The Regioselectivity of the Asymmetric Intermolecular Heck Reaction with Planar Chiral Diphosphine – Oxazoline Ferrocenyl Ligands

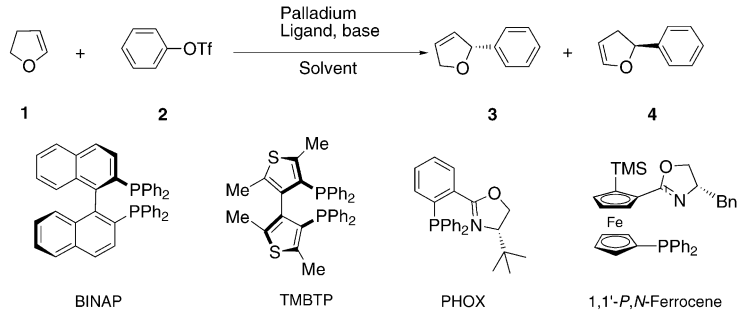
Tao Tu,[a] Wei-Ping Deng,[a] Xue-Long Hou,*[a] Li-Xin Dai,*[a] and Xi-Cheng Dong[b]

Abstract: A series of novel planar chiral diphosphine-oxazoline ferrocenyl ligands were synthesized and used efficiently in the palladium-catalyzed asymmetric intermolecular Heck reaction of 2,3-dihydrofuran with aryl triflate and cyclohexenyl triflate. The tuning of the regioselectivity was realized by means of different palladium precursors and by changing the electronic factor of the ligands. A plausible rationale based on the existed mechanism is provided.

Keywords: electronic effects · ferrocenyl ligands · Heck reaction · palladium · regioselectivity

Introduction

Since the first reports in the late 1980s,[1] the asymmetric Heck reaction has received considerable attention,[2] in particular, the intramolecular mode has been widely applied in organic synthesis.[3] The asymmetric intermolecular reaction between an olefin and an aryl source has been devised mainly for cyclic substrates (predominantly dihydrofuran), which was first reported by Hayashi and co-workers in 1991.[4] High enantioselectivities have been achieved by the use of bidentate ligands, usually diphosphines or phosphine-oxazolines.[4, 5] When these ligands are employed in the reaction of dihydrofuran (**1**) with phenyl triflate (**2**), two different products **3** and **4** are obtained (Scheme 1) as a result of the possibility of double-bond isomerization. For diphosphine-type ligands, such as BINAP,[4] TMBTP,[6, 7] and others,[8, 9] the compound with the migrated double bond, 2-phenyl-2,3-dihydrofuran (**4**), is obtained as the major product;[4, 10] while for P,N-type ligands, such as PHOX,[5] 1,1′-*P*,*N*-ferrocene ligand[11] and others,[12, 13, 14] the 2-phenyl-2,5-dihydrofuran (**3**) is formed predominantly. However, the reason for these strikingly different regioselectivities or how to control the regioselectivity is not clear.[15, 16] To understand the controlling or tuning of the regioselectivity, it is important to gain an insight into the mechanism of the asymmetric intermolecular Heck reaction.



Scheme 1. The asymmetric intermolecular Heck reaction with 2,3-dihydrofuran and phenyl triflate.

In our previous studies of chiral ferrocenyl ligands[17, 18] and the role played by their planar chirality,[11] we designed and synthesized a series of new diphosphine – oxazoline ferrocenyl ligands, which belong to a system synthetically convenient for modification,[19] and applied them to the asymmetric Heck reaction. Herein, we disclose the results of the use of these diphosphine – oxazoline ferrocenyl ligands in the asymmetric intermolecular Heck reaction. The regioselectivity of this reaction depends on different palladium sources as well as the electronic factor of the ligands.

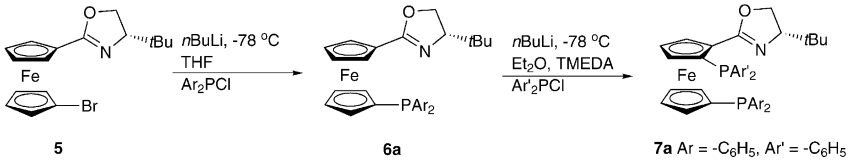
Results and Discussion

Synthesis of ligand (S,S_p)-7a: As shown in Scheme 2, ferrocenyl – oxazoline derivative **5**, that bears a *tert*-butyl group on

[a] Prof. X.-L. Hou, Prof. L.-X. Dai, T. Tu, Dr. W.-P. Deng
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
354 Fenglin Lu, Shanghai 200032 (China)
Fax: (+86) 21-6416-7519
E-mail: Xlhou@pub.sioc.ac.cn., Dailx@pub.sioc.ac.cn.

[b] Dr. X.-C. Dong
Key Laboratory of Computer Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
354 Fenglin Lu, Shanghai 200032 (China)
Fax: (+86) 21-6416-7519
E-mail: Dongxc@pub.sioc.ac.cn

 DOI: 10.1002/chem.200204450



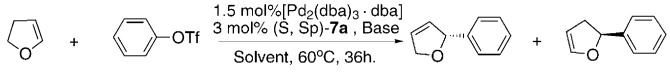
5 6a **7a** Ar = -C_6H_5, Ar' = -C_6H_5

Scheme 2. Synthesis of the planar chiral diphosphine – oxazoline ferrocenyl ligand (S,S_p)-**7a**.

the oxazoline ring,[20] was treated with *n*BuLi in THF at $-78\,^{\circ}C$ for 0.5 h, followed by trapping with Ph_2PCl to afford 1-diphenyl-phosphino-1′-oxazolinylferrocene (**6a**). Directed diastereoselective *ortho*-lithiation of **6a** according to Richard's and our procedure,[11a, 21] followed by trapping with chlorodiphenylphosphine, gave diphosphine – oxazoline ferrocenyl ligands (S,S_p)-**7a**, which contained not only a diphosphine fragment but also a phosphine – oxazoline fragment.

Asymmetric Heck reaction: With 1.5 mol% of catalyst, prepared in situ from $[Pd_2(dba)_3 \cdot dba]$ and 3 mol% of ligand (S,S_p)-**7a**, the reaction of **1** with **2** in THF was completed in 36 h with a high conversion to afford a mixture of regioisomers **3** and **4** in a ratio of 28:72 (Table 1, entry 1). The enantiomeric excess (*ee*) of product **3** was 97.1% *ee*, while that of the double-bond migration product **4** was low for a kinetic resolution process in the reaction.[10]

Table 1. Regioselective and enantioselective Heck reaction of 2,3-dihydrofuran.



1 **2** **3** **4**

Entry	Base	Solvent	Conversion [%][a]	Ratio of **3**/**4**[a]	*ee* [%][b] **3**(*R*)[c]	**4**(*S*)[c]
1	*i*Pr_2NEt	THF	98	28:72	97	29
2	PS	THF	98	40:60	96	30
3	Et_3N	THF	99	67:33	98	13
4	NaOAc	THF	80	55:44	98	29
5	*i*Pr_2NEt	toluene	96	40:60	91	10
6	*i*Pr_2NEt	DMF	90	35:65	93	nd
7	*i*Pr_2NEt	$(CH_2Cl)_2$	80	25:75	98	nd

[a] The conversion and ratio of **3**/**4** were determined by GC with *n*-undecane as the internal standard based on phenyl triflate (**2**). [b] Determined by GC on a Chiraldex G-PN column. [c] The absolute configuration of the products was assigned by comparison of the sign of specific rotations with literature data.[4, 5] nd = not determined.

To improve the regioselectivity of the reaction, the effect of bases and solvents was studied.[5, 10] With a Proton Sponge as the base, the ratio of **3**:**4** increased to 40:60 (Table 1, entry 2). However, when triethylamine was employed, product **3** was obtained as major product with 98.3% *ee* (Table 1, entry 3). Inorganic bases, such as NaOAc, gave higher ratios than diisopropylethylamine, but with lower conversion (Table 1, entry 4). Solvents more polar than toluene, such as DMF or 1,2-dichorlethane, favored the formation of isomer **4** (Table 1, entries 6 and 7).

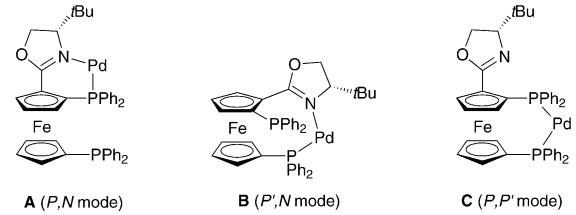
In view of the fact that $[Pd(OAc)_2]$ and $[Pd_2(dba)_3 \cdot dba]$ are two commonly used precursors of palladium species in the asymmetric Heck reaction, $[Pd(OAc)_2]$ was used instead of $[Pd_2(dba)_3 \cdot dba]$ in the reaction. Interestingly, a reversed ratio 67:33 for the two isomers **3** and **4** was obtained, whereby isomer **3** was formed with 96.8% *ee* (Table 2, entries 2 and 1). Furthermore, when the nonpolar solvent toluene was employed, an exciting ratio 95:5 was observed for **3** and **4** (Table 2, entry 3). When a proton sponge and trietheylamine were used instead of diisopropylethylamine, the observed regioselectivities did not improved (Table 2, entries 4 and 5). When $[Pd(O_2CCF_3)_2]$ was used in toluene, a ratio of 84:16 was obtained with a conversion of 65% (Table 2, entry 6). Again, The polar solvent favored the formation of isomer **4** (Table 2, entry 7). It seems that $[Pd(dba)_3 \cdot dba]$ favors the formation of product **4**, while $[Pd(OAc)_2]$ prefers the unisomerized product **3**.

Table 2. Effect of palladium precursors on the regioselectivity of Heck reaction.[a]

Entry	Palladium	Solvent	Base	Conversion [%][b]	Ratio of **3**/**4**[b]	*ee* [%][c] **3**(*R*)	**4**(*S*)
1	$[Pd(dba)_3 \cdot dba]$	THF	*i*Pr_2NEt	98	28:72	97	29
2	$[Pd(OAc)_2]$	THF	*i*Pr_2NEt	89	67:33	97	33
3	$[Pd(OAc)_2]$	toluene	*i*Pr_2NEt	85	95:5	97	26
4	$[Pd(OAc)_2]$	toluene	PS	70	83:17	94	39
5	$[Pd(OAc)_2]$	toluene	Et_3N	70	91:9	95	27
6	$[Pd(O_2CCF_3)_2]$	toluene	*i*Pr_2NEt	65	84:16	97	nd
7	$[Pd(O_2CCF_3)_2]$	THF	*i*Pr_2NEt	65	55:45	99	nd
8[d]	$[Pd(dba)_3 \cdot dba]$	THF	*i*Pr_2NEt	95	37:63	86	28
9[d]	$[Pd(dba)_3 \cdot dba]$	toluene	*i*Pr_2NEt	84	60:40	95	27
10[e]	$[Pd(dba)_3 \cdot dba]$	toluene	*i*Pr_2NEt	70	61:39	58	26
11[f]	$[Pd(dba)_3 \cdot dba]$	toluene	*i*Pr_2NEt	87	60:40	95	16

[a] The reaction was carried out with 1.5 mol% palladium precursor and 3 mol% ligand (S,S_p)-**7a** at $60\,^{\circ}C$ for 36 h. [b] The conversion and ratio of **3**/**4** were determined by GC with *n*-undecane as the internal standard based on phenyl triflate (**2**). [c] Determined by GC on a Chiral G-PN column. [d] Addition of 3 mol% $(nBu)_4NOAc$ (2 equiv/Pd) as additive. [e] Addition of 7.5 mol% $(nBu)_4NOAc$ (5 equiv/Pd) as additive. [f] Addition of 3 mol% LiOAc (2 equiv/Pd) as additive.

Ligand (S,S_p)-**7a** has three binding sites which means that there are three possible bidentate coordination modes: *N*,*P*, *N*,*P*′ and *P*,*P*′ (Scheme 3). We originally thought that the

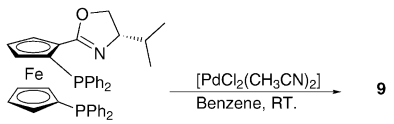


Scheme 3. Three possible coordination modes of (S,S_p)-**7a** with Pd^0.

difference in regioselectivity might be caused by the different coordination modes of the ligand with different palladium precursors, and the very high ratio of isomer **3** with $[Pd(OAc)_2]$ is probably caused by a *P*,*N* coordination mode.[5] Therefore, the ^{31}P NMR spectroscopy of ligand (S,S_p)-**7a** with

$[Pd_2(dba)_3 \cdot dba]$ and $[Pd(OAc)_2]$ in C_6D_6 were examined to assess what kind of coordination mode was taken in the reaction. The chemical shifts of the two phosphorus nuclei in the ligand (S,S_p)-**7a** were $\delta = -16.85$ (s) and -17.16 ppm (s) in C_6D_6. After reacting (S,S_p)-**7a** with $[Pd_2(dba)_3 \cdot dba]$ for 30 minutes, the corresponding phosphorus signals were shifted to downfield regions ($\delta = 25.97$ (brs) and 25.05 ppm (brs)). When phenyl triflate was added to the mixture, no obvious change of the phosphorus signals was found. These results indicate that ligand (S,S_p)-**7a** might function as a diphosphine ligand in this case (**C**, Scheme 3). It has been reported that diphosphine ligands with $[Pd(OAc)_2]$ usually afford product **4** predominantly;[10] however, when ligand (S,S_p)-**7a** and $[Pd(OAc)_2]$ were applied in this reaction, product **3** was obtained as the major product, although chelation of two phosphorus atoms with the palladium center was again revealed by ^{31}P NMR spectroscopy (the two phosphorus signals were also at $\delta =$ 25.97 (brs) and 25.05 ppm (brs)) in this case.[22]

To gain further structural information on palladium species coordinated to the diphosphine–oxazoline ferrocenyl ligand, the crystal structure of complex **9**, which was synthesized from ligand **8** and $[PdCl_2(CH_3CN)_2]$ in benzene, was examined by X-ray diffraction (Scheme 4 and Table 3). Ligand **8** bearing



8

Scheme 4.

Table 3. Selected crystal and structure refinement data for complex **9**·H_2O.

formula	$C_{40}H_{39}NO_2P_2Cl_2FePd$
fw	860.81
T[K]	293
crystal system	monoclinic
space group	$P2(1)$
a[Å]	9.3941(11)
b[Å]	20.155(2)
c[Å]	10.4647(12)
β[°]	113.055(2)
V[Å^3]	1823.1(4)
Z	2
ρ_{calcd}[g cm^{-3}]	1.568
μ[mm^{-1}]	1.162
F(000)	876
cryst size[mm]	$0.355 \times 0.270 \times 0.179$
T_{min}/T_{max}	0.55423/1.00000
θ range[°]	2.02–28.24
parameters	459
R_1[a], Rw	0.0433, 0.0810
GOF	0.910

[a] $[I > 2\sigma(I)]$

an isopropyl group on the oxazoline ring was similarly prepared as ligand **7a**. As can be seen in Figure 1, two phosphorus atoms chelate with the palladium center in **9**. This was further confirmation of the results from the ^{31}P NMR study. Thus, the difference in regioselectivity may be not

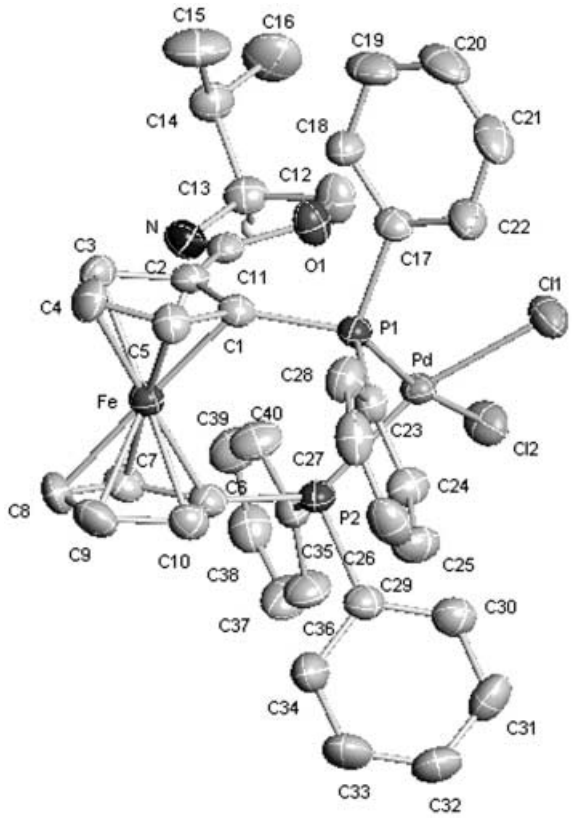
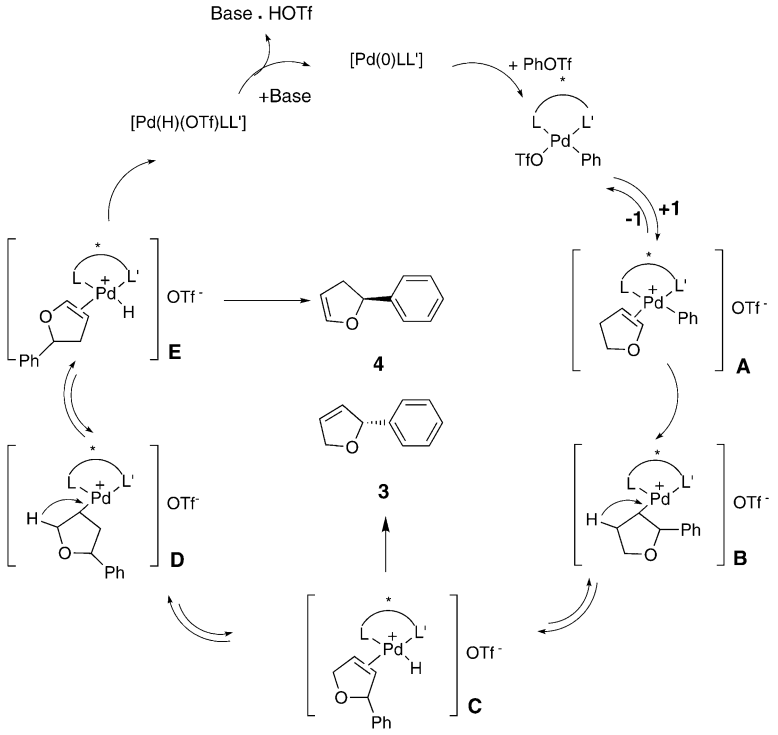


Figure 1. Structure of complex **9** (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Pd–P1 2.2850(13), Pd–P2 2.2913(15), Pd–Cl2 2.3375(14), Pd–Cl1 2.3457(16), P1–C1 1.813(6), P1–C23 1.809(6), P1–C17 1.833(5), P2–C6 1.816(6), P2–C29 1.821(6), P2–C35 1.823(6); P1-Pd-P2 99.75(5), P1-Pd-Cl2 170.65(5), P1-Pd-Cl1 86.35(5), P2-Pd-Cl2 86.80(5), P2-Pd-Cl1 162.22(6), Cl1-Pd-Cl2 89.35(6), C1-P1-Pd 115.08(18), C6-P2-Pd 122.75(18), C1-Fe-C6 109.1(2).

caused by the different coordination modes of ligand with palladium.

The six-membered heterometallocyclic ring in **9** formed by chelate coordination of ligand **8** is highly skewed (Figure 1). It can be seen that considerable steric hindrance exists between the oxazoline ring and the upper phosphino-phenyl ring. The P1-Pd-P2 bite angle of 99.75(5)° was larger than that measured for $[Cl_2Pd(dppf)]$ (99.07°)[23] and $[Cl_2Pd(BINAP)]$ (92.7°).[10] Hence, the diphosphine-oxazoline ferrocenyl ligand has higher reactivity than BINAP: a 1.5 mol% palladium source and 3 mol% (S,S_p)-**7a** were needed to complete the reaction within 36 h.[16]

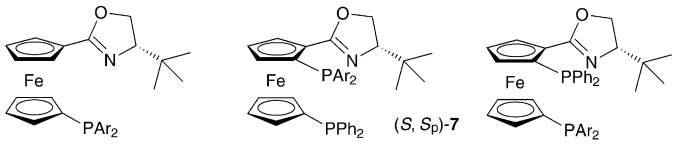
The generally accepted mechanism of the asymmetric intermolecular Heck reaction is depicted in Scheme 5.[10] Hayashi and co-workers explained the high enantioselectivity of product **4** through a kinetic resolution process and studied the relationship between the enantiomeric induction of product **4** and the ratio of **3**/**4** with this mechanism. Amatore and co-workers have provided a deep insight into the oxidative addition step of different palladium catalytic systems, and the different reactivities of various diphosphine ligands were compared.[16] However, there is no detailed discussion on the regioselectivity of the reaction, especially the electronic nature of the ligand and the palladium precursors.



Scheme 5. Proposed mechanism for the catalytic arylation of 2,3-dihydrofuran with phenyl triflate.

Herein, we attempt to rationalize the different regioselectivities of $[Pd(OAc)_2]$ and $[Pd(dba)_3 \cdot dba]$. Notably, the hydride–olefin complex **C** is a point of demarcation directed either to **3** or to the isomerized product **4**. Since the hydride–olefin complex **C** has a 16-electron square-planar structure, dissociation of the coordinated olefin should proceed by means of an associative mechanism involving an 18-electron transition state formed by nucleophilic attack of an incoming ligand at the palladium center. When $[Pd(OAc)_2]$ was used as a palladium source, acetate anions in the reaction system should possess sufficient nucleophilicity toward the cationic palladium center in **C** to cause the dissociation to give product **3**. However, when $[Pd(dba)_3 \cdot dba]$ was used, a similar nucleophilic attack could not occur, so that palladium would re-insert into the olefin to give complex **D**. A subsequent β-hydride elimination therefore proceeded more easily to give **4**. The nucleophilicity of an acetate anion should be more pronounced in a nonpolar media, such as toluene.[10, 24] Thus, when toluene was used as a solvent instead of THF, a higher regioselectivity could be observed (Table 2, entries 2 and 3). When palladium bistrifluoroacetate was used, the ratio of **3** and **4** was lower than that of $[Pd(OAc)_2]$ for the weaker nucleophilicity of the trifluoroacetate anion, despite the fact that **3** was the major product (Table 2, entry 6 versus 3). To investigate the effect of acetate anion as a nucleophile on the regioselectivity, the effect of the addition other acetate salts was also tested (Table 2, entries 8, 9, 10, and 11). When two equivalents of $(n\text{Bu})_4\text{NOAc}$ per equivalent of Pd were added to the reaction in the presence of $[Pd(dba)_3 \cdot dba]$ and THF, the ratio of **3/4** increased to 37:63 (compare the ratio of 28:72 for entry 1, Table 2). Furthermore, when toluene was used instead of THF, a higher ratio, namely 60:40, was obtained (Table 2, entry 9), which is consistent with the results for $[Pd(OAc)_2]$. A larger amount of $(n\text{Bu})_4\text{NOAc}$ did not change the ratio further (Table 2, entry 10). When two equivalents of LiOAc per equivalent of Pd was added to the reaction in the presence of $[Pd(dba)_3 \cdot dba]$ and toluene, a similar result was obtained as that with $(n\text{Bu})_4$-NOAc (Table 2, entry 11).

If this explanation is true, the electrophilicity of the cationic Pd atom of complex **C** might also influence the path toward **3** or **4**. Hence, ligands **7b–i** bearing different electron-donating or electron-withdrawing groups on phenyl rings of the phosphine were prepared with the same procedures as ligand (S,S_p)-**7a** (Scheme 6) and applied to the intermolecular asymmetric Heck reaction. The results are summarized in Table 4. All these ligands with $[Pd(OAc)_2]$ were able to catalyze the reaction of **1** and **2** in good conversions within 36 h and isomer **3** was formed with



6a: Ar = -C_6H_5
6b; Ar = -3,5-$(CF_3)_2C_6H_3$
6c; Ar = -3,5-$(CH_3)_2C_6H_3$
6d; Ar = -4-$(CF_3)C_6H_4$
6e; Ar = -4-$(OCH_3)C_6H_4$

7a: Ar = -C_6H_5
7b; Ar = -3,5-$(CF_3)_2C_6H_3$
7d; Ar = -3,5-$(CH_3)_2C_6H_3$
7f; Ar = -4-$(CF_3)C_6H_4$
7h; Ar = -4-$(OCH_3)C_6H_4$

7c: Ar = -3,5-$(CF_3)_2C_6H_3$
7e: Ar = -3,5-$(CH_3)_2C_6H_3$
7g: Ar = -4-$(CF_3)C_6H_4$
7 i: Ar = -4-$(OCH_3)C_6H_4$

Scheme 6. Planar chiral diphosphine–oxazoline ferrocenyl ligands modified with different electronic groups.

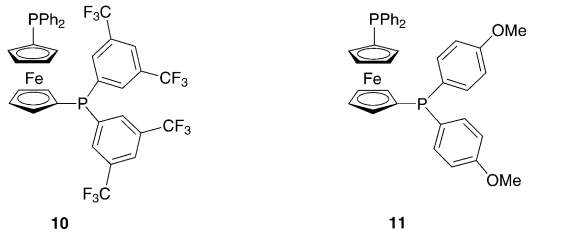
Table 4. Electronic effects of ligands on the regioselectity of Heck Reaction.[a]

Entry	Ligand	Palladium	Solvent	Conversion [%][b]	Ratio of **3/4**[b]	*ee* [%][c] **3**(*R*)	**4**(*S*)
1	**7b**	$[Pd(OAc)_2]$	toluene	72	94:6	75	13
2	**7c**	$[Pd(OAc)_2]$	toluene	67	**99:1**	92	nd
3	**7c**	$[Pd(dba)_3 \cdot dba]$	THF	86	89:11	94	20
4	**7d**	$[Pd(OAc)_2]$	toluene	77	90:10	98	nd
5	**7e**	$[Pd(OAc)_2]$	toluene	73	93:7	96	nd
6	**7f**	$[Pd(OAc)_2]$	toluene	98	95:5	97	29
7	**7g**	$[Pd(OAc)_2]$	toluene	80	64:36	83	29
8	**7h**	$[Pd(OAc)_2]$	toluene	67	83:17	98	29
9	**7i**	$[Pd(OAc)_2]$	toluene	65	14:86	86	27
10	**7i**	$[Pd(dba)_3 \cdot dba]$	THF	100	15:85	94	48
11	**7i**	$[Pd(dba)_3 \cdot dba]$	$(CH_2Cl)_2$	68	**8:92**	nd	19

[a] The reaction was carried out with 1.5 mol% palladium precursor and 3 mol% ligand in the presence of $i\text{Pr}_2\text{NEt}$ as base at 60 °C for 36 h. [b] The conversion and the ratio of **3/4** were determined by GC with *n*-undecane as the internal standard based on phenyl triflate (**2**). [c] Determined by GC on a Chiral γ-PG column. nd = not determined.

a high *ee* value. The best regioselectivity of 99:1 for **3** and **4** was observed with ligand **7c**, which has four strongly electron-withdrawing trifluoromethyl groups on the phenyl rings of the phosphine attached to the lower Cp ring (Table 4, entry 2); while a reversed ratio of 14:86 for the two isomers was found for ligand **7i**, which contains two electron-donating methoxy groups on the phenyl rings of phosphine (Table 4, entry 9). The diphosphine mode of coordination was supported by ^{31}P NMR spectroscopic studies in these two cases: when ligand **7c** and **7i** coordinate with Pd^0 in C_6D_6, the chemical shifts of the two phosphorus atoms all shifted to downfield (**7c**: $\delta = 23.63$ and 22.52 from -16.54 and -17.99 ppm; **7i**: $\delta = 25.48$ and 19.55 from -17.23 and -20.48 ppm). When ligand **7c** coordinated with Pd to form the hydride–olefin complex **C**, the electron-withdrawing trifluoromethyl groups could, in principle, lower the electron density on Pd^+, thereby making it more vulnerable to attack by an acetate anion and leading eventually to product **3**. However, because of the electron-donating effect of the methoxy group, ligand **7i** was able to enhance the electron density at the palladium center, leading to its re-insertion into the olefin to give isomer **4**. When $[Pd_2(dba)_3 \cdot dba]$ was used instead of $[Pd(OAc)_2]$ in THF, the regioselectivity of ligand **7c** was lower than that obtained with $[Pd(OAc)_2]$ in toluene (Table 4, entry 2 versus 3); while less change was found in the ratio of the two isomers when ligand **7i** was used (Table 4, entry 9 versus 10). When the more polar solvent 1,2-dichloroethane was used instead of THF, a better ratio of 8:92 for the two isomers was observed for ligand **7i** (Table 4, entry 11).

These results suggested that the different electronic nature of ligating atoms greatly affected the regioselectivity. However, when the modified phosphine group was attached to the upper Cp ring, the ring bearing an oxazoline group, the regioselectivity of the reaction changed a little compared to that with ligand **7a**. That is, the effect of the electronic nature of such ligand is not as significant as the ligand with modified groups on the lower Cp ring. It is possible that the oxazoline ring also acts as a electron-withdrawing group, therefore, the additional attached group at upper Cp ring has less effect than that at the lower Cp ring. To check the electronic effect of the ligand on the regioselectivity in more detail, the dppf analogues ligands **10** and **11** were synthesized. These ligands contain electron-withdrawing trifluoromethyl groups and the electron-donating methoxy group, respectively. When they were employed as the ligand with $[Pd(OAc)_2]$ and toluene in the Heck reaction, different regioselectivities were observed (Scheme 7). Ligand **10** provides product **3** predominantly, while **4** is the major product with ligand **11**. These results support our hypothesis that the electronic nature of the ligating atoms does affect the regioselectivity.

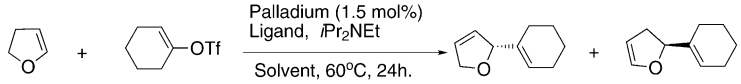


Scheme 7. The regioselectivities of Heck reaction catalyzed by ligands **10** and **11** with 1.5 mol% $[Pd(OAc)_2]$ in the presence of iPr_2NEt and toluene at 60 °C.

The literature shows that different regioselectivities are produced by *P,P* ligands and *P,N* ligands.[4, 5] Could this difference be explained by a similar rationale? To understand it, the atomic (Mulliken) charge of $[PdH\{(R)\text{-BINAP}\}]^+$ and $[PdH\{(S)\text{-PHOX}\}]^+$ were calculated at the PM3 level with Spartan 5.0.[25] The atomic (Mulliken) charge on the palladium center of $[PdH\{(R)\text{-BINAP}\}]^+$ is -0.041975, while that of $[PdH\{(S)\text{-PHOX}\}]^+$ is $+0.020161$. The electron density on Pd^+ of hydride–olefin complex **C** with PHOX should be much lower than that with BINAP. So, unisomerized isomer **3** was obtained as main product with PHOX, while with BINAP, isomerized product **4** was afforded predominantly owing to the rich electron density on the palladium center.

With these results in hand, other aryl and cyclohexenyl triflates were used to examine the above effect. Reactions of 2,3-dihydrofuran and these triflates with ligands **7a**, **7c**, and **7i** gave good enantioselectivities for 2,5-dihydrofuran derivatives and high conversion at 60 °C within 24–36 h (Table 5 and Table 6). In spite of the steric or electronic properties of triflates, the regioselectivities of the Heck reaction with these ligands also agree with our explanation. When 1-cyclohexenyltriflate was used with ligand **7i**, the regioselectivity was poor; however, isomer **14** was observed as the major product (Table 5, entry 3); When 4-nitrophenyl triflate was employed with ligand **7c**, the ratio of **16**:**17** was lower, but isomer **16** was still the main product (Table 6, entry 7). However, when ligand **7i** was employed, no 2,5-dihydrofuran derivatives were observed (Table 6, entry 9).

Table 5. Enantioselective and regioselective Heck reaction of 2,3-dihydrofuran with 1-cyclohexenyltriflate.

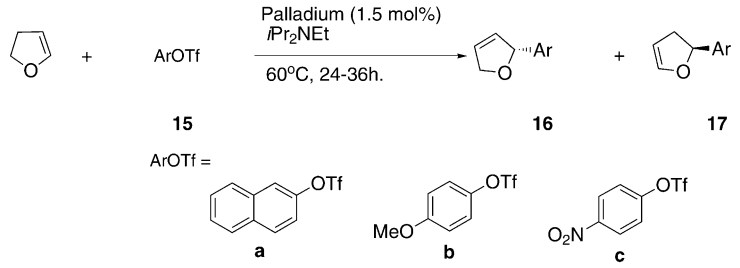


12 **13** **14**

Entry	Ligand	Palladium	Solvent	Conversion [%][a]	**13**/**14**[a]	*ee* [%][b] **13**(*R*)	**14**
1	**7c**	$[Pd(OAc)_2]$	toluene	99	97:3	80[c]	nd
2	**7a**	$[Pd(OAc)_2]$	toluene	98	92:8	90[c]	nd
3	**7i**	$[Pd(dba)_3 \cdot dba]$	$(CH_2Cl)_2$	87	35:65	40	nd

[a] The conversion and the ratio of **13**/**14** were determined by GC with *n*-undecane as the internal standard based on cyclohexenyl triflate (**12**). [b] Determined by GC on a Chiraldex B-PH column. [c] The absolute configuration of products was assigned by comparison of the sign of specific rotations with literature data.[5] nd = not determined.

Table 6. Enantioselective and regioselective Heck reaction of 2,3-dihydrofuran with different aryl triflates.



Entry	Ligand	Triflate	Palladium	Solvent	Conversion [%]	**16**/**17**	*ee* [%][f]	
							16(*R*)[f]	**17**(*S*)
1	**7c**	**15a**	$[Pd(OAc)_2]$	toluene	73[a]	90:10	66[c]	10[c]
2	**7a**	**15a**	$[Pd(OAc)_2]$	toluene	99[a]	83:17	78[c]	9[c]
3	**7i**	**15a**	$[Pd(dba)_3\cdot dba]$	$(CH_2Cl)_2$	83[a]	17:83	94[c]	14[c]
4	**7c**	**15b**	$[Pd(OAc)_2]$	toluene	91[b]	97:3	96[d]	nd
5	**7a**	**15b**	$[Pd(OAc)_2]$	toluene	67[b]	94:6	66[d]	nd
6	**7i**	**15b**	$[Pd(dba)_3\cdot dba]$	$(CH_2Cl)_2$	86[b]	0:100	–	9[d]
7	**7c**	**15c**	$[Pd(OAc)_2]$	toluene	100[b]	60:40	>99[e]	nd
8	**7a**	**15c**	$[Pd(OAc)_2]$	toluene	68[b]	49:51	96[e]	nd
9	**7i**	**15c**	$[Pd(dba)_3\cdot dba]$	$(CH_2Cl)_2$	82[b]	0:100	–	nd

[a] Conversion determined by GC with *n*-tridecane as the internal standard based on 2-naphthyl triflate (**15a**). [b] Conversion determined by GC with *n*-undecane as the internal standard based on aryl triflate (**15b** or **15c**). [c] Determined by HPLC on a Chiralcel OD-H column. [d] Determined by GC on a Rt-βDex column. [e] Determined by GC on a G-TA column. [f] The absolute configuration of the products was assigned by comparison of the sign of specific rotations with literature data.[4, 5] nd = not determined.

Conclusion

A study of the regioselectivity of the asymmetric Heck reaction was carried out utilizing a series of diphosphine-oxazoline ferrocenyl ligands and different palladium precursors. All these ligands can catalyze the reaction in high conversion and with 1.5 mol% catalyst loading. The tuning of the regioselectivity was realized by the use of palladium precursors and by varying the electronic nature of the ligands. A plausible mechanistic rationale was also provided. Furthermore, for 2,5-dihydrofuran derivatives, up to 99% *ee* was obtained. This is the first time that dramatic electronic effects have been observed and regioselectivity has been controlled in an asymmetric Heck reaction. These results may improve our understanding of the mechanisms of the asymmetric Heck reaction and provide a guide toward the design of ligands.

Experimental Section

General: All reactions and manipulations were performed in an argon atmosphere by means of standard Schlenk techniques. Anhydrous solvents were transferred by oven-dried syringes. Flaskware was flame-dried under a stream of argon. Melting points are uncorrected. NMR spectra were recorded at room temperature in $CDCl_3$ or C_6D_6 with 300 MHz (^{1}H), 121 MHz (^{31}P), and 288 MHz (^{19}F) instruments. The chemical shifts are given relative to TMS (as an internal reference) for ^{1}H NMR, 85% H_3PO_4 (as an external reference) for ^{31}P NMR, and CF_3COOH (as an external reference) for ^{19}F NMR spectroscopy. IR spectra were recorded in KBr with a Shimadze IR-440 infrared spectrophotometer. Mass spectra were recorded on a HP5989A mass spectrometer. Elemental analyses were carried out on a Foss-Heraus Vario instrument by the Analytic and Testing Center of SIOC, Chinese Academy of Sciences.

Materials: Tetrahydrofuran (THF), diethyl ether, benzene and toluene were distilled from sodium/benzophenone prior to use; CH_3CN and CH_2Cl_2 were distilled from CaH_2. All purchased reagents were used without further purification. The following starting materials were prepared according to literature procedures.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]ferrocene (6a):[11] Compound **5** (205 mg, 0.5 mmol) was dissolved in freshly distilled THF (4 mL) under argon and cooled to −78 °C. At this temperature, *n*BuLi (0.38 mL, 0.6 mmol, 1.6 M in *n*-hexane) was added, and then the resulting deep red solution was stirred for 20 min. Chlorodiphenylphosphine (0.13 mL, 0.7 mmol) was then added, and the resulting mixture was continually stirred and allow to warm to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was purified by chromatography (silica gel, ethyl acetate/petroleum 1:5) to give 227 mg of **5** (88% yield) as an orange oil. $[\alpha]_D^{20} = -132.6$ ($c = 0.35$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (s, 9H), 3.87 (dd, $J = 10.1$, 7.7 Hz, 1H), 4.09–4.24 (m, 6H), 4.40 (br s, 2H), 4.65–4.68 (m, 2H), 7.30–7.40 ppm (m, 10H).

Synthesis of 1-bis(3,5-bistrifluoromethylphenyl)phosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]ferrocene (6b): Prepared from **5** in 73% yield as a yellow powder. M.p. 40 °C; $[\alpha]_D^{20} = -91.2$ ($c = 0.75$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (s, 9H), 3.90 (dd, $J = 9.78$, 7.64 Hz, 1H), 3.89–4.18 (m, 3H), 4.21 (m, 3H), 4.53 (m, 2H), 4.68 (d, $J = 12.83$ Hz, 2H), 7.77 (dd, $J = 11.0$, 6.4 Hz, 4H), 7.90 ppm (s, 2H); ^{31}P NMR ($CDCl_3$): $\delta = -14.32$ ppm (s, 1P); ^{19}F NMR ($CDCl_3$): $\delta = 13.05$ ppm (s, 12F); MS (EI): *m*/*z* (%): 767 ($[M]^+$, 100), 768 ($[M+1]^+$, 43.22), 766 ($[M-1]^+$, 15.97), 253 (50.40); IR (KBr): $\tilde{\nu} = 2960$, 1662, 1480, 1355, 1280, 1185, 1136, 970, 899, 844, 705, 682, 508 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{26}F_{12}FeNOP$: C 51.65, H 3.42, N 1.83; found: C 51.74, H 3.68, N 1.66.

Synthesis of 1-bis(3,5-dimethylphenyl)phosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]ferrocene (6c): Prepared from **5** in 80% yield as a yellow powder. M.p. 45 °C; $[\alpha]_D^{20} = -143.4$ ($c = 0.745$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (s, 9H), 2.27 (s, 12H), 3.87 (dd, $J = 9.77$, 7.64 Hz, 1H), 4.12 (d, $J = 7.95$ Hz, 3H), 4.19 (m, 3H), 4.37 (m, 2H), 4.65 (m, 2H), 6.97 ppm (t, $J = 7.33$ Hz, 6H); ^{31}P NMR ($CDCl_3$): $\delta = -16.74$ ppm (s, 1P); MS (EI): *m*/*z* (%): 552 ($[M+1]^+$, 100), 553 ($[M+2]^+$, 40.06), 468 (43.17), 253(33.90); IR (KBr): $\tilde{\nu} =$ 2951, 1658,1581, 1464, 1299, 1260, 1115, 1026, 969, 846, 693, 492 cm^{-1}; elemental analysis calcd (%) for $C_{33}H_{38}FeNOP$: C 71.87, H 6.95, N 2.54; found: C 71.47, H 6.99, N 2.43.

Synthesis of 1-bis(4-trifluoromethylphenyl)phosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]ferrocene (6d): Prepared from **5** in 85% yield as a yellow powder. M.p. 39 °C; $[\alpha]_D^{20} = -105.5$ ($c = 1.39$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (s, 9H), 3.87 (dd, $J = 10.38$, 7.64 Hz, 1H), 4.08 (m, 3H), 4.19 (m, 3H), 4.47 (t, $J = 1.22$ Hz, 2H), 4.70 (d, $J = 10.99$ Hz, 2H), 7.45 (t, $J =$ 7.64 Hz, 4H), 7.58 ppm (d, $J = 7.33$ Hz, 4H); ^{31}P NMR ($CDCl_3$): $\delta =$ −16.30 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): $\delta = 13.18$ ppm (s, 6F); MS (EI): *m*/*z* (%): 631 ($[M]^+$, 100), 632 ($[M+1]^+$, 39.32), 633 ($[M+2]^+$, 12.43), 630 ($[M-1]^+$, 50.40), 253 (67.15); IR (KBr): $\tilde{\nu} = 2958$, 1660, 1486, 1396, 1324, 1166, 1128, 1061, 1017, 970, 832, 698, 502 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{28}F_6FeNOP$: C 58.97, H 4.47, N 2.22; found: C 59.28, H 4.77, N 2.17.

Synthesis of 1-bis(4-methyoxylphenyl)phosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]ferrocene (6e): Prepared from **5** in 40% yield as a yellow powder. M.p. 42 °C; $[\alpha]_D^{20} = -117.7$ ($c = 0.525$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (s, 9H), 3.80 (s, 6H), 3.87 (dd, $J = 9.77$, 7.33 Hz, 1H), 4.10 (m, 3H), 4.20 (m, 3H), 4.36 (s, 2H), 4.67 (d, $J = 11.61$ Hz, 2H), 6.85 (d, $J = 7.49$ Hz, 4H), 7.27 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): $\delta = -20.40$ ppm (s, 1P); MS (EI): *m*/*z* (%): 555($[M]^+$, 100), 556 ($[M+1]^+$, 27.75), 556 (27.75), 245(14.01); IR

(KBr): $\tilde{\nu}$ = 2953, 1658, 1593, 1498, 1284, 1246, 1176, 1116, 1095, 1029, 968, 826, 796, 491 cm^{-1} cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{34}FeNO_3P$: C 67.04, H 6.17, N 2.52; found: C 66.55, H 6.27, N 2.40

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (7a): A solution of **6a** (258 mg, 0.5 mmol) and TMEDA (0.1 mL, 0.7 mmol) in diethyl ether (6 mL) under argon was cooled to −78 °C. To this solution was added *n*BuLi (0.4 mL, 0.64 mmol) and the mixture was stirred at −78 °C for 2 h. Chlorodiphenylphosphine (0.13 mL, 0.7 mmol) was then added and the dry-ice bath was removed. The resulting mixture was continually stirred for 20 min, and then quenched with saturated $NaHCO_3$, diluted with diethyl ether, washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting residue was purified by column chromatography (ethyl acetate/petroleum 1:10) to afford 309 mg of compound **7a** as a yellow powder (yield 88%). M.p. 70 °C; $[\alpha]_D^{20}$ = −130.5 (c = 1.485, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.75 (s, 9H), 3.43 (s, 1H), 3.75 (dt, J = 39.0, 8.1 Hz, 2H), 3.94 (t, J = 1.5 Hz, 1H), 4.13–4.21 (m, 3H), 4.26 (t, J = 1.6 Hz, 1H), 4.49 (t, J = 1.7 Hz, 1H), 4.89 (s, 1H), 7.10–7.40 ppm (m, 20H); ^{31}P NMR ($CDCl_3$): δ = −17.24 (s, 1P), −17.47 ppm (s, 1P); MS (EI): m/z (%): 679 ([M]$^+$, 100), 680 ([M+1]$^+$, 44.33), 622 (34.59); IR (KBr): $\tilde{\nu}$ = 2953, 1662, 1479, 1434, 1164, 1141, 1027, 979, 831, 742, 702, 696, 501 cm^{-1}; elemental analysis calcd (%) for $C_{41}H_{39}FeNOP_2$: C 72.47, H 5.78, N 2.06; found: C 72.39, H 5.77, N 2.24.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-bis(3,5-bistrifluoromethyl)phenylphosphinoferrocene (7b): After directed diastereoselective *ortho*-lithiation of **6a**, the resulting mixture was treated with chloro-bis-3,5-bistrifluoromethylphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7b** was obtained as a yellow powder in 68% yield. M.p. 183 °C; $[\alpha]_D^{20}$ = −262.5 (c = 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 9H), 3.14 (t, J = 2.16 Hz, 1H), 3.60 (dd, J = 9.77, 7.33 Hz, 1H), 3.74 (s, 1H), 4.07 (dd, J = 15.36, 8.86 Hz, 1H), 4.13(dd, J = 18.33, 8.86 Hz, 1H), 4.41 (m, 3H), 4.49 (s, 1H), 4.98(t, J = 1.22 Hz, 1H), 7.14–7.28 (m, 10H), 7.58 (d, J = 6.72 Hz, 2H), 7.77 (s, 2H), 7.79 (s, 1H), 7.88 ppm (s, 1H); ^{31}P NMR ($CDCl_3$): δ = −16.54 (s, 1P), −17.99 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): δ = 13.12 ppm (d, J = 52.85 Hz, 12F); MS (EI): m/z (%): 951 ([M]$^+$, 100), 952 ([M+1]$^+$, 47.55), 950 ([M−1]$^+$, 22.30), 893 (23.28); IR (KBr): $\tilde{\nu}$ = 2958, 1660, 1480, 1436, 1353, 1278, 1181, 1141, 983, 895, 844, 699, 682, 518, 501 cm^{-1}; elemental analysis calcd (%) for $C_{45}H_{35}F_{12}FeNOP_2$: C 56.80, H 3.71, N 1.47; found: C 56.78, H 4.02, N 1.33.

Synthesis of 1-bis(3,5-bistrifluoromethyl)phenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (7c): After directed diastereoselective *ortho*-lithiation of **6b**, the resulting mixture was treated with chlorodiphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7c** was obtained as a yellow powder in 71% yield. M.p. 67 °C; $[\alpha]_D^{20}$ = −146.5 (c = 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.77 (s, 9H), 3.46 (s, 1H), 3.75 (m, 3H), 4.22 (m, 3H), 4.53 (m, 1H), 4.63 (s, 1H), 4.91(s, 1H), 7.16–7.44 (m, 10H), 7.66 (dd, J = 18.33, 6.11 Hz, 4H), 7.69 ppm (d, J = 11.61 Hz, 2H); ^{31}P NMR ($CDCl_3$): δ = −15.17 (s, 1P), −17.62 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): δ = 13.05 ppm (d, J = 0.75 Hz, 12F); MS (EI): m/z (%): 951 ([M]$^+$, 100), 952 ([M+1]$^+$, 48.48), 874 (26.96); IR (KBr): $\tilde{\nu}$ = 2958, 1666, 1480, 1435, 1354, 1279, 1186, 1138, 979, 898, 844, 742, 702, 682, 501 cm^{-1}; elemental analysis calcd (%) for $C_{45}H_{35}F_{12}FeNOP_2$: C 56.80, H 3.71, N 1.47; found: C 56.36, H 3.96, N 1.37.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-bis(3,5-dimethyl)phenylphosphinoferrocene (7d): After directed diastereoselective *ortho*-lithiation of **6a**, the resulting mixture was treated with chloro-bis-[3,5-dimethyl]-phenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7d** was obtained as a yellow powder in 68% yield. M.p. 75 °C; $[\alpha]_D^{20}$ = −51.9 (c = 0.875, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 9H), 2.24 (d, J = 20.17 Hz, 12H), 3.45 (s, 1H), 3.73 (m, 2H), 3.93(s, 1H), 4.18 (m, 2H), 4.26 (s, 1H), 4.50 (s, 2H), 4.92(s, 1H), 6.73 (m, 3H), 7.01 (m, 3H), 7.25 ppm (m, 10H); ^{31}P NMR ($CDCl_3$): δ = −16.42 (s, 1P), −17.30 ppm (s, 1P); MS (EI): m/z (%): 736 ([M]$^+$, 36.75), 735 ([M−1]$^+$, 100), 678 (75.44); IR (KBr): $\tilde{\nu}$ = 2951, 1663, 1583, 1478, 1434, 1126, 1027, 979, 846, 742, 695, 502 cm^{-1}; elemental analysis calcd (%) for $C_{45}H_{47}FeNOP_2$: C 73.47, H 6.44, N 1.90; found: C 73.74, H 6.90, N 1.83.

Synthesis of 1-bis(3,5-dimethyl)phenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (7e): After directed diastereoselective *ortho*-lithiation of **6c**, the resulting mixture was treated with chlorodiphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7e** was obtained as a yellow powder in 93% yield. M.p. 65 °C; $[\alpha]_D^{20}$ = −126.5 (c = 0.61, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 9H), 2.22 (d, J = 8.56 Hz, 12H), 3.45 (t, J = 1.22 Hz, 1H), 3.70 (dd, J = 9.78, 7.95 Hz, 1H), 3.78 (dd, J = 15.89, 9.48 Hz, 1H), 3.88(t, J = 1.84 Hz, 1H), 4.16 (dd, J = 9.78, 8.55 Hz, 1H), 4.22 (t, J = 2.45 Hz, 1H), 4.28 (t, J = 1.22 Hz, 1H), 4.48 (t, J = 1.22 Hz, 2H), 4.90(t, J = 1.22 Hz, 1H), 6.88 (m, 6H), 7.15–7.42 ppm (m, 10H); ^{31}P NMR ($CDCl_3$): δ = −16.94 (s, 1P), −17.61 ppm (s, 1P); MS (EI): m/z (%): 736 ([M]$^+$, 100), 737 ([M+1]$^+$, 47.31), 735 ([M−1]$^+$, 89.25), 679 (33.74); IR (KBr): $\tilde{\nu}$ = 2951, 1662, 1583, 1478, 1434, 1141, 1027, 979, 846, 742, 694, 501 cm^{-1}; elemental analysis calcd (%) for $C_{45}H_{47}FeNOP_2$: C 73.47, H 6.44, N 1.90; found: C 73.59, H 6.22, N 1.71.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-bis(4-trifluoromethyl)phenylphosphinoferrocene (7f): After directed diastereoselective *ortho*-lithiation of **6a**, the resulting mixture was treated with chlorobis(4-trifluoromethyl)phenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7f** was obtained as a yellow powder in 94% yield. M.p. 165 °C; $[\alpha]_D^{20}$ = −210.0 (c = 0.635, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.80 (s, 9H), 3.29 (d, J = 1.23 Hz, 1H), 3.68 (dd, J = 9.78, 7.33 Hz, 1H), 3.85 (m, 1H), 3.92 (t, J = 7.34 Hz, 3H), 4.16 (dd, J = 18.33, 9.17 Hz, 1H), 4.30 (t, J = 3.06 Hz, 1H), 4.36 (s, 1H), 4.47 (m, 2H), 4.95 (t, J = 1.22 Hz, 1H), 7.10–7.30 (m, 12H), 7.40–7.57 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): δ = −17.47 (s, 1P), −17.69 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): δ = 13.27 ppm (s, 6F); MS (EI): m/z (%): 815 ([M]$^+$, 100), 816 ([M+1]$^+$, 40.77), 758 (28.83); IR (KBr): $\tilde{\nu}$ = 2955, 1659, 1606, 1480, 1434, 1395, 1323, 1168, 1133, 1059, 1015, 977, 833, 745, 697, 599, 502 cm^{-1}; elemental analysis calcd (%) for $C_{43}H_{37}F_6FeNOP_2$: C 63.33, H 4.57, N 1.72; found: C 63.34, H 4.82, N 1.69.

Synthesis of 1-bis(4-trifluoromethyl)phenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (7g): After directed diastereoselective *ortho*-lithiation of **6d**, the resulting mixture was treated with chlorodiphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7g** was obtained as a yellow powder in 80% yield. M.p. 80 °C; $[\alpha]_D^{20}$ = −145.0 (c = 0.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, 9H), 3.37 (d, J = 1.22 Hz, 1H), 3.71 (dd, J = 20.77, 9.48 Hz, 1H), 3.78 (dd, J = 15.89, 9.51 Hz, 1H), 3.89 (t, J = 1.83 Hz, 3H), 4.15 (dd, J = 18.33, 9.77 Hz, 1H), 4.20 (m, 1H), 4.29 (t, J = 1.22 Hz, 1H), 4.55 (m, 2H), 4.93 (t, J = 1.22 Hz, 1H), 7.12–7.55 ppm (m, 16H); ^{31}P NMR ($CDCl_3$): δ = −16.78 (s, 1P), −17.37 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): δ = 13.22 ppm (s, 6F); MS (EI) m/z (%): 815 ([M]$^+$, 81.17), 759 (28.74), 739 (27.13), 574 (33.47), 265 (30.57); IR (KBr): $\tilde{\nu}$ = 2955, 1664, 1607, 1479, 1435, 1396, 1324, 1166, 1128, 1060, 1016, 979, 831, 743, 696, 499 cm^{-1}; elemental analysis calcd (%) for $C_{43}H_{37}F_6FeNOP_2$: C 63.33, H 4.57, N 1.72; found: C 63.62, H 5.07, N 1.89.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-bis(4-methoxyl)phenylphosphinoferrocene (7h): After directed diastereoselective *ortho*-lithiation of **6a**, the resulting mixture was treated with chlorobis(4-methoxyl)phenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7h** was obtained as a yellow powder in 83% yield. M.p. 77 °C; $[\alpha]_D^{20}$ = −129.2 (c = 0.905, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 9H), 3.42 (m, 1H), 3.74 (s, 3H), 3.77 (m, 3H), 3.83 (s, 3H), 3.91 (m, 1H), 4.13 (m, 1H), 4.21 (t, J = 2.44 Hz, 1H), 4.48 (m, 2H), 4.88 (t, J = 1.22 Hz, 1H), 6.80 (dd, J = 25.28, 7.95 Hz, 4H), 7.09 (dd, J = 8.55, 7.33 Hz, 2H), 7.22–7.41 ppm (m, 12H); ^{31}P NMR ($CDCl_3$): δ = −17.23 (s, 1P), −20.48 ppm (s, 1P); MS (EI): m/z (%): 740 ([M]$^+$, 100), 741 ([M+1]$^+$, 37.00), 683 (55.65); IR (KBr): $\tilde{\nu}$ = 2952, 1737, 1662, 1594, 1498, 1434, 1363, 1283, 1246, 1176, 1094, 1031, 979, 825, 743, 697, 494 cm^{-1}; elemental analysis calcd (%) for $C_{43}H_{43}FeNOP_2$: C 69.83, H 5.86, N 1.89; found: C 69.40, H 5.99, N 1.85.

Synthesis of 1-bis(4-methoxyl)phenylphosphino-1′-[(*S*)-*tert*-butyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (7i): After directed diastereoselective *ortho*-lithiation **6e**, the resulting mixture was treated with chlorodiphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **7i** was obtained as a yellow powder in 48% yield. M.p. 70 °C; $[\alpha]_D^{20}$ = −159.7 (c = 0.595, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.74 (s, 9H), 3.41 (s, 1H), 3.79 (s, 6H), 3.60–3.90 (m, 3H), 4.16 (t, J = 9.17 Hz, 1H), 4.25 (s, 2H), 4.48 (d, J = 9.17 Hz, 2H), 4.90(s, 1H), 6.79 (dd, J = 17.11, 8.56 Hz, 4H), 7.14–7.41 ppm (m, 14H); ^{31}P NMR ($CDCl_3$): δ = −16.96 (s, 1P), −21.06 ppm (s, 1P); MS (EI): m/z (%): 739

([M]$^+$, 100), 738 ([$M-1$]$^+$, 90.77), 740 ([$M+1$]$^+$, 36.95), 682 (61.77); IR (KBr): $\tilde{\nu}$ = 2951, 1661, 1593, 1497, 1434, 1352, 1284, 1246, 1176, 1095, 1029, 978, 825, 743, 696, 530, 500 cm^{-1}; elemental analysis calcd (%) for $C_{43}H_{43}FeNOP_2$: C 69.83, H 5.86, N 1.89; found: C 69.76, H 5.94, N 1.90.

Synthesis of 1-diphenylphosphino-1′-[(*S*)-isopropyl-2,5-oxazolinyl]-2′-(S_p)-diphenylphosphinoferrocene (8): After directed diastereoselective *ortho*-lithiation of 1-[(*S*)-isopropyl-2,5-oxazolinyl]-1′-bromoferrocene, which was synthesized according to a literature procedure,[11a] the resulting mixture was treated with chlorodiphenylphosphine as described above. After chromatography (ethyl acetate/petroleum 1:10) of the crude product, **8** was obtained as a yellow powder in 84% yield. M.p. 70 °C; $[\alpha]_D^{20} = -54$ (c = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.64 (d, J = 6.8 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H), 1.63 (m, 1H), 3.44 (m, 1H), 3.70 (t, J = 8.2 Hz, 1H), 3.80–3.91 (m, 1H), 3.96 (m, 1H), 4.18–4.30 (m, 3H), 4.48–4.51 (m, 2H), 4.92(t, J = 1.2 Hz, 1H), 7.18–7.48 ppm (m, 20H); ^{31}P NMR ($CDCl_3$): $\delta = -16.49$ (s, 1P), −17.28 ppm (s, 1P); MS (EI): m/z (%): 666 ([M]$^+$, 100), 480 (70.40), 393 (38.65), 183 (39.60); IR (KBr): $\tilde{\nu}$ = 2955, 1658, 1478, 1433, 1026, 980, 741, 695, 498 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{37}FeNOP_2$: C 72.19, H 5.60, N 2.11; found: C 72.10, H 5.60, N 1.94.

X-ray diffraction study of complex 9: A solution of ligand **8** (66.6 mg, 0.1 mmol) in benzene (2.0 mL) was added with stirring to a mixture of $[PdCl_2(CH_3CN)_2]$ (26 mg, 0.1 mmol) in benzene (1.0 mL), and the mixture was stirred overnight. The orange precipitate that formed was collected by filtration, washed with benzene, and dried under vacuum. The crude product was dissolved in CH_2Cl_2, layered with hexane, and allowed to stand at room temperature to give red crystals (76 mg, 90% yield): anal. calcd for $C_{40}H_{37}Cl_2FeNOP_2Pd \cdot H_2O$: C 55.81, H 4.75, N 1.63; found: C 55.80, H 4.44, N 1.47.

CCDC-204150 (complex **9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Synthesis of 1-bis(3,5-bistrifluoromethyl)phenylphosphino-1′-diphenylphosphinoferrocene (10): 1-Bromo-1′-diphenylphosphinoferrocene[26] (225 mg, 0.5 mmol) was dissolved in fresh distilled THF (4 mL) under argon and cooled to −78 °C. At this temperature, *n*BuLi (0.38 mL, 0.6 mmol, 1.6 M in *n*-hexane) was added. The resulting deep red solution was stirred for 20 min. Chlorobis(3,5-dimethyl)phenylphosphine (300 mg, 0.6 mmol) was then added, and resulting mixture was continually stirred and allowed to warm to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was purified by chromatography (silica gel, petroleum) to give **10** (330 mg, 80% yield) as a yellow powder. ^{1}H NMR ($CDCl_3$): δ = 3.90 (dd, J = 3.8, 1.8 Hz, 2H), 4.09 (dd, J = 3.8, 1.8 Hz, 2H), 4.28 (t, J = 1.5 Hz, 2H), 4.43 (t, J = 1.5 Hz, 2H), 7.22–7.40 (m, 10H), 7.66 (d, J = 6.5 Hz, 4H), 7.86 ppm (s, 2H); ^{31}P NMR ($CDCl_3$): $\delta = -13.66$ (s, 1P), −17.12 ppm (s, 1P); ^{19}F NMR ($CDCl_3$): δ = 13.07 ppm (s, 12F); MS (EI): m/z (%): 826 ([M]$^+$, 100), 828 ([$M+2$]$^+$, 37.78), 827 ([$M+1$]$^+$, 63.15), 825 ([$M-1$]$^+$, 81.16), 613 (24.21); IR (KBr): $\tilde{\nu}$ = 3074, 2932, 1355, 1279, 1135, 1029, 898, 829, 743, 682, 495 cm^{-1}; elemental analysis calcd (%) for $C_{38}H_{24}F_{12}FeP_2$: C 55.23, H 2.93; found: C 55.53, H 3.00.

Synthesis of 1-bis(4-methoxy)phenylphosphino-1′-diphenylphosphinoferrocene (11): After directed lithiation of 1-bromo-1′-diphenylphosphinoferrocene at −78 °C, the resulting mixture was treated with chlorobis(*p*-methoxy)phenylphosphine as in the procedure for ligand **10**. After chromatography (petroleum) of the crude product, **11** was obtained as an orange oil in 53% yield. ^{1}H NMR ($CDCl_3$): δ = 3.79 (s, 6H), 3.97 (ddd, J = 9.4, 3.8, 1.9 Hz, 2H), 4.25 (dt, J = 14.1, 1.8 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 7.12 (dd, J = 9.8, 7.1 Hz, 2H), 7.21–7.29 ppm (m, 18H); ^{31}P NMR ($CDCl_3$): $\delta = -16.26$ (s, 1P), −20.05 ppm (s, 1P); MS (EI): m/z (%): 614 ([M]$^+$, 100), 616 ([$M+2$]$^+$, 26.78), 615 ([$M+1$]$^+$, 93.64), 538 (20.59), 537 (21.52); IR (KBr): $\tilde{\nu}$ = 2833, 1592, 1496, 1283, 1245, 1176, 1094, 1028, 825, 742, 696, 490 cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{32}FeO_2P_2$: C 70.37, H 5.25; found: C 70.18, H 5.08.

General procedure of the asymmetric intermolecular Heck reaction: The palladium species (15 μmol), diphosphineoxazoline ferrocenyl ligand (30 μmol), and solvent (5 mL) were placed under argon in an Schlenk tube with a magnetic stirring bar. After the reaction mixture had been allowed to sitr for 30 min, cyclohexenyl or aryl triflate (1 mmol) and *n*-undecane or *n*-tridecane (20 mg) (an internal GC standard) were added, followed by the addition of 2,3-dihydrofuran (**1**, 0.38 mL, 4 mmol) and base (2 mmol). The mixture was stirred at 60 °C under argon until the reaction was complete according to GC analysis. The reaction mixture was diluted with additional petroleum ether and the resulting red suspension was filtered through Celite and washed with Et_2O. The combined organic solutions were concentrated to give a red oil, which was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) to afford 2,5-dihydrofuran and 2,3-dihydrofuran derivatives as colorless oils.

All conversions of different triflates were determined by GC and *ee* values were determined by chiral GC or HPLC. Absolute configuration of products was assigned through comparison of the sign of specific rotations with literature data.[4, 5]

Phenyl triflate (2): GC (PE-XL, EC-5 (Altech); 30 m × 0.32 mm, 90–110 °C, N_2: 16 psi): t_R = 2.5 min (**2**), t_R = 3.8 min (*n*-undecane), t_R = 6.6 min (**4**), t_R = 8.0 min (**3**); GC (PE-XL, Chiraldex G-PN (Astec); 20 m × 0.25 mm, 90–115 °C, 1 °C min^{-1}, N_2: 10 psi): **3:** 11.9 min (*S*), 12.2 (*R*); **4**: 28.4 min (*S*), 28.9 (*R*).

Cyclohexenyl triflate (12): GC (PE-XL, EC-5 (Altech); 30 m × 0.32 mm, 120–140 °C, N_2: 15.7 psi): t_R = 1.0 min (**12**), t_R = 2.0 min (*n*-undecane), t_R = 3.5 min (**14**), t_R = 3.6 min (**13**); GC (PE-XL, Chiraldex B-PH (Astec); 20 m × 0.25 mm, 100 °C, 20 min, N_2: 6 psi): **13:** 11.9 min (*S*), 12.1 (*R*).

2-Naphthyl triflate (15a): GC (PE-XL, EC-5 (Altech); 30 m × 0.32 mm, 120–250 °C, N_2: 16 psi): t_R = 4.0 min (**15a**), t_R = 9.4 min (*n*-tridecane), t_R = 23.5 min (**17a**), t_R = 26.5 min, (**16a**); HPLC (Chiralcel OD-H; 0.46 m × 25 cm, 0.5 mL min^{-1}, heptane/isopropanol 90:10, detection at 220 nm): **16a:** 13.7 min (*S*), 14.31 (*R*); **17a**: 14.6 min (*S*), 16.0 (*R*).

4-Methoxyphenyl triflate (15b): GC (PE-XL, EC-5 (Altech); 30 m × 0.32 mm, 120–250 °C, N_2: 16 psi): t_R = 3.4 min **(15b)**, t_R = 2.0 min (*n*-undecane), t_R = 8.3 min (**17b**), t_R = 9.7 min (**16b**); GC (PE-XL, *Rt*-β-Dex (Restek); 30 m × 0.25 mm, 100–180 °C, 1 °C min^{-1}, N_2: 10 psi): **16b:** 71.3 min (*S*), 71.8 min (*R*); **17b:** 65.4 min (*S*), 65.9 min (*R*).

4-Nitrophenyl triflate (15c): GC (PE-XL, EC-5 (Altech); 30 m × 0.32 mm, 120–250 °C, N_2: 16 psi): t_R = 2.0 min (*n*-undecane), t_R = 5.1 min (**15c**), t_R = 16.6 min (**17c**), t_R = 19.4 min (**16c**); GC (PE-XL, Chiraldex G-TA (Astec); 20 m × 0.25 mm, 120–170 °C, 1 °C min^{-1}, N_2: 12 psi): **16c**: 45.0 min (*R*), 46.1 min (*S*).

Acknowledgement

Financial support from the National Natural Science Foundation of China, Chinese Academy of Sciences, the Major Basic Research Development Program (Grant No. G2000077506), and the National Outstanding Youth Fund. We thank Professor H. N. C. Wong and Professor Z.-G. Zhang for inspiring discussions.

[1] a) Y. Sato, M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1989**, *54*, 4738; b) N. E. Carpenter, D. J. Kucera, L. E. Overman, *J. Org. Chem.* **1989**, *54*, 5846.

[2] Reviews: a) C. Bolm, J. P. Hildebrand, K. Muñiz, N. Hermanns, *Angew. Chem.* **2001**, *113*, 3382; *Angew. Chem. Int. Ed.* **2001**, *40*, 3284; b) M. Shibasaki, E. M. Vogl in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, 458; c) O. Loiseleur, M. Hayashi, M. Keenan, N. Schmees, A. Pfaltz, *J. Organomet. Chem.* **1999**. *576*, 16; d) M. Beller, T. H. Riermeier, G. Stark in *Transition Metals for Organic Synthesis* (Eds: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, *Vol. 1*, 208.

[3] a) F. Diederich, P. J. Stang, *Metal–Metal Cross-Coupling Reaction*, Wiley-VCH, **1999**; b) M. Shibasaki, C. D. J. Boden, A. Kojima, *Tetrahedron*, **1997**, *53*, 7371; c) S. E. Gibson, R. J. Middleton, *Contemp. Org. Synth.* **1996**, *3*, 447; d) E. Negishi, C. Copéret, S. Ma, S.-Y. Liou, F. Liu, *Chem. Rev.* **1996**, *96*, 365.

[4] a) F. Ozawa, Y. Kobatake, T. Hayashi, *Tetrahedron Lett.* **1993**, *34*, 2505; b) F. Ozawa, T. Hayashi, *J. Organomet. Chem.* **1992**, *428*, 267; c) F. Ozawa, A. Kubo, T. Hayashi, *J. Am. Chem. Soc.* **1991**, *113*, 1417.

[5] a) O. Loiseleur, M. Hayashi, N. Schmees, A. Pfaltz, *Synthesis* **1997**, 1338; b) O. Loiseleur, P. Meier, A. Pfaltz, *Angew. Chem.* **1996**, *108*, 218; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200.
[6] a) L. F. Tietze, K. Thede, R. Schimpf, F. Sannicolò, *Chem. Commun.* **2000**, 583; b) T. Benincori, O. Piccolo, S. Rizzo, F. Sannicolò, *J. Org. Chem.* **2000**, *65*, 8340; c) L. F. Tietze, K. Thede, F. Sannicolò, *Chem. Commun.* **1999**, 1811.
[7] Contrary to usual expectations, diphosphine TMBTP gave an isomerized product with 2,3-dihydrofuran; when this ligand was employed in the reaction with dihydropyrrole mainly an unisomerized product was obtained: L. F. Tietze, K. Thede, *Synlett* **2000**, 1470.
[8] a) K. Selvakumar, M. Valentini, P. S. Pregosin, A. Albinati, F. Eisenträger, *Organometallics* **2000**, *19*, 1299; b) A. Albinati, P. S. Pregosin, M. Tschoerner, *Organometallics* **1999**, *18*, 670; c) G. Trabesinger, A. Albinati, N. Feiken, R. W. Kunz, P. S. Pregosin, M. Tschoerner, *J. Am. Chem. Soc.* **1997**, *119*, 6315.
[9] N. G. Andersen, R. McDonald, B. A. Keay, *Tetrahedron: Asymmetry* **2001**, *12*, 263.
[10] a) F. Ozawa, A. Kubo, Y. Matsumoto, T. Hayashi, *Organometallics* **1993**, *12*, 4188; b) T. Hayashi, A. Kubo, F. Ozawa, *Pure Appl. Chem.* **1992**, *64*, 421.
[11] a) W.-P. Deng, S.-L. You, X.-L. Hou, L.-X. Dai, Y.-H. Yu, W. Xia, J. Sun, *J. Am. Chem. Soc.* **2001**, *123*, 6508; b) W.-P. Deng, X.-L. Hou, L.-X. Dai, X.-W. Dong, *Chem. Commun.* **2000**, 1483; b) W.-P. Deng, X.-L. Hou, L.-X. Dai, Y.-H Yu, W. Xia, *Chem. Commun.* **2000**, *4*, 285.
[12] a) S. R. Gilberston, D. Xie, Z. Fu, *J. Org. Chem.* **2001**, *66*, 7240; b) S. R. Gilberston, Z. Fu, *Org. Lett.* **2001**, *3*, 161.
[13] a) A. J. Hennessy, D. J. Connolly, Y. M. Malone, P. J. Guiry, *Tetrahedron Lett.* **2000**, *41*, 7757; b) A. J. Hennessy, Y. M. Malone, P. J. Guiry, *Tetrahedron Lett.* **1999**, *40*, 9163.
[14] a) A. V. Malkov, M. Bella, I. G. Stará, P. Kočovský, *Tetrahedron Lett.* **2001**, *42*, 3045; b) Y. Hashimoto, Y. Horie, M. Hayashi, K. Saigo, *Tetrahedron: Asymmetry*, **2000**, *11*, 2205; c) M. Ogasawara, K. Yoshida, T. Hayashi, *Heterocycles* **2000**, *52*, 195; d) J. Priego, J. C. Carretero, *Synlett* **1999**, 1603.
[15] For recent mechanistic advances, see: a) K. K. S. Hii, T. D. W. Claridge, J. M. Brown, *Angew. Chem.* **1997**, *109*, 1033; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 984; b) M. Ludwig, S. Strömberg, M. Svensson, B. Åkermark, *Organometallics* **1999**, *18*, 970.
[16] C. Amatore, G. Broeker, A. Jutand, F. Khalil, *J. Am. Chem. Soc.* **1997**, *119*, 5176.
[17] a) S.-L. You, X.-Z. Zhu, Y.-M. Luo, X.-L. Hou, L.-X. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 7471; b) S.-L. You, X.-L. Hou, L.-X. Dai, X.-Z. Zhu, *Org. Lett.* **2001**, *3*, 149; c) S.-L. You, X.-Z. Zhu, X.-L. Hou, L.-X. Dai, *Acta Chimica Sinica* **2001**, *10*, 1667; d) S.-L.You, X.-L. Hou, L.-X. Dai, B.-X. Cao, J. Sun, *Chem. Commun.* **2000**, 1933; e) S.-L.You, X.-L. Hou, L.-X. Dai, *Tetrahedron: Asymmetry* **2000**, *11*, 1495.
[18] a) X.-L. Hou, L.-X. Dai, W.-P. Deng, S.-L.You, Y.-G. Zhou, *Pure Appl. Chem.* **1999**, *71*, 1401; b) W.-P. Deng, X.-L. Hou, L.-X. Dai, *Tetrahedron: Asymmetry* **1999**, *10*, 4689; c) S.-L. You, Y.-G. Zhou, X.-L. Hou, L.-X. Dai, *Chem. Commun.***1998**, *24*, 2765; d) X.-D. Du, L.-X. Dai, X.-L. Hou, L.-J. Xia, M.-H. Tang, *Chin. J. Chem.* **1998**, *16*, 90.
[19] a) A. Tongi, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062; b) A. Tongi, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475; *Angew. Chem.* **1996**, *108*, 1581.
[20] A. Chesney, M. R. Bryce, R. W. J. Chubb, A. S. Batsanov, J. A. K. Howard, *Synthesis* **1998**, 413.
[21] C. J. Richards, A. W. Mulvaney, *Tetrahedron: Asymmetry* **1996**, *7*, 1419.
[22] F. Ozawa, A. Kubo, T. Hayashi, *Chem. Lett.* **1992**, 2177.
[23] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* **1984**, *106*, 158.
[24] For the nucleophilicity of anions in different solvents, see: M. B. Smith, J. March, *March's Advanced Organic Chemistry: Reaction, Mechanism and Structure*, Wiley, **2001**, 438–445.
[25] The structural parameters of the [Pd{(*R*)-BINAP}] moiety are taken from the X-ray structure of [$PdCl_2${(*R*)-BINAP}];[10] and the structural parameters of the [Pd{(*R*)-PHOX}] moiety are taken from the X-ray structure of [Pd(allyl){(*R*)-PHOX}]: J. Sprinz, M. Kiefer, G. Helmchen, *Tetrahedron Lett.* **1994**, *35*, 1523.
[26] T.-Y. Dong, L.-L. Lai, *J. Organomet. Chem.* **1996**, *509*, 131.

Received: September 25, 2002
Revised: February 24, 2003 [F4450]

