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The catalytic activity of Palladium(II) complexes containing PN ligands in the Heck and Suzuki C-C coupling reactions

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Abstract: A range of iminophosphine (PN) ligands ($(C_6H_5)_2P$-C_6H_4-CH=NR (R=-$C_6H_3(2\text{-}CH_3)(4\text{-}OH)$ (**1a**), -$CH_2CH_2C_6H_4(4\text{-}OH)$ (**1b**) and -$C_5H_3N(2\text{-}CH_3)$ (**1c**)) have been synthesized starting from 4-amino-3-methylphenol, 4-(2-aminoethyl)phenol and 2-amino-3-methylpyridine with 2-(diphenylphosphino)benzaldehyde. The PN ligands were reacted with $Pd(cod)Cl_2$ to give corresponding new $Pd(PN)Cl_2$ metal complexes, (**2a**, **2b** and **2c**). The Heck and Suzuki C-C coupling reactions were examined with catalysts **2a**-**2c** and showed high conversions under the determined conditions with para substituted aryl halides.

Keywords*:* iminophosphine, palladium complexes, Heck coupling, Suzuki coupling

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INTRODUCTION

The palladium-catalyzed cross-coupling reactions of aryl halides with arylboronic acids (Suzuki reaction) and with olefins (Heck reaction) provides a powerful methodology for constructing $C(sp^2)$-$C(sp^2)$ bonds (1). The reason for the intense research is the fact that C-C coupling reactions have been relatively used in several fields such as pharmacological agents, herbicides, and the synthesis of natural products, *etc*. Consequently, researchers have been working to find better catalysts and achieve better yields in these areas which are important for both industrial and scientific purposes (2,3).

Cyclopalladated catalysts display superior catalytic activities in cross-coupling reactions. Phospha-palladacycles were found to be highly efficient catalysts for Heck and Suzuki coupling reactions (4). Although phosphine ligands and their palladium complexes are widely used to catalyze the cross-coupling reactions for a variety of substrates, there have not been enough publications about the application of the iminophosphines and their palladium complexes in C-C coupling reactions. Besides that, the use of iminophosphine ligands, containing both soft phosphorus and hard nitrogen atoms, are generally increases the catalytic activity compared to the homo donor PP and NN ligands. The reason for this is that phosphorus atom can stabilize Pd center in a low oxidation state due to the π-acceptor character, while σ-donor ability of the nitrogen atom makes the Pd center more sensitive to the oxidative addition during the catalytic cycle. So PN ligands and their palladium(II) complexes have been identified as efficient catalysts for Heck (5,6) and Suzuki (7,8) reactions.

In this study, we have prepared new palladium(II) complexes (**2a-c**) to be used in the Heck and Suzuki cross-coupling reactions. The results demonstrate that PN type phosphine palladium(II) complexes are easily synthesized, and are also highly efficient complexes for the C-C cross-coupling reactions.

MATERIALS AND METHODS

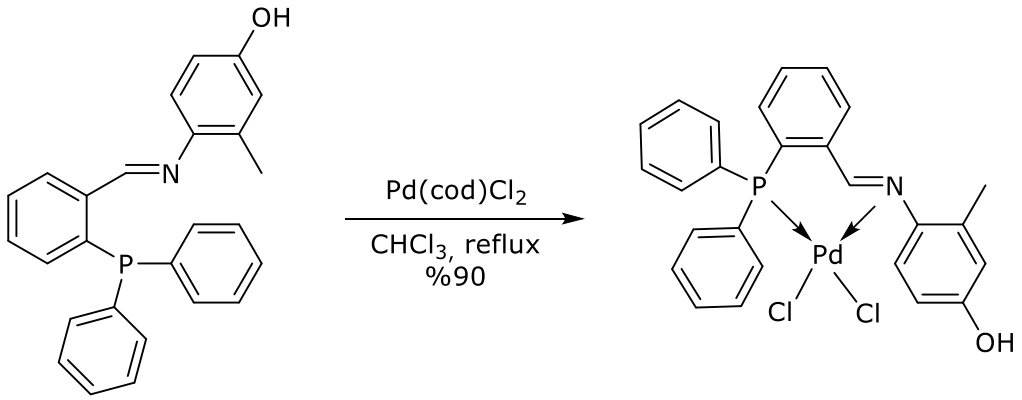
All reactions were carried out under nitrogen or argon atmosphere using conventional Schlenk glassware. All solvents were dried using established procedures and then immediately distilled under nitrogen atmosphere prior to use. 4-amino-3-methylphenol, 4-(2-aminoethyl)phenol, and 2-amino-3-methylpyridine obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) were used without further purification. The $[Pd(cod)Cl_2]$ (9) and 2-(diphenylphosphino)benzaldehyde (10) were prepared as described in the literature.

Microanalysis was performed using a LECO CHNS 932 instrument. The ^{1}H NMR (400.1 MHz) and $^{31}P\{^{1}H\}$ NMR (162.0 MHz) spectra were recorded at 25 °C with DMSO-d_6 and $CDCl_3$ on a Bruker NMR spectrometer; ^{13}C NMR were recorded on a Varian Mercury 100.6 MHz NMR spectrometer. $^{31}P\{^{1}H\}$ NMR spectra were recorded with complete proton decoupling and reported in ppm using 85% H_3PO_4 as external standard. The coupling products were analyzed by a Perkin Elmer Clarus 500 series gas chromatograph equipped with a flame ionization detector and Elite-1 capillary column with 30 m×0.25 mm×0.25 µm film thickness. Thin-layer chromatography (TLC) was used for monitoring the reactions.

Preparation of Pd(II) complexes

The **1a-c** were prepared as described in the literature (11).

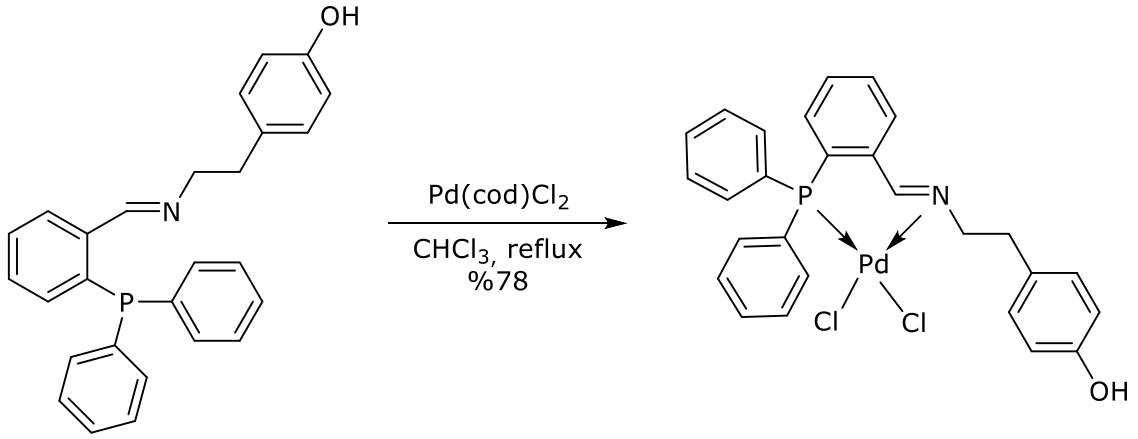
Preparation of [$PdCl_2$(Ph_2P-C_6H_4-CH=N-C_6H_3(2-CH_3)(4-OH))] (2a)



Scheme 1: Synthesis of complex **2a.**

To a solution of $Pd(cod)Cl_2$ (145 mg, 0.51 mmol) in $CHCl_3$ (10 mL) was added **1a** (200 mg, 0.51 mmol). The mixture was stirred for 6 h. Then the addition of diethyl ether caused to form a yellow solid which was filtered off and dried to give the title compound **2a**. Yield 263 mg (90%), mp.: 255-256 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ (ppm) 9.47 (s, 1H), 8.59 (s, 1H), 8.20-8.12 (dd, *J*= 6.9, 4.2 Hz, 1H), 7.95 (t, *J=8.3 Hz*, 1H), 7.81 (t, *J=7.6 Hz* 1H), 7.73-7.69 (m, 2H), 7.65-7.59 (m, 4H), 7.54-7.48 (m, 4H), 7.02 (dd, *J*=10.3, 7.8 Hz, 1H), 6.78-6.74 (m, 1H), 6.58-6.52 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ (ppm) 168.12 (d, J_{PC}=8.9 Hz, 1C, CH=N), 156.06 (s, 1C), 143.93 (s, 1C), 137.77 (d, J_{PC}=8.6 Hz, 1C), 136.55 (d, J_{PC}=15.7 Hz, 2C), 134.87 (d, J_{PC}=7.4 Hz, 1C), 133.95 (s, 1C), 133.53 (d, J_{PC}=11.0 Hz, 4C), 132.28 (d, J_{PC}=2.7 Hz, 1C), 131.27 (s, 1C), 129.16 (d, J_{PC}=11.8 Hz, 4C), 126.44 (s, 1C), 125.84 (s, 1C), 124.53 (s, 2C), 119.88 (s, 1C), 116.62 (s, 1C), 112.19 (s, 1C), 18.66 (s, 1C). ^{31}P NMR (162.0 MHz, DMSO-d_6): δ (ppm) 28.78 (s). Anal. calcd. for $C_{26}H_{22}Cl_2NOPPd$: C, 54.52; H, 3.87; N, 2.45 %. Found: C, 53.73; H, 4.37; N, 2.09 %. **2b** and **2c** were prepared as described in procedure **2a.**

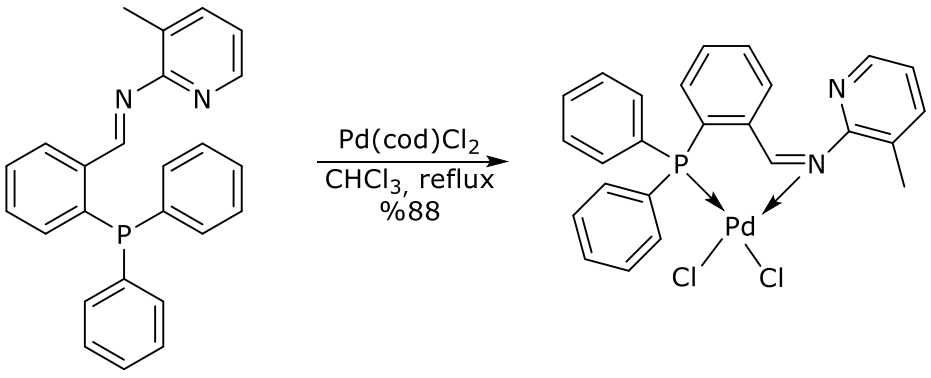
2.2.4. Preparation of [$PdCl_2(Ph_2P\text{-}C_6H_4\text{-}CH{=}N\text{-}(CH_2)_2\text{-}C_6H_4\text{-}(4\text{-}OH))$] (2b)



Scheme 2: Synthesis of complex **2b.**

Yield 233 mg (78%), mp.: 203-204 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ (ppm) 9.23 (s, OH, 1H), 8.53 (s, CH=N, 1H), 7.96-7.90 (m, 2H), 7.78 (t, *J*=7.5 Hz 1H), 7.71 (td, *J*=6.4, 1.0 Hz, 2H), 7.61 (td, *J*=7.6, 2.7 Hz, 4H), 7.47 (dd, *J*=12.9, 7.3 Hz, 4H), 7.01 (dd, *J*=10.0, 8.0 Hz, 1H), 6.80 (d, *J*=8.4 Hz, 2H), 6.59 (d, *J*=8.4 Hz, 2H), 4.46 (t, *J*=15.5 Hz, NCH_2, 2H), 2.69 (t, *J*=15.6 Hz, CH_2Ph, 2H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ (ppm) 165.70 (d, J_{PC}=8.9 Hz, 1C, CH=N), 155.86 (s, 1C), 136.72 (d, J_{PC}=16.1 Hz, 1C), 136.50 (d, J_{PC}=8.6 Hz, 4C), 134.30 (d, J_{PC}=7.9 Hz, 1C), 133.72 (d, J_{PC}=11.1 Hz, 2C), 133.34 (d, J_{PC}=2.2 Hz, 1C), 132.33 (d, J_{PC}=2.7 Hz, 1C), 129.46 (s, 1C), 129.08 (d, J_{PC}=11.9 Hz, 4C), 127.55 (s, 1C), 125.99 (s, 1C), 125.39 (s,1C), 119.72 (d, J_{PC}=9.6 Hz, 4C), 115.19 (s, 1C), 66.82 (s, 1C), 35.93 (s, 1C). ^{31}P NMR (162.0 MHz, DMSO-d_6): δ (ppm) 30.93 (s). Anal. calcd. for $C_{27}H_{24}Cl_2NOPPd$: C, 55.27; H, 4.12; N, 2.39 %. Found: C, 54.67; H, 4.67; N, 2.17 %.

2.2.4. Preparation of [$PdCl_2(Ph_2P\text{-}C_6H_4\text{-}CH{=}N\text{-}C_6H_3N\text{-}(2\text{-}CH_3))$] (2c)



Scheme 3: Synthesis of complex **2c.**

Yield 250 mg (88%), mp.: 165 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ(ppm) 8.82 (s, 1H, HC=N), 8.31-8.24 (m, *2*H), 7.98 (t, *J*=7.6 Hz, 1H), 7.87 (t, *J*=7.6 Hz, 1H), 7.72-7.66 (m, 3H), 7.66-

7.59 (m, 6H), 7.56 (d, *J*=7.2 Hz, 2H), 7.29 (dd, *J*=7.6, 4.8 Hz, 1H), 7.17 (dd, *J*=10.1, 7.9 Hz, 1H), 2.25 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, DMSO-*d*$_6$): δ (ppm) 168.93 (d, J_{PC}=8.5 Hz, C̲H=N), 161.53 (s, 1C), 145.06 (s, 1C), 139.31 (s, 1C), 138.83 (d, J_{PC}=8.4 Hz, 2C), 135.81 (d, J_{PC}=15.7 Hz, 1C), 135.52 (d, J_{PC}=7.5 Hz, 2C), 134.43 (s, 1C), 133.67 (d, J_{PC}=11.0 Hz, 2C), 132.20 (d, J_{PC}=2.6 Hz, 1C), 129.06 (d, J_{PC}=11.9 Hz, 4C), 128.40 (s, 1C), 126.79 (s, 1C), 126.26 (d, J_{PC}=14.1 Hz, 4C), 123.22 (s, 1C), 18.10 (s, 1C, C̲H$_3$). ^{31}P NMR (162.0 MHz, DMSO-*d*$_6$): δ (ppm) 28.03 (s). FT-IR, (KBr, cm^{-1}) υ: 3063 (CH_{Ar}), 2982 (CH_3), 1614 (C=N), 1432 (P-Ph). Anal. calcd. for $C_{25}H_{21}Cl_2N_2PPd$: C, 53.84; H, 3.80; N, 5.02 %. Found: C, 54.69; H, 3.34; N, 4.00 %.

General procedure for the Heck coupling reaction

A Schlenk tube was charged with the base (1.20 mmol) and the organic solvent (2.0 mL) under nitrogen atmosphere followed by aryl halide (1.00 mmol), olefin (1.20 mmol), and Pd(II) catalyst (1.00 % mol). The flask was sealed under N_2 atmosphere and placed in an oil bath and then the reaction mixture was stirred at appropriate temperatures for required times. After completion of the reaction, the mixture was cooled and extracted with ethyl acetate (3x20 mL). The extracts were washed with brine and dried over $MgSO_4$ and then the solvent was evaporated.

General procedure for the Suzuki coupling reaction

A Schlenk tube was charged with the base (2.00 mmol) and the organic solvent/H_2O (3.0/3.0 mL) under nitrogen atmosphere followed by aryl halide (1.00 mmol), phenylboronic acid (1.50 mmol) and Pd(II) catalyst (1.00 % mol). The flask was sealed under N_2 atmosphere and placed in an oil bath and then the reaction mixture was stirred at appropriate temperatures for required times. The reaction mixture was cooled and poured into water (5 mL) and extracted with $CHCl_3$ (3x20 mL). The extracts were washed with brine and dried over $MgSO_4$ and the solvent was then evaporated.

RESULTS AND DISCUSSION

The ligands, **1a**-**c,** were previously synthesized by treating 2-(diphenylphosphino)benzaldehyde (*o*-$Ph_2PPhCHO$) with appropriate primary amines 4-amino-3-methylphenol, 4-(2-aminoethyl)phenol and 2-amino-3-methylpyridine, respectively. The Pd(II) complexes **(2a-2c)** of the iminophosphine ligands were prepared under argon atmosphere using Schlenk techniques as shown in Schemes 1-3.

Characterization of the iminophosphine ligands and their Pd(II) complexes

The synthesized compounds were characterized using FT-IR and ^{1}H, ^{13}C, and ^{31}P-NMR. Quantizations were carried out with elemental analysis.

The ν_{N-H} and $\nu_{C=O}$ bands in the free amine and aldehyde compounds have totally disappeared in Schiff base ligands after the condensation. The displacement of C=N stretching frequencies from 1610-1636 cm^{-1} (**1a**: 1620, **1b**: 1636, **1c**:1610 (11)) in the free Schiff base ligands to lower values of 1603-1613 cm^{-1} (**2a**: 1603, **2b**: 1613, **2c**: 1604 cm^{-1}) in the complexes indicating the coordination of imine nitrogen to the palladium center (12–16).

^{1}H NMR evaluation of the compounds

The ^{1}H NMR spectrum of complexes **2a-c** displayed singlets at δ 8.59, 8.53, and 8.82 ppm, respectively, which confirmed the coordination of the imine (-CH=N) nitrogen to the palladium center (free ligands; **1a**; 8.89 ppm, **1b**; 8.88 ppm, and **1c**; 9.57 ppm) (11,17–20). On the other hand, ^{1}H-NMR spectra of the compounds demonstrate that the -OH peaks for **2a** and **2b** were observed at 9.47 and 9.43 ppm, respectively. As in the complexes -OH peaks slightly shifted to downfield comparing to the iminophosphine ligands. The aliphatic -CH_3 peaks in the structure of **2a** (2.09 ppm) and **2c** (2.25 ppm) appeared as a singlet, and the -CH_2-CH_2 peaks were found as triplet in the structure of **2b** occurring at 2.69 (N-CH_2) and 4.46 ppm (CH_2Ph) (21,22).

^{13}C NMR evaluation of the compounds

According to the ^{13}C-NMR spectra of the ligands, the peaks of the imine (-<u>C</u>H=N) carbon appeared in the region between 161.1 and 155.3 ppm indicating that the iminophosphine ligands were formed from the reaction of 2-(diphenylphosphino)benzaldehyde and amines (23). Furthermore, the -C-OH peaks for **1a**, **1b**, **2a** and **2b** appeared at 156.50, 156.06, 156.52 and 155.86 ppm, respectively. The -CH_3 peaks in the structure of **1a** and **2a** appear at 17.54 and 18.66 ppm as for the -CH_2-CH_2- peaks in the structure of **2b** occur at 66.82 (N-CH_2) and 35.93 (CH_2Ph) ppm. The ^{13}C NMR peaks of the phenyl carbons appeared at 143.93-112.19 **(2a)**, 136.72-115.19 **(2b)** and 145.06-123,22 ppm **(2c)** (24).

^{31}P NMR Evaluation of the Compounds

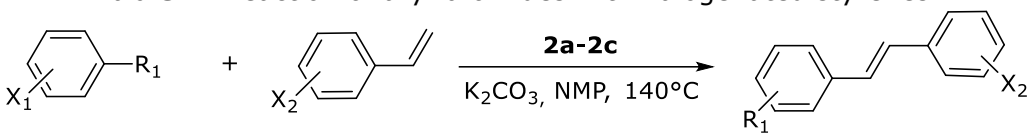
^{31}P-NMR peaks appeared at -13.54 (**1a**), -13.97 (**1b**), -13.76 (**1c**), 28.78 (**2a**), 30.93 (**2b**) and 28.03 (**2c**), respectively. The ^{31}P NMR signals of the complexes which appeared downfield shift shows that the ligands are coordinated to the palladium center via phosphorus atom (25). Based on NMR and FT-IR analysis of the ligands and palladium complexes, the ligands are coordinated to the palladium atom through the imine nitrogen and the phosphorus atom (26,27).

Elemental analysis for C, H and N of ligands **1a**-**1c** and Pd(II) complexes **2a**-**2c** have indicated that the metal-ligand ratio of complexes was 1:1.

Heck Reaction

First of all, the optimal conditions for the catalytic application of Pd(II) complexes in Heck reaction were identified. Different bases (NEt_3, Na_2CO_3, NaOAc and K_2CO_3), different temperatures (80, 100, 120 and 140 °C) and different solvents (toluene, 1,4-dioxane, DMF, and NMP) were tested to determine the optimum conditions. The progress of the reaction was monitored by GC analysis. Among the preliminary studies, K_2CO_3 was found to be best base and the N-methylpyrolidone (NMP) was found to be most suitable solvent at 140 °C. After optimization of the reaction conditions, the reactions of electronically activated and deactivated aryl bromides and aryl chlorides with substituted styrenes were also examined and moderate to good yields were obtained using catalysts **2a-c**. The results are given in Table 1. All of the reactions are performed with 1.0 mol% of catalysts in NMP as solvent at 140 ˚C with K_2CO_3 acting as base.

Table 1: Reaction of aryl bromides with halogenated styrenes.

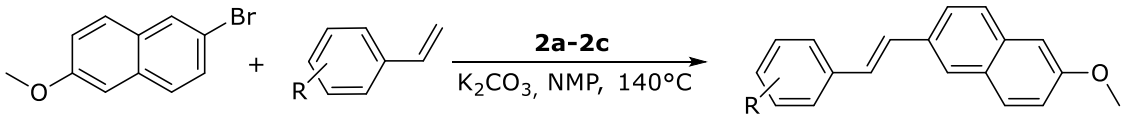


				Conv. (%)[a]		
Entry	**X_1**	**R_1**	**X_2**	**2a**	**2b**	**2c**
1	*o*-Br	$CO(CH_3)$	*o*-Cl	93	42	98
2	*m*-Br	$CO(CH_3)$	"	96	97	89
3	*p*-Br	$CO(CH_3)$	"	98	92	94
4	*p*-Br	COH	"	88	45	71
5	Br	H	"	50	85	17
6	*o*-Br	$CO(CH_3)$	*m*-Cl	62	72	14
7	*m*-Br	$CO(CH_3)$	"	96	99	76
8	*p*-Br	$CO(CH_3)$	"	98	91	88
9	*p*-Br	COH	"	93	98	98
10	Br	H	"	58	63	48
11	*o*-Br	$CO(CH_3)$	*p*-Cl	76	79	87
12	*m*-Br	$CO(CH_3)$	"	96	98	99
13	*p*-Br	$CO(CH_3)$	"	94	98	99
14	*p*-Br	COH	"	85	85	94
15	Br	H	"	87	49	75
16	*o*-Br	$CO(CH_3)$	*o*-Br	72	17	91
17	*m*-Br	$CO(CH_3)$	"	64	46	88
18	*p*-Br	$CO(CH_3)$	"	93	36	95
19	*p*-Br	COH	"	85	10	91
20	Br	H	"	10	6	7
21	*o*-Br	$CO(CH_3)$	*m*-Br	76	50	59
22	*m*-Br	$CO(CH_3)$	"	90	97	99
23	*p*-Br	$CO(CH_3)$	"	97	98	47
24	*p*-Br	COH	"	60	97	96
25	Br	H	"	12	5	4
26	*o*-Br	$CO(CH_3)$	*p*-Br	72	64	18
27	*m*-Br	$CO(CH_3)$	"	83	97	98
28	*p*-Br	$CO(CH_3)$	"	88	78	99
29	*p*-Br	COH	"	86	90	93
30	Br	H	"	5	1	21

[a]Reaction conditions: aryl bromide (1.00 mmol), styrene (1.20 mmol), K_2CO_3 (1.20 mmol) and 0.01 mmol catalyst in NMP (2.0 mL), 140 °C, 6h.
[b]Conversions were determined by GC based on aryl halide.

The results from the Table 1 indicate that the highest conversion (99%) (Table 1, entries 12, 13, 22, and 28) was achieved with the catalyst **2c** for the reaction between *m*- and *p*-bromo acetophenone, and *m*- and *p*-bromo styrene and *m*-chloro styrene. The reason why the yield in ortho position is lower than that in *m*- or *p*- position is that the substrate is unable to approach to the active center of Pd(0). The lowest conversion (5%) (Table 1, entry 30) was observed in the reaction of bromobenzene with *p*-bromostyrene. When $C(O)CH_3$ or C(O)H substituted aryl bromides were used, the yields were generally high. $C(O)CH_3$ or C(O)H groups activate the phenyl ring and it results in a higher yield. In general, the conversions were high in the test reactions conducted with aryl halides including electron-withdrawing groups as the substitutes. The conversion rates came out lower in the coupling reactions of bromobenzene. In addition, some low conversions are determined due to the occurrence of palladium black and its influence on the reaction rate (Table 1, entry 25, 30, 50, and 60) (28,29).

Table 2: Palladium-catalyzed coupling reactions of 2-bromo-6-methoxy naphthalene with styrenes[a].



		Conv.		
Entry	**R**	**2a**	**2b**	**2c**
1	*o*-Cl	38	60	55
2	*m*-Cl	70	56	63
3	*p*-Cl	92	79	79
4	*o*-Br	27	16	19
5	*m*-Br	32	23	15
6	*p*-Br	17	28	16
7	*o*-CH_3	57	61	45
8	*m*-CH_3	72	84	84
9	*p*-CH_3	95	77	n.r.
10	*o*-OCH_3	99	37	93

[a]Reaction conditions: 2-bromo-6-methoxy naphthalene (1.00 mmol), olefin (1.20 mmol), K_2CO_3 (1.2 mmol) and 0.01 mmol catalyst in NMP (2 mL), 140 °C, 6h.
[b]Conversions were determined by GC based on aryl halide.

Finally, Heck reaction was carried out with 2-bromo-6-methoxynaphthalene which is an important chemical in medicinal chemistry and used in the synthesis of naproxen (30). In the reaction between the substituted styrenes and 2-bromo-6-methoxynaphthalene using the

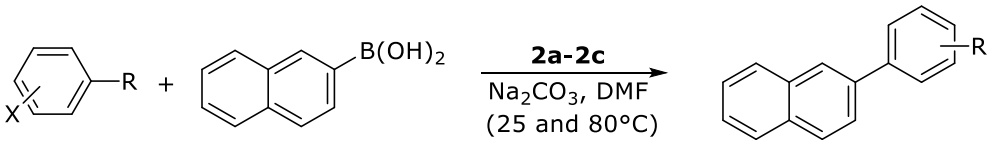
catalyst **2a** *o*-methoxy styrene gave the highest conversion (99%) (Table 2, entry 10) while *p*-bromo styrene gave the lowest conversion (17%) (Table 2, entry 6). The reaction yield was found high when active groups such as -methyl and -methoxy bound to the phenyl ring. It was determined to be low when halogens were used. This is because -methoxy or -methyl groups increase the interest of the substrates to Pd(0), and it causes an easier binding. When halogens on the phenyl ring are compared, the conversion found from the -chloro attached to phenyl ring was partially higher than that of the -bromo attached to phenyl ring (Table 2). The electron-withdrawing effect of -chloro group is higher than that of -bromo group, and it reduces the electron density of 2-bromo-6-methoxy naphthalene. This increases the interest of 2-bromo-6-methoxy naphthalene to Pd(0).

Suzuki Reaction

The same way as in the Heck C-C coupling reaction, firstly, the optimal conditions for defining the catalytic efficiency of Pd(II) complexes were determined for the Suzuki reaction. In order to determine the optimal conditions, organic and inorganic bases (NEt_3, Na_2CO_3, NaOAc, and K_2CO_3), different temperatures (80, 100, 120, and 140 °C) and solvents (toluene, 1,4-dioxane, DMF and NMP) were tested in the reaction of bromo benzene and phenyl boronic acid. At the end of the reaction, samples were analyzed with GC. The results confirm that the conversion was low at 80 °C in NMP when compared to other solvents such as toluene, 1,4-dioxane, and DMF.

After determining optimal conditions, the results showed that the conversion rose up to as high as 99 percent at the temperature of 80 °C, in the presence of Na_2CO_3 in the DMF solvent. The catalytic experiments were conducted with different aryl halide and boronic acid derivatives at 80 and 25 °C (31). Comparing among -bromo acetophenones, p-bromo acetophenone is slightly higher than ortho- and *m*-bromo acetophenone (Table 3, entries 3, 8 and 13). The bromo-positioned at meta- and para- causes a steric hindrance, and it results in partially low conversion. Therefore, the substrate cannot be coordinated to the Pd center well.

Table 3: The results of the reactions between aryl bromide and 2-naphthalene boronic acid.



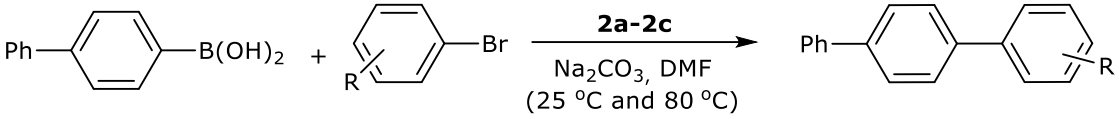
Entry	Catalyst	X	R	Conv. (%)[a]	
				25°C	80°C
1	**2a**	*o*-Br	$CO(CH_3)$	60	65
2	"	*m*-Br	$CO(CH_3)$	53	55
3	"	*p*-Br	$CO(CH_3)$	69	68
4	"	*p*-Br	C(O)H	77	79
5	"	Br	H	65	68
6	**2b**	*o*-Br	$CO(CH_3)$	2	9
7	"	*m*-Br	$CO(CH_3)$	10	63
8	"	*p*-Br	$CO(CH_3)$	98	98
9	"	*p*-Br	C(O)H	85	91
10	"	Br	H	46	49
11	**2c**	*o*-Br	$CO(CH_3)$	67	82
12	"	*m*-Br	$CO(CH_3)$	39	54
13	"	*p*-Br	$CO(CH_3)$	77	89
14	"	*p*-Br	C(O)H	80	93
15	"	Br	H	61	66

[a]Reaction conditions: aryl bromide (1.00 mmol), 2-naphthaleneboronic acid (1.20 mmol), K_2CO_3 (1.20 mmol) and 0.01 mmol catalyst in DMF/H_2O 2/2 mL), 6h.
[b]Conversions were determined by GC based on aryl halide.

According to the GC analyses, the Suzuki reaction of 4-biphenylboronic acid and aryl bromide using the catalyst **2b**, the highest conversions of 99 percent (Table 4, entries 8 and 9), were achieved in the reactions with *p*-bromoacetophenone and *p*-bromobenzaldehyde. The reason why the conversions from the aldehyde and ketone group in para position are higher than those for ortho and meta aldehyde and ketone group is that the steric hindrance is low in para position, and it easily coordinates to Pd(II) center (Table 3, entry 6).

For the reaction between biphenyl and aryl bromide, the highest conversion was obtained 74% at 25 °C and 92% at 80 °C. The lowest conversion at 25 and 80 °C was calculated to be 12% and 15%, respectively (Table 4, entry 1). As shown in Table 4 entry 9, catalyst **2b** gave excellent results for the synthesis of carbaldehyde derivative compounds in the room temperature.

Table 4. The Suzuki reaction between aryl bromides and 4-biphenylboronic acid.

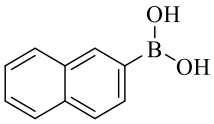
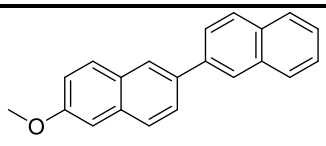
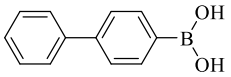
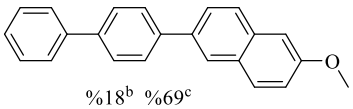
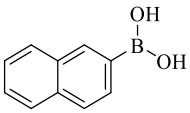
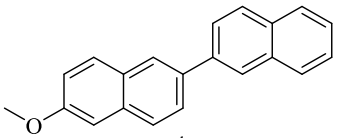
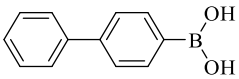
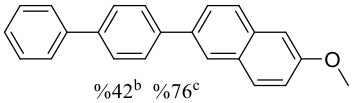
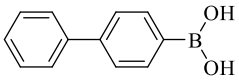
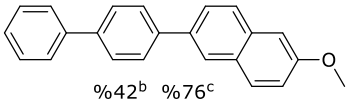
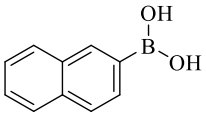
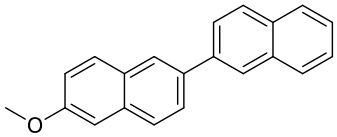


Entry	Catalyst	R	Conv. (%)[a]	
			25 °C	80 °C
1	**2a**	*o*-CO(CH_3)	12	15
2	"	*m*-CO(CH_3)	25	74
3	"	*p*-CO(CH_3)	47	67
4	"	*p*-C(O)H	74	92
5	"	H	60	87
6	**2b**	*o*-CO(CH_3)	4	20
7	"	*m*-CO(CH_3)	15	76
8	"	*p*-CO(CH_3)	91	99
9	"	*p*-C(O)H	**99**	**99**
10	"	H	67	87
11	**2c**	*o*-CO(CH_3)	-	12
12	"	*m*-CO(CH_3)	57	66
13	"	*p*-CO(CH_3)	65	79
14	"	*p*-C(O)H	98	98
15	"	H	51	65

[a]Reaction conditions: aryl halide (1.00 mmol), 4-biphenylboronic acid (1.20 mmol) K_2CO_3 (1.20 mmol) and 0.01 mmol cat., DMF/H_2O 2/2 mL), 6h.
[b]Conversions were determined by GC based on aryl halide.

When the catalytic efficiencies were analyzed with GC, the best conversion percentage in the reactions between 2-bromo-6-methoxy naphthalene, 2-naphthalene boronic acid and 4-biphenyl boronic acid was determined to be 91 percent when the catalyst **2b** was used and 69 percent with the catalyst **2a** (Table 5, entries 2-3). As seen in Table 5, the conversions were found to be low or average. Due to the steric effect of the substrates, the substrates are inability to approach to palladium active center, and it results in low conversions.

Table 5: The results of the reaction between 2-bromo-6-methoxy naphthalene and arylboronic acids.

Entry	Catalyst	$ArB(OH)_2$	Product and conv. (%)[a]
1	**2a**		 %30[b] %39[c]
2	″		 %18[b] %69[c]
3	**2b**		 %32[b] %91[c]
4	″		 %42[b] %76[c]
5	**2c**		 %42[b] %76[c]
6	″		 %36[b] %71[c]

Reaction conditions: 2-bromo-6-methoxy naphthalene (1 mmol), arylboronic acid (1.20 mmol), K_2CO_3 (1.20 mmol) and 0.01 mmol of catalyst, DMF/water, 2/2 mL, 6h.
[a]Conversions were determined by GC based on 2-bromo-6-methoxynaphthalene.
[b]25 °C.
[c]80 °C.

CONCLUSIONS

A new series of iminophosphine-Pd(II) complexes with PN ligands have been synthesized and characterized using spectroscopic techniques. The $^{31}P\{^{1}H\}$ NMR and FTIR results of the complexes indicate that the coordination of the iminophoshine ligand with Pd(II) occurs via phosphorus and nitrogen atoms. The complexes have been tested as catalysts for Heck and Suzuki reactions. The C-C coupling reactions put into practice with catalysts **2a**-**2c** show high conversions under the determined conditions with para- substituted aryl halides. Besides, the high conversion of some substrates at 25 °C shows that the catalysts are active.

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REFERENCES

1. Aydemir M, Baysal A, Gümgüm B. Synthesis and characterization of tris{2-(N,N-bis(diphenylphosphino) aminoethyl} amine derivatives: Application of a palladium(II) complex as a pre-catalyst in the Heck and Suzuki cross-coupling reactions. J Organomet Chem. 2008 Dec;693(26):3810–4.

2. Scrivanti A, Beghetto V, Matteoli U, Antonaroli S, Marini A, Crociani B. Catalytic activity of η2-(olefin)palladium(0) complexes with iminophosphine ligands in the Suzuki–Miyaura reaction. Role of the olefin in the catalyst stabilization. Tetrahedron. 2005 Oct;61(41):9752–8.

3. Nadri S, Joshaghani M, Rafiee E. Biphenyl-based phosphine: A well-defined, air-stable, and efficient ligand for the Mizoroki–Heck reaction. Appl Catal Gen. 2009 Jun;362(1–2):163–8.

4. Herrmann WA, Böhm VP., Reisinger C-P. Application of palladacycles in Heck type reactions. J Organomet Chem. 1999 Mar;576(1–2):23–41.

5. Iyer S, Kulkarni GM, Ramesh C. Mizoroki–Heck reaction, catalysis by nitrogen ligand Pd complexes and activation of aryl bromides. Tetrahedron. 2004 Feb;60(9):2163–72.

6. Reddy KR, Surekha K, Lee G-H, Peng S-M, Liu S-T. Palladium(II) Complexes with Phosphorus−Nitrogen Mixed Donors. Efficient Catalysts for the Heck Reaction. Organometallics. 2000 Jun;19(13):2637–9.

7. Doherty S, Knight JG, Scanlan TH, Elsegood MR, Clegg W. Iminophosphines: synthesis, formation of 2, 3-dihydro-1H-benzo [1, 3] azaphosphol-3-ium salts and N-(pyridin-2-yl)-2-diphenylphosphinoylaniline, coordination chemistry and applications in platinum group catalyzed Suzuki coupling reactions and hydrosilylations. J Organomet Chem. 2002;650(1):231–248.

8. Cheng J, Wang F, Xu J-H, Pan Y, Zhang Z. Palladium-catalyzed Suzuki–Miyaura reaction using aminophosphine as ligand. Tetrahedron Lett. 2003;44(37):7095–7098.

9. Drew D, Doyle JR, Shaver AG. Cyclic Diolefin Complexes of Platinum and Palladium. In: Cotton FA, editor. Inorganic Syntheses [Internet]. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2007 [cited 2017 Nov 24]. p. 47–55. Available from: http://doi.wiley.com/10.1002/9780470132449.ch11

10. Laue S, Greiner L, Wöltinger J, Liese A. Continuous application of chemzymes in a membrane reactor: Asymmetric transfer hydrogenation of acetophenone. Adv Synth Catal. 2001;343(6–7):711–720.

11. Keleş M, Şahinoğlu C, Emir DM, Mart M. New iminophosphine–Ru (II) complexes and their application in hydrogenation and transfer hydrogenation. Appl Organomet Chem. 2014;28(10):768–772.

12. Nobre SM, Monteiro AL. Pd complexes of iminophosphine ligands: A homogeneous molecular catalyst for Suzuki–Miyaura cross-coupling reactions under mild conditions. J Mol Catal Chem. 2009;313(1):65–73.

13. Jeffery JC, Rauchfuss TB, Tucker PA. Metal complexes of diiminodiphosphines. Structural and reactivity patterns. Inorg Chem. 1980 Nov;19(11):3306–15.

14. Rülke RE, Kaasjager VE, Wehman P, Elsevier CJ, van Leeuwen PWNM, Vrieze K, et al. Stable Palladium(0), Palladium(II), and Platinum(II) Complexes Containing a New, Multifunctional and Hemilabile Phosphino−Imino−Pyridyl Ligand: Synthesis, Characterization, and Reactivity. Organometallics. 1996 Jan;15(13):3022–31.

15. Crochet P, Gimeno J, Borge J, García-Granda S. Novel ruthenium(ii) complexes containing imino- or aminophosphine ligands for catalytic transfer hydrogenation. New J Chem. 2003 Jan 20;27(2):414–20.

16. Kwong H-L, Lee W-S, Lai T-S, Wong W-T. Ruthenium catalyzed asymmetric transfer hydrogenation based on chiral P,N,O Schiff base ligands and crystal structure of a ruthenium(II) complex bearing chiral P,N,O Schiff base ligands. Inorg Chem Commun. 1999 Feb;2(2):66–9.

17. Reddy KR, Surekha K, Lee G-H, Peng S-M, Chen J-T, Liu S-T. Study of Insertion of Olefins and/or Carbon Monoxide into Phosphine- Imine Palladium Methyl Complexes. Organometallics. 2001;20(7):1292–1299.

18. Wang C, Friedrich S, Younkin TR, Li RT, Grubbs RH, Bansleben DA, et al. Neutral Nickel(II)-Based Catalysts for Ethylene Polymerization. Organometallics. 1998 Jul;17(15):3149–51.

19. Lavery A, Nelson SM. Dinuclear intermediates in the oxidation of pendant olefinic groups of palladium (II)-co-ordinated Schiff-base ligands. J Chem Soc Dalton Trans. 1984;(4):615–620.

20. Alder MJ, Cross WI, Flower KR, Pritchard RG. Azo-phosphine containing complexes of Group 6 metal carbonyls: crystal and molecular structure of [Mo(CO)5{1-(4-ethylphenylazo)-6-diphenylphosphino-naphthalen-2-ol}]. J Organomet Chem. 1998 Oct;568(1–2):279–85.

21. Korostylev A, Bondarev O, Lyubimov S, Kovalevsky AY, Petrovskii P, Davankov V, et al. New palladium (II) complexes of (N, N-dimethylamino) alkoxy-1, 3, 2-oxazaphospholidine ligands. Inorganica Chim Acta. 2000;303(1):1–6.

22. Mahamo T, Mogorosi MM, Moss JR, Mapolie SF, Chris Slootweg J, Lammertsma K, et al. Neutral palladium(II) complexes with P,N Schiff-base ligands: Synthesis, characterization and application as Suzuki–Miyaura coupling catalysts. J Organomet Chem. 2012 Apr;703:34–42.

23. Radulović V, Bacchi A, Pelizzi G, Sladić D, Brčeski I, Andjelković K. Synthesis, Structure, and Antimicrobial Activity of Complexes of Pt(II), Pd(II), and Ni(II) with the Condensation Product of 2-(Diphenylphosphino)benzaldehyde and Semioxamazide. Monatshefte Für Chem - Chem Mon. 2006 Jun;137(6):681–91.

24. Mogorosi MM, Mahamo T, Moss JR, Mapolie SF, Slootweg JC, Lammertsma K, et al. Neutral palladium (II) complexes with P, N Schiff-base ligands: Synthesis, characterization and catalytic oligomerisation of ethylene. J Organomet Chem. 2011;696(23):3585–3592.

25. Keleş M, Yılmaz MK. Palladium(II) complexes with aminomethylphosphine ligands as catalysts for the heck reaction. Heteroat Chem. 2012;23(5):466–71.

26. Keles M, Aydin Z, Serindag O. Synthesis of palladium complexes with bis(diphenylphosphinomethyl)amino ligands: A catalyst for the Heck reaction of aryl halide with methyl acrylate. J Organomet Chem. 2007 Apr;692(10):1951–5.

27. Garrou PE. .DELTA.R-ring contributions to phosphorus-31 NMR parameters of transition-metal-phosphorus chelate complexes. Chem Rev. 1981 Jun;81(3):229–66.

28. Smith RC, Bodner CR, Earl MJ, Sears NC, Hill NE, Bishop LM, et al. Suzuki and Heck coupling reactions mediated by palladium complexes bearing trans-spanning diphosphines. J Organomet Chem. 2005 Jan;690(2):477–81.

29. Pramick MR, Rosemeier SM, Beranek MT, Nickse SB, Stone JJ, Stockland, RA, et al. Coupling of Aryl Halides with Aryl Boronic Acids with $P(C_6H_5)(2\text{-}C_6H_4Cl)_2$ as the Supporting Ligand. Organometallics. 2003 Feb;22(3):523–8.

30. Harrington PJ, Lodewijk E. Twenty Years of Naproxen Technology. Org Process Res Dev. 1997 Jan;1(1):72–6.

31. Sabounchei SJ, Panahimehr M, Ahmadi M, Nasri Z, Khavasi HR. Four-coordinate Pd(II) complexes containing non-symmetric phosphorus ylides: Synthesis, characterization, and catalytic behavior towards Suzuki reaction. J Organomet Chem. 2013 Jan;723:207–13.