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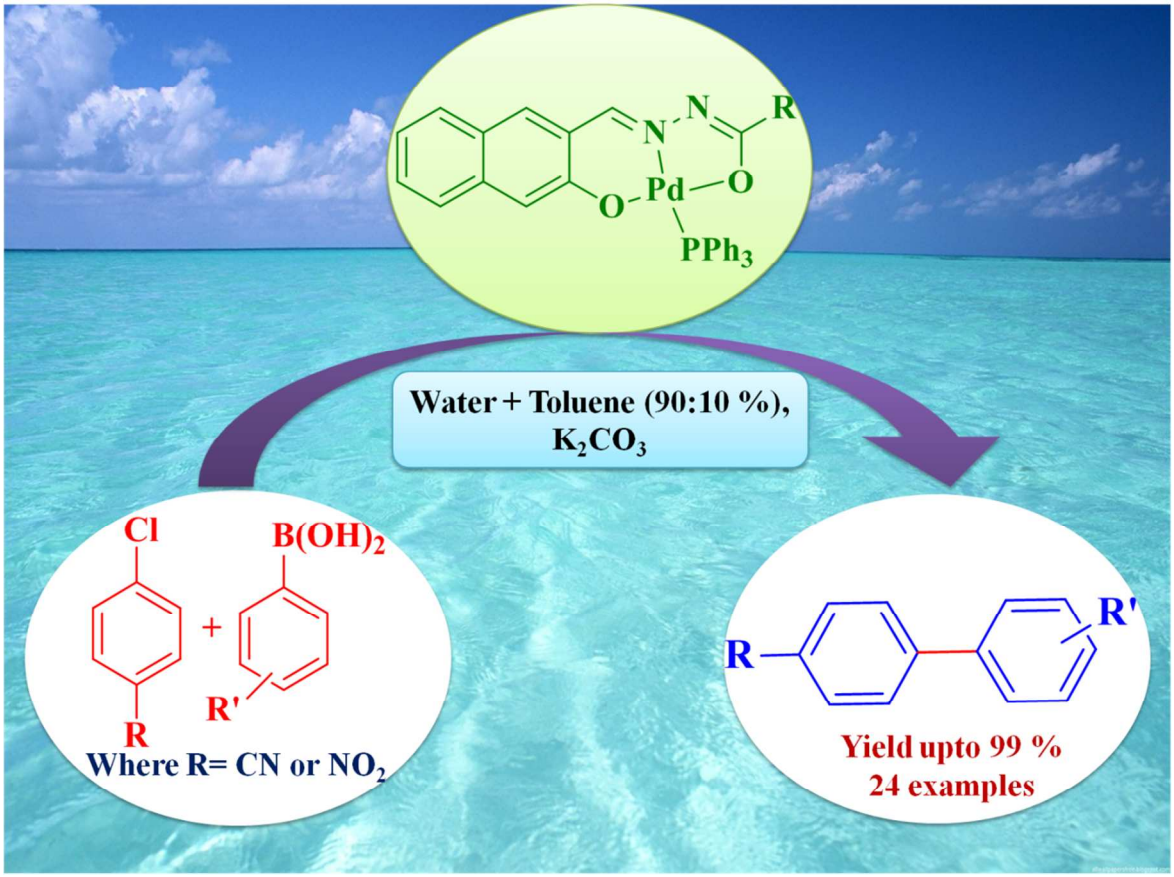
Robust and recyalble pincer type palladium(II) complexes for Suzuki-Miyaura coupling of challenging aryl chlorides in aqueous-organic media



# Palladium(II) complexes containing ONO tridentate hydrazone for Suzuki-Miyaura coupling of aryl chlorides in aqueous-organic media

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## Abstract

Facile synthesis of three new palladium(II) complexes bearing heterocyclic hydrazone ligands are presented along with their structural characterization using IR, $^{1}H$ and $^{13}C$ NMR spectra. Molecular structures of the complexes determined by single-crystal XRD revealed a distorted square-planner geometry around the metal ion to which the hydrazone was attached in a tridentate fashion. Catalytic activity of these complexes tested towards the Suzuki-Miyaura cross coupling reaction of substituted aryl boronic acids with aryl chlorides in water-toluene system (90:10%) without using any promoting additives or phase transfer agents, proved that they are highly active with 0.01 mol % loading under optimized conditions to afford 99% yield of the coupled product. Effects of temperature, solvent and base on the cross-coupling reaction were carried out as well. These complexes showed significant catalytic activity up to five cycles.

## Introduction

Transition metal-catalyzed C–C and C–X (X = heteroatom) bond forming reactions are a supreme tool in synthetic organic chemistry. The formation of C–C bonds were achieved by Kumada, Heck, Negshi, Suzuki-Miyaura, Hiyama, Sonogashira and Stille coupling reactions.[1] Among those, the palladium catalyzed Suzuki-Miyaura cross-coupling (SMC) reaction has triggered considerable enthusiasm in the synthetic chemistry community. SMC stands out as the most capable and helpful methodology for the synthesis of biphenyl derivative segments of numerous compounds such as pharmaceuticals, herbicides, natural products, polymers, organic electroluminescence materials and ligands.[2] It is widely utilized for C–C coupling reactions due to low toxicity of boronic acids, stability at ambient conditions and the facile removal of boron-containing side products. SMC reaction permits the utilization of organic solvents and inorganic bases, endures numerous other functional groups, unaffected by steric hindrance of the substrates and it's suitable for modern procedures.[3] The importance of palladium catalyzed cross-coupling reaction has been highlighted by the 2010 Nobel Prize in chemistry awarded to Professors Heck, Negishi and Suzuki.[4] Though wealth of information are available on both homogeneous and heterogeneous SMC reactions of aryl bromides or iodides with palladium catalysts,[5] relatively less is published with aryl chlorides as substrate due to the difficulty in the activation of C–Cl bond compared to C–Br or C–I bonds.[6]

Over a longer period, large number of palladium complexes bearing carbene, imine, oxime, phosphorus and other Schiff base ligands has been successfully employed for cross-coupling reactions.[7] In general, hydrazone is a class of Schiff base ligand that exhibits a wide range of analytical and biological applications.[8] Their transition metal complexes are well exploited as anticancer drugs and show great promise as chemotherapeutic agents.[9] In the recent years, hydrazone based palladium complexes emerge as a powerful catalytic system for the construction of C–C bond.[10]

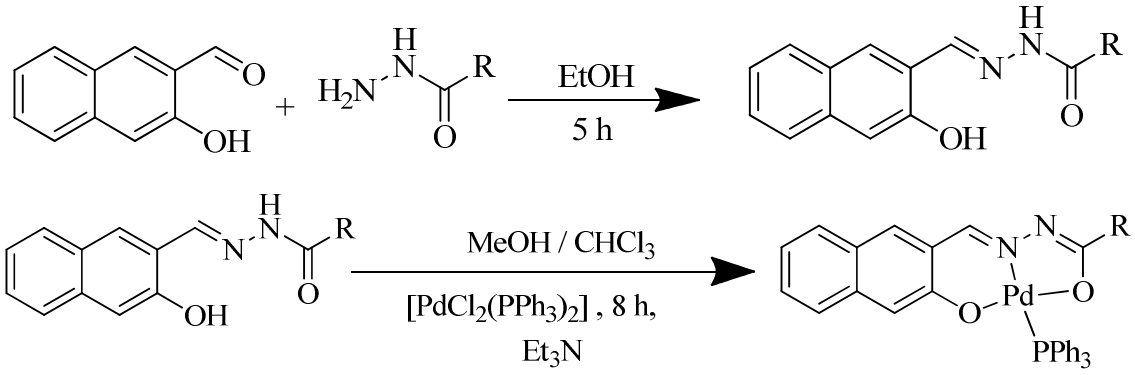
Pincer type palladium(II) complexes are widely utilized as a catalyst in coupling reactions.[11] The ONO tridentate heterocyclic hydrazone Pd(II) complexes may show similar behavior as their coordination mode is similar to that of pincer type complexes.[11] In our group, we are currently investigating the synthesis and biological applications of hydrazone based transition metal complexes.[9, 12] These complexes have shown promising biological activity and as part of our

continuing study into the versatility of hydrazone metal complexes,[12] we now turn our attention to evaluate some hydrazone containing palladium complexes as catalysts for the Suzuki-Miyaura coupling reaction.

Herein, we report the synthesis and structural characterization of three new palladium complexes bearing heterocyclic hydrazone ligands (furoichydrazone ($H_2L1$), thiopenehydrazone ($H_2L2$) and nicotinichydrazone ($H_2L3$)) and their catalytic activity towards SMC reaction of challenging aryl chlorides[13] with substituted aryl boronic acids in water-toluene media. To the best of our insight, utilizing palladium(II) complexes containing heterocyclic hydrzone ligand as catalysts for SMC reaction of aryl chlorides has not been published earlier.

**Results and discussion**

Reactions of palladium precursor $[PdCl_2(PPh_3)_2]$ with the heterocyclic hydrazones ($H_2L1$, $H_2L2$ and $H_2L3$) yielded complexes of the type $[Pd(L)(PPh_3)]$ as depicted in Scheme 1. Based on $^1H$, $^{13}C$ NMR and single-crystal XRD data, we observed that the hydrazone ligand is coordinated to the palladium ion in a tridentate fashion by replacing both the chloride ions and a molecule of triphenylphosphine from the starting precursor.




Where R = 2-furyl or 2-thiophenyl or 4-pyridyl

**Scheme 1** Synthetic route of ligands and their corresponding palladium complexes

The FT-IR spectra of the ligands $H_2L1$, $H_2L2$ and $H_2L3$ showed medium bands at 3442, 3399 and 3484 $cm^{-1}$ respectively, due to the presence of O−H group. Similarly, a strong band observed at 3046, 3090 and 3054 $cm^{-1}$ indicated the presence of N–H group in the free ligands. All the three ligands exhibited an intense C=O absorption at 1641, 1675 and 1613 $cm^{-1}$ respectively. In the spectra of complexes **1**, **2** and **3** absence of the strong band due to O−H indicated the deprotonation of naphthol oxygen and its coordination to palladium ion. The N–H and C=O stretching vibrations are also not observed in the spectra of complexes and thus proved that the ligand experienced a tautomerization and consequently coordinated via the imidolate oxygen to palladium(II) ion. In the spectra of palladium complexes **1**, **2** and **3** new bands were seen at 1526, 1577 and 1588 $cm^{-1}$ due to the occurrence of C=N−N=C group in addition to the appearance of a new, sharp band at 1185, 1186 and 1182 $cm^{-1}$ responsible for the C−O group. From the above discussed IR spectral features, it is clear that the hydrazones $H_2L1$, $H_2L2$ and $H_2L3$ were coordinated to palladium(II) ion via the naphtholate oxygen, the azomethine nitrogen and imidolate oxygen in complexes **1**, **2** and **3**.[14]

In order to confirm the coordination of hydrazone ligand in the new palladium complexes, $^{1}H$ & $^{13}C$ NMR spectra of complexes **1**, **2** and **3** were recorded. None of the complexes displayed any signal due to N−H proton revealed that an imidolate oxygen is coordinated to the palladium ion. Similarly, the non-existence of any resonance attributable to the O−H group of naphthalene ring revealed a deprotonation prior to its coordination to palladium ion in the complexes **1**, **2** and **3**. Sharp singlets found at δ 9.4, 8.5 and 8.9 ppm were assigned as due to that of azomethine proton of the coordinated hydrazone in the respective complexes. All the aromatic protons of coordinated triphenylphosphine and hydrazone of the palladium complexes (**1, 2** and **3**) showed their resonances in the region of δ 7.2 – 8.2 ppm. The $^{13}C$ NMR spectra of all the Pd(II) complexes displayed signals at δ 164.2, 160.0 and 165.4, ppm respectively owing to the imidolate carbon (N=C–O) involved in the coordination. The signal corresponding to the azomethine carbon of the hydrazone in complexes **1**, **2** and **3** were shifted downfield and appeared at δ 163.1, 147.2 and 160.0 ppm respectively. The signals appeared in the region of δ 110.6 –147.2 ppm were accounted to various aromatic carbons of the hydrazone as well as tripenylphosphine ligands of complexes **1**, **2** and **3**.[15]

The molecular structure of complexes **1**, **2** and **3** were determined by single-crystal X-ray diffraction in order to identify the exact coordination mode of hydrazone ligands in the newly synthesized complexes. All the complexes tested here crystallize in a primitive monoclinic system, space group $P2_1/n$. The ORTEP diagrams (Fig.1-3) reveal that the hydrazone ligand is coordinated to the palladium ion in a tridentate manner via the naphtholate oxygen, azomethine nitrogen and the deprotonated imidol, each forming five membered and six membered chelate rings. The Pd(II) ion adopted a distorted square-planar geometry satisfied by the hydrazone ligand as binegative tridentate ONO donor and the fourth site is occupied by a triphenylphosphine. The bond lengths and bite angles are very similar to those observed for other palladium(II) complexes.[16] The bite angles (°) around Pd(II) ion in the complexes **1**, **2** and **3** are N(1) – Pd(1) – O(1) = 93.86 (6), 93.21 (5) and 93.27 (10) respectively. Similarly, N(1) – Pd(1) – O(2) = 80. 26 (6), 80.72 (5), 80.24 (10) ; O(1) – Pd(1) – O(2) = 173.64 (6), 173.89 (4), 173.50 (9) and N(1) – Pd(1) – P(1) = 178.52 (5), 175.52 (4), 178.83 (8) respectively (Table 1 in the ESI).[16] The Pd – N(1), Pd – O(1) and Pd(1) – O(2) bond length (Å) of the complexes **1**, **2** and **3** are within the range reported for palladium complexes[16] Pd(1) – N(1) = 1.9674 (16), 1.9638 (12), 1.9720 (3); Pd(1) – P(1) = 2.2956 (5), 2.2743 (5), 2.2996 (9) respectively. In all the complexes, the length of C(12) – O(2) bond is shorter when compared to C(3) – O(1) bond (Table 1 in the ESI). The shortening of the above bond is due to the deprotonation of imidol group to coordinate with palladium ion in all the complexes.[17] Selected bond angles and bond lengths are gathered in Table 1 in the ESI. Details on the data collection and structure refinements are summarized in Table 2 in the ESI.

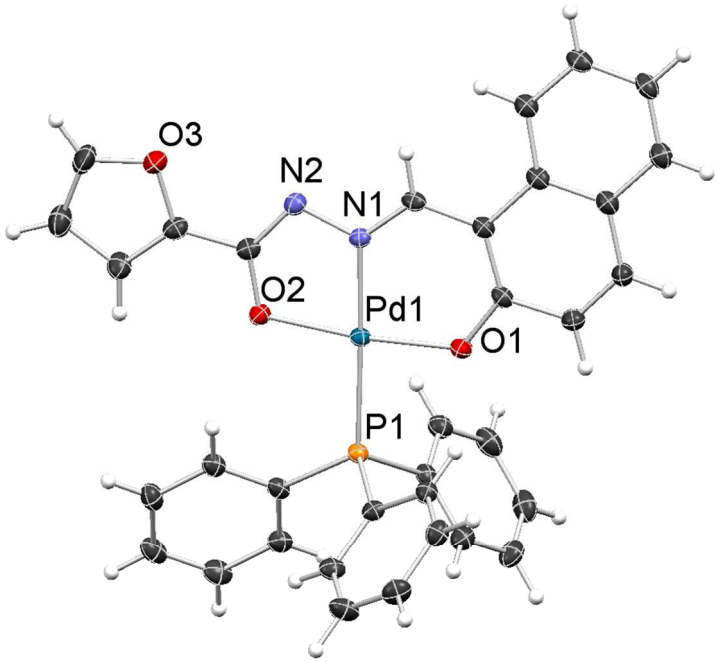



**Fig. 1** ORTEP diagram of complex **1**; displacement parameters at their 50% probability level.

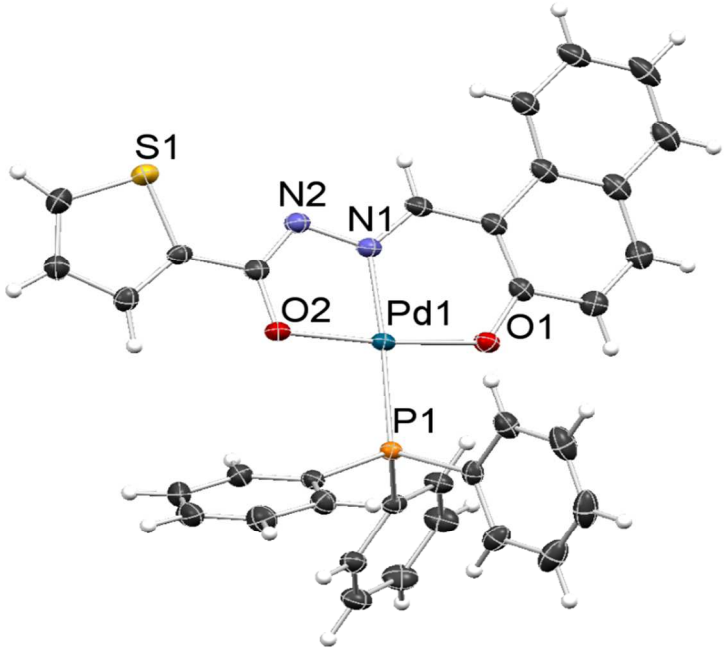



**Fig. 2** ORTEP diagram of complex **2**; displacement parameters at their 50% probability level.

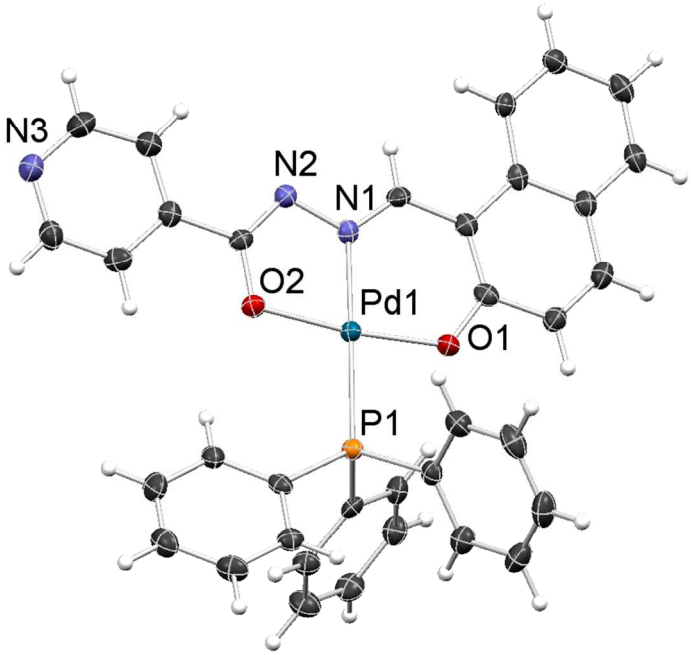



**Fig. 3** ORTEP diagram of complex **3**; displacement parameters at their 50% probability level.

Investigation on the catalytic activity of above synthesized Pd(II) complexes were performed against *p*-cholorobenzonitrile and 1-chloro-4-nitro-benzene with substituted aryl boronic acids in the presence of catalyst, inorganic base and solvent. Previous reports on the coupling reactions using *p*-cholorobenzonitrile and 1-chloro-4-nitro-benzene revealed that it was difficult to activate C–Cl bonds in them.[6] Hence, we selected the challenging aryl chlorides[13] namely, *p*-cholorobenzonitrile and 1-chloro-4-nitro-benzene for SMC with substituted aryl boronic acids in presence of the new palladium complexes as homogeneous catalysts.

Our investigations commenced with optimization of reaction conditions. For this purpose, *p*-chlorobenzonitrile (3 mmol) and phenylboronic acid (4 mmol) were used as model substrates in the presence of complex **2** as a catalyst (0.01 mol %). Various inorganic and organic bases listed in the Table 1 were surveyed identifying $K_2CO_3$ as a suitable base to increase yield (Table 1, entries 2–9). In our attempt to perform this coupling reaction in neat water, no progress was observed due to the fact that the catalyst is insoluble (Table 1, entry 1). Hence, we included some organic solvents to dissolve the catalyst in the reaction media. The impact of different polar and non-polar solvents on the yield of coupling reaction has been considered (Table 1, entries 10–

17). Amongst the solvents examined, water-toluene mixture gave the best yield (Table 1, entry 11). Further, various ratios of water-toluene mixtures were analyzed, a ratio of 90:10% giving better yield (Table 1, entries 18–22). When the SMC reaction was carried out in room-temperature, the yield of coupled product was only 15% after 19 h. However, upon raising the temperature from 50 to 110 °C, maximum yield was obtained at 90 °C (94%) after 10 h followed by a decrease in the yield at 100 and 110 °C to 87 and 76%, respectively. Further heating to 120 °C had no influence on the quantity of the coupled product (Fig. 4).

Among the catalysts (Table 1, entries 23–25), complex **1** showed superior catalytic activity towards SMC reaction of a series of aryl boronic acids with two different aryl chlorides. The higher catalytic potential of complex **1** is attributed to the presence of a furyl moiety at the terminal carbon of the coordinated hydrazone ligand.[18 a] In general, phosphine ligands like triphenylphosphine, phosphanes, phosphane oxides bearing Pd complexes help to activate C–Cl bonds in electron-deficient and electron-rich aryl chlorides.[18 b]

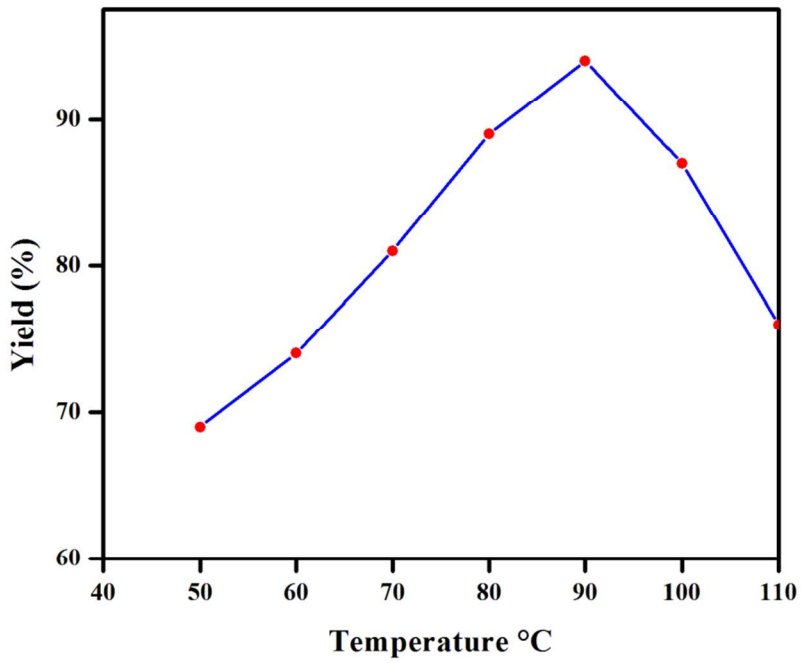
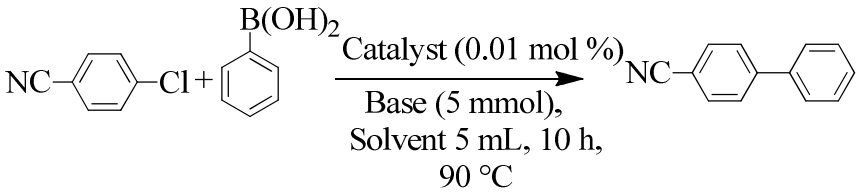



**Fig. 4** Effect of temperature on the SMC reaction.

**Table 1** Optimization of reaction conditions




| Entry | Catalyst | Base | Solvent | Yield (%) |
|---|---|---|---|---|
| 1 | Complex 2 | No base | $H_2O$ | No reaction |
| 2 | Complex 2 | No base | $H_2O$ / benzene | 12 |
| 3 | Complex 2 | KOH | $H_2O$ / benzene | 76 |
| 4 | Complex 2 | $K_2CO_3$ | $H_2O$ / benzene | 89 |
| 5 | Complex 2 | NaOH | $H_2O$ / benzene | 81 |
| 6 | Complex 2 | $Na_2CO_3$ | $H_2O$ / benzene | 83 |
| 7 | Complex 2 | $CH_3COONa$ | $H_2O$ / benzene | 40 |
| 8 | Complex 2 | $Et_3N$ | $H_2O$ / benzene | 25 |
| 9 | Complex 2 | Pyridine | $H_2O$ / benzene | 16 |
| 10 | Complex 2 | $K_2CO_3$ | $H_2O$ / benzene | 89 |
| 11 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene | 92 |
| 12 | Complex 2 | $K_2CO_3$ | $H_2O$ / $CHCl_3$ | 65 |
| 13 | Complex 2 | $K_2CO_3$ | $H_2O$ / DMF | 63 |
| 14 | Complex 2 | $K_2CO_3$ | $H_2O$ / $CH_3CN$ | 60 |
| 15 | Complex 2 | $K_2CO_3$ | $H_2O$ / THF | 18 |
| 16 | Complex 2 | $K_2CO_3$ | $H_2O$ / DMSO | 35 |
| 17 | Complex 2 | $K_2CO_3$ | $H_2O$ / *n*-propanol | 22 |

| | | | | |
|---|---|---|---|---|
| 18 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (10 %) | 94 |
| 19 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (20 %) | 92 |
| 20 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (30 %) | 85 |
| 21 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (40 %) | 81 |
| 22 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (50 %) | 76 |
| 23 | Complex 1 | $K_2CO_3$ | $H_2O$ / toluene (10 %) | 98 |
| 24 | Complex 2 | $K_2CO_3$ | $H_2O$ / toluene (10 %) | 92 |
| 25 | Complex 3 | $K_2CO_3$ | $H_2O$ / toluene (10 %) | 89 |

Low catalyst stacking tests (Table 2, entries 1–3) showed best execution utilizing 0.01 mol % of complex **1**. Reducing catalyst stacking from 0.01 – 0.0001 mol % under optimized conditions resulted in low yield in accordance with previous reports.[19] Utilizing 0.0001 mol % of catalyst increased turnover.

**Table 2** Effect of low catalyst stacking on SMC reaction

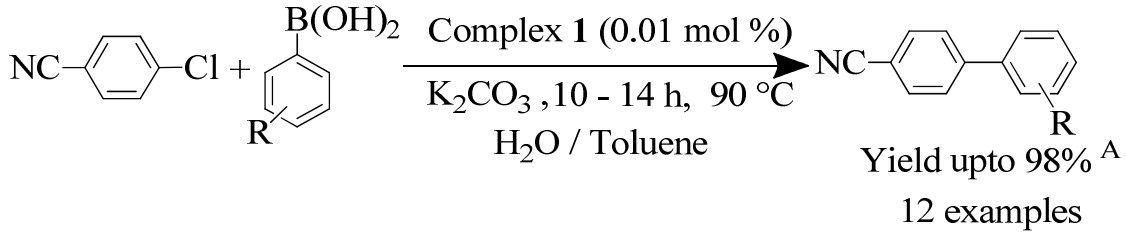
| Entry | Catalyst (mol %) | Yield (%) | TON |
|---|---|---|---|
| 1 | 0.01 | 98 | 9,800 |
| 2 | 0.001 | 90 | 90,000 |
| 3 | 0.0001 | 71 | 710,000 |

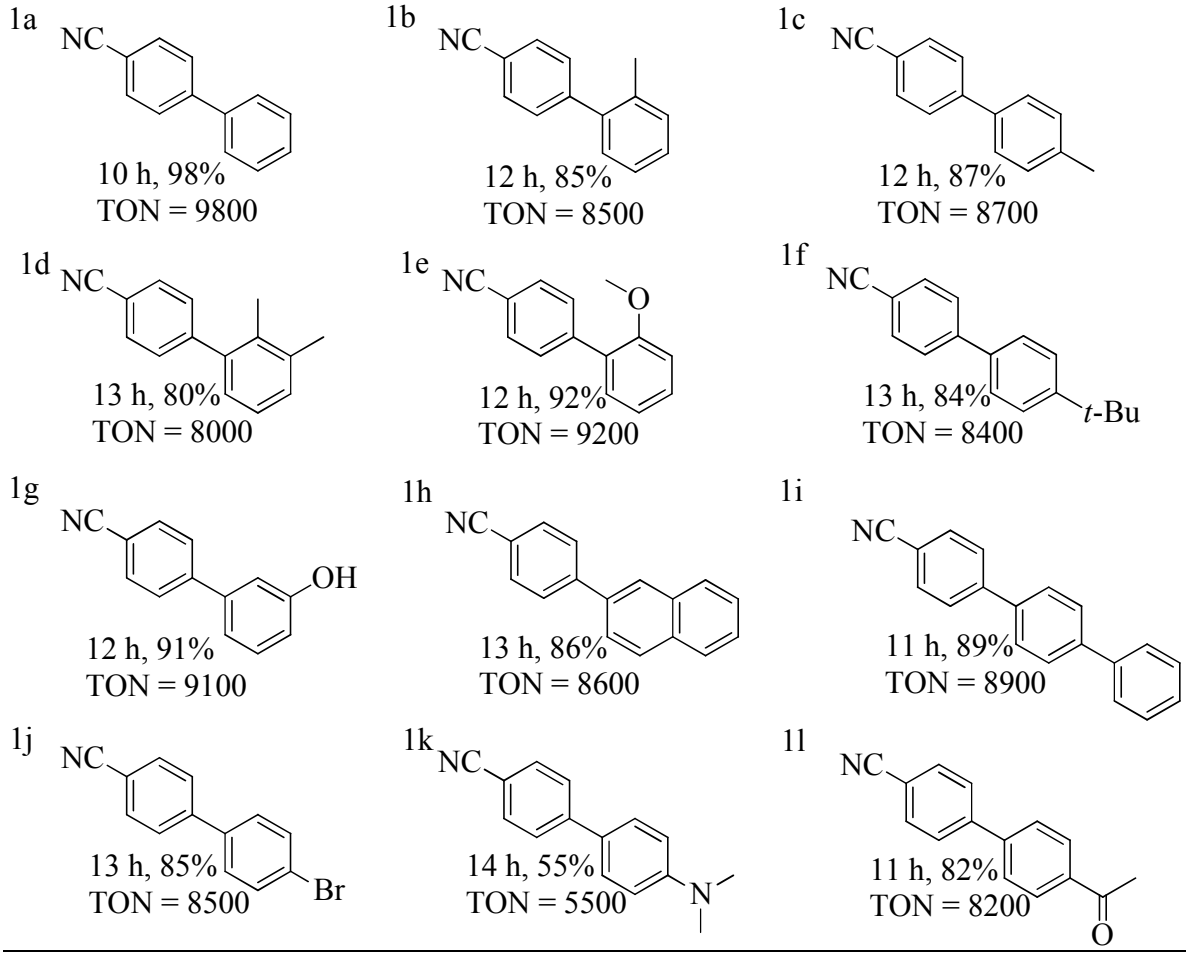
With the optimized reaction conditions in hand, we examined the scope of the SMC reaction of *p*-chlorobenzonitrile with diverse aryl boronic acids with catalyst **1** (0.01 mol %) (Table 3). Here, *p*-chlorobenzonitrile featuring a moderately deactivating nitrile group, is an ideal coupling partner for SMC reaction, while the other coupling partner aryl boronic acid bears both electron donating and withdrawing groups. Aryl boronic acids having deactivating groups such as –Br, –$COCH_3$, produce good yields within 10–14 h (Table 3, entries 1j and 1l). In the case of aryl boronic acids with activating groups such as –$CH_3$, –$OCH_3$, *t*–$(CH_3)_3C$–, –OH, and –$NR_2$, a yield of 55–92% were achieved (Table 3, entries 1c, 1e, 1f, 1g and 1k,). Remarkably, sterically demanding aryl boronic acids were also smoothly converted to the corresponding products in

85–90% yield (Table 3, entries 1c, 1h, and 1i). Gratifyingly, the coupling reaction was also operative for aryl boronic acid with high steric hindrances at a 80–85% yield (Table 3, entries 1b, 1d and 1e).

Encouraged by these results, we next performed the SMC reaction of 1-chloro-4-nitro-benzene as one of the partners instead of *p*-chlorobenzonitrile considering the fact that the former aryl chloride is also a challenging substrate possessing a strongly deactivating $NO_2$ group at *para* position.[13] Reaction conditions were very similar to those optimized for *p*-chlorobezonitrile except that the nitro substituted aryl chloride was reactive enough to couple with aryl boronic acids at room-temperature within 4–7 min. Coupling with aryl boronic acids containing both activating and deactivating groups were proceeded smoothly (Table 4 entries 2a–2l).

**Table 3** SMC reaction of *p*-chlorobenzonitrile with substituted aryl boronic acids using complex **1** as catalyst.

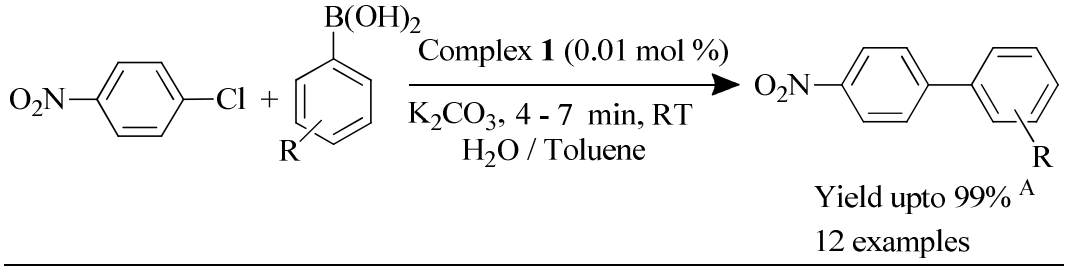


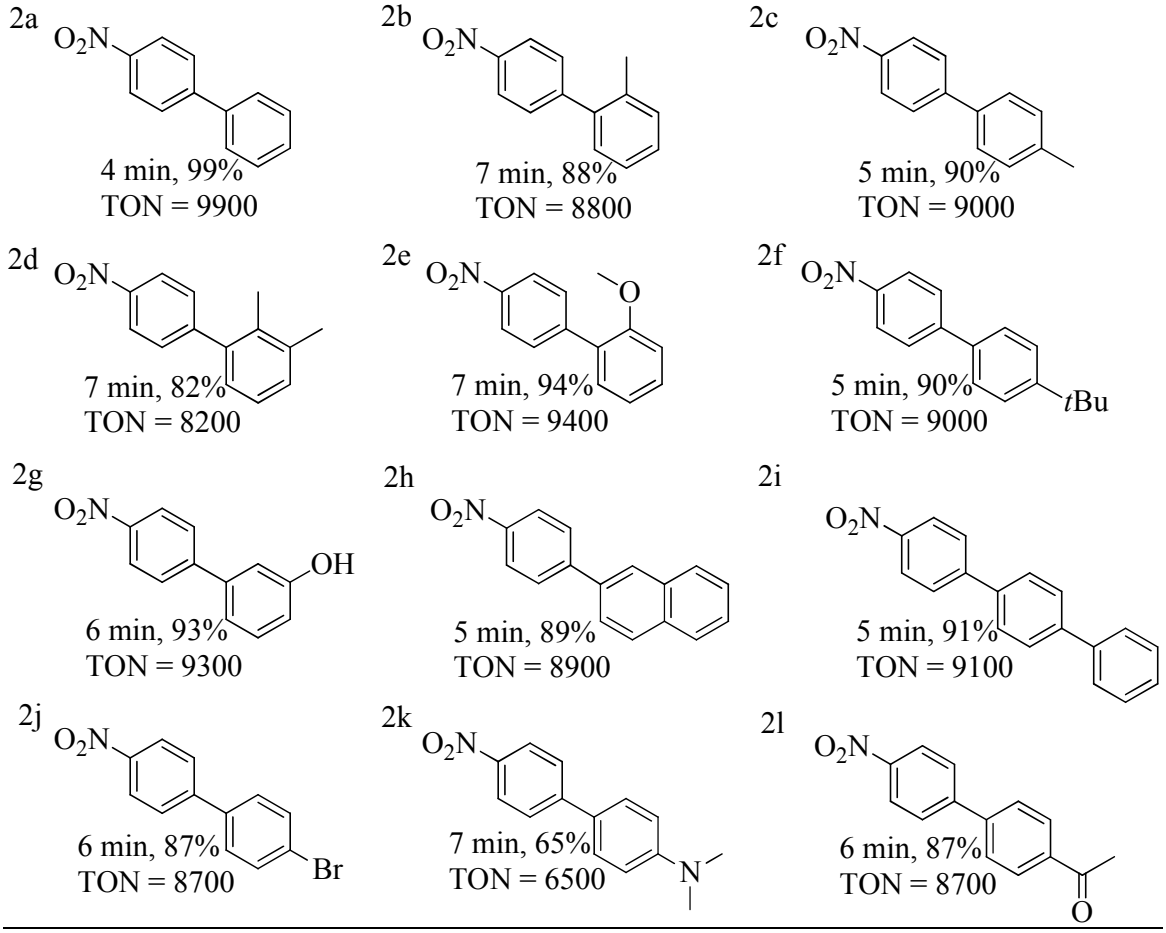




Reaction conditions: *p*-chlorobenzonitrile (3.0 mmol), aryl boronic acid (4.0 mmol), 0.01 mol % of complex **1**, $K_2CO_3$ (5.0 mmol), $H_2O$ (4.5 mL) and toluene (0.5 mL) stirred for 10–14 h at 90 °C.

[A] Isolated yield after column chromatography, TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

**Table 4** SMC reaction of 1-chloro-4-nitro-benzene with substituted aryl boronic acids using complex **1** as catalyst.



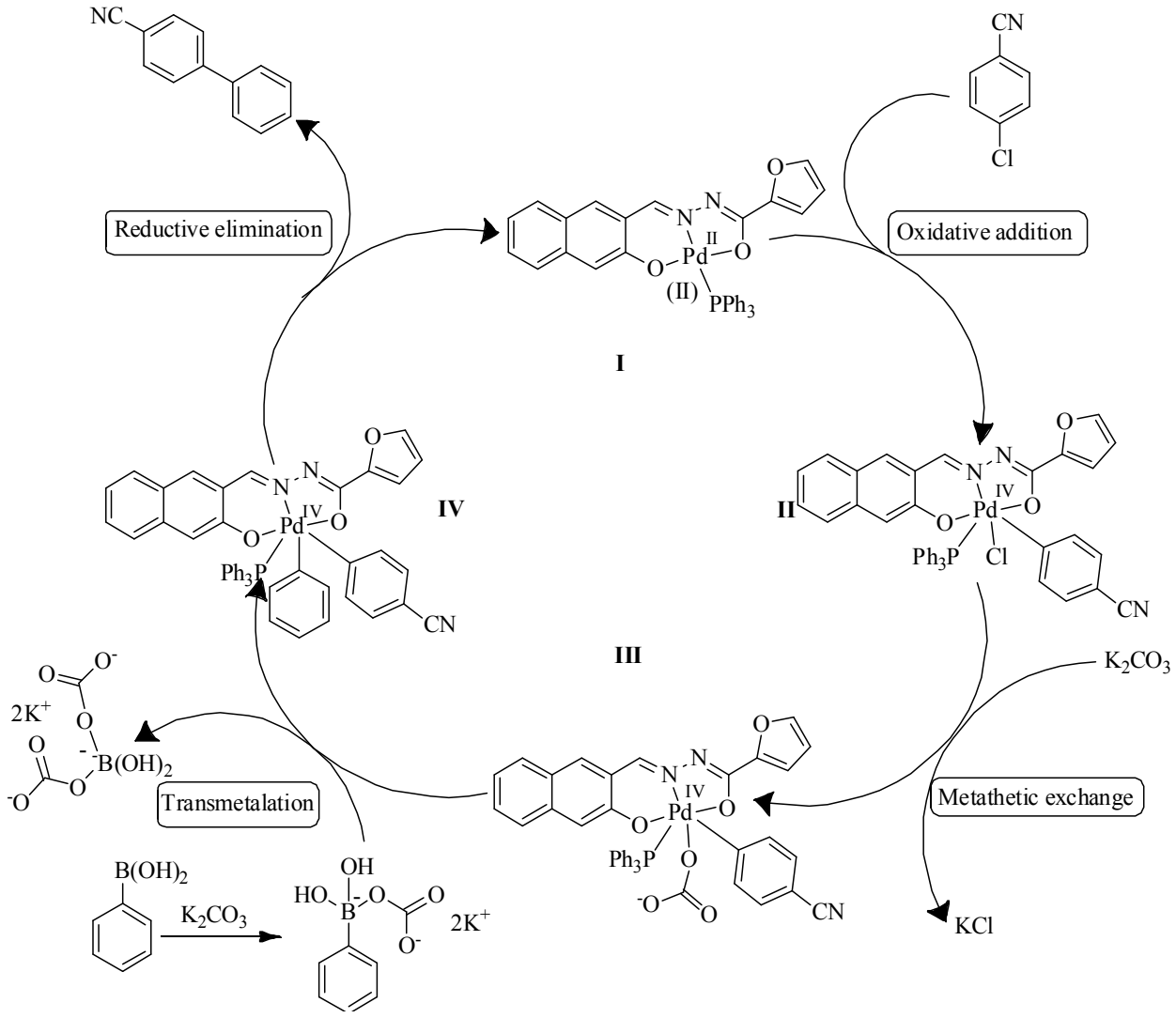




Reaction conditions: 1-chloro-4-nitro-benzene (3.0 mmol), aryl boronic acid (4.0 mmol), 0.01 mol % of complex **1**, $K_2CO_3$ (5.0 mmol), $H_2O$ (4.5 mL) and toluene (0.5 mL) stirred for 4–7 min. at room-temperature.

[A] Isolated yield after column chromatography, TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

**Mechanism for the SMC reaction**

Generally, pincer type ligand can increase the electron density at palladium(II) centre and facilitate the generation of Pd(IV) species. Therefore, Pd(IV) intermediates are considered as reactive intermediates in the mechanism of the SMC reaction of aryl halides at higher temperature.[11, 20 a] Advantageously, Pd(II)/Pd(IV) cycle helps facile reductive elimination from Pd(IV) intermediate. However, Pd(IV) intermediates are unstable and hence, it can't be isolated.[20 a] Based on these facts and previous reports,[20 b, c] a possible mechanism for SMC reaction was proposed in Scheme 2. The active species, palladium(II) hydrazone complex underwent the oxidative addition of *p*-chlorobenzonitrile to give an intermediate II. Addition of base to an intermediate II triggered a metathetic process to generate an intermediate III. Transmetallation of phenylboronic acid to an intermediate III produced an intermediate IV which on reductive elimination gave the desired cyanobiphenyls followed by the regeneration of Pd(II) active species. The mechanism for the SMC reaction involving 1-chloro-4-nitro-benzene and aryl boronic acids is very similar to the one depicted in Scheme 2.




**Scheme 2** Plausible mechanism for SMC reaction of *p*-chlorobenzonitrile with phenylboronic acid.

## Reusability of catalyst

Recovery and reusability of the catalyst was studied in a reaction that involved *p*-chlorobenzonitrile (3.0 mmol), phenylboronic acid (4 mmol), $K_2CO_3$ (5 mmol) and catalyst (0.01 mol %) in water-toluene (4.5-0.5 mL) at 90 °C. After completion of the reaction, the mixture was extracted with ethyl acetate to separate the catalyst and the product by column chromatography.

The recovered catalyst was dried and utilized for the next cycle under the same reaction conditions. Though a marginal decrease in the catalytic activity of the selected complex **1** was observed upon moving from the first to fifth cycle, there occurred a significant loss in its performance after the fifth cycle and yielded only 45% of the coupled product in the sixth cycle (Fig. 5). The identity of the catalyst after the reaction was confirmed by comparing its physical data (melting point and $R_f$ value) with the original complex.

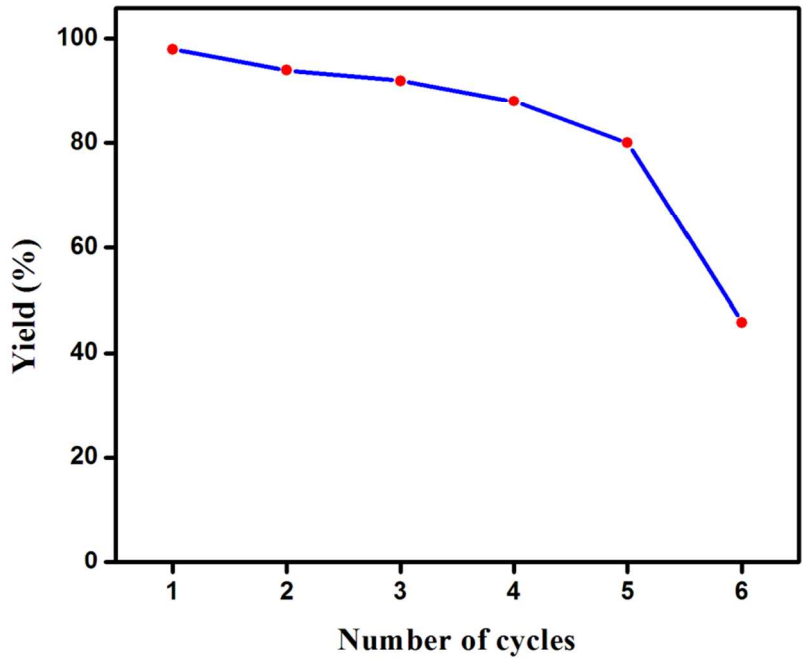



**Fig. 5** Reusability of catalyst **1**

H.M Lee *et al* reported recently [21] that zwitter ionic phosphine complexes were highly efficient at room-temperature for SMC reactions between sterically hindered aryl chloride and aryl boronic acids in an aqueous media. 94% of products were reported for the coupling reaction between *p*-chlorobenzonitrile and phenylboronic acid during 7 h. However, in the present report, we achieved 98% of the coupled product from the same substrates in 10 h by utilizing the newly synthesized palladium(II)-hydrazone complex **1** as a catalyst with comparably low catalyst loading.

## Conclusion

This study presented the synthesis and spectral characterization of three new palladium(II) complexes bearing heterocyclic hydrazone ligands. X-ray diffraction data of all these complexes

confirmed a distorted square-planar geometry around palladium(II) ion satisfied by ONO tridentate coordination of hydrazone ligands and a triphenylphosphine as a fourth ligand. One of the new complexes acted as a fabulous catalyst for Suzuki-Miyaura coupling of *p*-chlorobenzonitrile or 1-chloro-4-nitro-benzene with substituted aryl boronic acids in water-toluene media. Extension of the scope of this catalyst to aryl boronic acids possessing a range of functional groups attested that a smooth coupling occurred in all the cases under optimized conditions without the formation of either homocoupled products of boronic acids or coupling at the hydroxyl group present in boronic acid. Hence, we believe that this methodology involving a robust palladium based homogeneous catalyst towards the Suzuki-Miyaura coupling offers a novel route to synthesis a series of substituted biaryl segments.

## Experimental procedure

**Reagents and materials.** All reagent grade chemicals were used without further purification unless otherwise specifically mentioned. Solvents were purified and dried according to standard procedures.[22] Elemental analysis (C, H, N and S) were performed on a Vario EL III Elemental analyzer instrument. IR spectra (4000–400 $cm^{-1}$) were recorded on a Nicolet Avatar Model FT-IR spectrophotometer. Melting points were determined with a Lab India instrument. $^{1}H$ and $^{13}C$ NMR spectra were recorded in deuterated $CHCl_3$ as solvent on BRUKER 400 and 100 MHZ instruments, respectively.

## Synthesis of the ligands

Pincer type heterocyclic hydrazone ligands ($H_2L$) were synthesized by condensing equimolar amounts of *o*-hydroxy napthaldehyde with diverse hydrazides such as furoic acid hydrazide ($H_2L1$), thiophenecarboxylic acid hydrazide ($H_2L2$) and nicotinic acid hydrazide ($H_2L3$) in ethanol according to a literature method (Scheme 1).[9(b)] The reaction mixture was then refluxed on a water bath for 5 h and poured into crushed ice. The corresponding solid hydrazone formed was filtered, washed several times with distilled water and recrystallized from ethanol with 85–90% yield. The purity of the ligands were checked by various analytical techniques and is in accordance with literature reports.[9(b)]

**Synthesis of palladium complexes [Pd(L1)($PPh_3$)] (1)**

A solution of [$PdCl_2(PPh_3)_2$] (0.100 g, 143 mM) in chloroform (20 $cm^3$) was added drop wise to the hot methanolic (15 $cm^3$) solution of ligand $H_2L1$ (0.40 g, 143 mM) and two drops of triethylamine were added. The reaction mixture was refluxed for 8 h and thereafter kept at room-temperature for crystallization. Red colored crystal needles suitable for X-ray studies were obtained on slow evaporation of the reaction mixture over of 45 days. Yield: 85%, mp: 241−243 °C. Elemental analysis calculated for (%): $C_{34}$ $H_{25}$ $N_2$ $O_3P$ Pd: C, 63.12; H, 3.89; N, 4.33. Found (%) C, 62.98; H, 3.44; N, 4.01. UV-visible (solvent: DMSO, nm): 319, 327, 383 and 425. Selected IR bands (KBr, ν in $cm^{-1}$): 1605 (imidolate N=C–O), 1526 (C=N) and 1185 (naphtholate C–O). $^1$H NMR ($CDCl_3$, δ ppm) 9.42 (s, 1H), 8.45 (d, *J* = 8 Hz, 4H), 8.29 (dd, *J* = 1.2, 1.2 Hz, 3H), 8.01 − 8.03 (m, 3H), 7.97 (d, *J* = 1.2 Hz, 5H), 7.84 (t, *J* = 7.8 Hz, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.36 − 7.40 (m, 4H).$^{13}$C NMR ($CDCl_3$, δ ppm) 164.2, 146.4, 136.5, 129.9, 128.7, 127.4, 127.3, 126.8, 125.7, 119.9, 118.5, 115.0, 114.8.

**Synthesis of [Pd(L2)($PPh_3$)] (2)**

Complex **2** was prepared by the same procedure as that described for complex **1** with $H_2L2$ (0.42 g, 0.143 mM) and [$PdCl_2(PPh_3)_2$] (0.100 g, 0.143 mM). Red colored crystals of the product were obtained on slow evaporation of the reaction mixture over the period of two months. The crystals obtained were suitable for X-ray diffraction. Yield: 80%, mp: 261−264 °C. Elemental analysis calculated for (%): $C_{34}$ $H_{25}$ $N_2$ $O_2$ P Pd S: C, 61.59; H, 3.80; N, 4.23; S, 4.84. Found (%) C, 61.02; H, 3.34; N, 4.05; S, 4.26. UV-visible (solvent: DMSO, nm): 266, 328, 376 and 444. IR bands (KBr, ν in $cm^{-1}$): 1776 (imidolate N=C–O), 1588 (C=N) and 1186 (naphtholate C–O). $^1$H NMR ($CDCl_3$, δ ppm) 8.57 (s, 1H), 8.14 (s, 6H), 8.02 − 8.08 (m, 7H), 7.99 (d, *J* = 7.2 Hz, 4H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 4 Hz, 2H), 7.40 − 7.56 (m, 3H). $^{13}$C NMR ($CDCl_3$, δ ppm) 160.0, 147.2, 135.9, 136.5, 129.6, 129.0, 128.6, 120.4, 118.1, 116.7, 114.4, 110.6.

**Synthesis of [Pd(L3)($PPh_3$)] (3)**

Complex **3** was prepared using the same procedure as described for **1** by the reaction of $H_2L3$ (0.42 g, 0.143 mM) and [$PdCl_2(PPh_3)_2$] (0.100 g, 0.143 mM). After the completion of reaction the solute was kept at room-temperature. Needle shape orange crystals of X-ray diffraction quality were obtained after 50 days. Yield: 79 %. mp: 254 − 257 °C. Elemental

analysis calculated for (%): $C_{35}$ $H_{26}$ $N_3$ $O_2$ P Pd : C, 63.89; H, 3.98; N, 6.39. Found (%) C, 63.15; H, 3.22; N, 6.16. UV-visible (solvent: DMSO, nm): 308, 340, 370 and 420. IR bands (KBr, ν in $cm^{-1}$): 1693 (imidolate N=C–O), 1577 (C=N), 1182 (naphtholate C–O) and 501(C=N in ring). $^1$H NMR ($CDCl_3$, δ ppm) 8.92 (s, 1H), 8.21 (s, 2H), 8.01 – 8.04 (t, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 5.6 Hz, 8H), 7.77 (d, *J* = 2.8 Hz, 3H), 7.55 (t, *J* = 6.4 Hz, 4H), 7.46 (t, *J* = 3.6 Hz, 3H), 7.23 – 7.29 (m, 3H). $^{13}$C NMR ($CDCl_3$, δ ppm) 165.4, 160.0, 148.23, 135.9, 131.5, 129.9, 129.7, 128.7, 121.4, 117.7, 115.4, 112. 8.

**Single-crystal X-ray diffraction studies**

**Data collection:** Single-crystal X-ray diffraction data of complexes **1, 2** and **3** were collected on Bruker APEX II single-crystal X-ray diffractometer. The data was integrated and scaled using SAINT / SADABS from within the APEX2 software package by Bruker (Version 2.1-4). Indexing and unit cell refinement indicated a primitive monoclinic lattices in all three complexes with space group $P2_1/n$. Solution by direct methods (SHELXS, SIR97)[23] produced a complete heavy atom phasing models consistent with the proposed structures. The structure was completed by difference Fourier synthesis with SHELXL97.[24, 25] Scattering factors are from Waasmair and Kirfel[26] Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Å. Isotropic thermal parameters Ueq were fixed such that they were 1.2 Ueq of their parent atom Ueq for CH's and 1.5 Ueq of their parent atom Ueq in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

**Catalysis**

**General procedure for Suzuki-Miyaura C–C coupling reactions**

Pd(II) hydrazone complex **1** (0.01 mol %) in toluene (0.5 mL) was added to a mixture of *p*-chlorobenzonitrile or 1-chloro-4-nitro-benzene (3.0 mmol) and aryl boronic acid (4 mmol), $K_2CO_3$ (5 mmol) in water (4.5 mL) taken in a 20-mL round bottom flask. After stirring for 10–14 h at 90 °C or 4–7 min. at room-temperature, the reaction mixture was cooled. The mixture was extracted with ethyl acetate to separate the catalyst and the product by column chromatography method. The identity of the coupled products were confirmed by $^1$H and $^{13}$C NMR data (See ESI).

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