14**: less than 5% of substrate was hydrogenated by **7c** and **7d**, while 99% of conversion was achieved by **7b**. For the other two α -functionalized olefins (entry 8 and 9), full conversions were achieved by **7b** with 75% and 76% *ee*, respectively.

We have previously developed a selectivity model to rationalize and predict the absolute configuration of the product from hydrogenation.^[12] The olefin coordinates *trans* to phosphorous which is in agreement with other proposed mechanisms.^[13] As shown in Figure 2 (a), the phenyl group on the pyridine ring

occupies quadrant 3 which is the most hindered quadrant. Quadrant 1 and 4 are the least hindered sites in a *trans* position to each other. The ligand partly occupies quadrant 2 and makes it semi-hindered in steric bulk. In the Figure 2 (b), a simplified model, using *trans*- α -methylstilbene as an example, the smallest substituent, hydrogen, should be positioned in the most hindered quadrant 3, and the most sterically demanding substituents, the two phenyl rings, will be located in quadrant 1 and 4. This selectivity model predicts the stereo chemical outcome of the hydrogenation reaction (Figure 2, c), which is in agreement with the experimental results. In the case of conjugated α,β -unsaturated esters, electronic effects should be taken into consideration. The hydrogenation product of *trans*- α -methyl cinnamate (Table 1, entry 7) gave the (*R*)-mismatched configuration with the selectivity model, which is opposite to what was observed experimentally. This is a common phenomenon with certain α -methyl cinnamate substrates, and is probably due to the strong electronic effect that prevents hydride insertion at the electron-rich terminus on $\text{C}=\text{C}$ double bond and leads to formation of a sterically disfavoured but electronically favoured product.

Figure 2. Selectivity model applied in predicting the absolute configuration

Conclusions

In this study, bicyclic pyridine-phosphine ligands were prepared and their iridium complexes were evaluated by asymmetric hydrogenation of various olefins with good conversions and enantioselectivities. In most cases, the five-membered iridium complexes **7a** and **7b** resulted in better catalysts than the six-membered ring **7c** and **7d** did. We found that these catalysts gave competitive results with other heterocyclic iridium complexes. The carbon phosphorous bond in these ligands makes them relatively stable and allows their isolation and “*in situ*” use for other reactions.

Experimental Section

General method: All reagents used were commercially available. CH_2Cl_2 was freshly distilled from CaH_2 under nitrogen. THF was freshly distilled from sodium-benzophenone under nitrogen. Chromatographic separations were performed on Kiesel gel 60 H silica gel (particle size: 0.063-0.100mm). Thin layer chromatography (TLC) was performed on aluminum plates coated with Kieselgel 60 (0.20mm, UV254) and visualized under ultraviolet light ($\nu = 254\text{nm}$), or by staining with ethanolic phosphomolybdic acid and heating. ^1H NMR spectra were recorded

Table 1. Asymmetric hydrogenation of tri-substituted olefins with **7a-7d**

Entry	Substrate	7a		7b		7c		7d	
		conv.	ee	conv.	ee	conv.	ee	conv.	ee
1	8	84%	97% (S)	99%	99% (S)	17%	76% (S)	26%	87% (S)
2	9	99%	93% (S)	99%	90% (S)	91%	35% (S)	99%	90% (S)
3	10	99%	91% (R)	99%	76% (R)	87%	77% (R)	97%	48% (R)
4	11	94%	80% (S)	99%	78% (S)	17%	50% (S)	35%	65% (S)
5	12	99%	94% (S)	99%	84% (S)	99%	99% (S)	99%	87% (S)
6	13	99%	94% (S)	99%	79% (S)	99%	90% (S)	99%	92% (S)
7	14	46%	78% (R)	99%	77% (R)	< 5%		< 5%	
8	15	33%	99% (S)	99%	75% (S)	42%	31% (S)	62%	66% (S)
9	16	48%	77% (S)	99%	76% (S)	50%	14% (S)	67%	46% (S)

at 500 MHz or 300 MHz in CDCl₃ and referenced internally to the residual CHCl₃ peak (7.26 ppm). ¹³C NMR spectra were recorded at 100 or 75 MHz in CDCl₃ and referenced to the central peak of CDCl₃ (77.0 ppm). ³¹P NMR spectra were recorded at 121.47 MHz in CDCl₃. Chemical shifts are reported in ppm (δ scale). Enantiomeric excesses were determined either using HPLC with a chiral column and a diode array detector at 220 and 254 nm or by GC with a chiral column and an MS detector. Optical rotations were recorded on a thermostated polarimeter using a sodium lamp (589nm) and a 1.0 dm cell. HRMS (ESI) data were obtained using a Bruker microTOF-Q II instrument operating at ambient temperature. IR spectra were measured using a Perkin Elmer FT-IR apparatus.

Preparation of carboxylated pyridine derivatives **2a** and **2b**

nBuLi (2.5M in hexane, 2.0 equiv.) was added to a solution of **1a** or **1b** (1.0 mmol) and diisopropylamine (1.0 mmol) in dry Et₂O (20 ml) at -30 °C under argon atmosphere. The mixture was stirred at -30 °C for 1 h, and then dimethyl carbonate (1.1 mmol) was added. The solution was stirred at -30 °C for 1h, then it was allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was quenched by adding ammonium chloride (saturated aqueous solution) and the aqueous phase was extracted with Et₂O. Combined organic phases were washed further with brine and dried over MgSO₄ and filtered off. Removing the solvent under vacuum gave a crude product, which was purified by flash column chromatography (pentane: ethyl acetate = 10: 1) to give the pure product in 86% and 90% isolated yield for **2a** and **2b**. The racemic mixture was separated by preparative HPLC (Chiralcel

OD-column, 20×250mm, hexane : isopropanol = 99.5 : 0.5, 3mLmin⁻¹)

(S)-Methyl 2-chloro-6, 7-dihydro-5H-cyclopenta [b] pyridine-7-carboxylate (S)-2a: Obtained in 86% yield. [α]_D^{25.0} = 21.1 (c 1, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.50 (d, *J* = 8.0Hz, 1H), 7.15 (d, *J* = 8.0Hz, 1H), 4.09 (dd, *J* = 6.0, 8.5Hz, 1H), 3.75 (s, 3H), 3.11 (m, 1H), 2.90 (m, 1H), 2.45 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 173.3, 162.3, 150.0, 136.5, 135.3, 122.9, 52.5, 51.0, 29.2, 28.2. IR (neat, cm⁻¹): 1731, 1568, 1421, 1164, 823. HRMS (ESI) *m/z* = 212.0473, calcd. for C₁₀H₁₁ClNO₂ [M + H]⁺: 212.0478

(S)-Methyl 2-chloro-5,6,7,8-tetrahydroquinoline-8-carboxylate 2b: Obtained in 90% yield. [α]_D^{25.0} = 26.34 (c 0.2, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.41 (t, *J* = 8Hz, 1H), 7.16 (d, *J* = 8Hz, 1H), 3.98 (m, 3H), 3.76 (s, 3H), 2.85 (m, 1H), 2.76 (m, 1H), 2.25 (m, 1H), 2.12 (m, 1H), 1.95 (m, 1H), 1.83 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 174.1, 154.2, 148.2, 140.0, 131.5, 122.8, 52.3, 47.8, 27.7, 26.7, 19.9. IR (neat, cm⁻¹): 2948, 1732, 1566, 1442, 1430, 1161, 1135, 1003, 814. HRMS (ESI) *m/z* = 248.0449, calcd. for C₁₁H₁₂ClNO₂Na [M + Na]⁺: 248.0454

Preparation of pyridine alcohols **3a** and **3b**

To a solution of esters **2a** or **2b** (1.0 mmol) in THF (10ml), DIBAL-H (1.0 M in THF, 2.5 eq) was added dropwise at -78 °C under argon atmosphere. After addition, the reaction mixture was stirred at -78 °C for another 2hr and then warmed up to room temperature for 1hr. After the reaction completed, ammonium chloride (saturated aqueous solution) was added and the aqueous phase was extracted with dichloromethane. Combined organic phases were washed further with brine, dried over MgSO₄ and

filtered off. The crude product was purified by flash column chromatography (dichloromethane: methanol = 20: 1) to give the pure product.

(S)-(2-Chloro-6,7-dihydro-5H-cyclopenta[b]pyridin-7-yl)methanol 3a: Obtained in 87% yield. $[\alpha]^{25.0}_D = 8.2$ (c 1, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 3.90 (m, 1H), 3.81 (dd, *J* = 7.5, 10.5 Hz, 1H), 3.47 (brs, 1H), 3.35 (m, 1H), 2.92 (m, 2H), 2.28 (m, 1H), 1.84 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 167.3, 149.3, 136.3, 135.1, 122.1, 65.5, 46.9, 28.9, 26.5. IR (neat, cm⁻¹): 2940, 1568, 1418, 1237, 1167, 1033, 875, 8181. HRMS (ESI) *m/z* = 184.0524, calcd. for C₉H₁₁ClNO [M + H]⁺: 184.0529

(S)-(2-Chloro-5,6,7,8-tetrahydroquinolin-8-yl)methanol 3b: Obtained in 87% yield. $[\alpha]^{25.0}_D = 8.2$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 3.82-3.76 (m, 2H), 2.99 (m, 1H), 2.77-2.66 (m, 2H), 1.98-1.91 (m, 2H), 1.71 (m, 1H), 1.47 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 160.3, 147.5, 139.9, 131.4, 121.9, 67.0, 42.4, 28.2, 25.8, 21.2. IR (neat, cm⁻¹): 2940, 1568, 1418, 1237, 1167, 1033, 875, 8181. HRMS (ESI) *m/z* = 184.0524, calcd. for C₉H₁₁ClNO [M + H]⁺: 184.0529

Preparation of 4a and 4b

Alcohol **3a** or **3b** (1.0 mmol), PhB(OH)₂ (1.5 mmol) and DPPFPdCl₂DCM (0.1 mmol) were added into toluene (20 ml), followed by K₂CO₃ (2.0 mmol) and H₂O (1 ml). The mixture was heated to reflux under argon atmosphere overnight. After completion, reaction mixture was cooled to room temperature and extracted with diethyl ether. Combined organic phases were washed further with brine and dried over MgSO₄ and filtered off. Removing the solvent under vacuum gave the crude product, which was purified by flash column chromatography (pentane: ethyl acetate = 5: 1) to give the pure product.

(S)-(2-Phenyl-6,7-dihydro-5H-cyclopenta[b]pyridin-7-yl)methanol 4a: Obtained in 78% yield. $[\alpha]^{25.0}_D = 29.3$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.54 (m, 2H), 7.45 (m, 2H), 7.38 (m, 1H), 4.98 (brs, 1H), 3.99 (m, 1H), 3.86 (t, *J* = 10 Hz, 1H), 3.48 (m, 1H), 2.93 (dd, *J* = 5.5, 9.5 Hz, 2H), 2.28 (m, 1H), 1.71 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 167.5, 155.2, 139.1, 135.7, 133.2, 128.7, 126.7, 118.9, 66.6, 46.1, 29.3, 26.1. IR (neat, cm⁻¹): 2941, 1586, 1572, 1431, 1226, 1025, 833, 747, 692. HRMS (ESI) *m/z* = 226.1226, calcd. for C₁₅H₁₆NO [M + H]⁺: 226.1232

(S)-(2-Phenyl-5,6,7,8-tetrahydroquinolin-8-yl)methanol 4b: Obtained in 80% yield. $[\alpha]^{25.0}_D = 27.7$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 7.86 (d, *J* = 7 Hz, 2H), 7.58-7.50 (m, 4H), 7.38 (m, 1H), 3.82-3.87 (m, 2H), 3.14 (m, 1H), 2.82-2.78 (m, 2H), 2.03-1.96 (m, 2H), 1.77 (m, 1H), 1.45 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 160.1, 154.1, 139.1, 138.3, 131.1, 129.0, 126.8, 118.7, 100.3, 67.9, 42.1, 28.7, 26.4, 21.9. IR (neat, cm⁻¹): 3352, 2935, 1563, 1442, 1428, 1137, 1032, 992, 870, 837. HRMS (ESI) *m/z* = 240.1383, calcd. for C₁₆H₁₈NO [M + H]⁺: 240.1388

Iodination of 4a and 4b

To a solution of compound **4a** or **4b** (1.0 mmol) in dry dichloromethane (15 ml), iodine (3.0 mmol), triphenylphosphine (3.0 mmol) and imidazole (3.0 mmol) were added. The mixture was stirred at room temperature overnight. After completion, the reaction mixture was diluted with dichloromethane and washed with saturated aqueous sodium thiosulfate solution. The separated organic phase was further washed with brine and dried over MgSO₄ and filtered off. Removing the solvent under vacuum gave a crude product, which was purified by flash column chromatography (pentane: diethyl ether = 5: 1) to give the pure product.

(S)-7-(Iodomethyl)-2-phenyl-6,7-dihydro-5H-cyclopenta[b]

pyridine 5a: Obtained in 87% yield. $[\alpha]^{25.0}_D = 18.4$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 8.01 (m, 2H), 7.55 (m, 2H), 7.47 (m, 2H), 7.40 (m, 1H), 3.89 (m, 1H), 3.51 (m, 2H), 2.95 (m, 2H), 2.5 (m, 1H), 1.96 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 164.9, 156.4, 139.9, 135.8, 133.6, 129.0, 128.9, 127.1, 119.2, 47.8, 31.5, 28.4, 12.3. IR (neat, cm⁻¹): 1586, 1571, 1442, 1431, 1163, 832, 765, 691. HRMS (ESI) *m/z* = 336.0244, calcd. for C₁₅H₁₅IN [M + H]⁺: 336.0249

(S)-8-(iodomethyl)-2-phenyl-5, 6, 7, 8-tetrahydroquinoline 5b:

Obtained in 90% yield. $[\alpha]^{25.0}_D = 31.1$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8 Hz, 1H), 7.47-7.42 (m, 3H), 7.39 (m, 1H), 3.96 (dd, *J* = 3, 6.5 Hz, 1H), 3.81 (t, *J* = 9 Hz, 1H), 3.11 (m, 1H), 2.80-2.77 (m, 2H), 2.09 (m, 1H), 1.92-1.89 (m, 2H), 1.81 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 156.9, 154.7, 139.5, 137.8, 131.3, 128.8, 128.6, 126.9, 118.4, 42.6, 29.9, 29.2, 20.8, 14.9. IR (neat, cm⁻¹): 2937, 1558, 1459, 1448, 1178, 831, 758, 689. HRMS (ESI) *m/z* = 350.0400, calcd. for C₁₆H₁₇IN [M + H]⁺: 350.0406

General procedure for borane-protected N,P-Ligands 6a-6d

nBuLi (2.5M in hexane, 1.5 eq) was added to a solution of Ar₂P(BH₃)H (0.5 mmol) in dry THF (15 mL) at -78 °C under argon atmosphere. The solution was stirred for a further 10 min at -78 °C then 1 hr at room temperature. Substrate **5a-5b** (0.4 mmol) dissolved in THF was added dropwise to reaction mixture at 0 °C and stirred at 0 °C for another 1 hr. After addition, the reaction mixture was warmed to room temperature and stirred over night. When the reaction was completed, NaHCO₃ (saturated aqueous solution) was added and the aqueous phase was extracted with dichloromethane. Combined organic phases were washed further with brine and dried over MgSO₄ and filtered off. Removing the solvent under vacuum gave a crude product, which was purified by flash column chromatography (pentane: diethyl ether = 10: 1) to give the pure product.

(S)-7-((Diphenylphosphino)methyl)-2-phenyl-6,7-dihydro-5H-

cyclopenta[b]pyridine borane adduct 6a: Obtained in 91% yield. $[\alpha]^{25.0}_D = 17.5$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ 8.06 (d, *J* = 12.0 Hz, 2H), 7.94 (m, 2H), 7.78 (m, 2H), 7.55-7.43 (m, 11H), 3.61 (m, 1H), 3.46 (m, 1H), 2.80 (m, 2H), 2.43 (m, 1H), 1.67 (m, 1H), 1.4-0.6 (brm, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 166.3 (d, *J* = 13.6), 155.7, 139.7, 135.1, 132.9, 132.5 (d, *J* = 8.7), 131.3 (d, *J* = 2.7 Hz), 129.1, 128.9, 128.8, 128.7, 126.9, 118.6, 41.1, 33.0, 30.2 (d, *J* = 3.8 Hz), 29.1. ³¹P NMR: δ 16.6. IR (neat, cm⁻¹): 2379, 1587, 1435, 1107, 1061, 736, 693. HRMS (ESI) *m/z* = 406.1890, calcd. for C₂₇H₂₇BNP [M + H]⁺: 406.2010.

(S)-7-((Dio-tolylphosphino)methyl)-2-phenyl-6,7-dihydro-5H-

cyclopenta[b]pyridine borane adduct 6b: Obtained in 60% yield. $[\alpha]^{25.0}_D = 3.3$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ 8.18-8.02 (m, 3H), 7.89 (m, 1H), 7.58-7.10 (m, 11H), 3.82 (t, *J* = 15.0 Hz, 1H), 3.32 (m, 1H), 2.81 (m, 2H), 2.36 (m, 2H), 2.26 (s, 3H), 2.12 (s, 3H), 1.71 (m, 1H), 1.7-0.8 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 166.5 (d, *J* = 14.2 Hz), 155.5, 142.3 (d, *J* = 5.2 Hz), 139.6, 135.2, 134.2, 132.9, 132.8, 131.9 (d, *J* = 8.3 Hz), 131.5 (d, *J* = 15 Hz), 128.7, 126.9, 126.6 (d, *J* = 7.5 Hz), 118.5, 40.9, 33.1, 29.6, 29.1, 21.8 (d, *J* = 4.5 Hz). ³¹P NMR: δ 17.5. IR (neat, cm⁻¹): 2373, 1585, 1442, 1135, 1061, 823, 737, 693. HRMS (ESI) *m/z* = 436.2365, calcd. for C₂₉H₃₂BNP [M + H]⁺: 436.2365

(S)-8-((Diphenylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahy-

droquinoline borane adduct 6c: Obtained in 99% yield. $[\alpha]^{25.0}_D = 3.0$ (c 1.00, CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ 8.12-8.02 (m, 4H), 7.78-7.71 (m, 2H), 7.53-7.38 (m, 11H), 3.76 (dt, *J* = 0.2, 14.7 Hz, 1H), 3.30 (m, 1H), 2.77 (m, 2H), 2.28 (m, 2H), 1.90-1.71 (m, 3H), 1.50-0.82 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 158.7

(d, $J=12.7$ Hz), 154.3, 139.8, 137.8, 133.0 (d, $J=8.7$ Hz), 132.1 (d, $J=8.7$ Hz), 131.2, 131.1, 128.9, 128.8, 128.7, 126.8, 118.0, 37.1 (d, $J=1.4$ Hz), 31.0 (d, $J=3.6$ Hz), 30.1, 28.9, 20.6. ^{31}P NMR : δ 16.8. IR (neat, cm^{-1}): 3676, 2988, 2380, 1459, 1065, 736, 692. HRMS (ESI) m/z = 422.2208, calcd. For $\text{C}_{28}\text{H}_{39}\text{BNP}[\text{M} + \text{H}]^+$: 422.2209
(S)-8-((Dio-tolylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroquinoline borane adduct 6d: Obtained in 54% yield, $[\alpha]^{25.0}_{\text{D}} = 13.2$ (c 1.00, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 8.29 (dd, $J=8.1$, 14.1Hz, 1H), 7.98 (m, 2H), 7.82 (dd, $J=7.8$, 12.3Hz, 1H), 7.52-7.11 (m, 11H), 3.88 (t, $J=15.6$ Hz, 1H), 3.11 (m, 1H), 2.77 (m, 2H), 2.40 (m, 1H), 2.24 (s, 3H), 2.10 (s, 3H), 1.87 (m, 2H), 1.6801.57 (brm, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 154.4, 142.9 (d, $J=4.2$ Hz), 142.0 (d, $J=6.3$ Hz), 138.0, 134.9, 132.4 (d, $J=12.0$ Hz), 132.0 (d, $J=8.3$ Hz), 131.8 (d, $J=8.3$ Hz), 131.6 (d, $J=2.3$ Hz), 131.0 (d, $J=2.3$ Hz), 128.8, 126.8, 126.7, 126.53 (d, $J=1.5$ Hz), 118.1, 37.3, 30.5, 29.9, 29.1, 21.9 (d, $J_{\text{CP}}=4.3$ Hz), 20.6. ^{31}P NMR : δ 18.0. IR (neat, cm^{-1}): 3057, 2927, 2380, 1458, 1064, 909, 741. HRMS (ESI) m/z = 449.2440, calcd. For $\text{C}_{30}\text{H}_{34}\text{BNP}[\text{M} + \text{H}]^+$: 449.2480

General procedure for preparation of iridium complex 7a-7d

Borane protected N,P-ligand (1mmol) was dissolved in Et_2NH (10 ml for 1 mmol of substrate) and stirred at room temperature under argon overnight; the Et_2NH was removed under vacuum and the residue was filtered through short deactivated silica gel using (pentane: diethyl ether = 1: 1) followed by removing the solvent. The free N,P-ligand and $[\text{Ir}(\text{COD})\text{Cl}]_2$ were dissolved in dichloromethane under argon. This solution was heated to reflux for 1hour. After cooling to room temperature, water and $\text{NaBARF} \cdot 3\text{H}_2\text{O}$ were added and stirred vigorously for 2 hours at room temperature. The organic phase was separated and washed with brine, dried over MgSO_4 and filtered off. Removing the solvent under vacuum gave a crude product, which was purified by flash column chromatography (pentane: dichloromethane = 3: 2) to give the pure product.

(S)-[1,5-Cycloocatdien-7-((diphenylphosphino)methyl)-2-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridin-iridium(I)]-tetrakis-(3,5-bis-(trifluoromethyl)-phenyl)-borat 7a: Obtained in 76% yield. $[\alpha]^{25.0}_{\text{D}} = 2.9$ (c 0.75, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 7.71-7.43 (m, 27H), 7.24-7.17 (m, 2H), 4.35 (m, 2H), 4.16 (m, 1H), 3.06 (m, 2H), 2.84 (m, 4H), 2.22-1.61 (m, 8H), 1.24 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 166.7 (d, $J=2.0$ Hz), 161.9 (dd, $J=50.0$ Hz), 160.4, 139.4, 138.3, 136.4, 134.9, 133.7, 132.5, 132.4, 132.1, 131.6, 131.3, 130.6 (d, $J=10.0$ Hz), 130.1, 129.8, 129.7, 129.4, 129.3, 129.2, 128.8 (m), 128.4, 126.4 (d, $J=20.0$ Hz), 125.5, 122.9, 119.3, 117.6, 92.6 (d, $J=7.5$ Hz), 83.6 (d, $J=17.3$ Hz), 68.6, 66.6, 46.7 (d, $J=5.5$ Hz), 36.6 (d, $J=4.8$ Hz), 34.6, 30.0, 29.8, 29.3, 28.8, 28.7, 28.1, 24.4. ^{31}P NMR : δ 12.7. IR (neat, cm^{-1}): 2924, 1610, 1454, 1437, 1352, 1272, 1115, 885, 836, 744, 712, 694, 681. HRMS (ESI) m/z = 694.2211, calcd. For $\text{C}_{35}\text{H}_{36}\text{IrNP}[\text{M}-\text{BARF}]^+$: 694.2215.

(S)-[1,5-Cycloocatdien-7-((dio-tolylphosphino)methyl)-2-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridin-iridium(I)]-tetrakis-(3,5-bis-(trifluoromethyl)-phenyl)-borat 7b: Obtained in 80% yield. $[\alpha]^{25.0}_{\text{D}} = 24.5$ (c 2.0, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 7.87-7.39 (m, 26H), 7.12 (m, 1H), 4.42 (m, 1H), 4.21 (m, 2H), 3.07 (m, 3H), 2.95-2.40 (m, 6H), 2.32-2.06 (m, 5H), 2.05-1.90 (m, 3H), 1.43-1.23 (m, 2H), 1.23-1.00 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 166.7, 162.0 (dd, $J=50.0$ Hz), 160.9, 142.48, 140.51, 139.5, 138.6, 136.3, 135.0, 133.8, 133.1, 132.6, 132.2, 131.8 (d, $J=2.7$), 131.4, 130.2, 129.8, 129.3, 129.01-128.86 (m), 128.53-128.42 (m), 128.18, 127.02 (d, $J=10.0$ Hz), 126.6, 126.4, 122.9, 119.4, 117.7 (m), 93.9, 85.2, 67.2 (d, $J=5.0$ Hz), 66.4 (m), 46.6 (d, $J=5.6$ Hz), 36.9 (m), 34.4, 30.4, 30.2, 29.9, 28.7, 28.4 (m), 27.9 (m),

24.6, 23.3 (m), 23.1. ^{31}P NMR : δ 20.8. IR (neat, cm^{-1}): 2925, 1610, 1452, 1436, 1353, 1273, 1117, 886, 839, 745, 681. HRMS (ESI) m/z = 722.2524, calcd. For $\text{C}_{37}\text{H}_{40}\text{IrNP}[\text{M}-\text{BARF}]^+$: 708.2371.

(S)-[1,5-Cycloocatdien-8-((diphenylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroquinolin-iridium(I)]-tetrakis-(3,5-bis-(trifluoromethyl)-phenyl)-borat 7c: Obtained in 89% yield. $[\alpha]^{25.0}_{\text{D}} = 15.7$ (c 0.2 CHCl_3). ^1H NMR (CDCl_3 , 500 MHz): δ 7.79-7.63 (m, 10H), 7.63-7.48 (m, 12H), 7.48-7.39 (m, 5H), 7.34-7.28 (m, 2H), 4.52 (m, 1H), 4.31 (m, 1H), 4.10 (m, 1H), 3.14 (m, 1H), 2.84 (m, 2H), 2.70 (m, 1H), 2.55 (m, 1H), 2.51-2.32 (m, 2H), 2.19 (m, 1H), 2.08-1.84 (m, 3H), 1.81-1.67 (m, 3H), 1.40-1.31 (m, 1H), 1.15-1.04 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 162.6 (dd, $J=50.0$ Hz), 160.2, 141.2, 138.8, 135.0, 133.2 (d, $J=10.5$ Hz), 132.6-132.1 (m), 132.0-131.4 (m), 130.6-130.2 (m), 129.9, 129.8, 129.6, 129.5, 129.3, 128.9, 126.7, 124.8, 124.2, 123.0, 119.3, 117.7, 88.0, 69.5, 68.8, 41.0, 36.1, 35.8, 32.2, 32.1, 29.9, 29.4, 28.3, 23.6, 20.0. ^{31}P NMR : δ 3.7. IR (neat, cm^{-1}): 2923, 1609, 1461, 1436, 1353, 1274, 1118, 886, 838, 738, 712, 681, 695. HRMS (ESI) m/z = 708.2367, calcd. For $\text{C}_{36}\text{H}_{38}\text{IrNP}[\text{M}-\text{BARF}]^+$: 722.2528

(S)-[1,5-Cycloocatdien-8-((dio-tolylphosphino)methyl)-2-phenyl-5,6,7,8-tetrahydroquinolin-iridium(I)]-tetrakis-(3,5-bis-(trifluoromethyl)-phenyl)-borat 7d: Obtained in 87% yield. $[\alpha]^{25.0}_{\text{D}} = 10.0$ (c 0.3 CHCl_3). ^1H NMR (CDCl_3 , 500 MHz): δ 7.84-7.67 (m, 12H), 7.67-7.55 (m, 3H), 7.55-7.49 (m, 5H), 7.49-7.26 (m, 6H), 7.23-7.11 (m, 1H), 4.68-4.33 (m, 2H), 4.19 (m, 1H), 3.01-2.67 (m, 1H), 2.67-2.36 (m, 4H), 2.23-2.00 (m, 5H), 1.95-1.83 (m, 2H), 1.83-1.48 (m, 5H), 1.22-0.94 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 161.6 (dd, $J=50$ Hz), 169.0, 141.0, 139.2, 135.1, 132.7, 131.7, 131.5, 130.2, 129.8-129.3 (m), 128.5-129.0 (m), 127.1, 127.0-126.6 (m), 125.8, 123.0, 119.4, 117.7, 41.0 (d, $J=6$ Hz), 36.5, 34.8, 31.8 (m), 30.8, 30.2, 29.4, 28.2, 24.0, 23.1, 22.7, 19.6. ^{31}P NMR : δ 40.7. IR (neat, cm^{-1}): 2951, 1609, 1461, 1353, 1272, 1115, 886, 838, 736, 712, 681, 669. HRMS (ESI) m/z = 736.2681, calcd. For $\text{C}_{38}\text{H}_{42}\text{IrNP}[\text{M}-\text{BARF}]^+$: 736.2684

General procedure for asymmetric hydrogenation

Ir-complex (1.0 mol %) and substrate (0.25 mmol) were added into a vial, followed by dichloromethane (1 mL). The vial was placed in a high-pressure hydrogenation apparatus. The reactor was purged three times with H_2 (1 bar), then filled to H_2 (50 bar). The reaction was stirred at room temperature for 12 hours. Then the H_2 pressure was released and the solvent was removed *in vacuo*. The crude product was filtered through on a short plug of silica. Conversions were determined by ^1H NMR spectroscopy and enantiomeric excesses were determined by GC-MS or HPLC with a chiral column.^[4]

Supporting Information (see footnote on the first page of this article):

Copies of the ^1H NMR and ^{13}C NMR spectra for all key intermediates and final products.

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Entry for the Table of Contents ((Please choose one layout.))

Layout 2:

New pyridine derived N,P-chelated iridium catalysts were prepared and evaluated in asymmetric hydrogenation of tri-substituted olefins with high conversions and enantioselectivities.

(Asymmetric Hydrogenation)

Xu Quan, Vijay Singh Parihar, Milan Bera and Pher G. Andersson* (Page No. – Page No.)

Iridium Catalysts with Chiral Bicyclic Pyridine-Phosphine Ligands for Asymmetric Hydrogenation of Olefins

Keywords: Iridium / N,P-ligand / Pyridine/ Asymmetric Hydrogenation

Supporting Information

(S)-2a ¹H NMR

(S)-2b ^1H NMR

(S)-2b ^{13}C NMR

3a ^1H NMR

3a ^{13}C NMR

3b ¹H NMR

4a ^1H NMR

4b ^1H NMR

5a ¹H NMR

STANDARD CARBON PARAMETERS
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Temp: 25.0 C / 298.1 K
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INNOVA-500 "unity500"
User: QUANTA 2012
Date: 11-14-87
Pulse Sequence: zgpg30
Relax. delay: 1.000 sec
Acq. time: 0.000 sec
Width: 25996.3 Hz
368 repetitions
135.71 MHz
DRYDIPPLE H₁, 499.93 MHz
Power: 33 dB
continuously on
Data processing
Line broadening 1.0 Hz
F2 size: 131072
Total time 14 minutes

Pulse Sequence: szpul
Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
Pulse: zgpg30
NUC1: 13C
NUC2: 1H
Date_: 20120412
Time: 10.00
Pulse Sequence: szpul
Pulse: zgpg30
Acq. time: 3.000 sec
F2: 100.625 MHz
F1: 499.93 MHz
OBSERVE: 1H
DATA PROCESSING
Line broadening: 0.2 Hz
Gamma: 1.0000
Total time: 5 minutes

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7c ^1H NMR

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