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Phosphine free diamino-diol based palladium catalysts and their application in Suzuki–Miyaura cross-coupling reactions

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ABSTRACT

Inexpensive air and moisture stable diamino-diol ligands [(2-OH-$C_{10}H_6$)CH_2(μ-NC_4H_8N)CH_2($C_{10}H_6$-2-OH)] (**1**) and [(5-^{t}BuC_6H_3-2-OH)CH_2(μ-NC_4H_8N)CH_2(5-^{t}BuC_6H_3-2-OH)] (**2**) were synthesized by reacting corresponding alcohols with formaldehyde and piperazine. Treatment of ligands **1** and **2** with $Pd(OAc)_2$ in 1:1 molar ratio afforded neutral palladium complexes [Pd{($OC_{10}H_6$)CH_2(μ-NC_4H_8N)CH_2($C_{10}H_6$O)}] (**3**) and [Pd{(5-^{t}BuC_6H_3-2-O)CH_2(μ-NC_4H_8N)CH_2(5-^{t}BuC_6H_3-2-O)}] (**4**) in good yield. The palladium complexes **3** and **4** are employed in Suzuki–Miyaura cross-coupling reactions between phenylboronic acid and several aryl chlorides or bromides. They are found to be competent homogeneous catalysts for a variety of substrates to afford the coupled products in good to excellent yields. The crystal structures of compounds **2** and **4** are also reported.

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1. Introduction

Organometallic catalysis in air and using non-phosphorus catalysts has become an important goal in organic synthesis especially for the development of industrial process under simple, economical and environmentally friendly conditions. A broader family of palladium catalyzed coupling processes is known where a variety of transmetallating agents such as organomagnesium [1], organotin [2], organosilicon [3] and organozinc [4] reagents are routinely used. Palladium catalysed Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acid is among the most powerful C–C bond forming reactions available to synthetic chemists and its increasing popularity is due to its broad tolerance of different functional groups and ability to couple sterically demanding substrates under mild reaction conditions [5]. Further, the process involves non-toxic easy to handle reagents and also allows scale up production in industry [6]. Current technologies demand new catalysts, which are inexpensive, readily accessible, moisture- and air-stable and most importantly, highly effective under mild experimental conditions. To a certain extent this has been achieved by employing mainly phosphorus-based ligands as co-catalysts in organic solvents [7]. However, phosphorus-based auxiliary catalysts are often air and moisture sensitive, toxic and require inert atmosphere and mild reaction conditions.

In this context, several non-phosphorus [8] ligands containing mainly nitrogen donor atoms were designed and employed in various catalytic reactions with remarkable success. The transition metal complexes containing heterocyclic carbenes [8b,8c,8e] and nitrogen donor ligands such as imine and amine [8f,8g], oxime [8h,8i,8p], diazabutadiene derivatives [8a], imidazole [8d,8k], oxazoline [9] and bis(pyrimidine) [10] are widely employed in Suzuki–Miyaura cross-coupling reactions. In a few instances, Pd^{II} species were employed in catalytic reactions which undergo oxidative addition to give Pd^{IV} and revert back to Pd^{II} species [11]. Recently we reported a nitrogen based ligand and studied the catalytic activity of its *in situ* generated palladium(II) complex in carbon–carbon cross-couplings reactions such as Suzuki–Miyaura and Mizoraki–Heck coupling reactions [12]. Although, catalytic efficiency in these reactions was encouraging, we could not isolate the active palladium species responsible for the coupling reactions. In view of this, we slightly modified the ligand substituents and interacted with $Pd(acetate)_2$ and isolated Pd^{II} complexes which are used in catalytic studies. As a part of our interest on transition metal chemistry and catalytic investigations [13], we herein describe the synthesis of highly air and moisture stable palladium complexes containing diamino-diol ligands and their utility in Suzuki–Miyaura carbon–carbon cross-coupling reactions for both aryl bromides and chlorides.

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2. Results and discussions

The reactions of piperazine, 40% paraformaldehyde solution and 2-naphthol or 4-*tert*-butlylphenol under refluxing condition in methanol for 12 h afforded the colorless $[(HOC_{10}H_6)CH_2(\mu\text{-}NC_4H_8N)CH_2(C_{10}H_6OH)]$ (**1**) or $[(5\text{-}^tBuC_6H_3\text{-}2\text{-}OH)CH_2(\mu\text{-}NC_4H_8N)CH_2(5\text{-}^tBuC_6H_3\text{-}2\text{-}OH)]$ (**2**) in moderate yield. Treatment of ligands **1** and **2** with $Pd(OAc)_2$ in equimolar ratio at room temperature afforded $[Pd\{(OC_{10}H_6)CH_2(\mu\text{-}NC_4H_8N)CH_2(C_{10}H_6O)\}]$ (**3**) and $[Pd(5\text{-}^tBuC_6H_3\text{-}2\text{-}O)CH_2(\mu\text{-}NC_4H_8N)CH_2(5\text{-}^tBuC_6H_3\text{-}2\text{-}O)\}]$ (**4**), respectively, as shown in Scheme 1.

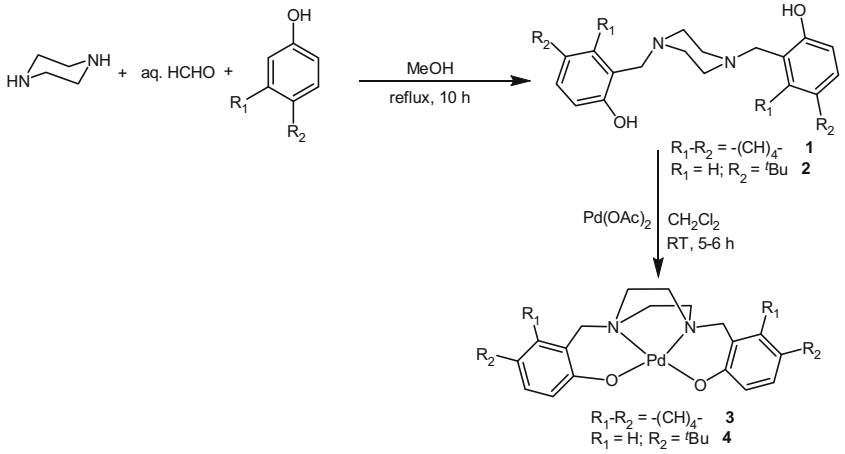
The ^1H NMR spectra of compounds **1** and **2** show sharp singlets at 4.06 and 3.72 ppm, respectively, for the methylene protons. The presence of the OH protons was confirmed by a D_2O exchange experiment. The mass spectra of the ligands **1** and **2** show molecular ion peaks at m/z 399.2 and 411.5 $[M+H]^+$, respectively. The $^{13}C\{^1H\}$ NMR and elemental analyses data are in good agreement with the proposed molecular structures. The molecular structure of ligand **2** and palladium complex **4** were confirmed by single crystal X-ray diffraction studies.

3. Molecular structures of 2 and 4

Perspective views of the molecular structures of **2** and **4** are shown in Figs. 1 and 2 while selected bond lengths and bond angles are given as captions to the figures. Crystal data and details of the structure determinations are given in Table 1.

Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of solvents from dichloromethane/petroleum ether mixtures (1:1) at room temperature. In the solid state, **2** possess crystallographically imposed centrosymmetry. The geometry about the nitrogen atom is distorted pyramidal with the sum of the bond angles being 330.2°. The N1–C11–C1 bond angle (112.62(9)°) in ligand **2** is comparable with that of similar ligand 1,4-bis(2-hydroxy-3,5-dimethylbenzyl)-piperazine [14]. In the crystal there is intramolecular hydrogen bonding between the tertiary nitrogen atom and the hydrogen atom of the phenoxo group leading to the formation of a six membered ring. The hydrogen bond distance for O1H1···N1 is 1.87(2) Å and the O1–H1···N angle is 152.4(17)°. In addition, there are weak, complementary C–H···O and C–H···π-ring interactions with the molecule at x, $1.5 - y$, $-0.5 + z$ (C8–H8b···center of gravity of ring C1–C6: 2.86 Å, 161°. C10–H10b···O2: 2.44 Å, 153°) and a C–H···O interaction with the molecule at $-x$, $2 - y$, $-z$ (C11–H11b···O2: 2.62 Å, 150°).

The complex **4** has a non-centrosymmetric structure with palladium as the central metal atom in a distorted square planar geometry with the corners being occupied by two tertiary nitrogen atoms (N1 and N2) and two phenolate oxygen atoms (O1 and O2). The conformation of the piperazine moiety is changed from chair to boat conformation during complexation. The *trans*-O2–Pd1–N1 and *trans*-O1–Pd1–N2 bond angles are, respectively, 171.01(13)° and 169.89(12)°, whereas the *cis* angles around the palladium vary from 74.10(14)° (N1–Pd1–N2) to 97.41(12)° (O2–Pd1–N2). The N2–C1–C13 bond angle is (115.02(3)°) slightly wider than that in the free ligand [N1–C11–C1, 112.62(9)°] due to the complexation. The Pd1–N1 and Pd1–N2 bond distances are 2.017(3) Å and 2.022(3) Å, respectively, whereas the Pd1–O1 and Pd2–O2 distances are 2.016(2) Å and 2.010(3) Å. As in **2**, there



Scheme 1. Synthesis of ligands and their palladium(II) complexes.

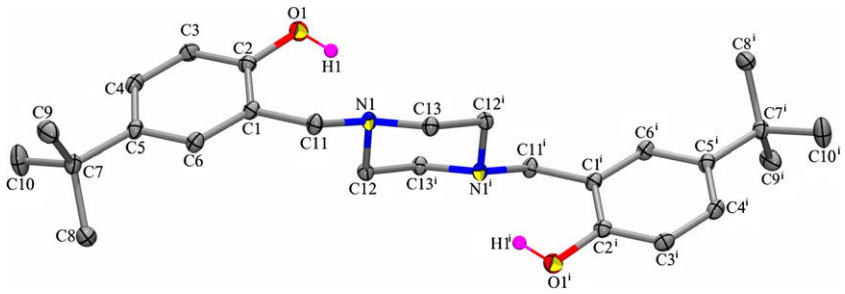


Fig. 1. An ORTEP view of molecular structure of **2**. Atoms $O1^i$, $N1^i$, etc. are related to O1, N1, etc. by the symmetry operation $2 - x$, $1 - y$, $1 - z$. All hydrogen atoms (except O1–H1 and $O1^i$–$H1^i$) were omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): O1–C2, 1.3673(13); N1–C12, 1.4719(13); N1–C13, 1.4692(14); N1–C11, 1.4747(13). Selected bond angles (°): C2–O1–H1, 104.3(12); C11–N1–C12, 111.70(8); C11–N1–C13, 109.63(8); C12–N1–C13, 108.87(8); C2–C1–C11, 121.04(9); C6–C1–C11, 120.13(10).

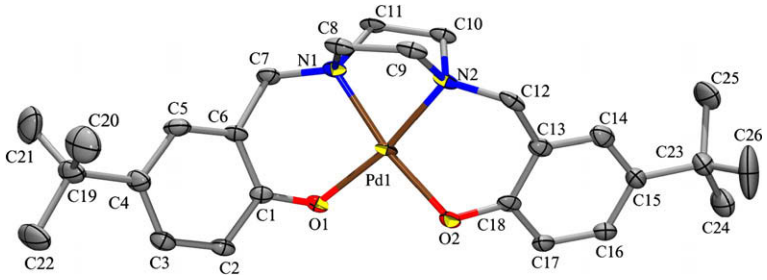


Fig. 2. An ORTEP view of molecular structure of **4**. All hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Pd1–O1, 2.016(2); Pd1–O2, 2.010(3); Pd1–N1, 2.017(3); Pd1–N2, 2.022(3); O1–C1, 1.333(4); N1–C7, 1.484(5). Selected bond angles (°): O1–Pd1–O2, 92.70(11); O1–Pd1–N1, 95.80(12); O1–Pd1–N2, 169.89(12); O2–Pd1–N1, 171.01(13); O2–Pd1–N2, 97.41(12); N1–Pd1–N2, 74.10(14); Pd1–O1–C1, 112.8(2); Pd1–N1–C7, 115.0(3).

Table 1
Crystallographic data for the compounds **2** and **4**

	2	**4**
Formula	$C_{26}H_{38}N_2O_2$	$C_{26}H_{36}N_2O_2Pd$
Formula weight	410.58	514.97
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	6.4837(5)	17.987(3)
b (Å)	8.2885(6)	12.503(2)
c (Å)	11.0749(8)	10.542(1)
α (°)	88.528(1)	90
β (°)	75.360(1)	92.111(2)
γ (°)	77.175(1)	90
V (Å^3)	561.19(7)	2369.2(6)
Z	1	4
ρ_{calc} (g cm^{-3})	1.215	1.444
μ (Mo Kα) (mm^{-1})	0.076	0.808
F(000)	224	1072
Crystal size (mm^3)	0.16 × 0.19 × 0.30	0.06 × 0.20 × 0.26
T (K)	100	100
2θ range (°)	2.5, 28.3	2.0, 28.4
Total no. of reflections	9891	20133
No. of independent reflections (R_{int})	2745 (0.023)	5615 (0.046)
R_1[a]	0.0392	0.0564
wR_2[b]	0.1094	0.1615
GOF (F^2)	1.065	1.0437

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]\}^{1/2} w = 1/[\sigma^2(F_o^2) + (xP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

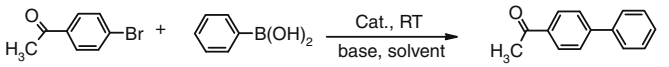
are complementary C–H···π-ring interactions with the molecule at $1-x$, $2-y$, $1-z$ (C11–H11a···center of gravity of ring C1–C6: 2.79 Å, 161°) and a weak C–H···O interaction with the molecule at $1+x$, y, z (C12–H12b···O1: 2.65 Å, 156°).

4. Suzuki–Miyaura cross-coupling reactions for aryl bromides

The room temperature Suzuki–Miyaura coupling reactions of aryl bromides with phenylboronic acid were carried out by employing the *in situ* generated palladium complexes of **1** or **2** with $Pd(OAc)_2$ in a 1:1 molar ratio. Both the systems are found to be highly active catalysts for the Suzuki–Miyaura cross-coupling reactions under mild reaction conditions. To optimize the reaction conditions, a series of reactions were carried out at room temperature with 4-bromoacetophenone and phenylboronic acid as a model reaction.

The effect of base on the coupling reaction was evaluated by taking 4-bromoacetophenone (0.5 mmol) with phenylboronic acid (0.75 mmol) in methanol at room temperature in presence of 0.5 mol% of the *in situ* generated catalyst with various bases (1 mmol). The results revealed that the inorganic bases used were more effective than Et_3N (Table 2) and hence the economically cheaper K_2CO_3 was chosen as base for the coupling reactions.

Table 2
Effect of base and solvent on the Suzuki–Miyaura coupling reaction.[a]



Entry	Base	Solvent	Yield (%)[b]	Yield (%)[c]
1	K_3PO_4	MeOH	100	100
2	K_2CO_3	MeOH	100	100
3	Na_2CO_3	MeOH	100	100
4	Cs_2CO_3	MeOH	100	99
5	Et_3N	MeOH	83	80
6	K_2CO_3	DMF	98	82
7	K_2CO_3	Toluene	81	60
8	K_2CO_3	Dioxane	68	15
9	K_2CO_3	DCM	53	40
10	K_2CO_3	THF	38	32

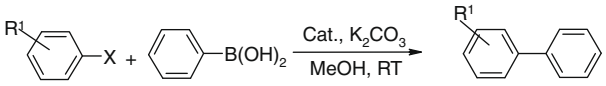
[a] *Reaction conditions*: 4-Bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.5 mol%), base (1 mmol) and solvent (5 mL). Conversion to the coupled product determined by GC based on 4-bromoacetophenone; average of two runs.
[b] Using catalyst **1**/$(Pd(OAc)_2$.
[c] Catalyst **2**/$(Pd(OAc)_2$.

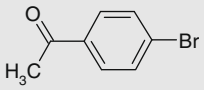
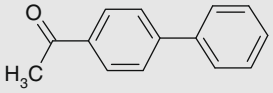
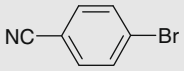
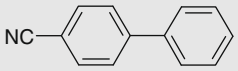
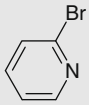
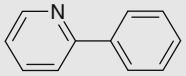
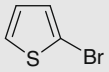
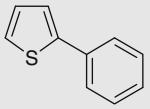
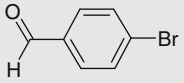
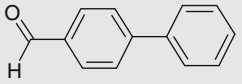
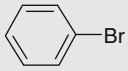
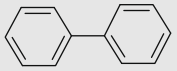
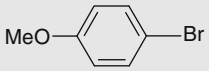
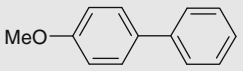
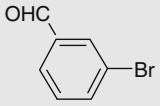
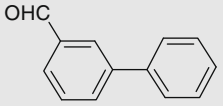
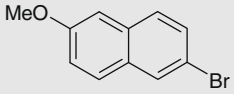
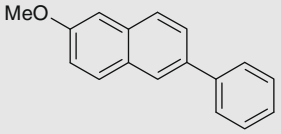
The solvents play an important role in the cross-coupling reactions. In the present study non-polar solvent like toluene gave moderate yield of the coupled product whereas polar solvents such as methanol or DMF are found to be more efficient (Table 2).

Under the optimized reaction conditions the Suzuki–Miyaura cross-coupling reactions were carried out for various aryl bromides (0.5 mmol) with phenylboronic acid (0.75 mmol) using K_2CO_3 (1 mmol) and 5–7 ml methanol at room temperature with the catalyst loading of 0.5–1 mol%. The reaction time has not been optimized. The results are displayed in Table 3. Electron-poor bromides such as 4-bromoacetophenone and 4-bromobenzonitrile were coupled with phenylboronic acid efficiently (entries 1, 2) in presence of $Pd(OAc)_2$/**1** or **2** catalyst mixture. The coupling reactions of some bromo heterocycles were also carried out with phenylboronic acid. Use of 2-bromopyridine and 2-bromothiophene produced excellent yield. The electron-poor 4-bromobenzaldehyde coupled with phenylboronic acid in presence of ligand **1** with low catalyst loading afforded good conversion whereas in the presence of ligand **2** the yields were moderate (entry 5). The electronically neutral bromobenzene (entry 6) produced good amount of desired product when coupled with phenylboronic acid. The electron rich or deactivated 4-bromoanisole and 2-bromo-6-methoxynaphthalene also afforded good conversion (entry 7, 9) in the presence of ligand **1** or **2**. Under the same standard conditions, 3-bromobenzaldehyde furnished the desired biaryls in good yield (entry 8).

The high efficiency of these catalysts at room temperature makes them valuable. To our knowledge, only few catalysts are known for Suzuki–Miyaura cross-coupling reactions which are effective at room temperature [22a–i]. The comparison data

Table 3
Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid.[a]



Entry	Aryl halides	Product	Ref.	Ligand (mol%)	Yield (%)[b]
1			[15]	**1**(0.5) **2**(0.5)	100[c] 100[c]
2			[16]	**1** (0.5) **2** (1)	100[c] 100[c]
3			[17]	**1** (1) **2** (1)	100 100
4			[18]	**1** (1) **2** (1)	94 100
5			[19]	**1** (0.5) **2** (0.5)	97[c] 72[c]
6			[18]	**1** (1) **2** (1)	96 92
7			[18]	**1** (0.5) **2** (1)	90 96
8			[20]	1 (1) **2** (1)	85 93
9			[21]	**1** (1) **2** (1)	79 100

[a] *Reaction conditions*: Aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1 mmol), MeOH (5 mL).
[b] Conversion to the coupled product determined by GC based on aryl bromide.
[c] Isolated yield.

presented in Table 4 show the efficiency of these new catalysts towards the coupling reactions.

It is important to evaluate the catalytic activity in the Suzuki–Miyaura coupling reactions at lower concentrations. We therefore examined the effect of catalyst loading in the reaction between 4-bromobenzonitrile and 4-bromoacetophenone with phenylboronic acid (Table 5). The results are encouraging with the catalysts showing good activity at room temperature. In order to asses the effectiveness of the ligands, blank reaction containing only the metal precursor, $Pd(OAC)_2$ was tested which showed 16.6% conversion with relatively low TON of 1326 (entry 1). The ligand supported catalysts showed around 8000 TON (entry 2) with ligand **2**. Very high turnover number was observed at 0.00005 mol% catalyst concentration (entry 4). Similarly when we carried out the coupling reactions by taking 4-bromoacetophenone and phenylboronic acid, 7600 and 66 000 TONS were achieved for catalyst loading of 0.0125 and 0.0005 mol%, respectively (entries 5, 6), indicating the efficiency of the catalyst systems.

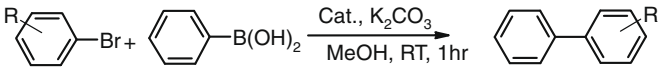
5. Suzuki–Miyaura cross-coupling reactions for aryl chlorides

Optimized conditions for the Suzuki–Miyaura coupling of aryl chlorides with phenylboronic acid in the presence of $Pd(OAc)_2$/**1** or **2** mixture catalyst (1–4 mol%) were found to be combination of aryl chloride (0.5 mmol) with phenylboronic acid (0.753 mmol) using 4 mol% *in situ* catalyst systems $Pd(OAc)_2$/**1** or **2** in DMF with K_2CO_3 (1.0 mmol) as base at 110 °C under aerobic condition. The reaction time has not been optimized. Various aryl chlorides were utilized for the coupling reaction under the optimized reaction conditions and the results obtained were tabulated in Table 6. In

Table 4
Comparison with other catalytic systems.

Entry	Ar–Br	[Pd] (mol%)	Base	Solvent	Conditions	Yield (%)	Ref.
1	4-MeCOPhBr	$[PdCl_2(dppf)]$, 1 mol%	K_2CO_3	Toluene	70 °C, 2 h	94	[23]
2	4-MeCOPhBr	$Pd(OAc)_2$/diazobutadiene, 3 mol%	Cs_2CO_3	Dioxane	80 °C, 1 h	98	[8a]
3	4-MeCOPhBr	Bis(oxazolinyl)-pyrrole dimeric palladium complex, 0.01 mol%	K_2CO_3	Toluene	70 °C, 1 h	92	[24]
4	4-MeCOPhBr	Palladium(II) metallamacrocycle supported by an amino-functionalised ferrocene complex, 0.5 mol%	K_2CO_3	Methanol	RT, 1 h	99	[25]
5	4-MeOPhBr	$Pd(OAc)_2$/2-aryl-2-oxazolines, 2 mol%	Cs_2CO_3	Dioxane	80 °C, 4 h	61–96	[10]
6	4-MeCOPhBr	Oxime-derived palladacycle, 0.001 mol%	K_2CO_3	Toluene	110 °C, 0.5–1 h	77–99	[26]
7	4-MeCOPhBr	Oxime-derived palladacycles, 0.01 mol%	KOH	MeOH/H_2O	RT, 5 h–4 days	94–100	[8i]
8	4-MeCOPhBr	$C_{17}H_{21}Cl_2N_3OPd \cdot 2CHCl_3$, 0.2 mol%	Cs_2CO_3	Dioxane	80 °C, 1.5 h	98	[27]
9	4-MeCOPhBr	$Pd(OAc)_2$/**2**, 0.0125 mol%	K_2CO_3	Methanol	RT, 1 h	95	This work
10	4-MeCOPhBr	$Pd(OAc)_2$/**2**, 0.5 mol%	K_2CO_3	Methanol	RT, 1 h	100	This work
11	4-MeCOPhBr	$Pd(OAc)_2$/**2**, 0.0005 mol%	K_2CO_3	Methanol	RT, 0.5 h	33.0	This work
12	4-MeOPhBr	$Pd(OAc)_2$/**2**, 0.5 mol%	K_2CO_3	Methanol	60 °C, 3 h	96	This work

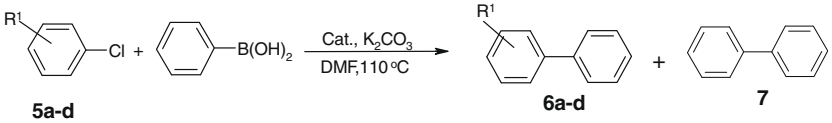
Table 5
Effect of low catalyst loading on the coupling reactions.[a]



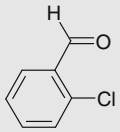
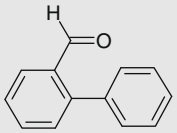
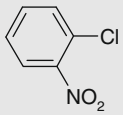
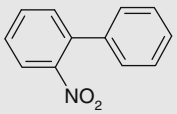
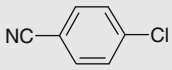
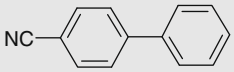
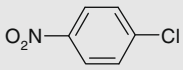
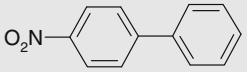
Entry	–R	Catalyst	Amount of catalyst (mol%)	Yield (%)[b]	TON[c]
1	–CN	$Pd(OAc)_2$	0.0125	16.6	1328
2	–CN	$Pd(OAc)_2$/**2**	0.0125	95.43	7634
3	–CN	$Pd(OAc)_2$/**2**	0.0005	34.69	69380
4	–CN	$Pd(OAc)_2$/**2**	0.00005	27.42	548400
5	$-COCH_3$	$Pd(OAc)_2$/**2**	0.0125	95.00	7600
6	$-COCH_3$	$Pd(OAc)_2$/**2**	0.0005	33.00	66000

[a] *Reaction conditions*: Aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1 mmol), MeOH (5 mL).
[b] Conversion to the coupled product determined by GC based on aryl bromide.
[c] In units of (mol of product)/(mol of Pd).

Table 6
Suzuki–Miyaura cross-coupling of aryl chlorides with phenylboronic acid.[a]



5a-d **6a-d** **7**

Entry	Aryl halides	Product	Ref.	Ligand	Yield (%)[b] **6**	Yield[b] (%) **7**
1			6a [28]	**1**	74	18
				2	92	7
2			6b [29]	**1**	87	8
				2	58	37
3			6c [16]	**1**	49	51
				2	72	21
4			6d [18]	**1**	45	54
				2	50	50

[a] *Reaction conditions*: Aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1 mmol), 4 mol% catalyst (1:1), DMF (5 mL).
[b] Conversion to the coupled product determined by GC, average of two runs.

all the cases, along with the expected coupled products, small quantities of biphenyl were also obtained as a result of homocoupling of phenylboronic acid. Under the standardized reaction conditions, the electron-poor *o*-chlorobenzaldehyde and *o*-chloronitrobenzene plus phenylboronic acid gave coupled product in excellent yields with less homocoupled product (entries 1, 2). The activated *p*-chlorobenzonitrile plus phenylboronic acid in the presence of **1** and **2** gave moderate yields of coupling product (entry 3). *p*-Substituted chlorides such as *p*-chloronitrobenzene afforded moderate amounts of coupled product under similar reaction conditions (entry 4).

These results suggested that these catalysts are quite effective in promoting C–C coupling under mild conditions for both bromo and chloro derivatives. All the catalytic runs generate palladium black due to the partial catalytic decomposition and the experimental data including the TEM analysis has confirmed that the palladium black is not the active catalyst [30] as there was no change in the particle size. Further, the homogeneous nature of the catalysis was checked by classical mercury test [31]. Addition of a drop of mercury to the reaction mixture did not affect the conversion of the reaction which suggests that the catalysis is homogeneous in nature, since heterogeneous catalysts would form an amalgam, there by poisoning it.

6. Conclusions

In summary, palladium complexes of diamino-diol ligands are very efficient catalysts for the Suzuki–Miyaura cross-coupling reactions under mild reaction conditions. Very good conversions of the coupled product were obtained using methanol as solvent in aerobic conditions for the aryl bromides at room temperature, whereas the aryl chlorides show good conversion rate under elevated temperature in DMF. The present system is highly air and moisture stable and the ligands can be synthesized readily from inexpensive and commercially available starting materials. Utilization of these catalysts in various other organic transformations such as Heck coupling, amination and dehalogenation reactions are in progress. Presently we do not have any experimental support to propose a mechanism for the catalytic pathway. In a typical Suzuki–Miyaura cross-coupling reaction, Pd^{II} species is reduced to Pd^{0} species prior to the oxidative addition. In the present case, similar speculation may lead to a Pd^{0} species containing only nitrogen donors which is less likely as nitrogen donor ligands can not stabilize Pd^{0} complexes. An alternative reaction path may involve a Pd^{II} species which can be oxidized to Pd^{IV} during the oxidative addition and is eventually reduced to the Pd^{II} species. However, further investigations are needed to substantiate one of these aspects and the work is in progress in this direction.

7. Experimental

Most of the bromo and chloro compounds, phenylboronic acid, naphthol and 4-*tert*-butyl phenol were purchased from Aldrich. Anhydrous K_3PO_4, and K_2CO_3 were purchased from *SIGMA* chemicals and *SDFINE* chemicals, respectively, and used as such received without further purification. Technical grade methanol and DMF were used for all catalytic reactions. All other reagents were used as received. Gas chromatographic analyses were performed on a Perkin–Elmer Clarus 500 GC and Hewlett Packard G 1800A GCD Systems equipped with a packed column. The ^1H and $^{13}C\{^1H\}$ NMR (δ in ppm) spectra were obtained on a Varian VXR 400 spectrometer operating at an appropriate frequencies of using TMS as standard. Positive shifts lie downfield of the standard in all the cases. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. Electro-spray ionization (EI) mass spectrometry experiments were carried out using Waters Q-Tof micro-YA-105. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR instrument as a KBr disk or in Nujol mull. Melting points were observed in capillary tubes and are uncorrected.

7.1. Synthesis of [(2-$HOC_{10}H_6$)CH_2(μ-NC_4H_8N)CH_2($C_{10}H_6$-2-OH)] (**1**)

A mixture of piperazine (1.49 g, 17.3 mmol) and 40% aqueous formaldehyde solution (3.9 mL, 52 mmol) were dissolved in methanol (40 mL) and heated to reflux for 2 h to give a clear solution. The solution was cooled to room temperature and 2-naphthol (5.0 g, 34.7 mmol) in methanol (60 mL) was added. The resulting reaction mixture was refluxed for a further 12 h and then cooled to room temperature. The colorless crystalline solid **1** was filtered off and dried in vacuum. M.p.: >250 °C. Anal. Calc. for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.57; N, 7.02. Found: C, 78.24; H, 6.49; N, 7.10%. FT-IR (KBr disc): ν_{OH} = 3445 (br) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 8.19 (s, *naphthyl*, H), δ 7.91 (d, J_{HH} = 8.4 Hz, *naphthyl*, H), δ 7.72 (d, J_{HH} = 7.6 Hz, *naphthyl*, H), δ 7.64 (d, J_{HH} = 8.8 Hz, *naphthyl*, H), δ *7.41–7.21* (m, *naphthyl*, H), δ 7.03 (d, J_{HH} = 8.8 Hz, *naphthyl*, H), 4.06 (s, CH_2, 4H), δ 3.18 (br s, NCH_2, 8H). MS (EI): *m/z* 399.2 $[M+H]^+$.

7.2. Synthesis of [(5-^{t}BuC_6H_3-2-OH)CH_2(μ-NC_4H_8N)CH_2(5-^{t}BuC_6H_3-2-OH)] (**2**)

This was synthesized by a procedure similar to that of **1**, using (7.51 g, 50 mmol) 4-*tert*-butyl phenol, piperazine (2.2 g, 25 mmol) and 40% aqueous formaldehyde solution (5.3 mL, 75.36 mmol). Yield: 65% (6.68 g, 16.3 mmol). Anal. Calc. for $C_{26}H_{38}N_2O_2$: C, 76.05; H, 9.32; N, 6.82. Found: C, 76.18; H, 9.43; N, 6.88%. FT-IR (KBr disc): ν_{OH} = 3444 (br) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.45 (br, *OH*, 2H), δ 7.19 (d, J_{HH} = 6.8 Hz, *phenyl*, 2H), δ 6.96 (s, *phenyl*, 2H), δ 6.75 (d, J_{HH} = 8.4 Hz, *phenyl*, 2H), 3.72 (s, CH_2, 4H), δ 2.93 (s, NCH_2, 4H), δ 2.37 (s, NCH_2, 4H) δ 1.27 (s, ^{t}*Bu*, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 155.2 (s, *phenyl*), 142.2 (s, *phenyl*), 125.8 (s, *phenyl*), 125.7 (s, *phenyl*), 120.2 (s, *phenyl*), 115.6 (s, *phenyl*), 61.8 (s, CH_2), 52.6 (s, NCH_2), 34.1 (s, $C(Me)_3$), 31.7 (s, CH_3). MS (EI): *m/z* 411.6 $[M+H]^+$.

7.3. Synthesis of [(2-$OC_{10}H_6$)CH_2(μ-NC_4H_8N)CH_2($C_{10}H_6$-2-O)Pd] (**3**)

A solution of $[Pd(OAc)_2]$ (0.028 g, 0.127 mmol) in dichloromethane (5 mL) was added dropwise to **1** (0.051 g, 0.127 mmol) also in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 6 h. The pale yellow precipitate formed was collected by filtration and washed with diethyl ether to give analytically pure product of **3** as a yellow crystalline solid. Yield: 77% (0.049 g, 0.098 mmol). M.p.: 236–240 °C (dec.). Anal. Calc. for $C_{26}H_{24}N_2O_2Pd$: C, 62.09; H, 4.81; N, 5.57. Found: C, 62.02; H, 4.90; N, 5.48%. ^1H NMR (400 MHz, DMSO-d_6): δ *8.23–7.12* (m, *naphthyl protons*), 4.0 (s, CH_2, 4H), δ 3.14 (br s, NCH_2, 8H). MS (EI): *m/z* 503.4 $[M+H]^+$.

7.4. Synthesis of [(2-O-5-^{t}BuC_6H_3)CH_2(μ-NC_4H_8N)CH_2(5-^{t}BuC_6H_3-2-O)Pd] (**4**)

This was synthesized by a procedure similar to that of **3** by reacting [(5-^{t}BuC_6H_3-2-OH)CH_2(μ-NC_4H_8N)CH_2(5-^{t}BuC_6H_3-2-OH)] (0.029 g, 0.072 mmol) and $[Pd(OAc)_2]$ (0.016 g, 0.072 mmol) at room temperature. Yield: 85% (0.032 g, 0.061 mmol). M.p.: 140–142 °C (dec.). Anal. Calc. for $C_{26}H_{36}N_2O_2Pd$: C, 60.63; H, 7.05; N, 5.44. Found: C, 60.67; H, 7.17; N, 5.55%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J_{HH} = 7.22 Hz, *phenyl*, 2H), δ 6.98 (s, *phenyl*, 2H), δ 6.82 (d, J_{HH} = 8.4 Hz, *phenyl*, 2H), 3.62 (s, CH_2, 4H), δ 2.91 (s, NCH_2, 4H), δ 2.32 (s, NCH_2, 4H) δ 1.26 (s, ^{t}*Bu*, 18H).

7.5. X-ray crystallography

Crystals of **2** and **4** were mounted in a Cryoloop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected for **2** using 606 scans in ω (0.3° per scan) at $\phi = 0$, 120 and 240° using the SMART software package [32a] while for **4** three sets of 400 frames, each of width 0.5° in omega, collected at $\phi = 0.00$, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in ϕ, collected at $\omega = -30.00$ and 210.00° employing the APEX2 [32b] program suite were used. The raw data were reduced to F^2 values using the SAINT+ software [33] and a global refinements of unit cell parameters using 3595 (for **2**) or 9962 (for **4**) reflections chosen from the full data set were performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS) [34]. The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package [35]. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

8. Typical procedure for Suzuki–Miyaura cross-coupling reactions

In a two-necked round bottom flask the appropriate amount of ligand, metal precursors and 5 mL of solvent were placed with a magnetic stir bar. After stirring for 5 min the aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol) and base (1 mmol) were added to the reaction flask. The reaction mixture was heated to the appropriate temperature for the required time (the course of reaction was monitored by GC analysis) and then the solvent was removed under reduced pressure. The resultant residual mixture was diluted with H_2O (8 mL) and Et_2O (8 mL), followed by extraction twice (2×6 mL) with Et_2O. The organic fraction was dried ($MgSO_4$), filtered, stripped of the solvent under vacuum and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC/GCMS analysis. Yields were calculated against consumption of the aryl halides. The crude material was purified by silica column chromatography using hexane-ethyl acetate as an eluent to give the desired biaryls. For experiments with low catalyst loading and for comparison of other Pd(II) sources, stock solution of appropriate concentration was prepared by dissolving 1.0 mg of the palladium catalyst in appropriate amount of DCM and used for each independent run.

8.1. 4-Acetylbiphenyl

White powder. M.p.: 126–128 °C, (lit. [15] 123 °C) Anal. Calc. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 86.20; H, 6.49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ *8.05–7.26* (m, *phenyl*, 9H), 2.65 (s, C*H*$_3$, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.0 (*C*=O), 146.0 (s, *phenyl*), 140.1 (s, *phenyl*), 136.0 (s, *phenyl*), 129.1 (s, *phenyl*), 129.6 (s, *phenyl*), 128.4 (s, *phenyl*), 127.5 (s, *phenyl*), 127.4 (s, *phenyl*), 26.7 (*C*H$_3$). MS (EI): *m/z* 196.0 [M]$^+$.

8.2. [1,1′-Biphenyl]-4-carbonitrile

White powder. M.p.: 83–85 °C., (lit. [16] 85–86 °C) ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.77–7.26* (m, *phenyl*, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.9 (s, *phenyl*), 139.4 (s, *phenyl*), 132.8 (s, *phenyl*), 129.3 (s, *phenyl*), 128.8 (s, *phenyl*), 127.9 (s, *phenyl*), 127.4 (s, *phenyl*), 119.1 (*C*≡N), 111.1 (*C*–C≡N). Anal. Calc. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.81. Found: C, 86.22; H, 5.03; N, 7.70%. MS (EI): *m/z* 179.0 [M]$^+$.

8.3. 4-Phenylbenzaldehyde [19]

Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.98–7.25* (m, *phenyl*, 9H), 10.04 (s, C*H*O, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1 (*C*=O), 147.3 (s, *phenyl*), 139.8 (s, *phenyl*), 135.3 (s, *phenyl*), 130.4 (s, *phenyl*), 130.2 (s, *phenyl*), 129.2 (s, *phenyl*), 128.9 (s, *phenyl*), 128.6 (s, *phenyl*), 128.4 (s, *phenyl*), 127.8 (s, *phenyl*), 127.5 (s, *phenyl*). MS (EI): *m/z* 182.0 [M]$^+$.

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Appendix A. Supplementary material

CCDC 690771 and 690772 contain the supplementary crystallographic data for **2** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.019.

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