

# 1,1'-Bis(oxazolinyl)ferrocene-based palladium catalysts: Synthesis, X-ray structures and applications in Suzuki and Heck coupling reactions

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Received 31 October 2005; received in revised form 1 December 2005; accepted 7 December 2005

Available online 27 January 2006

## Abstract

1,1'-Bis(oxazolinyl)ferrocene-based palladium dichloride complexes **2a** and **2b** were synthesized. X-ray single-crystal diffraction analyses showed that they are of the *N,N'*-chelating type, and that the coordination mode of **2a**, which has an isopropyl group, is of the *cis* type, whereas that of **2b**, which has a *tert*-butyl group, is the *trans* one. These two complexes were employed as catalysts for Suzuki and Heck reactions, and showed high catalytic activities in coupling reactions with various aryl halides and counterparts (phenylboronic acid or *n*-butyl acrylate). Particularly, the catalyst **2a** afforded the coupled product of aryl bromide with phenylboronic acid at room temperature.

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**Keywords:** Catalyst; Palladium; Ferrocene; Oxazoline; Coordination modes; Suzuki; Heck

## 1. Introduction

Palladium catalyzed cross-coupling reactions constitute one of the most useful methods of forming carbon–carbon bonds and carbon–heteroatom (N, O and S) bonds [1]. Many different reaction types have been reported, such as Kumada and co-workers [2], Negishi [3], Milstein and Stille [4], Hatanaka and Hiayama [5], Miyaura and Suzuki [6], Sonogashira et al. [7], Heck [8] and Hartwig-Buchwald [9] cross-coupling reactions. They have been widely used for the synthesis of valuable organic compounds such as pharmaceuticals and agrochemicals [10]. In most cases, the choice of ligand plays a major role in the efficiency of the reaction. Recently, a number of efficient ligands have been reported in order to expand the scope of the reaction substrates that can be used under mild conditions [4c,6d,11]. However, these ligands systems, mostly phosphine derivatives, suffer from drawbacks such as their high sensitivity to air and moisture and, consequently, inert atmosphere conditions are required for effi-

cient catalysis. As one of the methods of overcoming these problems, nitrogen donor ligands have been employed as ligands in many transition metal catalyzed transformation reactions [12]. Nitrogen-based catalysts allow for the generation of catalytically active complexes which are complementary to the known phosphine-based systems.

Our and other research groups have reported that chiral 1,1'-bis(oxazolinyl)ferrocene derivatives, which are mainly based on the phosphine donor group, were synthesized diastereoselectively, and showed high catalytic activities in palladium catalyzed asymmetric allylic alkylation reactions [13]. In addition, the palladium complexes of 1,1'-bis(oxazolinyl)ferrocenes having diphenylphosphinyl groups have been studied with NMR spectroscopy and X-ray crystallography. They showed *N,P*-chelating or *P,P*-chelating modes depending on their structural features. A couple of years ago, Ikeda and co-workers reported their NMR studies of the palladium complexes of 1,1'-bis(oxazolinyl)ferrocenes, in which they suggested that the 1:2 palladium complexes of the ligand and palladium was formed [14]. However, we obtained the *N,N*-chelating type palladium complexes from the same ligands.

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There have been several reports in which oxazoline-based ligands were used in palladium catalyzed cross-coupling reactions [15]. However, to the best of our knowledge, 1,1'-bis(oxazolanyl)ferrocenes **1**, which have only nitrogen donor groups, have never been used as ligands in palladium catalyzed cross-coupling reactions, even though nitrogen donor ligands are known to be less sensitive to air and water than phosphine donor ligands. Herein, we report our findings that the coordination modes of 1,1'-bis(oxazolanyl)ferrocene ligands toward palladium are dependent on the substituted group in the oxazoline ring, and that these complexes show high catalytic activities in Suzuki and Heck reactions.

## 2. Results and discussion

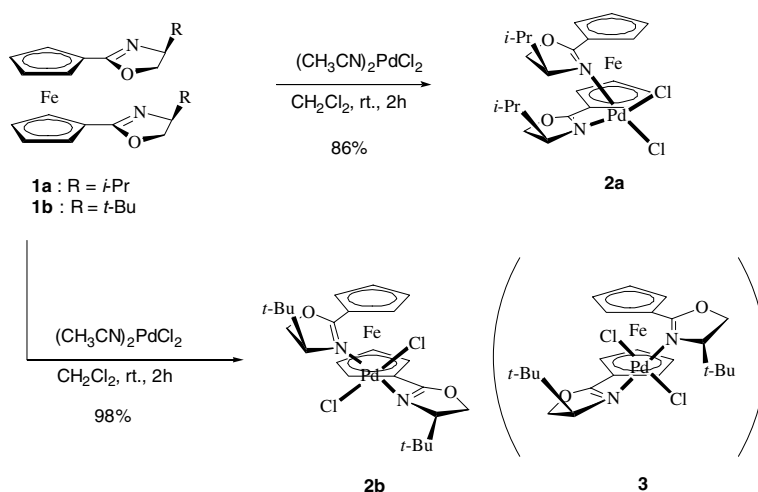
### 2.1. Synthesis and X-ray crystallography of 1,1'-bis(oxazolanyl)ferrocene palladium dichloride complexes

The coordination modes of 1,1'-bis(oxazolanyl)ferrocenes toward palladium were examined (Scheme 1). When 1,1'-bis(oxazolanyl)ferrocene (**1a**) bearing an isopropyl group on the oxazoline ring was treated with 1.0 equivalent of  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  in  $\text{CH}_2\text{Cl}_2$  at room temperature, the palladium dichloride complex **2a** was obtained with 86% yield. The complex is a thermally robust red solid that is stable in air both in the solid form and in solution. The  $^1\text{H}$  NMR spectrum of the corresponding metal complex exhibits two noteworthy features. First, the oxazolanyl protons and the protons of the cyclopentadienyl rings in ferrocene are shifted downfield from the values observed for the free ligand. Second, the magnetically equivalent protons in the free ligand, whose equivalence is derived from the centrosymmetry of ferrocene, are transformed into two sets of non-equivalent signals. These results imply that the palladium and ligand are combined in a 1:1 molar ratio to form an  $N,N'$ -type chelating complex and that their coordination mode is not  $C_2$ -symmetry. Next, 1,1'-bis(oxazoli-

nyl)ferrocene (**1b**) having a *t*-butyl group on the oxazoline ring was reacted with  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  in the same way. The complex **2b** was obtained with almost quantitative yield and exhibited the same stability. However, in contrast to **2a**, the  $^1\text{H}$  NMR spectrum of the resulting complex exhibits only one set of signals that are mostly shifted downfield from the values observed for the free ligand, indicating that the complex is a  $C_2$ -symmetric  $N,N'$ -type chelating one. Moreover, this result also implies that the coordination mode of **2b** is different from that of **2a**.

In order to define the exact coordination modes of each complex, the solid state molecular structures of **2a** and **2b** were determined by X-ray diffraction, and these are depicted in Figs. 1 and 2, respectively, together with the principal bond lengths and bond angles. As elucidated from the crystallographic data, both two palladium complexes are of the  $N,N'$ -chelating type, and **2a** has the *cis* coordination mode, while **2b** has the *trans* one.

In the case of the *cis* palladium complex of the 1,1'-bis(oxazolanyl)ferrocene (**2a**), only one conformer is able to be formed. However, in the case of the *trans* complex, there are two possible conformers that can be formed, viz. one in which each substituted group (e.g. *tert*-butyl) on the oxazoline ring faces the *endo* side of the ferrocene moiety, and the other in which they face the *exo* side. Of these two possible conformers, only **2b** was obtained, whereas the other possible conformer **3** was not detected in the  $^1\text{H}$  NMR spectrum of the reaction mixture. This exclusive formation of one conformer of the *trans* complex may be due to the existence of two types of steric repulsion. One type of repulsion between both *tert*-butyl groups on the oxazoline rings leads to the *trans* coordination mode rather than the *cis* one, while the other type of repulsion between the *tert*-butyl groups and the ferrocene moiety leads to the *exo* conformer. This finding suggests that the geometry and conformation of the palladium complex of 1,1'-bis(oxazolanyl)ferrocene is dependent on the size of the substituted group on the oxazolanyl ring. In contrast



Scheme 1. Synthesis of 1,1'-bis(oxazolanyl)ferrocene palladium dichlorides, **2a** and **2b**.

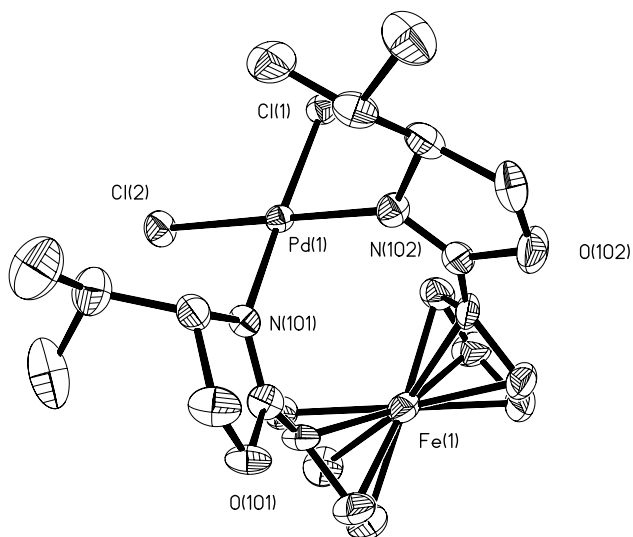


Fig. 1. X-ray structure of **2a** with 50% probability. Selected bond distances (Å): Pd(1)–N(101) = 2.055(6), Pd(1)–N(102) = 2.041(7), Pd(1)–Cl(1) = 2.322(2), Pd(1)–Cl(2) = 2.309(2). Selected bond angles (°): N(101)–Pd(1)–N(102) = 88.5(3), N(102)–Pd(1)–Cl(2) = 179.4(2), N(101)–Pd(1)–Cl(2) = 90.91(19), N(102)–Pd(1)–Cl(1) = 88.01(2), N(101)–Pd(1)–Cl(1) = 176.51(19), Cl(1)–Pd(1)–Cl(2) = 92.43(7).

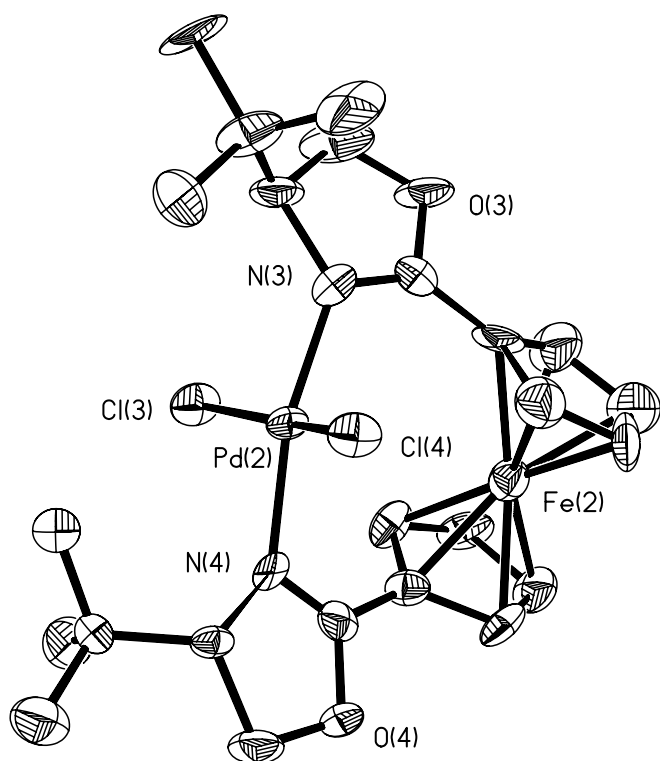


Fig. 2. X-ray structure of **2b** with 50% probability. Selected bond distances (Å): Pd(2)–N(3) = 1.993(12), Pd(2)–N(4) = 1.997(10), Pd(2)–Cl(3) = 2.331(4), Pd(2)–Cl(4) = 2.317(3). Selected bond angles (°): N(3)–Pd(2)–N(4) = 1165.9(5), N(3)–Pd(2)–Cl(4) = 93.6(3), N(4)–Pd(2)–Cl(4) = 87.8(3), N(3)–Pd(2)–Cl(3) = 88.1(4), N(4)–Pd(2)–Cl(3) = 93.7(3), Cl(4)–Pd(2)–Cl(3) = 166.62(15).

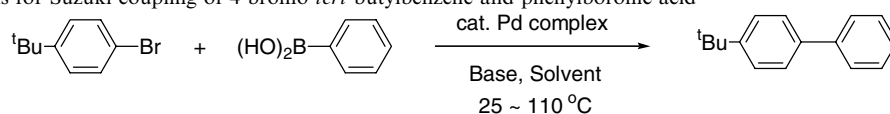
to our results, based on their  $^1\text{H}$  NMR experimental data, Ikeda and co-workers suggested that the palladium complexes of 1,1'-bis(oxazoliny)ferrocenes did form a 1:2

complex of ligand-to-metal [14]. The different results between our complexes and theirs might be the nature of the solvent used. When the coordinating solvent-like  $\text{CH}_3\text{CN}$  was used, 1:2 complex is formed, while non-coordinating solvent-like  $\text{CH}_2\text{Cl}_2$  gave 1:1 complex. This rationalization is supported by the following experiment. When the complexation reaction between **1b** and  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  performed in  $\text{CD}_3\text{CN}$ , the  $^1\text{H}$  NMR spectrum showed the same pattern as that reported by Ikeda and co-workers, suggesting 1:2 complex was formed. Moreover, their complexation behavior was independent of the substituted group on the oxazoliny ring. It is well known that the coordination mode (*cis* or *trans*) of a chelating ligand is dependent on the donor atom-metal-donor atom bite angle, which is derived from the length and flexibility of the ligand backbone [16]. The general feature of chelating ligands is their *cis*-coordination. Of course, there have been several reports of *trans*-chelating ligands in palladium complexes; for example, phosphine ligands based on the xanthene framework [17] or on the ferrocene unit [18], nitrogen ligands such as bis-pyridine [19] and carbene type ligands such as bis-imidazolylidene [20].

## 2.2. Suzuki cross-coupling reactions

The complexes prepared in this work were employed as catalysts for Suzuki and Heck reactions. These reactions were used as a standard test reaction to probe the reactivity of these new palladium complexes. First, the catalysts **2a** and **2b** were applied to the Suzuki cross-coupling reaction with phenylboronic acid and 4-bromo-*tert*-butylbenzene. Table 1 summarizes the results obtained from the screening of a variety of bases and solvents for model substrates that undergo C–C coupling reactions. Several trends are readily apparent. The catalyst **2a** with its *cis*-chelating mode showed a faster cross-coupling reaction rate than the *trans*-chelating catalyst **2b** (entries 1 and 13). As shown in Fig. 3, the catalyst **2a** afforded the coupled product in 70% yield within 30 min and almost quantitative yield in 2 h. However, the complex **2b** showed only 50% yield even after 2 h, and required a longer reaction time to produce a yield of more than 90% of the coupled product. Various less expensive bases were examined for their effect on the reaction efficiency in the toluene solvent.  $\text{K}_2\text{CO}_3$  was the most effective (entry 1) and  $\text{K}_3\text{PO}_4$  showed comparable results (entry 2).  $\text{KF}$  displayed moderate efficiency, generating the coupled product in 65% yield (entry 3). Sodium bases such as  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4$  showed low activities (entries 4 and 5). Interestingly, although they are commonly used and effective bases for Pd/phosphine Suzuki-type reactions [6d,21],  $\text{Cs}_2\text{CO}_3$  and  $\text{CsF}$  proved to be fairly ineffective in the present system (entries 6 and 7). Among the tested solvents, the non-polar solvent toluene was found to be the most productive, whereas polar aprotic solvents, such as DMF, NMP, THF and dioxane, and polar protic solvents, such as *i*-PrOH, afforded low coupled product yields (entries 8–12). A similar beneficial effect of

Table 1  
Optimization of conditions for Suzuki coupling of 4-bromo-*tert*-butylbenzene and phenylboronic acid<sup>a</sup>



Entry	Pd (mol%)	Catalyst	Solvent	Base	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)
1	0.5	2a	Toluene	K <sub>2</sub> CO <sub>3</sub>	60	2	98
2	0.5	2a	Toluene	K <sub>3</sub> PO <sub>4</sub>	60	2	94
3	0.5	2a	Toluene	KF	60	2	65
4	0.5	2a	Toluene	Na <sub>2</sub> CO <sub>3</sub>	60	2	18
5	0.5	2a	Toluene	Na <sub>3</sub> PO <sub>4</sub>	60	2	27
6	0.5	2a	Toluene	Cs <sub>2</sub> CO <sub>3</sub>	60	2	10
7	0.5	2a	Toluene	CsF	60	2	5
8	0.5	2a	DMF	K <sub>2</sub> CO <sub>3</sub>	60	12	40
9	0.5	2a	NMP	K <sub>2</sub> CO <sub>3</sub>	60	12	10
10	0.5	2a	THF	K <sub>2</sub> CO <sub>3</sub>	60	12	62
11	0.5	2a	Dioxane	K <sub>2</sub> CO <sub>3</sub>	60	12	14
12	0.5	2a	<i>i</i> -PrOH	K <sub>2</sub> CO <sub>3</sub>	60	12	57
13	0.5	2b	Toluene	K <sub>2</sub> CO <sub>3</sub>	60	10	94
14	1.0	2a	Toluene	K <sub>2</sub> CO <sub>3</sub>	25	24	92
15 <sup>c</sup>	4.2 × 10 <sup>-3</sup>	2a	Toluene	K <sub>2</sub> CO <sub>3</sub>	110	24	82

<sup>a</sup> Reaction conditions: 1.0 mmol aryl halide, 1.1 mmol PhB(OH)<sub>2</sub>, 1.5 mmol base, 2.0 ml solvent.

<sup>b</sup> Yields determined by GC.

<sup>c</sup> 10.0 mmol scale of aryl halide used.

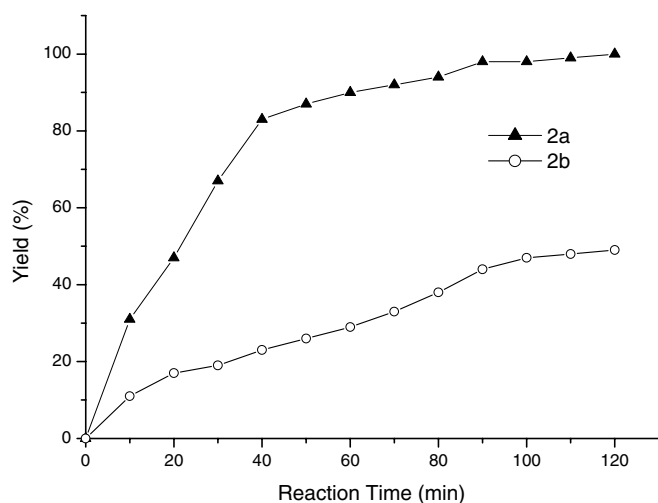


Fig. 3. Reaction profile for the Suzuki cross-coupling reaction of 4-bromo-*tert*-butylbenzene and phenylboronic acid using catalyst **2a** (▲) and **2b** (○) at 60 °C.

non-polar solvents on coupling reactions was also observed for phosphine-based systems [6d]. For room temperature couplings, the reaction required a 1.0 mol% catalytic loading of the complex **2a** (entry 14). The reaction needed an elevated temperature and long reaction time for a high turnover number (TON = 19,524) to be obtained for the complex **2a** (entry 15). To the best of our knowledge, there have been only a few reports of N-coordinated palladium complex mediated Suzuki cross-coupling reactions of aryl bromides at room temperature [22]. This result implies that complex **2a** can be employed as a catalyst in Suzuki cross-

coupling reactions for aryl bromides bearing thermally unstable moiety.

The Suzuki cross-coupling of activated and deactivated aryl bromides or aryl chloride with phenylboronic acid were carried out in the presence of 0.5 mol% of catalyst **2a** to give the cross-coupled products (Table 2). Bromobenzene reacted with phenylboronic acid in 2 h to give biphenyl in 98% isolated yield (entry 1). The activated substrates reacted with phenylboronic acid to give the corresponding cross-coupled products in generally good isolated yield (entries 2 and 9–12). Some of the deactivated substrates required an elevated temperature to give the products in high yield (entries 5 and 7). The sterically hindered 2-bromotoluene resulted in high yields. However, the very sterically congested and deactivated substrate, bromomesitylene, reacted with phenylboronic acid to give the cross-coupled product in only modest yield (entries 14 and 15). The use of 2-bromo and 3-bromo pyridines, which have the potential to bind to palladium through the nitrogen atom, gave 46% and 89% yields, respectively (entries 16 and 17). More vigorous conditions were required to effect the Suzuki cross-coupling of aryl chlorides (entries 18 and 19).

### 2.3. Heck cross-coupling reactions

Afterwards, the Heck reactions of 4-bromotoluene and *n*-butyl acrylate were carried out with various bases and solvents. The use of a phosphate base generally leads to higher yields for the coupling reactions, and in this case K<sub>3</sub>PO<sub>4</sub> gave the product in 94% yield (entries 1 and 2). Car-

Table 2  
Suzuki cross-coupling reactions by catalyst **2a**<sup>a</sup>

X = Br, Cl

Entry	ArBr	Temperature (°C)	Time <sup>b</sup> (h)	Yield <sup>c</sup> (%)	Entry	ArBr	Temperature (°C)	Time <sup>b</sup> (h)	Yield <sup>c</sup> (%)
1		60	2	98	11		60	2	99
2		60	2	99	12		60	2	98
3		60	2	96	13		60	2	92
4		60	3	64	14		60	3	40
5		90	2	90	15		90	2	68
6		60	3	60	16		60	2	46
7		90	2	86	17		60	2	89
8		60	2	91	18		80	4	26
9		60	2	99	19		110	6	45
10		60	2	98					

<sup>a</sup> Reaction conditions: 1.0 equiv of aryl halide, 1.1 equiv of phenylboronic acid, 0.5 mol% **2a**, 1.5 equiv of K<sub>2</sub>CO<sub>3</sub>, toluene (0.1 M).

<sup>b</sup> Reaction times were not optimized.

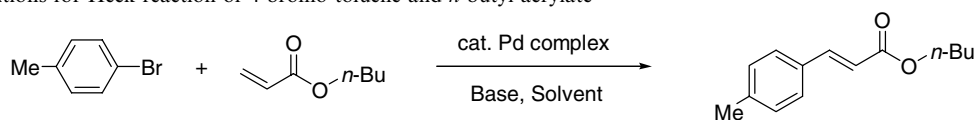
<sup>c</sup> Isolated yields of compounds are an average of at least two runs. All compounds are characterized by comparison of <sup>1</sup>H and <sup>13</sup>C NMR spectra with authentic samples or literature data.

bonate bases, such as K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>, gave the products in modest to low yields (entries 3–5). Organic bases such as Et<sub>3</sub>N showed low activity (entry 7). *N*-Methylpyrrolidione (NMP), which is a cyclic amide solvent, was the best solvent in this system. Other non-cyclic amide sol-

vents such as DMF and DMA led to the coupled product being generated in moderate yield. The catalysts **2a** and **2b** showed similar product yields of 94% and 90%, respectively (entries 1 and 12) at a concentration of 0.1 mol%, and their turnover number were 4650 and 4500, respectively, when



Table 3  
Optimization of conditions for Heck reaction of 4-bromo-toluene and *n*-butyl acrylate<sup>a</sup>



Entry	Pd (mol%)	Catalyst	Solvent	Base	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)
1	0.1	2a	NMP	K <sub>3</sub> PO <sub>4</sub>	140	3	94
2	0.1	2a	NMP	Na <sub>3</sub> PO <sub>4</sub>	140	3	80
3	0.1	2a	NMP	K <sub>2</sub> CO <sub>3</sub>	140	3	65
4	0.1	2a	NMP	Na <sub>2</sub> CO <sub>3</sub>	140	3	70
5	0.1	2a	NMP	Cs <sub>2</sub> CO <sub>3</sub>	140	3	24
6	0.1	2a	NMP	NaOAc	140	3	50
7	0.1	2a	NMP	Et <sub>3</sub> N	80	12	3
8	0.1	2a	DMF	K <sub>3</sub> PO <sub>4</sub>	140	6	59
9	0.1	2a	DMA	K <sub>3</sub> PO <sub>4</sub>	140	6	53
10	0.02	2a	NMP	K <sub>3</sub> PO <sub>4</sub>	140	8	93
11	0.002	2a	NMP	K <sub>3</sub> PO <sub>4</sub>	140	12	8
12	0.1	2b	NMP	K <sub>3</sub> PO <sub>4</sub>	140	3	90
13	0.02	2b	NMP	K <sub>3</sub> PO <sub>4</sub>	140	12	90

<sup>a</sup> Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol *n*-butyl acrylate, 2.0 mmol base, 2.5 ml solvent.

<sup>b</sup> Yields determined by GC.

they were used at a concentration of 0.02 mol% (entries 10 and 13). At a concentration of 0.002 mol%, the catalyst **2a** led to the coupled product being generated in only 8% yield (entry 11). In contrast to these results, Ueda and co-workers reported that *trans*-chelating complexes exhibited higher catalytic activities in Heck reactions for aryl iodides than *cis*-chelating complexes [19c]. However, their *trans*-chelating complex produced the coupled product of aryl bromide in very low yield (1–4%) (see Table 3).

A wide range of electronically and structurally diverse aryl bromides can be cross-coupled efficiently with *n*-butyl acrylate under these optimized conditions. The results are summarized in Table 4. It is noteworthy that the use of deactivated, electron-rich aryl bromides as well as activated, electron-poor ones also resulted in high yields.

### 3. Conclusion

In summary, the 1,1'-bis(oxazoliny)ferrocene palladium dichloride complexes **2a** and **2b** were synthesized with 86% and 98% yields, respectively. Their *N,N'*-type chelating modes were determined by X-ray single-crystal diffraction. It was found that the complex **2a** operates in the *cis* mode, and complex **2b** in the *trans* mode. Moreover, the compound **1b** afforded only one of two possible *trans*-chelating palladium complexes. Complexes **2a** and **2b** were employed as catalysts in Suzuki and Heck reactions, and showed high catalytic activities. The catalyst **2a** showed a faster reaction rate than the catalyst **2b** in Suzuki reactions, however, their reactivities were not significantly different in Heck reactions. In particular, the catalyst **2a** afforded the coupled product of an aryl bromide with phenylboronic acid at room temperature. Based on these results, further investigations into the use of chiral catalysts in asymmetric reactions are under way.

## 4. Experimental

### 4.1. General procedures

The reagents and solvents were obtained from commercial sources and were generally used without further purification. 1,1'-Bis(oxazoliny)ferrocenes (**1**) were prepared according to the procedures described in the literature [13a]. Naphthalene was used as a standard in the quantitative GC experiments using response factors determined from isolated products. All NMR spectra were recorded in CDCl<sub>3</sub> with a Bruker AM 300 spectrometer. Chemical shifts are given in  $\delta$  ppm downfield from Me<sub>4</sub>Si ( $\delta$  0, <sup>1</sup>H) or CDCl<sub>3</sub> ( $\delta$  77, <sup>13</sup>C) as an internal standard. Elemental analyses were performed by the Center for Biofunctional Molecules, Pohang University of Science and Technology.

### 4.2. Synthesis of [1,1'-bis{(S)-4-isopropylloxazolin-2-yl}ferrocene]palladium(II) dichloride (**2a**)

A solution of **1a** (172 mg, 0.42 mmol) and (CH<sub>3</sub>CN)<sub>2</sub>-PdCl<sub>2</sub> (109 mg, 0.42 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was stirred at room temperature for 2 h, and then the volatiles were removed in vacuo. The residue was washed with hexane and dried in vacuo, giving **2a** as a red solid (212 mg, 0.36 mmol, yield 86%), which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane at -18 °C to produce red crystals of **2a**. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.74 (m, 1H), 6.88 (m, 1H), 4.68 (m, 1H), 4.64 (m, 1H), 4.61 (m, 1H), 4.53 (t, *J* = 1.2 Hz, 1H), 4.49 (m, 2H), 4.48 (m, 1H), 4.31 (m, 1H), 4.20–4.05 (m, 4H), 2.95 (m, 1H), 2.41 (m, 1H), 1.83 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 6H), 0.69 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  171.8, 170.08, 99.86, 86.54, 74.00, 72.92, 72.75, 72.57, 71.83, 71.51, 70.19, 69.36, 68.58, 68.25, 31.96, 29.45, 22.37, 19.59, 18.23, 15.03. Anal. found:

Table 4  
Heck cross-coupling reactions by catalyst **2a**<sup>a</sup>

Entry	ArBr	Yield <sup>b</sup> (%)	Entry	ArBr	Yield <sup>b</sup> (%)
1		97	5		96
2		98	6		95
3		94	7		88
4		85	8		92

<sup>a</sup> Reaction conditions: 1.0 equiv of aryl halide, 1.5 equiv of butyl acrylate, 2.0 equiv of K<sub>3</sub>PO<sub>4</sub>, 0.1 mol% **2a**, NMP(0.2 M) at 140 °C for 3 h.

<sup>b</sup> Isolated yields of compounds are an average of at least two runs. All compounds are characterized by comparison of <sup>1</sup>H and <sup>13</sup>C NMR spectra with authentic samples or literature data.

C, 45.00; H, 4.72; N, 4.60. Calc. for C<sub>22</sub>H<sub>28</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>Pd:  
C, 45.12; H, 4.82; N, 4.78%.

#### 4.3. Synthesis of [1,1'-bis{(S)-4-tert-butylloxazolin-2-yl}ferrocene]palladium(II) dichloride (**2b**)

A solution of **1b** (149 mg, 0.341 mmol) and (CH<sub>3</sub>CN)<sub>2</sub>-PdCl<sub>2</sub> (88 mg, 0.34 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was stirred at room temperature for 2 h, and then the volatiles were removed in vacuo. The residue was washed with *n*-hexane and dried in vacuo, giving **2b** as a dark red solid (204 mg, 0.333 mmol, yield 98%), which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane at -18 °C to produce dark red crystals of **2b**. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.95 (t, *J* = 1.4 Hz, 2H), 4.87 (t, *J* = 1.4 Hz, 2H), 4.69 (t, *J* = 1.3 Hz, 2H), 4.44 (m, 4H), 4.21 (m, 4H), 1.14 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 171.78, 80.39, 74.02, 72.38, 70.85, 70.23, 69.67, 34.42, 26.43. Anal. found: C, 46.61; H, 4.94; N, 4.99. Calc. for C<sub>24</sub>H<sub>32</sub>Cl<sub>2</sub>Fe-N<sub>2</sub>O<sub>2</sub>Pd: C, 46.97; H, 5.26; N, 4.56%.

#### 4.4. Suzuki cross-coupling reactions

The aryl halide (2.0 mmol), phenylboronic acid (2.2 mmol), and the catalyst **2a** or **2b** (0.01 mmol, 0.5 mol%) were combined with K<sub>2</sub>CO<sub>3</sub> (3.0 mmol) in a small round-bottom flask. Toluene was added and the flask was sealed with a septum. The flask was maintained in an

oil bath at the appropriate temperature until the starting material was consumed, as determined by GC and TLC. The reaction mixture was poured into 20 mL of saturated aqueous ammonium chloride and extracted (3 × 20 mL) with Et<sub>2</sub>O. The combined ether extracts were washed with brine (60 mL), dried over MgSO<sub>4</sub>, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with 5% ethyl acetate in hexanes.

#### 4.5. Heck cross-coupling reactions

The aryl bromide (2.0 mmol), *n*-butyl acrylate (3.0 mmol) and the catalyst **2a** or **2b** (0.002 mmol, 0.1 mol%) were combined with K<sub>3</sub>PO<sub>4</sub> (4.0 mmol) in a small round-bottom flask. NMP was added and the flask was sealed with a septum. The flask was maintained in an oil bath at 140 °C until the starting material was consumed, as determined by GC and TLC. The reaction mixture was poured into 20 mL of saturated aqueous ammonium chloride and extracted (3 × 20 mL) with Et<sub>2</sub>O. The combined ether extracts were washed with brine (60 mL), dried over MgSO<sub>4</sub>, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with 5% ethyl acetate in hexanes.

#### 4.6. X-ray crystallographic study of **2a** and **2b**

Suitable crystals of the complexes **2a** and **2b** were obtained by layering concentrated solutions of the compounds in dichloromethane with *n*-hexane and allowing slow diffusion at  $-18\text{ }^{\circ}\text{C}$ . The crystals were sealed in capillaries before collecting the intensity data with an Enraf-Nonius CAD4 diffractometer using monochromated Mo  $K\alpha$  ( $\lambda = 0.71013\text{ \AA}$ ) radiation. The raw data collected were processed to produce conventional intensity data using the program, SAINT. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of the Patterson and difference Fourier methods provided by the program package, SHELXTL. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated and included in the final cycle of refinement.

##### 4.6.1. Crystal data for **2a**

Empirical formula =  $\text{C}_{46}\text{H}_{58}\text{Cl}_8\text{Fe}_2\text{N}_4\text{O}_4\text{Pd}_2$ , formula weight = 1339.06, red crystals,  $0.1 \times 0.3 \times 0.3\text{ mm}^3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 14.664(2)$ ,  $b = 18.691(4)$ ,  $c = 26.825(7)\text{ \AA}$ ,  $V = 5455.0(17)\text{ \AA}^3$ ,  $Z = 4$ , density =  $1.630\text{ Mg/m}^3$ , absorption coefficient =  $1.606\text{ mm}^{-1}$ ,  $T = 188(2)\text{ K}$ , 10,281 unique reflections measured,  $R(F)$  for all data = 0.0549,  $R_w(F)$  for all data = 0.1303, goodness-of-fit = 1.096.

##### 4.6.2. Crystal data for **2b**

Empirical formula =  $\text{C}_{51}\text{H}_{74}\text{Cl}_{10}\text{Fe}_2\text{N}_4\text{O}_6\text{Pd}_2$ , formula weight = 1518.14, dark red crystals,  $0.20 \times 0.20 \times 0.05\text{ mm}^3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.4354(2)$ ,  $b = 12.7792(2)$ ,  $c = 45.4510(4)\text{ \AA}$ ,  $V = 6061.17(16)\text{ \AA}^3$ ,  $Z = 8$ , density =  $3.327\text{ Mg/m}^3$ , absorption coefficient =  $3.087\text{ mm}^{-1}$ ,  $T = 188(2)\text{ K}$ , 24,888 unique reflections measured,  $R(F)$  for all data = 0.0970,  $R_w(F)$  for all data = 0.1844, goodness-of-fit = 1.244.

#### Acknowledgement

This work was financially supported by research fund of Chonnam National University in 2004.

#### Appendix A. Supplementary material

The crystallographic data used for the structural analysis were deposited with the Cambridge Crystallographic Data Centre, CCDC no 287803 for compound **2a** and no 287804 for **2b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EX, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.018.

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