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Asymmetric Arylation

Chiral Phosphorus–Olefin Ligands for the Rh^{I}-Catalyzed Asymmetric Addition of Aryl Boronic Acids to Electron-Deficient Olefins

Qian Chen,*[a] Liang Li,[a] Guangli Zhou,[b] Xiaoli Ma,[a] Lu Zhang,[a] Fang Guo,[a] Yi Luo,*[b] and Wujiong Xia*[a]

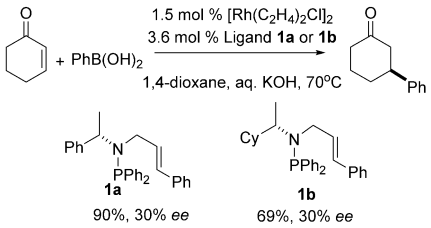
Abstract: New chiral phosphorus–olefin hybrid ligands derived from the rigid "privileged" L-proline have been conveniently prepared and applied in the rhodium-catalyzed asymmetric arylation of electron-deficient olefins with arylboronic acids at room temperature; this reaction provides the desired products in excellent yields and high enantioselectivities. The origin of observed stereoselectivity has been investigated by density functional theory (DFT) calculations.

Chiral molecules are important in the field of pharmaceuticals, agricultural chemicals, fine chemicals, and materials. Catalytic asymmetric synthesis of enantiomer-enriched compounds in the presence of a catalytic amount of metal complexes modified with various chiral ligands has been proven to be one of the most efficient approaches.[1] It will be a lasting topic of great interest in asymmetric catalysis for the design and application of novel chiral ligands, because a versatile chiral ligand has never been reported. In this regard, the exploitation of phosphorus- and nitrogen-based chiral ligands has given us a distinct impression.[2]

On the one hand, the discovery of organometallic complexes with olefin ligand(s) in organometallic chemistry has a long and continuing history.[3] However, the use of catalytic organometallic complexes with chiral olefin ligand(s) was only achieved recently by the research groups of Hayashi and Carreira; this encouraged a dramatic surge of research interest in asymmetric catalysis.[4] Subsequently, various diene ligands with bicyclic and acyclic skeletons have been designed and prepared.[5,6] As a coordination group, olefins are really fascinating due to its enormous potency, which can be installed into many "privileged" skeletons and/or combined with the other existing coordination atoms and/or functional groups. In fact, the recently developed olefin-containing chiral ligands, alkene, P-,[7] alkene, N-[8] and alkene, S-hybrid[9,10] ligands have shown novel coordination ability and higher catalytic performance in asymmetric catalysis, and attracted considerable attention from several research groups.

We have also engaged in this interesting research field and described that chiral *N-tert*-butylsulfinyl vinyl aziridines and C_2-symmetric chiral sulfurous diamides can be used as efficient chiral sulfur–olefin hybrid ligands for highly enantioselective rhodium-catalyzed asymmetric 1, 4-addition reactions.[11] In this context, considering the outstanding coordination ability of phosphorus, the exploitation of new ligands based on the olefin, P-hybrid compounds would unambiguously enrich the chiral ligand libraries and enhance their application in asymmetric organic synthesis. Herein, we describe the development of a new class of olefin, P-ligands based on the rigid "privileged" chiral pyrrolidine backbone.

We originally conceived that chiral phosphorus–olefin ligands would be obtained by combining a simple chiral phosphinamine with cinnamyl group. Therefore, we started our research by preparing chiral phosphorus–olefin compounds **1a** and **1b** and their application as ligands in the rhodium-catalyzed asymmetric 1,4-addition of phenyl boronic acid to cyclohexenone (Scheme 1). The chiral phosphorus–olefin compounds **1a** and **1b** can be directly obtained by a simple two-step procedure. Reductive amination of (*S*)-1-phenylethanamine or (*S*)-1-cyclohexylethanamine with cinnamaldehyde gave the corresponding secondary amine in high yield. *N*-phosphi-



Scheme 1. Initial attempts using chiral olefins, P-ligands for the Rh^{I}-catalyzed asymmetric arylation.

[a] *Prof. Dr. Q. Chen, L. Li, X. Ma, L. Zhang, F. Guo, Prof. Dr. W. Xia*
State Key Lab of Urban Water Resource and Environment (SKLUWRE)
School of Chemistry and Chemical Engineering
Harbin Institute of Technology
Harbin, Heilongjiang, 150080 (China)
E-mail: chenqian@hit.edu.cn

[b] *G. Zhou, Prof. Dr. Y. Luo*
State Key Laboratory of Fine Chemicals
School of Pharmaceutical Science and Technology
Dalian University of Technology
Dalian 116024 (China)

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nation of the secondary amines with chlorodiphenyl phosphine completed the synthesis of **1** in good yield. When **1a** and **1b** were used as a chiral ligand for the rhodium-catalyzed asymmetric 1,4-addition reaction, the adduct was obtained in good-to-high yield with promising enantioselectivity (30% *ee*).

Based on the above encouraging results, we designed a kind of novel chiral phosphorus–olefin ligand bearing a "privileged" chiral pyrrolidine backbone (Figure 1). We further envi-

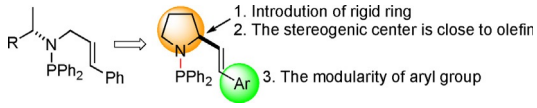
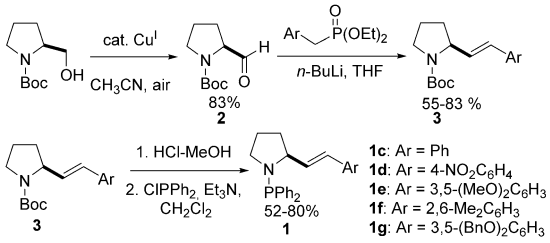


Figure 1. Design of new chiral phosphorus–olefin hybrid ligand.

sioned that the stereocontrol performance of the ligand in asymmetric catalysis can be improved by introducing a rigid five-membered cyclic backbone, which can be readily obtained from L-proline, and the chiral carbon of the ligand is closer to the alkenyl group compared to that of **1a** and **1b**. Furthermore, the modularity of aryl group would make it possible to discover ideal ligands. It should be noted that most of the reported chiral phosphorus–olefin ligands are prepared by chiral resolution or tedious synthetic procedures, and few are derived from natural chiral pool compounds.[7k] This is the first successful example of a designed chiral phosphorus–olefin hybrid ligand governed by natural amino acid, L-proline.

The synthesis of ligands **1c**–**1g** is shown in Scheme 2; this started from the commercially available (*S*)-(−)-1-Boc-2-pyrrolidinemethanol in several sample steps (Boc = *tert*-butoxycarbonyl).[12] Oxidation of the alcohol gave the corresponding aldehyde **2** in 83% yield using copper-catalyzed air oxidation.[13]

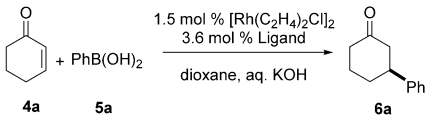


Scheme 2. Synthesis of chiral olefins, P-ligands derived from the L-proline.

A Horner–Wadsworth–Emmons olefination reaction of the aldehyde **2** with phosphonate afforded alkene **3** in good-to-high yields. Removal of the Boc group and subsequent *N*-phosphination with chlorodiphenyl phosphine completed the synthesis of **1** in moderate-to-high yields over two steps.

With chiral phosphorus–olefin ligands **1c**–**1g** in hand, the Rh^{I}-catalyzed 1,4-addition of phenylboronic acid **5a** with cyclohexenone **4a** was reexamined as the model reaction to evaluate its efficiency in asymmetric catalysis.[14] As expected, the product **6aa** was formed in excellent yield (>99%) and reasonably high enantioselectivity (85% *ee*) in the presence of

Table 1. Effect of the chiral phosphorus–olefin ligands in the Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohexenone.



4a 5a 6a

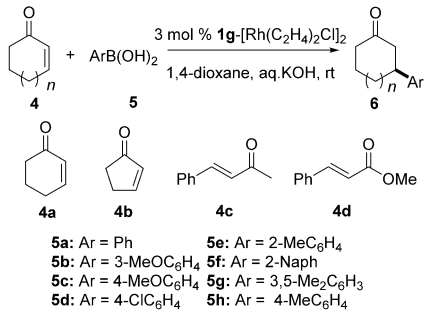
Entry[a]	Ligand	T [°C]	t [h]	Yield [%][b]	*ee* [%][c]
1	**1c**	70	3	99	85
2	**1c**	25	10	98	90
3	**1d**	25	10	98	90
4	**1e**	25	12	99	89
5	**1f**	25	12	89	81
6	**1g**	25	12	97	93

[a] All reactions were carried out with **4a** (0.5 mmol) and **5a** (2.5 mmol) in 1,4-dioxane (2.0 mL) unless otherwise noted. [b] Isolated yield. [c] Determined by chiral HPLC with hexane/2-propanol.

3 mol% Rh-**1c** complex at 70 °C (Table 1, entry 1). When the reaction temperature was reduced to room temperature (25 °C), the enantioselectivity increased to 90% *ee* (Table 1, entry 2). Then, electronic and steric effects of the aryl group in the chiral phosphorus–olefin ligands were examined (Table 1, entries 3–6). The electronic effect of aryl group in chiral phosphorus–olefin ligands has no distinct influence on catalytic activity, whereas the position of the substituent on the phenyl ring has a little influence on the enantioselectivity. For example, both ligands **1d** bearing electron-withdrawing substituted groups and **1e** bearing electron-donating substituted groups gave the products in excellent yield with 90% *ee* and 89% *ee*, respectively (Table 1, entries 3 and 4). However, the attempt to improve the enantioselectivity, by introducing two methyl groups at the *ortho*-position of benzene, has proven to be challenging, as a lower enantioselectivity (81% *ee*) despite maintaining higher yield (Table 1, entry 5) was obtained. The enantioselectivity of this catalytic reaction improved to 93% *ee* when ligand **1g** was used, in which the methyl substituent of 3,5-dimethoxyl benzene in ligand **1e** was replaced by benzyl (Table 1, entry 4 vs entry 6).

With the optimal reaction conditions in hand (Table 1, entry 6), the scope of this rhodium-catalyzed asymmetric 1,4-addition reaction was then investigated. As shown in Table 2, the substituents of substrate **5** may be either electron-rich or electron-deficient aryl groups, which had very little effect on the reaction stereoselectivity. For example, 3-methoxyphenyl and 4-methoxyphenyl, the aryl groups of which have electron-donating groups were successfully introduced to **4a**, thereby giving the corresponding product **6** with high enantioselectivity in excellent yields (Table 2, entries 2 and 3, 90% *ee*). 4-Chlorophenyl bearing an electron-withdrawing substituent was also introduced to **4a** to give **6ad** in good yield and excellent *ee* (93%) (Table 2, entry 4). The reaction of 2-methylphenyl, 2-naphthyl, 3,5-dimethylphenyl, and 4-methylphenyl boronic acid with **4a** gave the corresponding product **6** in excellent yield (90–98%) with good enantioselectivity (84–88% *ee*) (Table 2, entries 5–8). Then, cyclopentenone **4b** was examined as a substrate for this transformation. Thus, the reactions of cy-

Table 2. Rh/**1g**-catalyzed asymmetric addition of arylboronic acids **5** to α,β-unsaturated carbonyl compounds **4**.



4a 4b 4c 4d

5a: Ar = Ph **5e:** Ar = 2-MeC_6H_4
5b: Ar = 3-$MeOC_6H_4$ **5f:** Ar = 2-Naph
5c: Ar = 4-$MeOC_6H_4$ **5g:** Ar = 3,5-$Me_2C_6H_3$
5d: Ar = 4-ClC_6H_4 **5h:** Ar = 4-MeC_6H_4

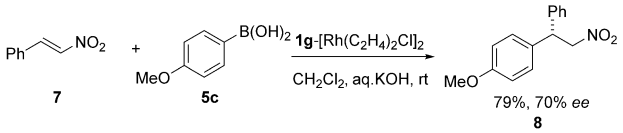
Entry[a]	4	$ArB(OH)_2$	*t* [h]	6	Yield [%][b]	*ee* [%][c]
1	**4a**	**5a**	10	**6aa**	97	93
2	**4a**	**5b**	8	**6ab**	93	90
3	**4a**	**5c**	8	**6ac**	99	90
4	**4a**	**5d**	8	**6ad**	70	93
5	**4a**	**5e**	10	**6ae**	98	87
6	**4a**	**5f**	12	**6af**	95	88
7	**4a**	**5g**	8	**6ag**	90	88
8	**4a**	**5h**	12	**6ah**	90	84
9	**4b**	**5a**	10	**6ba**	95	86
10	**4b**	**5c**	12	**6bc**	99	91
11	**4b**	**5e**	12	**6be**	96	93
12	**4b**	**5f**	12	**6bf**	95	84
13	**4b**	**5g**	10	**6bg**	98	90
14	**4c**	**5c**	10	**6cc**	73	87
15	**4d**	**5c**	12	**6dc**	95	92

[a] All reactions were carried out with **4a** (0.5 mmol) and **5a** (2.5 mmol) in 1,4-dioxane (2.0 mL) unless otherwise noted. [b] Isolated yield. [c] Determined by chiral HPLC with hexane/2-propanol.

clopentenone **4b** with several arylboronic acids, the aryl groups of which have electron-donating and electron-withdrawing substituted groups, took place smoothly to afford the corresponding **6** with good-to-high enantioselectivity (84–93% *ee*) in excellent yields (Table 2, entries 9–13). Furthermore, linear α,β-unsaturated carbonyl compounds were also good substrates for this transformation. The reaction of enone (*E*)-4-phenylbut-3-en-2-one **4c** with 4-methoxyphenyl boronic acid **5c** afforded **6cc** in good yield and high enantioselectivity (87% *ee*) (Table 2, entry 14). The reaction of methyl cinnamate **4d** with 4-methoxyphenyl boronic acid **5c** gave the product **6dc** in 95% yield with 92% *ee* (Table 2, entry 15).

Finally, we further examined the substrate scope other than α,β-unsaturated carbonyl compounds. Thus, the transformation of nitroalkene **7** to the synthetically useful intermediate **8** was carried out (Scheme 3). The enantioselective addition of 4-methoxyphenyl boronic acid **5c** to **7** in the presence of a rhodium/**1g** catalyst afforded product **8** in 79% yield with 70% *ee*.

The stereochemical pathway in our arylation of cyclohexenone **4a** with **1g** as the ligand is rationalized in Figure 2.[7c,f,h] After the initial transmetalation step, the phenylrhodium species has a *trans*-relationship between the phenyl group and the olefin of ligand **1g**. In the following step, cyclohexenone **4a** preferentially approaches the vacant position of rhodium with its α *si*-face to avoid the steric repulsion between the aryl



Scheme 3. Asymmetric addition of arylboronic acid **5c** to nitroalkene **7**.

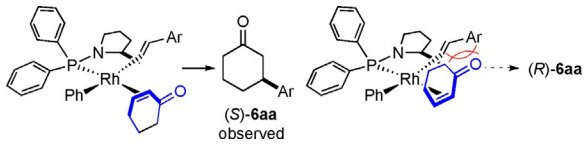


Figure 2. Proposed stereochemical model.

group of ligand and carbonyl or methyene of 6-position in cyclohexenone **4a**. Accordingly, the phenyl group in the metal center attacks the activated olefin from the α *si*-face to give the corresponding adduct (*S*)-**6aa**, which is in agreement with the observed result. The absolute configuration of **6aa** was determined to be *S* by comparing its optical rotation value with the literature.[15]

To see the transition structures related to the stereochemistry, DFT calculations were conducted (see the Supporting Information for computational details). As shown in Figure 3, cyclohexenone (**B**) would adopt the *si*-face to coordinate with phenylrhodium species (**A**) to give coordination complex (**C**), which is exergonic by 2.9 kcal mol^{-1}. Then **C** overcomes an energy barrier of 14.9 kcal mol^{-1} to give species **E** with (*S*)-configuration. However, the *re*-face insertion process has a higher energy barrier (17.8 kcal mol^{-1}), endergonic coordination complex (**D**, 2.1 kcal mol^{-1}) and thermodynamically less favorable addition product **F**. This result is in line with the observed stereochemical outcomes. It is noteworthy that all of the optimized structures show a strong interaction between the Rh and HC=CHPh double bond of the ligand, as suggested by the Rh–C distances of 2.19 Å–2.45 Å (see Figure S1 in the Supporting Information).

To further access the origin of the stereoselectivity, an energy decomposition analysis was carried out.[16] The result indicates that the catalyst moiety in the transition state **TS (D–F)** with (*R*)-configuration is more deformed due to the repulsion between the Ph group of the ligand and the carbonyl group and neighboring methylene of cyclohexanone moiety in comparison with **TS (C-E)** with (*S*)-configuration.[16] This is similar for the coordination complexes **D** and **C**. This could account for the stabilities of **C** and **TS (C–E)**, and why the (*S*)-configured addition product **E** is more favorable.

In conclusion, we have successfully developed a new type of chiral phosphorus–olefin hybrid ligands based on the rigid "privileged" *L*-proline backbone, and demonstrated their utility in enantioselective rhodium-catalyzed asymmetric arylation of electron-deficient olefins with arylboronic acids at room temperature. The adducts can be obtained in high yields and high enantioselectivities. DFT calcualtions suggest that the repulsion between the Ph group of ligand and the carbonyl and neigh-

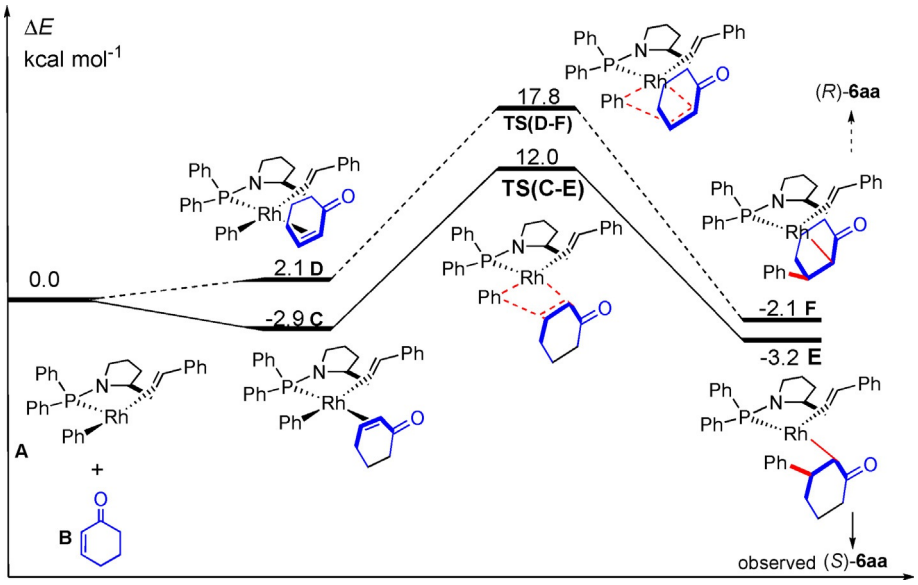


Figure 3. Computed energy profiles (energies in kcal mol^{-1}) for the different stereochemical pathways in the arylation of cyclohexenone and the arylrhodium species. Solid line denotes the *si*-face insertion to give the (*S*)-configuration, and the dashed line denotes the *re*-face insertion to give the (*R*)-configuration.

boring methylene of cyclohexanone accounts for the stereoselectivity. The simple synthesis and the modularity make this new type of ligand attractive and promising for asymmetric catalysis. Further modification of more effective chiral phosphorus–olefin hybrid ligands derived from L-proline and their applications in other asymmetric transformations is currently underway in our laboratory.

Experimental Section

General procedure for the synthesis of olefin from L-prolinal: To a solution of diethyl benzylphosphonate (1.5 mmol) in THF (5 mL) was added *n*BuLi (2.4 M in hexane, 0.63 mL, 1.5 mmol) at −78 °C over 5 min, and then the reaction mixture was stirred at the same temperature for 1 h. A solution of L-prolinal (1 mmol) in THF was added to the above solution. At this temperature, it was stirred for 1 h and then allowed to warm to room temperature. After being stirred overnight, water (20 mL) was added to quench the reaction. The aqueous phase was extracted by AcOEt (3×20 mL) and the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were isolated by silica gel column chromatography.

General procedure for the synthesis of the chiral olefin, P-ligands: AcCl (10 mmol) was slowly added to an oven-dried 25 mL flask charged with dried methanol (10 mL) at 0 °C. The resulting mixture was stirred for 1 hour at room temperature. A solution of olefin (1 mmol) in dried 1,4-dioxane (5 mL) was added to the reaction mixture. The resulting mixture was stirred for 3 h at room temperature. The solvent was removed and then an aqueous solution of 10% NaOH (10 mL) was added. The reaction mixture was extracted with CH_2Cl_2 and the organic phases were dried over Na_2SO_4 and evaporated under vacuum to give a colorless oil. To this oil in CH_2Cl_2 was added Et_3N (5 mmol) and PPh_2Cl (2 mmol) in CH_2Cl_2 at 0 °C. The mixture was stirred at room temperature for 6–10 h. The residue was purified by silica gel chromatography to give the desired ligand.

General procedure for rhodium(I)-catalyzed asymmetric 1,4-addition of phenylboronic acid to cycloalkenones: Under an atmosphere of N_2, a reaction flask was charged with $([Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 0.0075 mmol) and $PhB(OH)_2$ (2.5 mmol). Then, 1,4-dioxane (2.0 mL), ligand (0.018 mmol), cyclohexenone (0.5 mmol), and 4 M aqueous potassium hydroxide (0.5 mmol) were added successively to the flask. The mixture was stirred at room temperature. After dilution with AcOEt (20 mL), the mixture was washed with 10% aqueous NaOH and brine, and then dried over Na_2SO_4, concentrated under vacuum, and purified by silica gel column chromatography. The products were then analyzed by HPLC on a chiral stationary phase to determine the enantiomeric excess.

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Keywords: asymmetric arylation · electron-deficient olefins · ligands · L-proline · rhodium

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