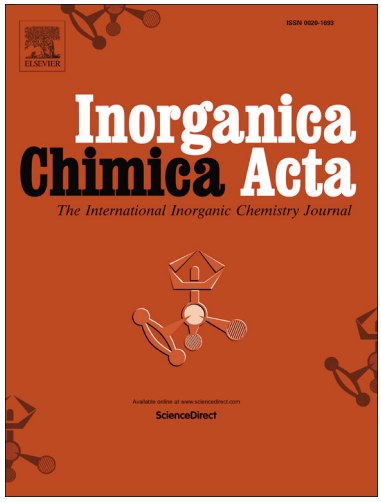

Research paper

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PII: S0020-1693(18)30620-0
DOI: https://doi.org/10.1016/j.ica.2018.06.013
Reference: ICA 18305

To appear in: *Inorganica Chimica Acta*

Received Date: 24 April 2018
Revised Date: 6 June 2018
Accepted Date: 7 June 2018

Please cite this article as: M. Kemal Yılmaz, S. İnce, S. Yılmaz, M. Keleş, Palladium(II) Catalyzed Suzuki C-C Coupling Reactions with Imino- and Amino-phosphine Ligands, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.06.013

Palladium(II) Catalyzed Suzuki C-C Coupling Reactions with Imino- and Amino-phosphine Ligands

Mustafa Kemal Yılmaz[a*], Simay İnce[b], Sevilay Yılmaz[c], Mustafa Keleş[b]

[a]Mersin University, Faculty of Arts and Sciences, Department of Chemistry, 33343 Mersin, Turkey

[b]Osmaniye Korkut Ata University, Faculty of Arts and Sciences, Department of Chemistry, 80000 Osmaniye, Turkey

[c]Çukurova University, Faculty of Arts and Sciences, Department of Chemistry, 01330 Adana, Turkey

ABSTRACT:

A new series of bidentate PN type imino- (**1-3**) and amino-phosphine ligands (**4-6**) and their palladium(II) complexes [Pd(PN)Cl_2] (**1a-6a**) have been synthesized and fully characterized using spectroscopic and analytical methods, including ^{31}P, ^{1}H, ^{13}C NMR and FTIR spectroscopy and high resolution mass spectroscopy. The catalytic activities of the Pd(II) complexes were investigated for the Suzuki C-C coupling reactions of phenylboronic acid with aryl bromides using a substrate to catalyst ratio of 500/1. The effect of base, temperature and solvent has been investigated, and the highest reaction rates were observed at 80°C in dimethylformamide (DMF) with K_2CO_3 as the base in 12 h. Under optimized reaction conditions, generally higher coupled product was obtained with substituted aryl bromides,

*Corresponding author Tel.: +90 324 361 00 01; fax: 90 324 361 00 73
e-mail: mkyilmaz@mersin.edu.tr (MK. Yılmaz)

including both electron-withdrawing (-formyl and -aceto) or -donating groups (-methyl and -methoxy) at -ortho or -para positions, except 2-bromoacetophenone which has bulkier -aceto group compared to the other aryl bromides.

Keywords: Iminophosphine, aminophosphine, palladium, Suzuki coupling

1. Introduction

The palladium catalyzed Suzuki C-C coupling reaction of organoboron compounds with aryl halides is one of the most important reaction for the preparation of new C-C bonds in organic synthesis which has been applied to many areas, such as pharmacological agents, herbicides and the synthesis of natural products etc. [1-8]. Therefore, researchers have improved and designed new ligands and catalyst systems to apply this type of reaction. Phosphines and their palladium complexes play an important role as catalysts for the Suzuki C-C coupling reactions [9,10]. Sterically hindered and electron rich phosphines, such as trialkylphosphines, ferrocenyldialkylphosphines and dialkylarylphosphines have been successfully applied in the Suzuki C-C coupling reactions for a variety of substrates [11,12]. However, in order to obtain more selective and active catalysts, hemilabile ligands are designed and applied in the Suzuki C-C coupling reactions. Combining soft and hard donor groups, phosphorus-nitrogen based (such as pyridine, quinazoline, pyrazole, imidazoline, oxazoline, thiazoline, oxazine based cyclic ligands or acyclic imine-N-donor ligands) have been applied in C-C coupling reactions to facilitate substrate interaction with the palladium center and stabilize the intermediates during the catalytic cycles. In addition, the presence of sp^3 (R-NH) or sp^2 (=N-R) hybridized nitrogen donor in the ligand system significantly affects the catalytic performance [13-17]. Herein, we report Suzuki C-C coupling reactions catalyzed by Pd(II) complexes of the imino-phosphine (**1a-3a**) and amino-phosphine ligands (**4a-6a**). A full report on the effect of solvent, base and temperature for the Suzuki C-C coupling reactions of aryl halides with arylboronic

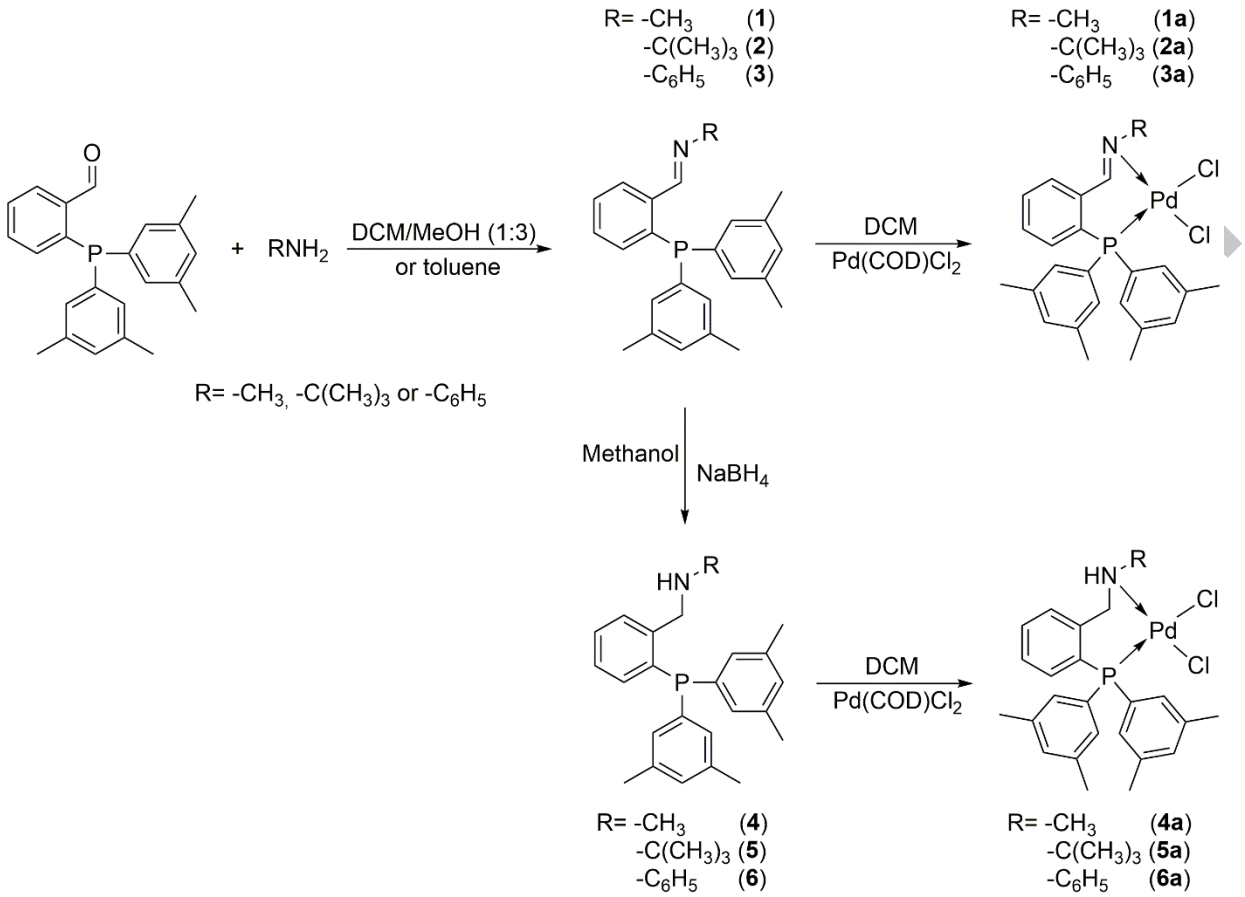
acid was also described. Under the optimized conditions, a variety of electron-donating or electron-withdrawing groups at ortho position on aryl bromide was well tolerated. The important advantages associated with our catalyst system are their stability towards air and moisture.

2. Experimental

2.1. General Comments

All of the reactions were performed under inert atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures [18] and then immediately distilled under argon atmosphere prior to being used. FTIR spectra of the ligands and complexes were recorded with a Perkin Elmer RX1 Spectrophotometer in the range between 4000-650 cm^{-1}. ^{1}H, ^{31}P, and ^{13}C NMR analysis were recorded in $CDCl_3$ at 400.2, 162.0, 100.6 and 376.5 MHz respectively, using Bruker Avance-400 NMR spectrometer at 25°C. The chemical shifts were given in ppm as δ downfield from $SiMe_4$ as an internal standard. Spin multiplicities were reported as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), triplet of doublet (td) with coupling constant (*J*) given in Hertz (Hz) or multiplet (m). Melting points were determined on a Mettler Toledo MP90 system and are uncorrected. Gas chromatography (GC-FID) analyses were performed on a Perkin Elmer Clarus 500 series gas chromatograph equipped with and a 30 m x 0.25 mm x 0.25 μm film thickness Rxi-5ms capillary column. HRMS measurements were performed with a Waters series SYNAPT G1 MS model high resolution mass spectrometer. Thin layer chromatography (TLC) was monitored on a silica gel plates (Merck Kieselgel 60 F254).

2.2. Preparation of ligands and complexes



Scheme 1. Synthesis of imino- and amino-phosphine ligands and palladium(II) complexes

2.2.1. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-methylmethanimine (1)

A 20 mL CH_2Cl_2/CH_3OH (1:3) solution of 2-(bis(3,5-dimethylphenyl)phosphino)benzaldehyde (0.39 g, 1.15 mmol), and ethanol solution (ca. 5 mL) of methylamine was conducted in Schlenk tube and stirred at room temperature. After 2 hours, the volatiles were removed under high vacuum. The yellow oily residue was recrystallized in methanol at -20°C overnight to give the pure imino-phosphine **1** as a white solid. 97% yield (0.40 g). **Melting point:** 95.2°C. **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 8.99 (d, J_{PH}= 3.8 Hz, CH=N, 1H), 8.01 (dd, *J*= 3.8, 7.5 Hz, ArH, 1H), 7.37 (t, *J*= 7.4 Hz, ArH, 1H), 7.29 (t, *J*= 7.4 Hz, ArH, 1H), 6.97 (s, ArH, 2H), 6.92 (dd, *J*= 5.3, 7.1 Hz, ArH, 1H), 6.88 (d, *J*= 8.2 Hz, ArH, 4H), 3.40 (d, *J*= 1.3 Hz, NCH_3, 3H), 2.25 (s, $ArCH_3$, 12H). **^{13}C NMR (100.6 MHz,**

$CDCl_3$): δ (ppm) 161.3 (d, J_{PC}= 24.8 Hz), 139.7 (d, J_{PC}= 11.1 Hz), 137.9 (d, J_{PC}= 7.4 Hz), 137.6 (d, J_{PC}= 19.0 Hz), 136.1 (d, J_{PC}= 9.0 Hz), 133.6 (s), 131.6 (d, J_{PC}= 20.0 Hz), 130.6 (s), 130.2 (s), 128.8 (s), 126.7 (d, J_{PC}= 4.4 Hz), 48.1 (s), 21.31 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -15.46. **FT-IR (KBr, cm^{-1}):** 1643 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+H]^+$ for $C_{24}H_{26}NP$ 360.1881; found $[M+H]^+$ 360.1896.

2.2.2. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-(*tert*-butyl)methanimine (2)

2-(bis(3,5-dimethylphenyl)phosphino)benzaldehyde (0.52 g, 1.51 mmol) and 25 mL *tert*-butyl amine was conducted in young's tube and stirred at 50°C overnight. After the required time, *tert*-butyl amine was removed and the yellow oily product was dried under high vacuum. (0.55 g, 92%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 8.71 (d, J_{PH}= 5.2 Hz, CH=N, 1H), 7.86 (m, ArH, 1H), 7.26 (t, J= 7.4 Hz, ArH, 1H), 7.16 (t, J= 7.1 Hz, ArH, 1H), 6.86 (d, J= 3.7 Hz, ArH, 4H), 6.84 (s, ArH, 2H), 6.78 (m, ArH, 1H), 2.16 (s, $ArCH_3$, 12H), 0.98 (s, $C(CH_3)_3$, 9H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 153.7 (d, J_{PC}= 22.3 Hz), 139.0 (d, J_{PC}= 16.0 Hz), 136.8 (d, J_{PC}= 7.8 Hz), 134.9 (d, J_{PC}= 8.7 Hz), 131.7 (d, J_{PC}= 1.8 Hz), 130.9 (d, J_{PC}= 20.3 Hz), 129.6 (s), 128.6 (s), 127.6 (s), 125.7 (d, J_{PC}= 3.8 Hz), 56.5 (s), 28.4 (s), 20.2 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -12.48. **FT-IR (KBr, cm^{-1}):** 1634 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+H]^+$ for $C_{27}H_{32}NP$ 402.2351; found $[M+H]^+$ 402.2362.

2.2.3. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-phenylmethanimine (3)

50 mL young's tube was charged with 2-(bis(3,5-dimethylphenyl)phosphino)benzaldehyde (0.52 g, 1.51 mmol) and aniline (0.14 mL, 1.51 mmol) and the mixture was dissolved in toluene. After the stirring at 120°C for 12 hours, the volatiles were removed and the yellow oily product was dried under high vacuum (0.58 g, 92%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ 9.02 (d, J_{PH}= 5.4 Hz, 1H), 8.15 (m, ArH, 1H), 7.35 (t, J = 7.5 Hz, ArH, 1H), 7.25 (td, J= 1.0,

7.5 Hz, ArH, 1H), 7.20 (m, 2H), 7.06 (m, ArH, 1H) 6.85 (m, ArH, 9H), 2.18 (s, $ArCH_3$, 12H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 159.3 (d, J_{PC}= 23.9 Hz), 152.0 (s), 139.5 (s), 138.1 (d, J_{PC}= 7.8 Hz), 135.9 (d, J_{PC}= 9.0 Hz), 133.5 (s), 131.9 (d, J_{PC}= 20.3 Hz), 130.8 (s), 128.9 (s), 128.81 (s), 127.5 (d, J_{PC}= 3.8 Hz), 125.8 (s), 121.1 (s), 21.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -13.83**. FT-IR (KBr, cm^{-1}):** 1619 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+H]^+$ for $C_{29}H_{28}NP$ 422.2038; found $[M+H]^+$ 422.2050.

2.2.4. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-methylmethanamine (4)

$NaBH_4$ (0.08 g, 2.15 mmol) was added to a solution of imino-phosphine ligand **1** in 15 mL methanol (0.19 g, 0.54 mmol) and the mixture was stirred for 1 hour at room temperature. The solvent was removed and the remaining product was dissolved in dichloromethane, and washed with H_2O. The resulting organic phase was dried with Na_2SO_4, solvent was removed and the pure amino-phosphine **4** was obtained as a colorless oily product. (0.19 g, 95%) **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 7.65 (dd, *J*= 7.1, 4.6 Hz, ArH, 1H), 7.30 (td, *J*= 7.5, 1.1 Hz, ArH, 1H), 7.19-7.13 (m, ArH, 1H), 7.06 (d, *J*= 12.7 Hz, ArH, 1H), 6.91 (s, ArH, 2H), 6.78 (d, *J*= 8.4 Hz, ArH, 4H), 4.12 (s, $ArCH_2$, 2H), 2.38 (s, NCH_3, 3H), 2.18 (s, $ArCH_3$, 12H). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -15.69. **HRMS (ESI):** calc. $[M+H]^+$ for $C_{24}H_{28}NP$ 362.2038; found $[M+H]^+$ 362.2050.

Ligand **5** and **6** were prepared using procedure for **4.**

2.2.5. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-(tert-butyl)methanamine (5)

96%, 0.51 g. **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 7.43-7.37 (m, ArH, 1H), 7.25-7.21 (m, ArH, 1H), 7.13 (d, *J*= 13.5 Hz, ArH, 1H), 7.07 (t, *J*= 7.0 Hz, ArH, 1H), 6.90 (s, 2H), 6.82 (d, *J*= 8.0 Hz, 4H), 3.81 (s, $ArCH_2$, 2H), 2.18 (s, $ArCH_3$, 12H), 0.93 (s, $C(CH_3)_3$, 9H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 137.9 (d, J_{PC}= 7.4 Hz), 136.6 (d, J_{PC}= 9.7 Hz), 136.2 (d,

J_{PC}=13.6 Hz), 133.4 (s), 131.8 (d, J_{PC}= 20.2 Hz), 130.5 (s), 129.9 (d, J_{PC}= 4.9 Hz), 129.5 (d, J_{PC}= 9.7 Hz), 129.1 (s), 126.99 (s), 50.7 (s), 45.9 (d, J_{PC}= 9.6 Hz, $ArCH_2$), 28.8 (s), 21.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -15.45. **HRMS (ESI):** calc. $[M+H]^+$ for $C_{27}H_{34}NP$ 404.2507; found $[M+H]^+$ 404.2528.

2.2.6. 1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-phenylmethanamine (6)

96%, 0.33 g. **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ 7.36 (m, ArH, 1H), 7.19 (t, *J*= 7.4 Hz, ArH, 1H), 7.10 (m, ArH, 1H), 6.98 (t, *J*= 7.8 Hz, ArH, 2H), 6.89 (s, ArH, 2H), 6.85 (m, 1H), 6.81 (d, *J*= 8.1 Hz, ArH, 4H), 6.55 (t, *J*= 7.2 Hz, ArH, 1H), 6.28 (d, *J*= 8.1 Hz, ArH, 2H), 4.38 (s, $ArCH_2$, 2H), 2.16 (s, $ArCH_3$, 12H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 146.8 (s), 142.1 (d, J_{PC}= 22.8 Hz), 136.9 (d, J_{PC}= 7.4 Hz), 135.2 (d, J_{PC}= 15.3 Hz), 134.9 (d, J_{PC}= 9.0 Hz), 132.54 (s), 130.7 (d, J_{PC}= 20.0 Hz), 129.6 (s), 127.7 (s), 126.9 (d, J_{PC}= 5.1 Hz), 126.2 (s), 116.2 (s), 111.9 (s), 45.9 (d, J_{PC}= 23.1 Hz, $ArCH_2$), 20.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) -16.06. **HRMS (ESI):** calc. $[M+H]^+$ for $C_{29}H_{30}NP$ 424.2194; found $[M+H]^+$ 424.2202.

2.3. Preparation of Pd(II) complexes

2.3.1. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-methylmethanimine}-palladium(II) (1a)

A solution of N-methyl-2-(bis(3,5-dimethylphenyl)phosphino)benzylimine (**1**) (0.32 g, 0.89 mmol) in CH_2Cl_2(10 mL) was added to a solution of $Pd(COD)Cl_2$ (0.25 g, 0.89 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 30 minutes at room temperature. After the completion of the reaction, the volatiles were removed in vacuo and diethyl ether was added to precipitate the yellow product. The resulting solid was washed with diethylether (4×5 mL) and dried under vacuum to give complex **1a**. Yield 95% (0.45 g). **^{1}H NMR (400.2 MHz, $CDCl_3$):**

δ (ppm) 8.01 (s, CH=N, 1H), 7.67-7.60 (m, ArH, 2H), 7.50 (t, *J*= 6.0 Hz, ArH, 1H), 7.10 (s, ArH, 2H), 7.03 (d, *J*= 13.4 Hz, ArH, 5H), 3.88 (s, NCH_3, 3H), 2.23 (s, $ArCH_3$, 12H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 164.4 (d, J_{PC}= 8.9 Hz), 138.6 (d, J_{PC}= 12.7 Hz), 136.8 (d, J_{PC}= 15.1 Hz), 135.1 (d, J_{PC}= 8.6 Hz), 134.3 (d, J_{PC}= 2.9 Hz), 133.5-133.4 (m), 132.4 (d, J_{PC}= 2.4 Hz), 131.9 (d, J_{PC}= 11.3 Hz), 125.1 (s), 124.5 (s), 123.7 (s), 123.2 (s), 54.3 (s), 21.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 32.23 (s). **FT-IR (KBr, cm^{-1}):** 1642 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{24}H_{26}Cl_2NPPd$ 560.0117; found $[M+Na]^+$ 560.0157.

The Pd(II) complexes **2a-6a** were prepared using procedure for **1a.**

2.3.2. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-(tert-butyl)methanimine}-palladium(II) (2a)

(0.51 g, 97%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 8.03 (s, CH=N, 1H), 7.73-7.62 (m, ArH, 3H), 7.46 (m, ArH, 2H), 7.11 (s, ArH, 3H), 6.94 (dd, *J*= 10.1, 7.8 Hz, ArH, 2H), 2.23 (s, $ArCH_3$, 12H), 1.40 (s, $C(CH_3)_3$, 9H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 164.8 (d, J_{PC}= 8.2 Hz), 138.9 (d, J_{PC}= 14.9 Hz), 138.5 (d, J_{PC}= 7.1 Hz), 135.1 (d, J_{PC}= 8.7 Hz), 134.2 (d, J_{PC}= 3.0 Hz), 133.3 (d, J_{PC}= *8.3 Hz*), 132.6 (d, J_{PC}= 3.9 Hz), 132.5 (d, J_{PC}= 2.6 Hz), 122.9 (s), 122.4 (s), 64.5 (s), 31.79 (s), 21.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 32.65 (s). **FT-IR (KBr, cm^{-1}):** 1619 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{27}H_{32}Cl_2NPPd$ 602.0586; found $[M+Na]^+$ 602.0677.

2.3.3. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-phenylmethanimine}-palladium(II) (3a)

(0.53 g, 97%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ 8.19 (s, CH=N, 1H), 7.84 (m, ArH, 1H), 7.78 (t, *J*= 7.2 Hz, ArH, 1H), 7.63 (t, *J*= 7.2 Hz, ArH, 1H), 7.42 (d, *J*= 7.4 Hz, ArH, 2H), 7.30 (m,

ArH, 3H), 7.19 (d, *J*= 13.1 Hz, ArH, 6H), 7.12 (m, ArH, 1H), 2.34 (s, $ArCH_3$, 12H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 164.9 (d, J_{PC}= 8.5 Hz), 151.8 (s), 138.8 (d, J_{PC}= 12.7 Hz), 136.9 (d, J_{PC}= 14.5 Hz), 136.3 (d, J_{PC}= 8.3 Hz), 134.3 (d, J_{PC}= 2.9 Hz), 133.9 (d, J_{PC}= 7.8 Hz), 133.8 (d, J_{PC}= 3.0 Hz), 132.7 (d, J_{PC}= 2.3 Hz), 131.9 (d, J_{PC}= 11.3 Hz), 128.6 (s), 128.1 (s), 125.2 (s), 124.6 (s), 123.4 (s), 21.3 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 31.23 (s). **FT-IR (KBr, cm^{-1}):** 1584 ($\nu_{C=N}$). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{29}H_{28}Cl_2NPPd$ 622.0273; found $[M+Na]^+$ 622.0345.

2.3.4. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-methylmethanamine}-palladium(II) (4a)

(0.49 g, 98%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 7.48 (t, *J*= 6.8 Hz, ArH, 1H), 7.36-7.28 (m, ArH, 3H), 7.26 (s, ArH, 1H), 7.05 (t, *J*= 14.4 Hz, ArH, 4H), 6.84-6.80 (m, ArH, 1H), 5.65 (s, NH, 1H), 3.90 (d, J_{PH}= 13.0 Hz, $ArCH_2$, 1H), 3.74 (m, $ArCH_2$, 1H), 2.50 (s, NCH_3, 3H), 2.22 (s, 12H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 138.9 (d, J_{PC}= 4.0 Hz), 138.7 (d, J_{PC}= 5.6 Hz), 138.1 (d, J_{PC}= 13.0 Hz), 134.2-133.9 (m), 133.6 (d, J_{PC}= 3.0 Hz), 132.6 (d, J_{PC}= 8.4 Hz), 132.2 (d, J_{PC}= 11.2 Hz), 131.9 (d, J_{PC}= 11.8 Hz), 129.9 (d, J_{PC}= 7.9 Hz), 127.5 (s), 126.9 (s), 125.2 (s), 124.6 (d, J_{PC}= *10.3 Hz*), 124.0 (s), 55.8 (d, J_{PC}= 11.0 Hz, $ArCH_2$), 39.3 (s), 21.4 (s). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 20.71 (s). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{24}H_{28}Cl_2NPPd$ 562.0273; found $[M+Na]^+$ 562.0707.

2.3.5. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-(tert-butyl)methanamine}-palladium(II) (5a)

(0.51 g, 98%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ (ppm) 7.46 (t, *J*= 7.5 Hz, ArH, 1H), 7.35-7.28 (m, ArH, 4H), 7.16 (d, *J*= 12.8, ArH, 2H), 7.15-7.08 (m, ArH, 2H), 7.00 (s, ArH, 1H), 5.43 (d, *J*= 22.4, NH, 1H), 4.44 (dd, J_{PH}= 14.7, 2.8 Hz, $ArCH_2$, 1H), 4.18 (ddd, J_{PH}=14.8, 6.8,

2.4 Hz, $ArCH_2$, 1H), 2.27 (s, $ArCH_3$, 6H), 2.17 (s, $ArCH_3$, 6H), 1.19 (s, $C(CH_3)_3$, 9H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ (ppm) 141.0 (d, J_{PC}= 14.5 Hz), 138.3 (t, J_{PC}= 12.8 Hz), 133.9 (d, J_{PC}= 1.53 Hz), 133.7 (d, J_{PC}= 3.0 Hz), 133.3 (d, J_{PC}= 2.9 Hz), 132.2 (d, J_{PC}= 11.2 Hz), 131.8 (d, J_{PC}= 3.2 Hz), 129.5 (d, J_{PC}= 7.5 Hz), 129.0 (s), 128.4 (s), 127.2 (s), 126.6 (s), 125.5 (s), 125.1 (s), 60.5 (s), 52.5 (d, J_{PC}= 9.5 Hz, $ArCH_2$), 30.8 (s), 21.4 (d, J_{PC}= 6.6 Hz). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 17.57 (s). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{27}H_{34}Cl_2NPPd$ 604.0743; found $[M+Na]^+$ 604.0748.

2.3.6. Dichloro{1-(2-(bis(3,5-dimethylphenyl)phosphinyl)phenyl)-N-phenylmethanamine}-palladium(II) (6a)

(0.53 g, 97%). **^{1}H NMR (400.2 MHz, $CDCl_3$):** δ 7.85 (s, ArH, 1H), 7.49-7.45 (m, ArH, 3H), 7.42 (s, ArH, 1H), 7.34 (dd, *J*= 4.5, 2.9 Hz, ArH, 2H), 7.24 (d, *J*= 13.7 Hz, ArH, 2H), 7.19 (s, ArH, 2H), 7.13 (m, ArH, 2H), 6.95 (m, ArH, 1H), 6.86 (dd, *J*= 8.4, 4.4 Hz, ArH, 1H), 6.33 (s, NH, 1H), 4.33 (d, J_{PH}= 13.1 Hz, $ArCH_2$, 1H), 4.13 (dd, J_{PH}= 10.6, 8.2 Hz, $ArCH_2$, 1H), 2.37 (s, $ArCH_3$, 6H), 2.29 (s, $ArCH_3$, 6H). **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 143.8 (s), 139.2 (d, J_{PC}= 14.0 Hz), 138.8 (d, J_{PC}= 12.2 Hz), 138.2 (d, J_{PC}= 12.9 Hz), 134.1 (d, J_{PC}= 2.8 Hz), 133.6 (d, J_{PC}= 2.8 Hz), 133.5 (d, J_{PC}= 3.1 Hz), 132.8 (d, J_{PC}= 8.5 Hz), 132.3 (d, J_{PC}= 11.2 Hz), 131.9 (d, J_{PC}= 11.2 Hz), 131.8 (d, J_{PC}= 2.1 Hz), 129.6 (d, J_{PC}= 8.0 Hz), 128.8 (s), 127.4 (s), 127.1 (s), 126.7 (s), 126.0 (s), 125.8 (s), 58.2 (d, J_{PC}= 11.5 Hz, $ArCH_2$), 21.4 (d, J_{PC}= 7.2 Hz). **^{31}P NMR (162.0 MHz, $CDCl_3$):** δ (ppm) 21.11 (s). **HRMS (ESI):** calc. $[M+Na]^+$ for $C_{29}H_{30}Cl_2NPPd$ 624.0430; found $[M+Na]^+$ 624.0494.

2.4. General procedure for Suzuki C-C coupling reactions

In a typical experiment, a sealed tube was charged with aryl bromide (0.10 mmol), phenylboronic acid (0.12 mmol), base (0.12 mmol), organic solvent-H_2O (3:3 mL) and

palladium catalyst (0.2 mol%), and the mixture was stirred at appropriate temperature. After the required reaction time, the mixture was cooled and poured out in $CHCl_3$ (20 mL) and washed with saturated ammonium chloride and brine solution. Then, the organic phase was dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product was chromatographed on silica gel and the isolated biphenyl product was characterized by ^{1}H, ^{13}C NMR, and GC.

3. Results and Discussion

3.1. Synthesis

The synthetic routes of the imino- and amino-phosphine ligands and their palladium(II) complexes were outlined in Scheme 1. 2-bis-(3,5-dimethylphenylphosphino)benzaldehyde [19,20] was firstly reacted with methylamine, *tert*-butylamine and aniline to afford 1-(2-(bis(3,5-dimethylphenyl)phosphino)phenyl)-N-methylmethanimine (**1**), 1-(2-(bis(3,5-dimethyl phenyl)phosphino)phenyl)-N-(*tert*-butyl)methanimine (**2**) and 1-(2-(bis(3,5-dimethylphenyl) phosphino)phenyl)-N-phenylmethanimine (**3**) as a white solid or colorless oily products, respectively [15,20,21]. The classical reduction of imine groups with $NaBH_4$ in methanol, followed by extraction with dichloromethane and water and dried over Na_2SO_4, afforded amino-phosphine compounds 1-(2-(bis(3,5-dimethylphenyl)phosphino)phenyl)-N-methylmethanamine (**4**), 1-(2-(bis(3,5-dimethylphenyl)phosphino)phenyl)-N-(*tert*-butyl)methanamine (**5**) and 1-(2-(bis(3,5-dimethylphenyl)phosphino)phenyl)-N-phenylmethanamine (**6**) as a colorless oily products [22-24].

The reaction of corresponding PN type ligands (**1**-**6**) with dichloro(1,5-cyclooctadiene) palladium(II) [25] in CH_2Cl_2 gave palladium(II) complexes (**1a**-**6a**) as yellow solids by the following general procedures. All the palladium(II) complexes have been found to be

completely air and moisture stable and can be handled in the air for weeks. They are readily soluble in methanol, dichloromethane, chloroform, dimethylformamide and acetonitrile, but poorly soluble in other commonly used organic solvents such as toluene, THF or 1,4-dioxane.

3.2. Characterization

All of the ligands and Pd(II) complexes have been fully characterized using FT-IR, ^{1}H, ^{31}P and ^{13}C NMR spectroscopy and they were further characterized by HRMS analysis. The ^{1}H NMR spectra of compound **1**, **2** and **3** showed a characteristic doublet for the imine proton which related to the coupling of the phosphorus with the imine hydrogen at 8.99 ppm (J_{PH}= 3.8 Hz), 8.71 ppm (J_{PH}= 5.2 Hz) and 9.02 (J_{PH}= 5.4 Hz), respectively. Also, the ^{13}C NMR spectra exhibited characteristic doublet signals of the imine carbons resonated at 161.3 (J_{PC}= 24.8 Hz) (**1**), 153.7 (J_{PC}= 22.3 Hz) (**2**) and 159.3 (J_{PC}= 23.9 Hz) ppm (**3**), respectively. The ^{1}H NMR spectra of Pd(II) complexes displayed singlet peaks at 8.01 (**1a**) 8.03 (**2a**) and 8.19 (**3a**) ppm, showing that the phosphine coordinated palladium considerably de-shielded compared to the free ligands. Meanwhile, based on ^{13}C NMR analysis, the signal of imine carbons of metal complexes de-shielded and were found to occur in the range 164.4-164.9 ppm (with 8.2-8.9 Hz), as compared to its PN ligands after complexations to the metal ion through imine nitrogen of the ligands. Besides that, all of the ^{1}H NMR peaks observed between 8.15-6.78 ppm, assigned to aromatic CH protons of ligands **(1-3)** and complexes (**1a-3a**). In addition, the methyl protons attached to the phenyl rings gave singlet peaks at 2.25, 2.16 and 2.17 ppm for compound **1, 2** and **3,** and the $NC\underline{H}_3$ and $C(C\underline{H}_3)_3$ resonances were observed at 3.40 (d, J_{PH}=1.3 Hz, probably due to phosphorus coupling) and 0.98 ppm (s) for compound **1** and **2**, as expected [15,17,26]. Reduction of the compounds **1-3** was performed in methanol with 4 mole equivalents $NaBH_4$ to give amino-phosphine ligands **(4-6)**. The ^{1}H NMR spectra of ligand **4-6** showed singlet resonance at 4.12 **(4),** 3.81 **(5)** and 4.38 **(6)** ppm which are assigned to Ar-CH_2

protons together with disappearance of imine doublet at 8.99, 8.71 and 9.02 ppm indicating the reduction of imine groups to amino- groups [15,17,22,24,27,28]. In ^{1}H NMR of palladium complexes, two sets of signals (3.90 (d) and 3.74 (m) for **4a**; 4.44 (dd) and 4.18 (ddd) for **5a**; 4.33 (d) and 4.13 (dd) for **6a**) were recorded for each proton of methylene group probably due to the rotation of -CH_2- hydrogens and coupling of phosphorus with the methylene hydrogen similar to that of phosphorus with corresponding imine hydrogen. The formation of palladium(II) complexes were also confirmed by ^{13}C NMR analysis. This is a downfield shift from 45.9-54.3 to 52.5-58.2 ppm observed for methylene carbons of the amino-phosphine ligands, further confirming the coordination of the nitrogen donor to the palladium center [20,21,29,30]. The ^{31}P NMR spectrum showed singlet resonances at -15.46, -12.48 and 13.83 ppm assigned to ligand **1-3** and after the reduction of imine group with excess $NaBH_4$, the signals were shifted to -15.69, -15.45 and -16.06 ppm for ligand **4-6,** respectively [17,29]. These signals have totally disappeared and low field singlet has newly formed (32.23 **(1a)**, 32.65 **(2a)**, 31.23 **(3a)**, 20.71 **(4a)**, 17.57 **(5a)** and 21.11 **(6a)** ppm) in the ^{31}P NMR spectra of the Pd(II) complexes which further support the coordination of the phosphorus atom to the palladium center [31,32]. Thus, as expected, the spectroscopic results and high resolution mass data together support the purposed structures (see the supporting information).

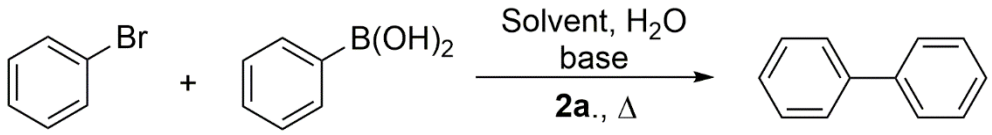
3.3. Suzuki coupling reactions

The nature of the base, solvent, temperature and catalyst amount is more important for the Suzuki C-C coupling reactions. So, we first chose bromobenzene and phenylboronic acid as the model substrates to optimize the catalytic conditions, including optimization of the bases, solvents and temperatures. For this purpose, we have tested common inorganic and organic bases such as KOH, K_2CO_3, Na_2CO_3, K_3PO_4, NaOAc, Et_3N, Bu^{t}OK, NaOH and DIPEA at 80°C as shown in Table 1 and in all cases the reactions were performed with 0.2 mol% of

catalyst. While the reaction proceeds with various bases and solvents, the best result was obtained with K_2CO_3 as the base and DMF was found to be the best solvent at 80°C (entries 2 and 12). Thereafter, coupling of phenylboronic acid was carried out in toluene as solvent and no coupling product was obtained (entry 20). It is well-known that generally non-polar solvents like toluene are not preferred for the Suzuki C-C coupling reactions as they allow for the lower solubility of both the substrates and catalysts used [20,21,33,34]. In addition, no coupling product was also observed in the absence of base (entry 10), which is essential to generate the catalytically active species and facilitate the transmetalation step. In Suzuki coupling reactions, the use of weak bases remains unable to activate phenylboronic acid, whereas strong bases limit the functional group tolerance [35]. The use of commonly inorganic bases such as KOH, Na_2CO_3, K_3PO_4, NaOH, and organic bases like Et_3N, NaOAc, Bu^tOK or DIPEA, lead to the formation of coupling products in moderate yields (entries, 1, 3-9, 11, and 13-19).

On the other hand, the reaction temperature has a great effect on the yield of coupling product. In high temperature Suzuki C-C coupling reactions, the effect of temperature results in palladium black formation whereas lower temperature does not accelerate the oxidative addition of aryl bromides which is rate determining step of a Suzuki C-C coupling reaction [13,36]. In order to study the effect of temperature on coupling of phenylboronic acid with bromobenzene, the reaction temperature was decreased to 50°C which decreased the yield of cross coupling product to 55% (entry 2). Thus, the best reaction temperature was found to be 80°C, which is adequately suitable for the activation of bromobenzene without palladium black formation.

Table 1. The effect of base, solvent and temperature on the Pd(II) catalyzed Suzuki C-C coupling reaction between bromobenzene and phenylboronic acid with catalyst **2a**[a]



Entry	Solvent	Base	Yield (80°C)[b]
1	DMF	KOH	60
2	DMF	K_2CO_3	89 (55)[c]
3	DMF	Na_2CO_3	60
4	DMF	NaOAc	61
5	DMF	Et_3N	69
6	DMF	Bu^tOK	40
7	DMF	K_3PO_4	64
8	DMF	NaOH	29
9	DMF	DIPEA	67
10	DMF	-	-
11	1,4-dioxane	KOH	70
12	1,4-dioxane	K_2CO_3	78
13	1,4-dioxane	Na_2CO_3	65
14	1,4-dioxane	NaOAc	34
15	1,4-dioxane	Et_3N	73
16	1,4-dioxane	Bu^tOK	67
17	1,4-dioxane	K_3PO_4	65
18	1,4-dioxane	NaOH	62
19	1,4-dioxane	DIPEA	55
20	toluene	K_2CO_3	-

[a]Reaction conditions: bromobenzene (0.1 mmol), phenylboronic acid (0.12 mmol), catalyst **2a** (0.2 mol%), base (0.12 mmol), solvent (2.0 mL), H_2O (2.0 mL), 12 h**.**
[b]Bıphenyl product was isolated from the reaction mixture and was characterized by ^1H, ^{13}C NMR, and GC
[c]50 °C.

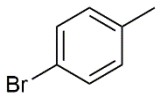
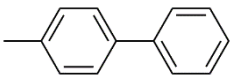
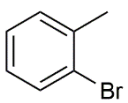
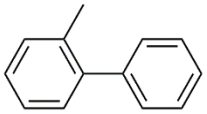
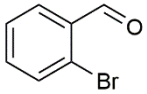
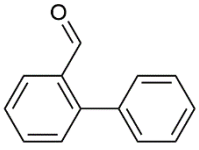
Next, the performance of Pd(II) catalysts on Suzuki C-C coupling reactions was further investigated for different aryl bromides and phenylboronic acid under the optimized conditions. The results are presented in Table 2. Coupling of phenylboronic acid with para-substituted aryl bromides gave desired coupled product with a good to excellent isolated yields by all catalysts in 12 hours (up to 99% yield, Table 2, entries 1, 4, 5, and 7). Generally, for the Suzuki C-C coupling reactions, the use of deactivated aryl bromides, substituted with electron donating groups such as -methyl or -methoxy, slows down the rate of the reaction [13,20,21].

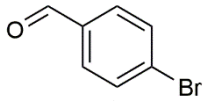
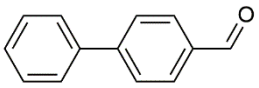
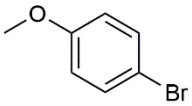
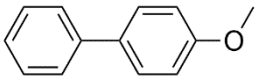
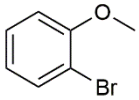
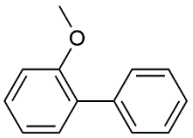
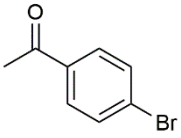
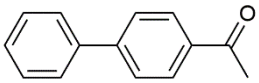
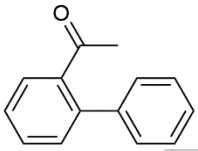
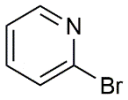
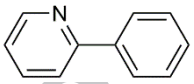
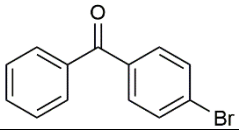
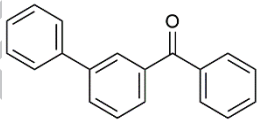
However, both electron-withdrawing and -donating groups on the phenyl ring at para position of aryl bromides did not seem to have a great effect on the product yields apparently. Comparing the efficiency of the catalysts, the poorest results (78%) are obtained with deactivated substrate 4-bromotoluene when **2a** and **4a** are used as catalysts (entry 1) while the coupling of another deactivated 4-bromoanisole with phenylboronic acid goes to almost completion (>99) in 12 h with all catalysts (entry 4). The catalytic system is also efficient for the coupling of 3-bromobenzophenone with phenylboronic acid and thus 3-phenylbenzophenone was obtained in high yields (86-97%, entry 10). On the other hand, the presence of electron-withdrawing or -donating groups in the ortho position on the aryl bromides, significantly influences the catalyst performance leading to reduced reaction rates [13,37]. This effect suggests that, with sterically hindered aryl bromides, the oxidative addition of the substrate to the palladium center is the rate determining step in the Suzuki C-C coupling reaction and ultimately decreasing the rate of reaction. Importantly, the coupling of ortho substituted substrates such as 2-bromotoluene, 2-bromoanisole and 2-bromobenzaldehyde with phenylboronic acid generally gave coupled products in moderate to good yields (from 43-89%) and steric effects of these groups were well tolerated (entries, 2, 3 and 6). But, in the case of 2-bromoacetophenone, only 10% and 12% desired product was obtained with catalyst **5a** and **6a**, respectively and no significant product was observed with catalyst **1a**-**4a**. These results clearly indicate that, the strong steric effect of the bulkier -aceto group in the 2-bromoacetophenone has a great influence on the catalytic activity of the complexes when comparing to the other sterically hindered substrates containing relatively less bulky substituents such as -methyl, -methoxy and -formyl groups (entries 2, 3, 6, and 8). Besides, the catalytic efficiency of our catalyst system is highly slowed down (<5 to 12%) for the heterocoupled product when 2-bromopyridine was used as a substrate (entry 9). The catalytic activities of palladium catalysts **1a**-**6a** were also tested in the Suzuki coupling of industrially important substrate 3-

bromobenzophenone with phenylboronic acid and good to excellent coupled product was isolated (86-97%, entry 10).

Normally, the presence of "imino group" rather than "amino group" in the ligand system will increase the σ-donor ability of the nitrogen donor and so the palladium center will be more susceptible to oxidative addition reactions, but surprisingly, comparing the results obtained for **1a-3a** and **4a-6a** catalysts, no significant difference was found in catalytic activity of the complexes. On the other hand, Mahamo and coworkers reported the use of well-defined methyl chloride and dichloride iminophosphine Pd(II) complexes as pre-catalysts in Suzuki C-C coupling reactions which have benzyl, furfuryl and thiophenyl groups on the imine nitrogen of the ligands. They observed that for this catalyst system, the presence of methylene group which bonded to nitrogen donor, reduced the steric crowding and improves conversions and activities [13]. However, comparing the results obtained from our catalyst system, sterically hindered substrates of both electron-withdrawing and electron-donating groups on the aryl bromide were well tolerated and the reactions were carried out under relatively mild temperature.

Table.2. The effect of the catalysts on the Suzuki C-C coupling reactions of between substituted aryl bromides and phenylboronic acid[a]

Entry	ArBr	Product	Yield (%)[b]					
			1a	**2a**	**3a**	**4a**	**5a**	**6a**
1			86	78	93	78	86	95
2			59	70	87	65	86	53
3			53	68	49	43	44	89

4			94	95	98	>99	94	97
5			>99	95	94	96	97	98
6			60	85	89	58	56	48
7			88	93	99	96	90	96
8			<5	<5	<5	<5	12	10
9			<5	25	20	<5	16	8
10			95	97	97	86	94	88

[a]Reaction conditions.: aryl bromide (0.1 mmol), phenylboronic acid (0.12 mmol), catalyst (0.2 mol%), K_2CO_3 (0.12 mmol), DMF (2.0 mL), H_2O (2.0 mL), T: 80°C, 12 h.
[b]Biaryl products were isolated from the reaction mixture and were characterized by ^1H, ^{13}C NMR, and GC.

4. Conclusion

Several new imino- and amino-phosphine ligands and their palladium(II) complexes have been synthesized and characterized by spectrocopic and analytical methods. Based on the NMR, FTIR and HRMS analyses, the imino- and amino-phosphine ligands acted as PN bidentate ligand and have bonded to the palladium center via nitrogen and phosphorus donors. These palladium(II) complexes were used as catalyst precursors for the Suzuki C-C coupling of substituted aryl bromides bearing activated or deactivated group at -ortho or -para positions.

The results show that, good to excellent coupling products were obtained for these imino- and amino-phosphine palladium catalysts and sterically hindered substrates were well tolerated.

Acknowledgements

This work was supported by the Osmaniye Korkut Ata University (Project Number: OKUBAP-2017-PT2-003).

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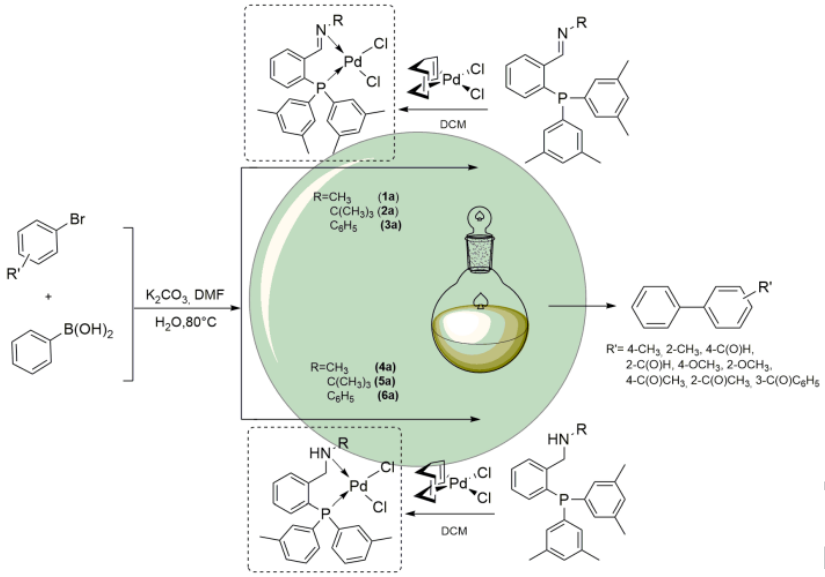
Graphical abstract



Research Highlights

- PN type imino- and amino phosphine ligands and their Pd(II) complexes have been synthesized.
- These Pd(II) complexes [Pd(PN)Cl_2] have been applied for the Suzuki C-C coupling reactions.
- Good to excellent coupling products were obtained and sterically hindered substrates were well tolerated.