# Synthesis, Characterization, and Crystal Structures of Three *cis/trans* Pyridine–Cyclopalladated Ferrocenylimine Complexes, and Their Catalysis in Suzuki Reactions

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Three new pyridine–cyclopalladated ferrocenylimine complexes 2a-c have been easily prepared and characterized by elemental analysis, ESI-MS, <sup>1</sup>H NMR, and IR spectra. Their detailed structures are determined by single-crystal X-ray analysis. Palladacycle 2a is found to be a *cis* complex in the solid state, while 2b and 2c are *trans* complexes. These complexes were found to be efficient for the Suzuki reaction of aryl bromides with phenylboronic acid. Typically, using 0.2 mol% of 2c in the presence of 1.5 equivalents of K<sub>2</sub>CO<sub>3</sub> as base in toluene at 100°C provided the coupled products in good to excellent yields.

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#### Introduction

The palladium-catalyzed Suzuki reaction is a versatile method for the formation of C-C bonds in organic synthesis,<sup>[1-3]</sup> and gives access to a wide range of biaryl compounds. For industrial applications it is necessary to develop highly active catalysts, which allow the use of low catalyst loadings and inexpensive but usually less reactive starting materials.<sup>[4]</sup> Recently, great progress has been made by using palladium complexes with bulky, electron-rich phosphine ligands.<sup>[5-7]</sup> In addition, cyclopalladated compounds (palladacycles) also provide efficient catalytic systems for the Suzuki coupling.<sup>[8-10]</sup> Indolese and coworkers<sup>[11]</sup> and Bedford et al.<sup>[12]</sup> have demonstrated that isolated or in-situ formed secondary or tertiary phosphine (e.g.,  $HP(Bu^t)_2$ ,  $HPCy_2$  or  $PCy_3$ ,  $PBu_3^t$ ) adducts of dimeric phosphorus- or nitrogen-containing palladacycles exhibit excellent activity at very low catalyst loadings when aryl chlorides, both activated and unactivated, are used as substrates in the Suzuki reaction. We have also found that tricyclohexylphosphine (PCy<sub>3</sub>)-cyclopalladated ferrocenylimine complexes are efficient catalysts for the coupling of aryl chlorides.<sup>[13,14]</sup> However, the high price usually associated with bulky phosphines along with difficulties to remove their decomposition byproducts have encouraged researchers to explore alternatives for phosphines. In this regard, the N-heterocyclic carbene (NHC) palladacycle complex developed by Nolan and coworkers<sup>[15,16]</sup> has been found to be able to couple unactivated aryl chlorides with arylboronic acids at room temperature in short reaction times although the catalyst loadings are relatively high (2 mol%).

During the past decade we have systematically studied the cyclopalladation of Schiff base-type ferrocenylimines<sup>[17–19]</sup> and some of the obtained palladacycles have been successfully used in Suzuki coupling.<sup>[13,14,20–22]</sup> To further explore the applications of cyclopalladated ferrocenylimines in



palladium-catalyzed coupling reactions, we prepared three new pyridine–cyclopalladated ferrocenylimine complexes 2a–c (Scheme 1) and examined their activity in the Suzuki reaction. Interestingly, complex 2a is found to adopt a *cis* configuration of the coordinated pyridine (py) to the imino nitrogen in the solid state. To our knowledge, there has been no report concerning the *cis* structure of monomeric imine and aminebased palladacycles.<sup>[12–14,17,19,21,23–26]</sup> The crystal structures of these phosphine-free palladacycles and their catalysis in Suzuki reactions are presented below.

#### **Results and Discussion**

Synthesis and Characterization of Complexes 2a-c

The chloride-bridged palladacyclic dimers  $1\mathbf{a}-\mathbf{c}$  were prepared according to published procedures.<sup>[17,21]</sup> Each of them was treated with 1.1 equivalents of pyridine per palladium in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 30 min to afford the corresponding adducts  $2\mathbf{a}-\mathbf{c}$  as red solids in 78–89% yield. All the new complexes are air- and moisture-stable both in the solid state and in solution. They are very soluble in chloroform, dichloromethane, and acetone, but insoluble in petroleum spirits and *n*-hexane.

Complexes 2a-c were characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS) analysis. The IR spectra of the free ferrocenylimines show an intense sharp band in the range 1620-1640 cm<sup>-1</sup>. For complexes 2a-c, this band shifts to lower energy  $(1547-1586 \text{ cm}^{-1})$ , which indicates that the imino nitrogen atom is coordinated to palladium through its lone pair.<sup>[13,17]</sup> The <sup>1</sup>H NMR spectrum of complex 2c is consistent with the proposed structure and indicates the presence of only one isomer in solution. The trans geometry of this isomer is confirmed by X-ray crystallographic analysis (see below). In contrast, the <sup>1</sup>H NMR spectra of 2a-b clearly show that they are a mixture of *cis* and trans isomers in solution. Comparison with the <sup>1</sup>H NMR spectroscopic data for complex 2c suggests that the major signals are attributable to the trans isomer. For example, the doublet at  $\delta$  9.03 and two triplets at  $\delta$  7.84 and 7.42 are assigned to the signals of pyridine protons in 2c. The corresponding signals of the major isomer in **2a** and **2b** appear at  $\delta$  9.03, 7.82, 7.39 and  $\delta$  9.02, 7.83, 7.41, respectively.

# Crystal Structures

The crystal structures of complexes 2a-c were determined to confirm the details. All the crystals were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirits at room temperature. The molecules are shown in Figs 1–3 (displacement ellipsoids are drawn at the 30% probability level). Selected bond lengths and angles are listed in Table 1.

As can be seen, the molecules of  $2b \cdot CH_2Cl_2$  and 2c adopt a *trans* configuration of the coordinated pyridine to the imino nitrogen. To the best of our knowledge, the crystal structures of all monomeric imine and amine-based palladacycles indicate that, in the solid state, the *trans* isomer crystallizes preferentially. Surprisingly, the single-crystal X-ray analysis of complex **2a** reveals a *cis* configuration in the solid state.

The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the nitrogen atom of the py, the chlorine atom, and the C6 and nitrogen atoms of the ferrocenylimine. The deviations of the Pd atoms from the planes are 0.0298, 0.0161, and 0.0224 Å for complexes 2a-c,

respectively. The bicyclic system formed by the palladacycle and the C<sub>5</sub>H<sub>3</sub> moiety is approximately coplanar (dihedral angles of 2.9°, 2.5°, and 2.2° for complexes **2a–c**, respectively). In each structure, the two Cp rings are almost parallel with dihedral angles of 5.8°, 4.0°, and 1.4°, respectively, for **2a–c**. In all cases the C(6)–Pd(1)–N(1) bond angle is around 80°, which is essentially identical to those in the corresponding PPh<sub>3</sub> or PCy<sub>3</sub>–cyclopalladated ferrocenylimines.<sup>[13,14,21,27]</sup> The Pd(1)–C(6) [1.971(4)Å], Pd(1)–N(1) [2.065(3)Å], and Pd(1)–N(2) [2.050(3)Å] bond lengths of *trans* complex **2c** are similar to those of related *trans* palladacycles with pyridine [1.890(5)–2.004(5)Å, 1.981(4)–2.082(2)Å, and 2.030(5)– 2.043(2)Å].<sup>[25,26]</sup> The Pd(1)–C(6) [2.205(5)Å], Pd(1)–N(1) [2.329(4)Å], and Pd(1)–N(2) [2.436(4)Å] bond lengths of *cis* complex **2a** are obviously longer than the above corresponding



**Fig. 2.** Molecular structure of complex **2b**·CH<sub>2</sub>Cl<sub>2</sub>. CH<sub>2</sub>Cl<sub>2</sub> and hydrogen atoms are omitted for clarity.



Fig. 1. Molecular structure of complex 2a. Hydrogen atoms are omitted for clarity.

values, which is attributed to the steric demand of the *cis* structure. The *trans* effect of the metalated carbanion may also be responsible for the longer Pd(1)–N(2) bond length of **2a**. For *trans* **2b**·CH<sub>2</sub>Cl<sub>2</sub>, the bond lengths around Pd are unexpectedly

Fig. 3. Molecular structure of complex 2c. Hydrogen atoms are omitted for clarity.

N2

Table 1. Selected bond lengths (Å) and angles [deg.] for 2a-c

Bonds and angles	2a	$2b\cdot \mathrm{CH}_2\mathrm{Cl}_2$	2c
Pd(1)-C(6)	2.205(5)	2.211(7)	1.971(4)
Pd(1)–N(1)	2.329(4)	2.321(6)	2.065(3)
Pd(1)-N(2)	2.436(4)	2.272(6)	2.050(3)
Pd(1)-Cl(1)	2.5929(16)	2.706(2)	2.4022(12)
N(1)-C(11)	1.465(6)	1.460(9)	1.285(5)
C(6) - Pd(1) - N(1)	80.31(18)	80.9(2)	81.43(15)
C(6)-Pd(1)-N(2)	176.72(18)	89.8(3)	93.84(16)
N(2)-Pd(1)-N(1)	96.56(15)	170.7(2)	174.75(12)
C(6) - Pd(1) - Cl(1)	92.44(15)	178.12(18)	176.97(13)
N(2)-Pd(1)-Cl(1)	90.73(12)	91.23(19)	89.16(10)
N(1)-Pd(1)-Cl(1)	172.35(11)	98.04(16)	95.59(9)

long. The Pd(1)–C(6) and Pd(1)–N(1) bond lengths of **2a** are also evidently longer than those of the corresponding *trans* PCy<sub>3</sub> and PPh<sub>3</sub>–cyclopalladated ferrocenylimines [2.019(6), 1.998(3), and 2.170(5), 2.136(3) Å],<sup>[14,27]</sup> while the Pd(1)–C(6) and Pd(1)–N(1) bond lengths of **2c** are slightly shorter than those of the corresponding PCy<sub>3</sub>–cyclopalladated ferrocenylimine [1.998(3) and 2.150(3) Å].<sup>[13]</sup>

Fig. 4 shows that the crystal structure of **2c** is different from those of complexes **2a**, **2b**·CH<sub>2</sub>Cl<sub>2</sub>, and the corresponding PCy<sub>3</sub>-cyclopalladated ferrocenylimine.<sup>[13]</sup> In complex **2c**, the chlorine atom not only forms a hydrogen bond with the adjacent C-H group of py (Cl1S ··· H21N = Cl1N ··· H21T = 2.816 Å), but also forms a hydrogen bond with the adjacent C-H group of the Cp ring (Cl1S ··· H4T = Cl1N ··· H4O = 2.902 Å), which are responsible for the construction of the one-dimensional network structure of **2c**.

### Suzuki Coupling Reaction

The coupling of 4-bromotoluene with phenylboronic acid was chosen as a model reaction to evaluate the effectiveness of the new cyclopalladated complexes 2a-c in a Suzuki reaction. The reaction was performed under a nitrogen atmosphere in anhydrous toluene in the presence of K<sub>2</sub>CO<sub>3</sub> as base at 100°C for 12 h. The palladacycles 2a and 2b had similar activity and produced the coupled products in 84 and 82% yields with a catalyst loading of 0.2 mol%. Palladacycle 2c was found to be the most active among the three catalysts: it gave the product in excellent isolated yield (93.4%) under the same reaction conditions (Table 2, entries 1–3).

In the following experiments, the Suzuki coupling reactions of a variety of electronically and structurally diverse aryl bromides with phenylboronic acid were investigated by using complex **2c** as catalyst under the same reaction conditions. Similar to the result of 4-bromotoluene, excellent yields (97–98%) were also obtained in the case of other electron-neutral aryl bromides such as bromobenzene and 1-bromonaphthalene (Table 2, entries 4, 5). For the very electron-rich 4-bromoanisole, the yield decreased slightly but was still very high (90%, entry 6). *ortho*-Substituents were tolerated and even the very sterically hindered 2-bromo-*m*-xylene provided the biaryl product in 75.8% isolated yield (entries 7–9). For electron-deficient aryl bromides such as 3-bromonitrobenzene and 4-bromobenzonitrile, the catalyst



Fig. 4. One-dimensional network structure of complex 2c formed by hydrogen bonds. Non-hydrogen bonding H atoms are omitted for clarity.

193

loadings could be lowered to 0.1 mol% without loss of activity (entries 10, 11). Coupling of heteroaryl bromides with phenylboronic acid with this catalyst system was also studied. 3-Bromopyridine was found to be an efficient coupling partner in this system that gave 92.9% isolated yield. The result was much better than that of 2-bromopyridine (entries 12, 13). Finally, with bromothiophenes moderate yields can be obtained under the same conditions (entries 14, 15).

# Conclusions

The three new phosphine-free palladacycles 2a-c were easily synthesized and structurally characterized. Single-crystal X-ray analysis confirmed the *cis* structure of palladacycle 2aas well as the *trans* structures of palladacycles 2b and 2c in the solid state. These complexes were found to be efficient

 Table 2.
 Suzuki coupling of aryl bromides with phenylboronic acid catalyzed by 2a-c

Entry	Aryl halide	Catalyst [mol%]	Product	Yield [%]
1	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Br	<b>2a</b> (0.2)	p-MePh–Ph	84.5
2	p-MeC <sub>6</sub> H <sub>4</sub> Br	<b>2b</b> (0.2)	p-MePh–Ph	82.1
3	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Br	<b>2c</b> (0.2)	<i>p</i> -MePh–Ph	93.4
4	PhBr	<b>2c</b> (0.2)	Ph–Ph	97.4
5	Br	<b>2c</b> (0.2)		98.0
6	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	<b>2c</b> (0.2)	p-MeOPh–Ph	90.3
7	Br	<b>2c</b> (0.2)	Me	89.9
8	o-MeC <sub>6</sub> H <sub>4</sub> Br	<b>2c</b> (0.2)	o-MePh–Ph	84.5
9	Me Br Me	<b>2c</b> (0.2)	2,6-Me <sub>2</sub> Ph–Ph	75.8
10	NO <sub>2</sub> Br	<b>2c</b> (0.1)	<i>m</i> -NO <sub>2</sub> Ph–Ph	98.5
11	p-NC-C <sub>6</sub> H <sub>4</sub> Br	<b>2c</b> (0.1)	p-NCPh-Ph	99.8
12	NBr	<b>2c</b> (0.2)	N Ph	61.9
13	Br	<b>2c</b> (0.2)	Ph	92.9
14	SBr	<b>2c</b> (0.2)	S Ph	68.3
15	S Br	<b>2c</b> (0.2)	√ Ph S Ph	62.1

catalysts for the Suzuki reaction of a variety of aryl bromides with phenylboronic acid.

#### **Experimental**

### General

All other chemicals were used as purchased. Solvents were dried and freshly distilled before use. Suzuki reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were determined with a Thermo Flash EA 1112 elemental analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer as KBr pellets. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl<sub>3</sub> with TMS as an internal standard. Mass spectra were measured on a LC-MSD-Trap-XCT instrument.

# General Method for the Synthesis of Pyridine– Cyclopalladated Ferrocenylimines **2a-c**

A solution of chloride-bridged palladacyclic dimer 1a-c (0.1 mmol) and pyridine (0.22 mmol) in dichloromethane (10 mL) was stirred at room temperature for 30 min. The product was separated by passing through a short silica gel column with ethyl acetate as eluent. The first band was collected to afford complex 2a-c after evaporation of the solvent.

# $[PdCl{[(\eta^5-C_5H_5)]Fe[(\eta^5-C_5H_3)C(CH_3)=NC_6H_4-4-CH_3]}(py)]$ **2a**

Yield 86.5%. mp 214°C (dec.). Found: C 53.3, H 4.2, N 5.3. Calc. for C<sub>24</sub>H<sub>23</sub>ClFeN<sub>2</sub>Pd: C 53.7, H 4.3, N 5.2%. v<sub>max</sub> (KBr)/cm<sup>-1</sup> 3088 w, 2923 w, 1598 m, 1548 s, 1470 s, 1443 s, 1321 m, 1232 m, 1105 m, 1062 w, 1015 w, 815 m. The complex exists as a mixture of cis- and trans-isomers in CDCl<sub>3</sub> solution, trans/cis  $\approx$  1.5:1.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>, trans-isomer) 9.03 (2H, d, J 5.0, pyH), 7.82 (1H, t, J 7.2, pyH), 7.39 (2H, t, J 6.4, pyH), 7.18 (2H, d, J 7.6, C<sub>6</sub>H<sub>4</sub>), 6.98 (2H, m, C<sub>6</sub>H<sub>4</sub>), 4.50 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.33 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.31 (1H, s, C<sub>5</sub>H<sub>3</sub>), 3.92 (1H, s, C<sub>5</sub>H<sub>3</sub>), 2.35 (3H, s, CH<sub>3</sub>), 2.02 (3H, s, CH<sub>3</sub>). δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>, *cis*-isomer) 8.25 (2H, d, J 4.4, pyH), 7.49 (1H, t, J 7.2, pyH), 6.98 (2H, m, overlapped with C<sub>6</sub>H<sub>4</sub> of *trans*-isomer, pyH), 6.85 (2H, m, C<sub>6</sub>H<sub>4</sub>), 6.62 (2H, br s, C<sub>6</sub>H<sub>4</sub>), 5.12 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.47 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.45 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.40 (5H, s, C<sub>5</sub>H<sub>5</sub>), 2.20 (3H, s, CH<sub>3</sub>), 2.02 (3H, s, overlapped with CH<sub>3</sub> of trans-isomer, CH<sub>3</sub>). m/z (ESI<sup>+</sup>) 501.0 (M<sup>+</sup> – Cl).

# $[PdCl{[(\eta^5-C_5H_5)]Fe[(\eta^5-C_5H_3)C(CH_3)=NC_6H_4-4-Br]}(py)]$ **2b**

Yield 89.3%. mp 239°C (dec.). Found: C 41.7, H 3.4, N 4.1. Calc. for C<sub>24</sub>H<sub>22</sub>BrCl<sub>3</sub>FeN<sub>2</sub>Pd: C 42.0, H 3.2, N 4.1%.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3058 w, 2371 w, 1601 w, 1547 s, 1469 s, 1443 m, 1230 m, 1102 w, 1065 m, 1004 m, 813 m. The complex exists as a mixture of *cis*- and *trans*-isomers in CDCl<sub>3</sub> solution, *trans/cis*  $\approx$  2.7:1.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>, *trans*-isomer) 9.02 (2H, d, *J* 5.1, pyH), 7.83 (1H, t, *J* 7.6, pyH), 7.50 (2H, d, *J* 8.2, C<sub>6</sub>H<sub>4</sub>), 7.41 (2H, t, *J* 6.7, pyH), 6.97 (2H, m, C<sub>6</sub>H<sub>4</sub>), 4.53 (1H, d, *J* 2.1, C<sub>5</sub>H<sub>3</sub>), 4.35 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.33 (5H, s, C<sub>5</sub>H<sub>5</sub>), 3.97 (1H, d, *J* 1.8, C<sub>5</sub>H<sub>3</sub>), 2.03 (3H, s, CH<sub>3</sub>).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>, *cis*-isomer) 8.28 (2H, d, *J* 4.7, pyH), 7.55 (1H, m, pyH), 7.19 (2H, d, *J* 7.9, C<sub>6</sub>H<sub>4</sub>), 7.06 (2H, t, *J* 6.4, pyH), 6.64 (2H, br s, C<sub>6</sub>H<sub>4</sub>), 5.16 (1H, s, C<sub>5</sub>H<sub>3</sub>), 4.49 (2H, s, C<sub>5</sub>H<sub>3</sub>), 4.40 (5H, s, C<sub>5</sub>H<sub>5</sub>), 2.03 (3H, s, overlapped with CH<sub>3</sub> of *trans*-isomer, CH<sub>3</sub>). *m/z* (ESI<sup>+</sup>) 566.8 (M<sup>+</sup> – Cl).

Parameter	2a	$2b \cdot CH_2Cl_2$	2c
Empirical formula	C24H23ClFeN2Pd	C24H22BrCl3FeN2Pd	C <sub>22</sub> H <sub>25</sub> ClFeN <sub>2</sub> Pd
Formula weight	537.14	686.95	515.14
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	$\overline{P}$ 1	P21/c
Crystal size [mm <sup>3</sup> ]	$0.20 \times 0.18 \times 0.17$	$0.20\times0.18\times0.16$	$0.20\times0.18\times0.17$
<i>a</i> [Å]	19.956(4)	11.439(2)	13.381(3)
<i>b</i> [Å]	17.662(4)	13.171(3)	15.466(3)
<i>c</i> [Å]	17.497(4)	13.955(3)	10.272(2)
α [deg.]	90	80.48(3)	90
$\beta$ [deg.]	92.23(3)	66.43(3)	105.12(3)
$\gamma$ [deg.]	90	73.39(3)	90
V [Å <sup>3</sup> ]	6162(2)	1843.7(6)	2052.2(7)
$D_{\rm c} [{\rm g}{\rm cm}^{-3}]$	1.158	1.237	1.667
Z	8	2	4
GOF (on $F^2$ )	1.093	1.061	1.041
Data/restraints/parameters	5442/0/262	5411/0/289	3550/0/245
$R_1, wR_2 [I > 2\sigma(I)]^A$	0.0577, 0.1218	0.0699, 0.1637	0.0347, 0.0925

Table 3. Crystallographic data and structure refinement for complexes 2a-c

<sup>A</sup> $R_1 = \sum ||F_0| - F_c|| / \sum |F_0|; wR_2 = [\sum (F_0^2 - F_c^2)^2 / \sum w (F_0^2)^2]^{1/2}.$ 

# $[PdCl{[(\eta^5-C_5H_5)]Fe[(\eta^5C_5H_3)CH=NCy]}(py)]$ **2***c*

Yield 78.5%. mp 238°C (dec.). Found: C 51.1, H 4.8, N 5.5. Calc. for  $C_{22}H_{25}ClFeN_2Pd$ : C 51.3, H 4.9, N 5.4%.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2925 s, 2851 m, 2372 w, 1586 s, 1446 s, 1405 w, 1321 w, 1293 w, 1236 w, 1102 w, 1066 m, 819 m.  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 9.03 (2H, d, *J* 5.0, pyH), 7.92 (1H, s, CH=N), 7.84 (1H, t, *J* 7.6, pyH), 7.42 (2H, t, *J* 7.0, pyH), 4.44 (1H, d, *J* 2.2, C<sub>5</sub>H<sub>3</sub>), 4.25 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.21 (1H, t, *J* 2.2, C<sub>5</sub>H<sub>3</sub>), 4.06 (1H, m, N-CHC<sub>5</sub>H<sub>10</sub>), 3.84 (1H, d, *J* 2.0, C<sub>5</sub>H<sub>3</sub>), 2.42 (1H, m, NCy), 2.10 (1H, m, NCy), 1.83 (2H, m, NCy), 1.72 (1H, m, NCy), 1.15–1.56 (5H, m, NCy). *m/z* (ESI<sup>+</sup>) 479.0 (M<sup>+</sup> – Cl).

# Suzuki Reactions

A prescribed amount of catalyst, aryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol),  $K_2CO_3$  (0.75 mmol), and toluene (2.0 mL) were placed in a Schlenk tube under nitrogen. The reaction mixture was then heated at 100°C for 12 h (time not optimized), and then allowed to cool. The reaction mixture was extracted three times with dichloromethane, and then the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and evaporated to dryness. The products were isolated by flash chromatography on silica gel. All the coupled products are known compounds and were characterized by <sup>1</sup>H NMR spectroscopy.

# Single-Crystal X-Ray Structure Determination

Intensity data of complexes **2a–c** were measured on a Rigaku– Raxis-IV X-ray diffractometer using graphite-monochromatized  $Mo_{K\alpha}$  radiation ( $\lambda$  0.71073 Å) at 291(2) K. All data were collected using the  $\omega$ –2 $\theta$  scan technique and corrected for Lorenz polarization effects. The three structures were solved by direct methods and expanded using Fourier techniques. All nonhydrogen atoms were described anisotropically; hydrogen atoms were included but not refined. The full-matrix least-squares calculations on  $F^2$  were applied on the final refinement. Their raw data were corrected and the structures were solved using the *SHELXL-97* program.<sup>[28]</sup> Compounds for **2a–c** have CCDC reference numbers 621235, 621238, and 621236, respectively. Details of the crystal structure determination of 2a-c are summarized in Table 3.

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