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FULL PAPER

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Iminophosphine palladium catalysts for Suzuki carbonylative coupling reaction

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Three iminophosphine ligands having soft phosphorus and hard nitrogen atoms and their Pd(II) complexes were synthesized and characterized using ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and Fourier transform infrared spectroscopic techniques. Also, electrochemical properties of the iminophosphines and their Pd(II) complexes were investigated in acetonitrile–tetrabutylammonium perchlorate solution with cyclic and square wave voltammetry techniques. All Pd(II) complexes were evaluated as catalysts for carbonylative cross-coupling reactions of aryl iodides with phenylboronic acid. The Suzuki carbonylation of aryl iodides at 80 °C under balloon pressure of carbon monoxide in the presence of K_2CO_3 as a base was examined, and good to high conversions and excellent selectivities were obtained.

KEYWORDS
electrochemistry, iminophosphines, palladium, Suzuki carbonylation

1 | INTRODUCTION

Palladium-catalysed carbonylative cross-coupling reactions of aryl halides with organoboron compounds play an important role in modern chemical transformations, and these types of reactions are widely applied for the synthesis of pharmaceuticals, agrochemicals and advanced materials.[1–3] While carbonyl compounds have been traditionally synthesized by multi-step syntheses, biologically important symmetric or unsymmetric diaryl ketones such as benzophenones can be obtained in one-step procedures using carbonylative cross-coupling reactions.[4,5] In such cases, these coupling reactions typically proceed in organic solvents, but they have also been applied successfully in green solvents such as water and ionic liquids.[6–9] Carbonylative Suzuki cross-coupling reactions are generally catalysed by palladium nanoparticles,[10,11] *in situ* generated palladium complexes with phosphines or N-heterocyclic carbene ligands or various commercially available palladium complexes,[7,12–15] palladium on carbon,[16] palladium nanoparticles immobilized on supported ionic liquid-like phases,[6] palladium supported on hollow magnetic mesoporous spheres,[17] palladium nanoparticles supported on nickel pyrazolate[18] or palladacycles.[19] However, to the best of our knowledge, there has been no study of carbonylative cross-coupling reactions of arylboronic acids with aryl iodides catalysed by PN-type bidentate iminophosphine ligand-based palladium complexes.[20]

In the study reported in this paper, we prepared, characterized and investigated the electrochemical behaviour of PN-type iminophosphine ligands and their Pd(II) complexes. All the Pd(II) complexes were also applied as catalysts for the carbonylative Suzuki cross-coupling reactions of aryl iodides with arylboronic acids under an atmospheric pressure of carbon monoxide. The results show that the iminophosphine palladium complexes can catalyse the carbonylative coupling reactions of aryl iodides with arylboronic acids

with good to high selectivity even under an atmospheric pressure of carbon monoxide.

2 | EXPERIMENTAL

2.1 | Materials and methods

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried using established procedures and then immediately distilled under nitrogen atmosphere prior to use.[21] (*S*)-α-Methylbenzylamine, (*S*)-α,4-dimethylbenzylamine, (*R*)-α-methyl-4-nitrobenzylamine hydrochloride and Pd(cod)Cl_2 were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and were used without further purification. 2-(Diphenylphosphino)benzaldehyde[22] and 1-(2-(diphenylphosphinyl)phenyl)-*N*-(1-phenylethyl) methaneimine[23] were prepared according to literature methods.

Microanalysis (C, H and N) was performed using a LECO CHNS 932 instrument. Fourier transform infrared (FT-IR) spectra of synthesized compounds were recorded with a PerkinElmer RX1 spectrophotometer in the range 650–4000 cm^{-1}. All ^1H NMR (400.1 MHz) and $^{31}P\{^1H\}$ NMR (162.0 MHz) spectra were recorded at 25 °C with deuterated DMSO or $CDCl_3$ with a Bruker NMR spectrometer. ^{13}C NMR spectra were obtained with a Varian Mercury 100.6 MHz spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded with complete proton decoupling using 85% H_3PO_4 as external standard. The Suzuki carbonylative cross-coupling products were analysed using GC/MS with an Agilent 7890A GC System 5975C MSD series gas chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm × 0.25 μm film thickness β-Dex capillary column and an Agilent 1200 (HPLC). TLC was used for monitoring the reactions.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques were performed using a CHI 6094D electrochemical analyser equipped with a three-electrode electrochemical cell system. An Ag/Ag^+ (10 mM Ag^+/ACN) reference electrode, a Pt wire as counter electrode and a glassy carbon electrode (3.0 mm in diameter) as working electrode were employed for the electrochemical studies.

Voltammetric experiments were performed at room temperature in acetonitrile (ACN) solution with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. High-purity argon was purged to the solution for 15 min to maintain deoxygenated condition and the passage of argon was also continued during the experiment. The working electrode was polished with alumina paste on a felt pad in order of 1.0, 0.3 and 0.05 μm particle size. The cleaning procedure was followed by sonication with an isopropyl alcohol–water mixture for 10 min and rinsing with acetone.

Electrochemical measurements were performed with 1 mM Pd(II) complexes. CV measurements were performed with a 100 mV s^{-1} scan rate between −1.5 and 1.5 V potential window starting from negative. SWV settings were: step potential, 4 mV; amplitude, 25 mV; frequency, 15 Hz.

2.2 | Preparation of ligands and complexes

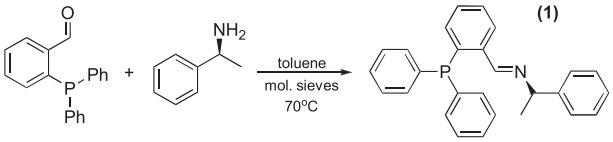
2.2.1 | Preparation of (*o*-PPh_2)$C_6H_4CH{=}NCH(CH_3)C_6H_5$ (1)

Ligand **1** was prepared (Scheme 1) according to a literature procedure.[24]

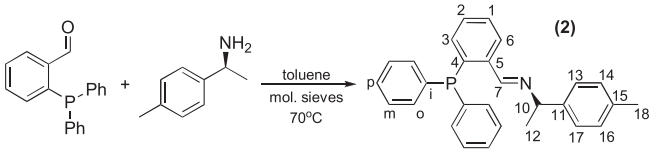
2.2.2 | Preparation of (*o*-PPh_2)$C_6H_4CH{=}NCH(CH_3)C_6H_4$(*p*-$CH_3$) (2)

2-(Diphenylphosphino)benzaldehyde (0.25 g, 0.86 mmol) with (*S*)-α,4-dimethylbenzylamine (0.13 mL, 0.86 mmol) were stirred for 12 h in dry toluene and in the presence of molecular sieves (4 Å) at 70 °C. The reaction was monitored by TLC (hexane–ethyl acetate, 3:1). Filtration and drying in vacuum afforded the desired yellow oily product (Scheme 2).

Yield 282 mg (81%). FT-IR (KBr, cm^{-1}): 1434, 1634, 3052. ^1H NMR (400.2 MHz, $CDCl_3$, δ, ppm): 8.83 (d, J = 4.8 Hz, 1H, H^7), 7.90 (m, 1H), 7.42 (m, 1H), 7.27–7.16 (m, 11H), 6.99 (m, 4H), 6.78 (m, 1H), 4.37 (q, J = 6.6 Hz, 1H, H^{10}), 2.30 (s, 3H, H^{18}), 1.32 (d, J = 6.6 Hz, 3H, H^{12}). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 158.0 (d, J = 20.4 Hz, C^7), 141.9 (s, C^{11}), 139.7 (d, J = 17.0 Hz, C^4), 137.4 (d, J = 19.5 Hz, C^i), 134.2 (d, J = 5.7 Hz, C^o), 134.0 (d, J = 5.6 Hz, C^m), 133.2 (s, C^1), 132.0 (s), 130.10 (s, C^2), 129.0 (s), 128.8 (s, C^p), 128.6 (d, J = 7.0 Hz), 128.1 (d, J = 4.2 Hz), 126.6 (s, C^6), 69.4 (s, C^{10}), 24.4 (s, C^{12}), 21.1 (s, C^{18}). ^{31}P NMR (162.0 MHz, $CDCl_3$, δ, ppm): −12.46 (s). Anal. Calcd for $C_{28}H_{26}NP$ (%): C, 82.53; H, 6.43; N, 3.44. Found (%): C, 82.64; H, 6.59; N, 3.49.



SCHEME 1 Preparation of ligand **1**[24]



SCHEME 2 Preparation of ligand **2**

2.2.3 | Preparation of (*o*-PPh_2) $C_6H_4CH{=}NCH(CH_3)C_6H_4$(*p*-$NO_2$) (3)

2-(Diphenylphosphino)benzaldehyde (0.25 g, 0.86 mmol) with (*R*)-α-methyl-4-nitrobenzylamine hydrochloride (0.18 g, 0.86 mmol) were stirred for 12 h in dry toluene, in the presence of molecular sieves (4 Å) and Et_3N (0.12 ml, 0.86 mmol) at 70 °C (Scheme 3). The reaction was monitored by TLC (hexane–ethyl acetate, 3:1). The solvent was evaporated under reduced pressure until dryness and diluted with CH_2Cl_2. The solution was washed with $NaHCO_3$ solution and water and combined organic phases were dried (Na_2SO_4) and the solvent evaporated. The residue was crystallized at −20 °C in methanol.

Yield 300 mg (80%). FT-IR (KBr, cm^{-1}): 1432, 1645, 3052. ^{1}H NMR (400.2 MHz, $CDCl_3$, δ, ppm): 8.90 (d, J = 4.7 Hz, 1H, H^{25}), 8.07 (d, J = 8.76 Hz, 2H, $H^{34,36}$), 7.96 (m, 1H, H^{24}), 7.35 (m, 14H), 6.89 (m, 1H), 4.48 (q, J = 6.6 Hz, 1H, H^{30}), 1.35 (d, J = 6.7 Hz, 3H, H^{32}). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 159.4 (d, J = 18.6 Hz, C^{25}), 152.4 (s, C^{31}), 139.1 (d, J = 16.8 Hz, C^{22}), 137.7 (d, J = 20.4 Hz, C^{i}), 136.7 (dd, J = 9.5, 4.8 Hz, C^{o}), 134.2 (s), 134.08 (d, J = 7.3 Hz, C^{m}), 133.9 (s, C^{19}), 133.5 (s), 130.5 (s, C^{20}), 128.7 (dd, J = 7.0, 5.9 Hz), 128.5 (d, J = 4.0 Hz), 127.4 (s), 123.6 (s, C^{24}), 69.1 (s, C^{30}), 24.7 (s, C^{32}). ^{31}P NMR (162.0 MHz, $CDCl_3$, δ, ppm): −12.36 (s). Anal. Calcd for $C_{27}H_{23}N_2O_2P$ (%): C, 73.96 H, 5.29; N, 6.39. Found (%): C, 74.12; H, 5.32; N, 6.43.

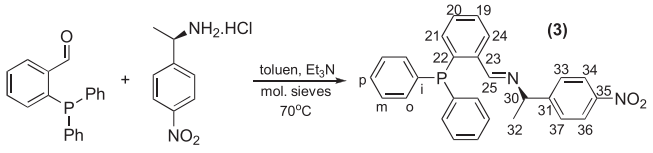
2.2.4 | Preparation of [$PdCl_2$(*o*-PPh_2) $C_6H_4CH{=}NCH(CH_3)C_6H_4$(*p*-$CH_3$)] (2a)

To a solution of Pd(cod)Cl_2 (0.28 g, 1.00 mmol) in dry CH_2Cl_2 (10 mL) was added **2** (0.40 g, 1.00 mmol). The mixture was stirred for 6 h at room temperature. Then, addition of diethyl ether caused a yellow solid which was filtered off and dried to afford the title compound **2a** (Scheme 4).

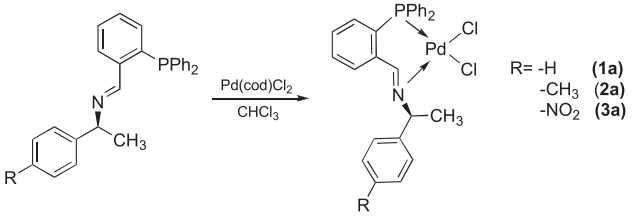
Yield 575 mg (85%); m.p. 228 °C. FT-IR (KBr, cm^{-1}): 1436, 1632, 3056. ^{1}H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 7.72 (d, J = 7.7 Hz, 1H), 7.69 (s, 1H, H^{25}), 7.62–7.44 (m, 1H), 7.44–7.38 (m, 2H), 7.34–7.23 (m, 2H), 7.20 (s, 1H), 6.82 (d, J = 7.7 Hz, 1H), 6.62 (q, J = 6.8 Hz, 1H), 3.41 (q, J = 7.02 Hz, 1H, H^{30}), 2.24 (s, 3H, H^{18}), 1.45 (d, J = 7.0 Hz, 3H, H^{12}). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 161.9 (d, J = 8.6 Hz, C^{7}), 152.4 (s, C^{11}), 138.3 (d, J = 16.8 Hz, C^{4}), 137.6 (d, J = 20.4 Hz, C^{i}), 136.3 (dd, J = 9.5, 4.8 Hz, C^{o}), 134.4 (s), 133.7 (d, J = 7.3 Hz, C^{m}), 133.2 (s, C^{1}), 131.7 (s), 129.8 (s, C^{2}), 129.4 (dd, J = 7.0, 5.9 Hz), 128.5 (d, J = 4.0 Hz), 128.3 (s), 124.4 (s, C^{6}), 69.7 (s, C^{10}), 21. 4 (s, C^{18}), 21.2 (s, C^{12}). ^{31}P NMR (162.0 MHz, $CDCl_3$, δ, ppm): 31.44 (s). Anal. Calcd for $C_{28}H_{26}Cl_2NPPd$ (%): C, 57.51 H, 4.48; N, 2.40. Found (%): C, 57.88; H, 4.69; N, 2.66. HRMS: calcd for $C_{28}H_{26}Cl_2NPPd$ (M^+) m/z 584.0292, found 584.0298.

2.2.5 | Preparation of [$PdCl_2$(*o*-PPh_2) $C_6H_4CH{=}NCH(CH_3)C_6H_4$(*p*-$NO_2$)] (3a)

Compound **3a** was prepared using a procedure similar to that described for **2a**. Yield 560 mg (78%); m.p. 113 °C (decomp.). FT-IR (KBr, cm^{-1}): 1436, 1632, 3059. ^{1}H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.23 (s, 1H, H^{25}), 7.90–7.19 (s, 16H, ar-CH), 7.05 (q, 1H), 6.88 (dd, 1H), 6.62 (q, J = 6.8 Hz, 1H), 3.48 (m, 1H, H^{30}), 1.63 (d, J = 7.0 Hz, 3H, H^{32}). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 162.0 (d, J = 18.6 Hz, C^{25}), 147.6 (s, C^{31}), 146.4 (d, J = 16.8 Hz, C^{22}), 137.1 (d, J = 20.4 Hz, C^{i}), 136.4 (dd, J = 9.5, 4.8 Hz, C^{o}), 134.3 (s), 133.9 (d, J = 7.3 Hz, C^{m}), 133.6 (s, C^{19}), 133.0 (s), 132.4 (s, C^{20}), 129.1 (dd, J = 7.0, 5.9 Hz), 128.9 (d, J = 4.0 Hz), 128.9 (s), 124.1 (s, C^{24}), 68.5 (s, C^{30}), 20.8 (s, C^{32}). ^{31}P NMR (162.0 MHz, $CDCl_3$, δ, ppm): 31.29 (s). Anal. Calcd for $C_{27}H_{23}Cl_2N_2O_2PPd$ (%): C, 52.66 H, 3.76; N, 4.55. Found (%): C, 52.98; H, 3.92; N, 4.77. HRMS: calcd for $C_{27}H_{23}Cl_2N_2O_2PPd$ (M^+) m/z 614.9987, found 614.9992.



SCHEME 3 Preparation of ligand **3**



SCHEME 4 Preparation of complexes **1a**, **2a** and **3a**[24]

2.3 | General procedure for Carbonylative Suzuki coupling reaction

The desired Pd(II) complex (0.01 mmol), base (1.2 mmol), phenylboronic acid (1.2 mmol), iodobenzene (1.0 mmol) and solvent (4.0 mL) were placed under argon atmosphere into a Schlenk tube and then pressurized with carbon monoxide at a pressure of 1 atm. Next the reaction was conducted for 4 h at 80 °C. After completion of the reaction, the Schlenk tube was cooled to room temperature, and the mixture was diluted with diethyl ether (8 mL) and then filtered through a pad of silica gel. Then the mixture was analysed using GC–MS with mesitylene as an internal standard to determine the conversion of iodobenzene.

3 | RESULTS AND DISCUSSION

3.1 | Characterization

Ligands **1**, **2** and **3** and Pd(II) complexes **1a**, **2a** and **3a** were synthesized by treating 2-(diphenylphosphino)benzaldehyde with the appropriate primary amine under argon atmosphere using a literature procedure.[24] All compounds are very soluble in dichloromethane, chloroform, ethanol and acetone, and insoluble in *n*-hexane and diethyl ether.

From the ^{1}H NMR spectra, displacement of doublet signal of azomethine proton from upfield in non-coordinated ligands (**2**: 8.58 ppm; **3**: 9.12 ppm as a doublet) to downfield in palladium complexes (**2a**: 7.69 ppm; **3a**: 8.23 ppm) as a singlet, due to back-bonding from the palladium centre, suggest the coordination of azomethine nitrogen to palladium metal.[25–27] The ligands show phosphorus coupling from the imine proton of the ligand in ^{1}H NMR spectra (4.6 Hz in **1**, 4.8 Hz in **2**, and 4.7 Hz in **3**), which points to a through-space coupling, indicating that the C*H*═N atom (C(7)H and C(25)H) is directed towards the lone pair of the phosphorus atom. In the ^{13}C NMR spectra, the methylene carbon appears as a doublet signal in the region 162.0–158.0 ppm (158.0 (20.4 Hz) (**2**), 159.4 (18.6) (**3**), 161.9 (8.6 Hz) (**2a**) and 162.0 ppm (8.8 Hz) (**3a**)) as expected. The coordination of the phosphorus donor to the metal centre is clear from the downfield shift of the ^{31}P{^{1}H} NMR signal compared to that of the free ligand which is approximately 40 ppm for the palladium complexes. From FT-IR analysis, the displacement of C═N stretching frequencies from 1634 (**2**) and 1645 (**3**) cm^{-1} for the free iminophosphine ligands to lower values of 1632 (**2a**) and 1632 (**3a**) cm^{-1} for the palladium complexes indicates the coordination of azomethine nitrogen to the Pd(II) centre. Microanalytical data for C, H and N of the Pd(II) complexes indicate that the metal-to-ligand ratio of the complexes is 1:1. Based on the elemental CHN analysis and FT-IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectral analysis, we suggest that the iminophosphine ligands act as PN-bidentate ligands and bond to the palladium atom through the azomethine nitrogen atom (C═N) and the phosphorus atom.

3.2 | Electrochemical characterization of synthesized complexes

Electrochemical characterization of the synthesized iminophosphine ligands (**1**, **2**, **3**) and their Pd(II) complexes (**1a**, **2a**, **3a**) was done using CV and SWV in an ACN–0.1 M TBAP solution system within the potential range − 1.5 to 1.5 V.

Figure 1 shows CV responses of ligand **1** and its Pd(II) complex **1a** on glassy carbon electrode with a 100 mV s^{-1} scan rate. The voltammogram of **1a** exhibited a wide oxidation peak and two reduction peaks. The anodic peak observed at anodic potentials was also observed in the CV curve of **1**. So these peaks were evaluated as ligand-based electrochemical processes and only cathodic side of the potential range is shown in the SWV plot (inset). Complex **1a** showed two cathodic peaks at −0.748 and −1.055 V, corresponding to the redox pairs Pd(II)/Pd(I) and Pd(I)/

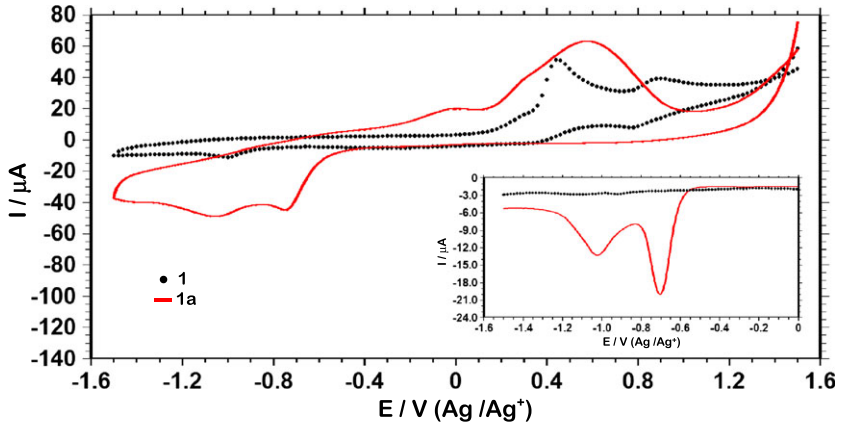


FIGURE 1 CV curves of 1 mM Schiff base ligand **1** and Pd(II) complex **1a** in 0.1 M TBAP–ACN on glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: SWV of **1** and **1a**; amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

Pd(0), respectively.[28,29] The second reduction peak was also related to the ligand-based reduction process in **1a**. There were no anodic reversible peaks on the reverse scan except a small oxidation peak at −0.041 V which is assigned to oxidation of Pd(I) to Pd(II). This process is the resultant of unstable Pd(II) + Pd(0) → 2Pd(I) reaction.[30] The data obtained from the CV traces of the Schiff base ligands and metal complexes are presented in Table 1.

The CV curves of **2a** (Figure 2) showed two irreversible redox processes during the negative scan. A comparison of the voltammetric responses of **2a** and **2** under the same potential region establishes that the first cathodic reduction peak at −1.030 V corresponds to **2**. The second reductive response at E_{pc} = −1.241 V and oxidation at E_{pa} = −1.139 V can be assigned to Pd(II) → Pd(I) reduction process. The observed $E_{1/2}$ value of the Pd(II)/Pd(I) redox pair is comparable to the value reported earlier.[31] The reduction of Pd(II) → Pd(I) is clearly observed from the SWV results at the inset.

The CV curves of Schiff base ligand **3** and Pd(II) complex **3a** are presented in Figure 3. The peaks in the negative potential region (0.0 to −1.5 V) related to **3** were also observed in the CV curve of **3a**. The inset shows the SWV curves of **3** and **3a**. The peak at −1.109 V is assigned to a quasi-reversible electrochemical response of Pd(II)/Pd(0) couple of **3a**, with potentials E_{pa} = −1.027 V and E_{pc} = −1.190 V. A weak peak observed at −0.231 V is related to Pd(I) → Pd(II) redox process. Formation of Pd(I) is explained with a subsequent proportionation process, Pd(0) + Pd(II) → 2Pd(I), in aprotic solvents. This behaviour is similar to that reported previously in CV studies of Pd(II) complexes.[32]

TABLE 1 Electrochemical parameters for Pd(II) complexes in 0.1 M TBAP–ACN solution

Compound	Redox couple	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)[a]	$E_{1/2}$ (V)[b]
1a	Pd(II)/Pd(I)	−0.748	−0.041	707	−0.395
	Pd(I)/Pd(0)	−1.055	—	—	—
2a	Pd(II)/Pd(I)	−1.241	−1.139	102	−1.190
3a	Pd(II)/Pd(0)	−1.190	−1.027	163	−1.109
	Pd(I)/Pd(II)	—	−0.231	—	—

[a]$\Delta E_p = E_{pa} - E_{pc}$.

[b]$E_{1/2} = (E_{pa} + E_{pc})/2$, v = 100 mV s^{-1}.

3.3 | Suzuki Carbonylation

The carbonylative cross-coupling reaction of iodobenzene with phenylboronic acid under an atmospheric pressure of carbon monoxide was chosen as a model reaction. The influences of various reaction parameters, such as solvent, catalyst loading, CO pressure and base, on the reaction were investigated.

Initially, the reaction was performed at 80 °C for 2 h in the presence of 1 mol% of catalyst (**1a**) with various bases (1.2 equiv.). The influence of base in the reaction was first examined and a significant effect of the base on the catalytic activity and yield was observed. Thus, when the reaction was carried out with K_2CO_3 as a base, 85% selectivity and 80% conversion were observed (Table 2, entry 5). Preliminary experiments showed that highly polar solvents, such as tetrahydrofuran (THF), 1,4-dioxane and ethanol, were required in order to obtain high reaction rates and yields (Table 2). The highest activity was obtained in 1,4-dioxane with K_2CO_3 as a base (Table 2, entry 5).

Entries 5, 6 and 7 of Table 2 show the effect of catalyst loading on the catalytic activity of complex **1a**. When 1 mol% of **1a** is used, 80% conversion and 85% selectivity are reached within 2 h of the reaction, while 75% conversion and 76% selectivity, and 74% conversion and 61% selectivity are reached in the same time when 0.4% and 0.2 mol%, respectively, are used. Comparing entries 5–7 of Table 2, substrate-to-catalyst ratio did not significantly decrease the conversion and selectivity when using 0.2% and 0.4 mol% catalyst. We also investigated the effect of the pressure of CO with pressures

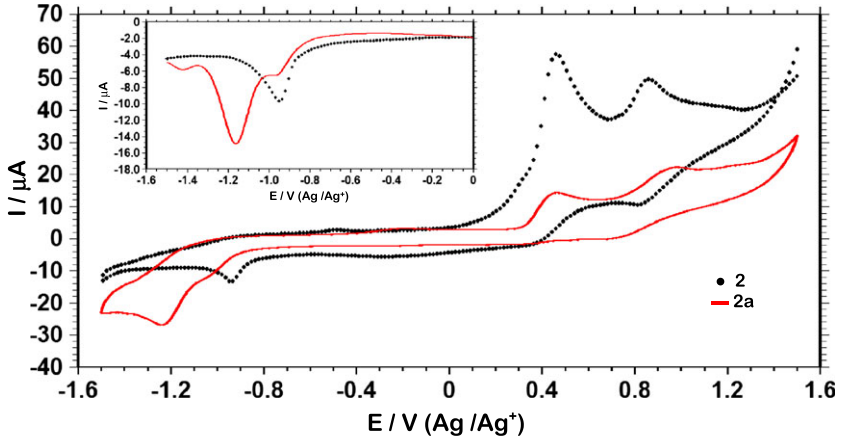


FIGURE 2 CV curves of 1 mM Schiff base ligand **2** and Pd(II) complex **2a** in 0.1 M TBAP–ACN on glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: SWV of **2** and **2a**; amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

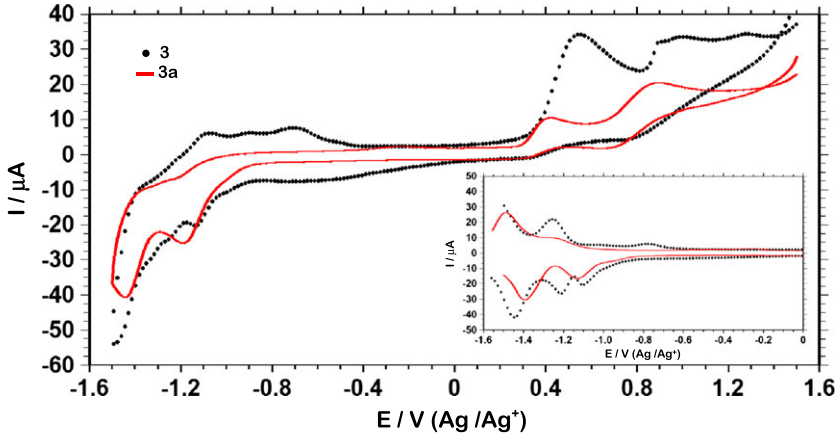
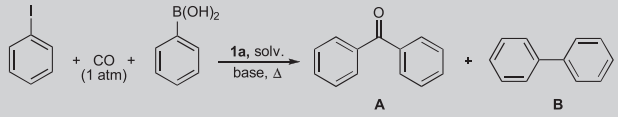


FIGURE 3 CV curves of 1 mM Schiff base ligand **3** and Pd(II) complex **3a** in TBAP–ACN on glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: SWV of **3** and **3a**; amplitude = 25 mV; frequency = 15 Hz; step potential = 4 mV)

TABLE 2 Effect of base, solvent and catalyst loading on Suzuki carbonylative coupling reaction of iodobenzene[a]



Entry	Solvent	Base	Conversion (%)[b]	Yield (A) (%)[b]	Yield (B) (%)[b]	Selectivity (A) (%)[c]
1	THF	Et_3N	63	4	5	45
2	1,4-Dioxane	Et_3N	64	5	-	100
3	Ethanol	Et_3N	79	4	4	50
4	THF	K_2CO_3	67	4	14	22
5	1,4-Dioxane	K_2CO_3	80	22	4	85
6	1,4-Dioxane	K_2CO_3 (S:C = 250)	75	19	6	76
7	1,4-Dioxane	K_2CO_3 (S:C = 500)	74 (75[d], 78[e])	17 (9[d], 8[e])	11 (3[d], 4[e])	61 (71[d], 68[e])
8	Ethanol	K_2CO_3	100	4	40	9
9	THF	Na_2CO_3	61	—	—	—
10	1,4-Dioxane	Na_2CO_3	60	5	—	100
11	Ethanol	Na_2CO_3	97	4	34	11
12	THF	K_3PO_4	58	—	—	—
13	1,4-Dioxane	K_3PO_4	69	4	5	45
14	Ethanol	K_3PO_4	64	—	—	—

[a]Iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol), solvent (4 mL), **1a** (0.01 mmol), 80 °C, 2 h.

[b]Mesitylene used as internal standard and coupled products analysed by GC–MS.

[c]Selectivity (A) (%) = 100 × Yield (A)/Yield (A + B).

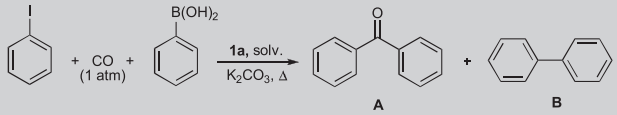
[d]CO (5 bar).

[e]CO (10 bar).

of 5 and 10 atm. However, when the CO pressure increased from 1 to 5 and 10 atm, the conversion of the reaction and the desired product selectivity did not increase obviously. Therefore, the Suzuki carbonylative coupling reaction was carried out with atmospheric pressure of CO, 0.2 mol% catalyst and K_2CO_3 in 1,4-dioxane at 80 °C.

To extend the scope of the reaction, water was also used for the Suzuki carbonylative coupling reaction, because water is a cheap, readily available nontoxic solvent and is environmentally friendly.[9] Therefore, we used water and water–1,4-dioxane solvent system for the Suzuki carbonlylative coupling reaction of iodobenzene and we also studied the effect of catalyst loading on the reaction (Table 3). It can be seen that both water and water–1,4-dioxane solvent system gave very poor selectivity of product compared to 1,4-dioxane. In addition, increasing the catalyst loading from 0.2 to 1.0 mol% did

TABLE 3 Effect of water on Suzuki carbonylative coupling reaction[a]



Entry	Solvent	S:C	Conversion (%)[b]	Yield (A) (%)[b]	Yield (B) (%)[b]	Selectivity (A) (%)[c]
1	H_2O	500	95	13	23	36
2	H_2O/1,4-dioxane	500	100	—	43	—
3	H_2O	100	97	13	20	40

[a]Iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol), solvent (4 mL), catalyst (**1a**), 80 °C, 2 h.

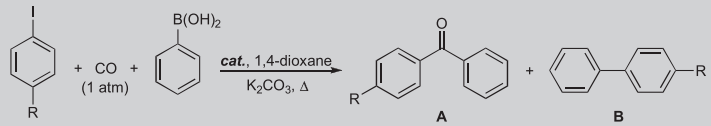
[b]Mesitylene used as internal standard and coupled products analysed by GC–MS.

[c]Selectivity (A) (%) = 100 × Yield (A)/Yield (A + B).

not improve the selectivity of the Suzuki carbonylative coupling product. As a result, we performed the coupling reaction of substituted aryl iodides in 1,4-dioxane as solvent.

After the optimized reaction conditions were identified for base and solvent, we also investigated the Suzuki carbonylative coupling of substituted aryl iodides with phenylboronic acid at 80 °C under balloon pressure of CO in 1,4-dioxane with the palladium catalysts (**1a**–**3a**). We found that when using **2a** as a catalyst it was possible to obtain 82% conversion and 89% selectivity with 4-fluoroiodobenzene after 2 h of the reaction (Table 4, entry 13). But the use of 4-iodotoluene as a substrate gave moderate conversion (64%) and 27% selectivity (entry 4). Similarly, the electron-rich aryl iodide 4-iodoanisole gave acceptable yield (60%) but with full selectivity (entry 11) in the presence of **3a** catalyst. However, when 4-nitroiodobenzene was used as a substrate no selectivity was found with any of the catalysts (entries 6–8). Moreover, the reaction of iodobenzene and phenylboronic acid catalysed by **2a** resulted in full selectivity in 2 h (entry 1).

TABLE 4 Suzuki carbonylative coupling reaction of substituted aryl iodides with catalysts **1a**–**3a**



Entry	R	Catalyst	Conversion (%)[b]	Yield (A) (%)[b]	Yield (B) (%)[b]	Selectivity (A) (%)[c]
1	H	**2a**	76	26	—	100
2	H	**3a**	72	5	22	19
3	4-CH_3	**1a**	35	—	26	—
4	4-CH_3	**2a**	64	9	24	27
5	4-CH_3	**3a**	44	—	26	—
6	4-NO_2	**1a**	76	—	29	—
7	4-NO_2	**2a**	73	—	34	—
8	4-NO_2	**3a**	75	—	32	—
9	4-OCH_3	**1a**	57	18	5	78
10	4-OCH_3	**2a**	56	19	9	68
11	4-OCH_3	**3a**	60	32	—	100
12	4-F	**1a**	72	18	5	78
13	4-F	**2a**	82	33	4	89
14	4-F	**3a**	77	32	4	89

[a]Aryl iodide (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (0.002 mmol), K_2CO_3 (1.2 mmol), 1,4-dioxane (4 mL), 80 °C, 2 h.

[b]Mesitylene as internal standard and coupled product analysed by GC–MS.

[c]Selectivity (A) (%) = 100 × Yield (A)/Yield (A + B).

4 | CONCLUSIONS

We have synthesized new iminophosphine–Pd(II) complexes and then characterized using NMR (^{1}H, ^{13}C, ^{31}P) and FT-IR techniques. Also, the electrochemical behaviour of the complexes was investigated and $E_{1/2}$ values of reversible redox processes were determined. *E*p values of irreversible processes have also been reported. We report the catalytic activity of the complexes in the carbonylative Suzuki coupling reaction of common aryl iodides with phenylboronic acid. Under our reaction conditions, we obtained good conversion and excellent selectivity when iodobenzene and 4-iodoanisole were used as substrates. It is noteworthy that these activities were observed with 0.02 mol% catalyst and under atmospheric pressure of carbon monoxide.

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SUPPORTING INFORMATION

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