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Cyclopalladated complexes of 2-(*m*-nitrophenyl)imidazolines: synthesis, characterization and catalytic activity in the Suzuki reaction under mild conditions

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Abstract Three cyclopalladated complexes of 2-(*m*-nitrophenyl)imidazolines have been easily prepared and characterized by spectroscopic analysis. The structure of one of the complexes has been determined by single-crystal X-ray analysis. The complexes are effective catalysts for the Suzuki reaction of aryl bromides with phenylboronic acid in aqueous solution at room temperature under air.

Introduction

The palladium-catalyzed Suzuki reaction is one of the most powerful methods to construct C–C bonds, particularly for the preparation of biaryl compounds [1, 2]. Recent developments in this area have been largely focused on the palladium catalysts that can activate notoriously unreactive aryl chlorides, and/or function under mild reaction conditions such as at room temperature, under air or in aqueous media. Substantial progress has been made by using simple palladium salts with bulky, electron-rich phosphines [3, 4] or *N*-heterocyclic carbenes (NHC) [5, 6]. The cyclopalladated compounds or palladacycles containing these ligands have also been reported to be efficient for the activation of aryl chlorides under relatively mild reaction conditions [7–12]. We have systematically studied the cyclopalladation reactions of Schiff base type ferrocenylimines and found that cyclopalladated ferrocenylimine complexes with tricyclohexylphosphine (PCy_3) or dicyclohexylphosphinobiphenyl ligands exhibit excellent activity at low catalyst loadings in the coupling of aryl chlorides with phenylboronic acid [13–15]. Some palladacyclic compounds can even promote the coupling of unactivated and sterically hindered aryl chlorides at room temperature although the catalyst loadings are relatively high (1–2 mol%) [7, 11, 12]. Furthermore, compared with other palladium catalytic systems, especially those with bulky alkylphosphines, the cyclopalladated complexes have some obvious advantages in their usually high stability toward air, moisture and heat. These properties allowed for catalytic experiments to be done in the presence of air and water [16–20]. Connecting with our interest in the palladacycles and their applications [13–15, 21–25], herein, we would like to report the synthesis and characterization of three cyclopalladated complexes with 2-(*m*-nitrophenyl) imidazolines (**2a**–**2c**) (Schemes 1, 2). It should be pointed out that the imidazoline-NH group in ligand (**1a**) was acetylated during the palladation reaction, giving the *N*-acetylated cyclopalladated complex (**2a**) (Scheme 2). The three palladium complexes were successfully applied in the Suzuki reactions of aryl bromides with phenylboronic acid in aqueous solution at room temperature under air. The results are presented in this paper.

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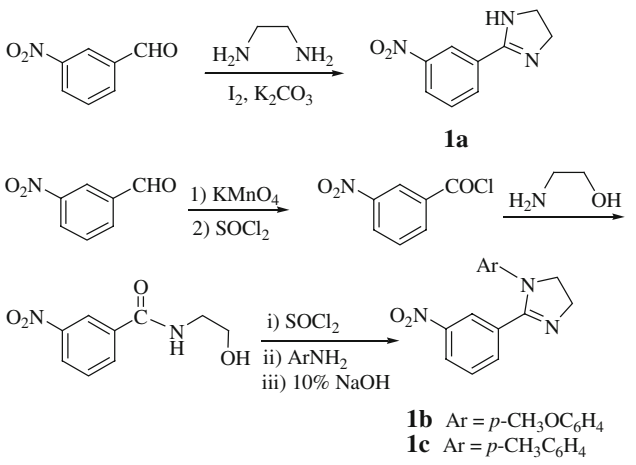
Experimental

Glacial acetic acid was dried by distilling from P_2O_5. *m*-Nitrobenzaldehyde, *m*-nitrobenzoic acid, *m*-nitrobenzoyl chloride and compound (**1a**) were prepared according to literature methods. All other chemicals were used as purchased. Melting points were measured using a WC-1



Scheme 1

microscopic apparatus and are uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard for ^{1}H and ^{13}C NMR and 85% H_3PO_4 as external standard for ^{31}P NMR. Mass spectra were performed on an Agilent LC/MSD Trap XCT instrument. HRMS were measured on a Micromass Q-TOF mass spectrometer (Waters, Manchester, UK) with an ESI source.

Synthesis of 2-(*m*-nitrophenyl)imidazolines (**1b**–**1c**)

To a stirred solution of 2-aminoethanol (0.15 mL, 2.5 mmol) and Et_3N (0.43 mL) in THF (10 mL) was added dropwise a solution of *m*-nitrobenzoyl chloride (371 mg, 2.0 mmol) in THF (10 mL) at room temperature. After stirring overnight, the reaction mixture was filtered and evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:1) as eluent, giving white solids of the corresponding amido alcohol 377 mg (90%). The obtained amido alcohol (377 mg, 1.8 mmol) was then reacted with thionyl chloride (5 mL) under reflux for 8 h. Excess thionyl chloride was evaporated. The residue was dissolved in dry diethyl ether (10 mL) and filtered. To this solution was added dry triethylamine (0.6 mL), followed by *p*-methoxyaniline or *p*-toluidine (2.7 mmol). After stirring for 4 h at room temperature, 10% NaOH (6 mL) was added and the mixture was stirred overnight. The aqueous mixture was extracted with dichloromethane and the combined organic layers were washed with saturated $NaHCO_3$, brine, dried over $MgSO_4$ and evaporated. The crude product was purified by preparative TLC on silica gel plates eluting with ethyl acetate/petroleum ether to afford compounds (**1b**–**1c**) as pale yellow oils.

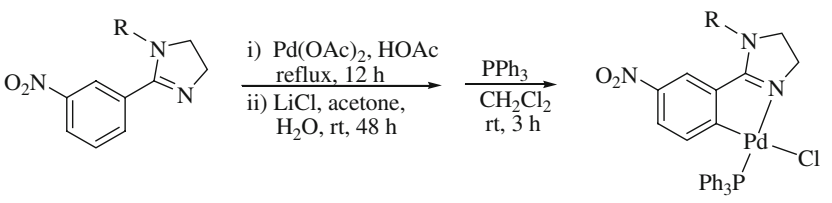
1b 56% yield. IR (KBr, cm^{-1}): *v* 2935, 2868, 1606, 1531, 1514, 1349, 1246, 1180, 1143, 1040, 997, 908, 833, 739, 696. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H, ArH), 8.16 (d, $J = 8.1$ Hz, 1H, ArH), 7.77 (d, $J = 7.7$ Hz, 1H, ArH), 7.42 (t, $J = 8.0$ Hz, 1H, ArH), 6.84 (d, $J = 8.8$ Hz, 2H, NAr), 6.75 (d, $J = 8.8$ Hz, 2H, NAr), 4.11–4.06 (*m*, 2H, CH_2), 3.99–3.94 (*m*, 2H, CH_2), 3.74 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (C=N), 156.9, 147.7, 135.8, 134.3, 132.7, 129.0, 125.7, 124.3, 123.7, 114.4, 55.4, 55.3, 53.2. MS (*m/z*, ESI$^+$): 298 (M + H). ESI-HRMS: M + H Calc. for $C_{16}H_{16}N_3O_3$: 298.1192, found: 298.1186. M + Na Calc. for $C_{16}H_{15}N_3NaO_3$: 320.1011, found: 320.1047.

1c 52% yield. IR (KBr, cm^{-1}): *v* 2928, 2869, 1609, 1525, 1349, 1141, 998, 909, 861, 816, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H, ArH), 8.18 (d, $J = 8.4$ Hz, 1H, ArH), 7.77 (d, $J = 7.7$ Hz, 1H, ArH), 7.43 (t, $J = 8.0$ Hz, 1H, ArH), 7.00 (d, $J = 8.0$ Hz, 2H, NAr), 6.74 (d, $J = 8.1$ Hz, 2H, NAr), 4.10–3.99 (*m*, 4H, CH_2CH_2), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (C=N), 147.9, 140.1, 134.5, 134.4, 132.9, 129.8, 129.1, 124.5, 123.8, 123.6, 54.8, 53.3, 20.8. MS (*m/z*, ESI$^+$): 282 (M + H). ESI-HRMS: M + H Calc. for $C_{16}H_{16}N_3O_2$: 282.1243, found: 282.1242. M + Na Calc. for $C_{16}H_{15}N_3NaO_2$: 304.1062, found: 304.1076.

Synthesis of cyclopalladated complexes (**2a**–**2c**)

A mixture of the appropriate 2-(*m*-nitrophenyl)imidazoline (**1a**–**1c**) (0.2 mmol) and $Pd(OAc)_2$ (54 mg, 0.24 mmol) in dry HOAc (60 mL) was refluxed for 12 h under a nitrogen atmosphere. The solvent was removed under reduced

Scheme 2



1a R = H
1b R = *p*-$CH_3OC_6H_4$
1c R = *p*-$CH_3C_6H_4$

2a R = $COCH_3$
2b R = *p*-$CH_3OC_6H_4$
2c R = *p*-$CH_3C_6H_4$

pressure and a solution of lithium chloride (102 mg, 2.4 mmol) in acetone/water (3:2, 35 mL) was added. The resulting solution was stirred at room temperature for 48 h then extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$ and filtered. Then to this filtrate was added Ph_3P (105 mg, 0.4 mmol). After stirring at room temperature for 3 h, CH_2Cl_2 was evaporated and the residue was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the cyclopalladated complexes (**2a**–**2c**) as orange solids.

2a m.p.: 186 °C. 21% yield. IR (KBr, cm^{-1}): ν 3447, 2924, 1709, 1595, 1511, 1437, 1382, 1341, 1305, 1222, 1096, 1060, 1024, 860, 749, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, $J = 2.8$ Hz, 1H, ArH), 7.73–7.70 (*m*, 6H, PPh_3), 7.48–7.45 (*m*, 3H, PPh_3), 7.42–7.37 (*m*, 7H, PPh_3 and ArH), 6.62 (dd, $J = 5.2$, 8.8 Hz, 1H, ArH), 4.34 (t, $J = 8.4$ Hz, 2H, CH_2), 4.23 (t, $J = 8.4$ Hz, 2H, CH_2), 2.42 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 168.9, 166.2, 144.1, 138.4, 137.9, 137.8, 135.2, 135.1, 131.1, 130.2, 129.6, 128.4, 128.3, 124.0, 123.9, 51.5, 49.3, 25.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.81. MS (*m/z*, ESI^+): 600 (M − Cl). ESI-HRMS: M − Cl Calc. for $C_{29}H_{25}N_3O_3PPd$: 600.0668, found: 600.0604.

2b m.p.: 168 °C. 36% yield. IR (KBr, cm^{-1}): ν 3426, 2928, 1712, 1590, 1510, 1435, 1252, 1095, 1023, 837, 749, 696. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (*m*, 6H, PPh_3), 7.47–7.46 (*m*, 3H, PPh_3), 7.40–7.39 (*m*, 6H, PPh_3), 7.23–7.20 (*m*, 4H, ArH and NAr), 7.02–7.00 (*m*, 2H, NAr), 6.66–6.61 (*m*, 1H, ArH), 4.34 (t, $J = 10.2$ Hz, 2H, CH_2), 4.11 (t, $J = 10.2$ Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3). ^{31}P NMR(162 MHz, $CDCl_3$): δ 41.35. MS (*m/z*, ESI^+): 664 (M − Cl). ESI-HRMS: M − Cl Calc. for $C_{34}H_{29}N_3O_3PPd$: 664.0981, found: 664.0944.

2c m.p.: 153 °C. 34% yield. IR (KBr, cm^{-1}): ν 3433, 3054, 2924, 2856, 1590, 1511, 1435, 1339, 1158, 1098, 1024, 868, 826, 749, 698. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.71 (*m*, 6H, PPh_3), 7.47–7.44 (*m*, 3H, PPh_3), 7.40–7.36 (*m*, 6H, PPh_3), 7.30–7.26 (*m*, 4H, ArH and NAr), 7.21 (d, $J = 8.2$ Hz, 2H, NAr), 6.63 (dd, $J = 4.7$, 8.5 Hz, 1H, ArH), 4.35 (t, $J = 10.2$ Hz, 2H, CH_2), 4.13 (t, $J = 10.2$ Hz, 2H, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 166.2, 143.5, 138.5, 138.4, 137.9, 137.4, 135.3, 135.2, 130.9, 130.7, 130.2, 128.2, 128.1, 126.4, 123.3, 123.2, 120.7, 56.5, 50.7, 21.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.33. MS (*m/z*, ESI^+): 648 (M − Cl). ESI-HRMS: M − Cl Calc. for: $C_{34}H_{29}N_3O_2$ PPd: 648.1032, found: 648.1005.

General procedure for the Suzuki reaction

A tube was charged with aryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.0 mmol), the catalyst (**2**) (0.0025 mmol), *n*-Bu_4NBr (0.5 mmol) and EtOH-H_2O (2 mL, v/v = 1/1) under air. The reaction mixture was stirred at room temperature for 12 h (time not optimized). Then water was added, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with water, dried over $MgSO_4$, filtered and evaporated. The products were isolated by flash chromatography on silica gel (the purified products were identified by comparison of melting points with the literature values or by their ^{1}H NMR spectra).

X-ray crystallography

The crystals of cyclopalladated complex (**2b**) were obtained by recrystallization from acetone/petroleum ether at room temperature. Crystallographic data for **2b**·0.5 CH_3COCH_3: $C_{34}H_{29}ClN_3O_3PPd{\cdot}0.5CH_3COCH_3$, 0.20 × 0.17 × 0.17 mm^3, triclinic, P-1, $a = 9.6401(19)$ Å, $b = 17.292(4)$ Å, $c = 20.719(4)$ Å, $\alpha = 78.71(3)°$, $\beta = 76.68(3)°$, $\gamma = 81.77(3)°$, $V = 3278.4(11)$ $Å^3$, $Z = 4$, $D_{Calc} = 1.478$ Mg m^{-3}, $\mu = 0.738$ mm^{-1}, $F(000) = 1488$. All diffraction data of the complex (**2b**) were collected with a Rigaku-Raxis-IV imaging plate area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. The diffraction data were corrected for Lorentz and polarization factors. The structure was solved by direct methods [26] and expanded using Fourier techniques and refined by full-matrix least-squares methods using the SHELXTL-97 program package [27] giving a final $R_1 = 0.0609$, $wR_2 = 0.1171$ and 10450 unique reflections with $I > 2\sigma$ (I) for complex (**2b**). Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. CCDC reference number 741291.

Results and discussion

Synthesis and spectroscopic characterization

The three 2-(*m*-nitrophenyl)imidazolines (**1a**–**1c**) were synthesized starting from *m*-nitrobenzaldehyde as shown in Scheme 1. The aldehyde group in *m*-nitrobenzaldehyde was directly converted to 2-imidazoline to yield (**1a**), according to the published procedure [28]. Compounds (**1b**) and (**1c**) were prepared by oxidation of *m*-nitrobenzaldehyde to *m*-nitrobenzoic acid with aqueous $KMnO_4$, followed by the reaction with thionyl chloride to give *m*-nitrobenzoyl chloride. Compounds (**1b**) and (**1c**) were then synthesized according to Scheme 1 [29]. The following cyclopalladation was carried out with the ligands (**1a**–**1c**) and 1.2 equivalent of $Pd(OAc)_2$ in refluxing acetic acid for 12 h, followed by the addition of LiCl to give the proposed chloride-bridged palladacyclic dimers. The dimers were subjected to a bridge-splitting reaction with

triphenylphosphine to afford the expected monomers (**2a**–**2c**). It was found that the imidazoline-NH group in ligand (**1a**) was acetylated during the palladation reaction. A possible reason for the acetylation was that small amounts of Ac_2O might be formed by the dehydration of HOAc with P_2O_5. Another possibility was that the –NH was acetylated by HOAc directly, promoted by $Pd(OAc)_2$, since the condensation of secondary amines with carboxylic acids is usually difficult under heating. Similar acetylations were observed in the platination and palladation reactions of *bis*(imidazoline)benzene ligands containing phenolic-OH groups [25]. All the new compounds were well characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ESI–MS and IR spectra. The IR spectra of the palladium complexes (**2a**–**2c**) show $\nu_{C=N}$ around 1,595 cm^{-1}, which is shifted to lower energy in comparison with the free 2-imidazolines (**1a**–**1c**) (around 1,609 cm^{-1}), indicating the existence of N–Pd coordination. In the ^{1}H NMR spectra, the signals of the cyclopalladated aryl ring protons in complexes (**2**) were significantly shifted upfield, while those of the *N*-aryl and imidazoline rings were shifted downfield relative to the corresponding signals in ligands (**1**). These shifts are indicative of the N–Pd coordination and C–Pd bond formation in the Pd complexes.

Crystal structure of complex (**2b**)

The structures of the cyclopalladated complexes were further confirmed by a single-crystal X-ray analysis of complex (**2b**). The molecule is shown in Fig. 1. There are two molecules in the asymmetric unit along with one molecule of acetone. As depicted in Fig. 1, the Pd atom is in a slightly distorted square-planar environment bonded to the C1 atom of the cyclopalladated aryl ring, the chlorine atom, the imidazolinyl imino-nitrogen atom and the P atom of PPh_3. A tricyclic system is thus formed by the cyclopalladated aryl ring, the five-membered palladacycle and the imidazoline ring. The three rings are approximately coplanar, with the interplanar angles between the cyclopalladated aryl ring or imidazoline ring on one hand, and the palladacycle on the other, being equal to 6.0 (10.4) and 5.2° (3.5°), respectively. However, the *N*-aryl ring is not coplanar with the three rings and the dihedral angle between *N*-aryl ring with the attached imidazoline ring is 66.4° (79.0°). All the bond distances and angles around the Pd(II) center are similar to those observed in the related cyclopalladated complexes with 2-oxazolines, of which the N–Pd–C bond angle (around 80°) is essentially identical [30, 31]. The coordinated PPh_3 is trans to the imino-nitrogen of imidazoline with an almost linear P–Pd–N angle.

Weak intermolecular hydrogen bonds are found in the crystal of **2b**. Due to the weak intermolecular hydrogen bonds between the Pd atom and the adjacent C–H group of

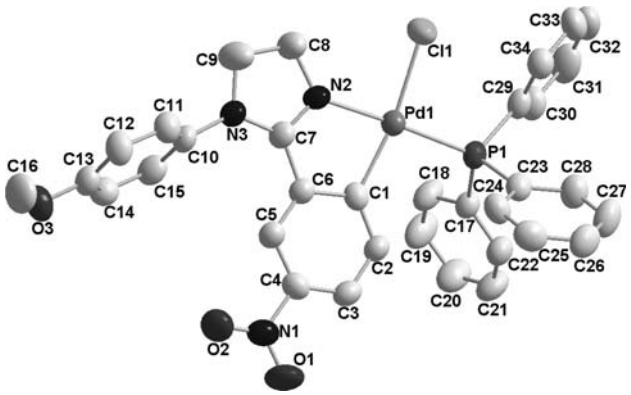


Fig. 1 Molecular structure of complex (**2b**) (representation of one of the two independent molecules in the asymmetric unit). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows (corresponding values for the unshown second structure are given in *brackets*): Pd(1)–C(1) 2.042(4) [2.023(4)], Pd(1)–N(2) 2.044(4) [2.064(4)], Pd(1)–P(1) 2.2783(12) [2.2675(12)], Pd(1)–Cl(1) 2.3744(15) [2.3726(13)] and C(1)–Pd(1)–N(2) 80.22(16) [80.45(16)], C(1)–Pd(1)–P(1) 97.58(13) [93.08(12)], N(2)–Pd(1)–P(1) 173.56(13) [172.45(11)], C(1)–Pd(1)–Cl(1) 166.27(12) [169.11(13)], N(2)–Pd(1)–Cl(1) 88.40(11) [90.73 (11)], P(1)–Pd(1)–Cl(1) 94.53(6) [95.24(5)]

N–Ar (C(15)···Pd(1) 3.753 Å, H(15)···Pd(1) 3.188 Å, C(15)–H(15)···Pd(1) 121°), one molecule (A) exists as a dimer. The other molecule (A′) also has a dimeric structure formed by two types of weak intermolecular hydrogen bonds between the Pd′ or Cl′ atom and the adjacent C–H group of N–Ar (C(11′)···Pd(1′) 3.753 Å, H(11B)···Pd(1′) 3.037 Å, C(11′)–H(11B)···Pd(1′) 135°; C(12′)···Cl(1′) 3.637 Å, H(12B)···Cl(1′) 2.863 Å, C(12′)–H(12B)···Cl(1′) 142°) [32–36]. It is noteworthy that there are also weak intermolecular hydrogen bonds between the two dimeric structures. One hydrogen bond is between O_2 of the nitro group and adjacent C–H group of PPh_3 (C(22′)···O(2) 3.367 Å, H(22B)···O(2) 2.704 Å, C(22′)–H(22B)···O(2) 129°). The other hydrogen bond involves the O3′ atom of the methoxy group and adjacent C–H group of C–Ar (C(3)···O(3′) 3.313 Å, H(3A)···O(3′) 2.606 Å, C(3)–H(3A)···O(3′) 133°) [37]. A 2D architecture of complex (**2b**) is thus constructed (Fig. 2).

Suzuki reaction

To evaluate the effectiveness of the cyclopalladated complexes (**2a**–**2c**) in the Suzuki reaction under mild reaction conditions, the coupling of bromobenzene with phenylboronic acid was first chosen as a model reaction. The reaction was performed using complex (**2a**) as the catalyst in the presence of *n*-Bu_4NBr under air in aqueous media at room temperature for 12 h. As shown in Table 1, the base and the solvent strongly affected the coupling reaction. When CH_3OH-H_2O was used as solvent, K_2CO_3 was found

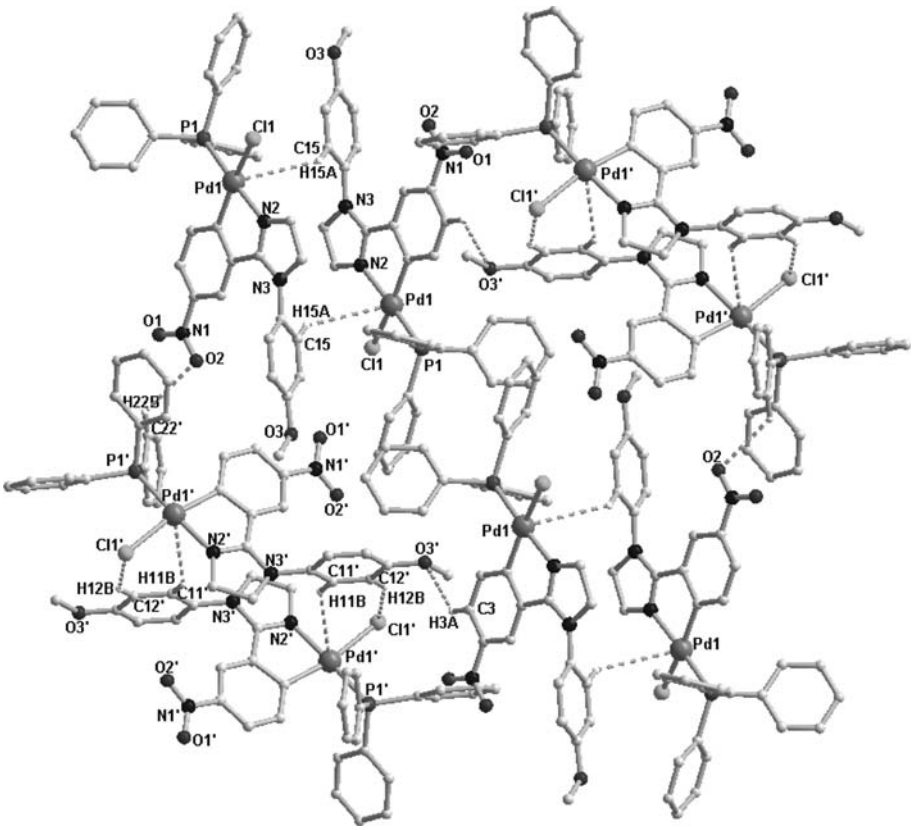
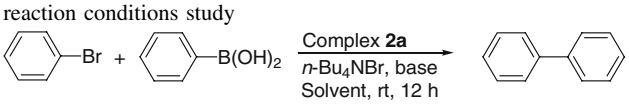


Fig. 2 2D architecture of complex (**2b**) formed by hydrogen bonds. Non-hydrogen bonding H atoms are omitted for clarity

to be the most effective among the tested bases such as K_2CO_3, KOH, $KF{\cdot}2H_2O$, K_3PO_4, Na_2CO_3, giving the biphenyl in a 86% yield with a catalyst loading of 0.5 mol% (entries 1–6). Several other solvents using K_2CO_3 as the base were also examined. Among them, EtOH-H_2O was the most productive and afforded the biphenyl in an almost quantitative yield (entry 7). CH_3OH and DMF-H_2O gave high yields (entries 8–9), while THF-H_2O and toluene-H_2O proved to be ineffective (entries 10–11).

With the appropriate combination of base and solvent (K_2CO_3 and EtOH-H_2O) in hand, the relative activities of three palladacycles (**2**) in the coupling of 3-bromotoluene with phenylboronic acid under the same conditions were compared. Palladacycle (**2c**) was found to be the most active among the three catalysts, giving the coupled product in 95% yield with a catalyst loading of 0.5 mol% (Table 2, entries 1–3). In the following experiments, therefore, the Suzuki coupling reactions of a variety of electronically and structurally diverse aryl bromides with phenylboronic acid were investigated using complex (**2c**) as the catalyst. Similar to the result obtained for 3-bromotoluene, excellent yields (99%) were also obtained in the case of other electron-neutral aryl bromides such as bromobenzene and 1-bromonaphthalene (entries 4–5). Several electron-deficient aryl bromides such as 4-chlorobromobenzene, 2-bromonitrobenzene and 4-bromobenzaldehyde were also efficiently converted to the corresponding biaryl products (entries 6–8). *Ortho*-substituents were tolerated

Table 1 Suzuki coupling of bromobenzene with phenylboronic acid: reaction conditions study



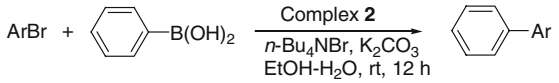
Entry	Base	Solvent	Yield[a] (%)
1	K_2CO_3	CH_3OH-H_2O	99[b]
2	K_2CO_3	CH_3OH-H_2O	86
3	KOH	CH_3OH-H_2O	45
4	$KF{\cdot}2H_2O$	CH_3OH-H_2O	Trace
5	K_3PO_4	CH_3OH-H_2O	55
6	Na_2CO_3	CH_3OH-H_2O	57
7	K_2CO_3	EtOH-H_2O	99
8	K_2CO_3	CH_3OH	94
9	K_2CO_3	DMF-H_2O	82
10	K_2CO_3	THF-H_2O	4
11	K_2CO_3	Toluene-H_2O	9

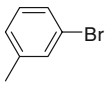
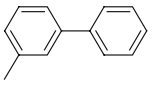
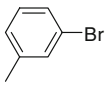
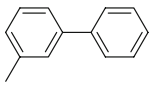
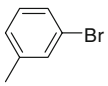
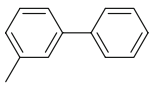
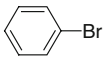
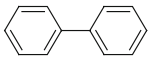
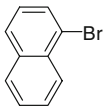
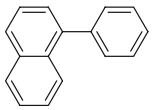
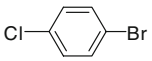
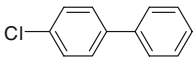
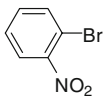
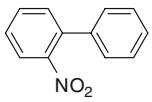
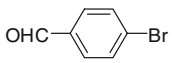
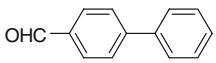
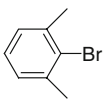
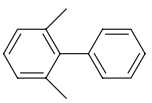
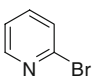
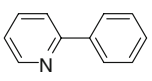
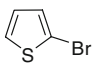
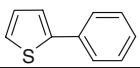
Reaction conditions: bromobenzene 0.5 mmol, $PhB(OH)_2$ 0.6 mmol, base 1.0 mmol, *n*-Bu_4NBr 0.5 mmol, solvent 2 mL (v/v = 1/1), 0.5 mol% of complex (**2a**), at room temperature under air for 12 h

[a] Isolated yields based on bromobenzene

[b] 1 mol% mol of complex (**2a**)

Table 2 Suzuki coupling reaction of aryl bromides with phenylboronic acid catalyzed by **2**



Entry	Complex **2**	ArBr	Product	Yield [a] (%)
1	**2a**			82
2	**2b**			90
3	**2c**			95
4	**2c**			99
5	**2c**			99
6	**2c**			98
7	**2c**			96
8	**2c**			88
9	**2c**			84
10	**2c**			70
11	**2c**			15

Reaction conditions: aryl bromides 0.5 mmol, $PhB(OH)_2$ 0.6 mmol, K_2CO_3 1.0 mmol, *n*-Bu_4NBr 0.5 mmol, EtOH-H_2O 2 mL (v/v = 1/1), 0.5 mol% of complex (**2**), at room temperature under air for 12 h

[a] Isolated yields based on aryl bromide

and even the very sterically hindered 2-bromo-*m*-xylene could provide the product in a good isolated yield (84%, entry 9). A moderate yield was obtained in the coupling of 2-bromopyridine with phenylboronic acid (70%, entry 10), while 2-bromothiophene was found to be a poor coupling partner in this system giving only a 15% yield (entry 11).

Conclusions

In conclusion, we have synthesized and characterized three cyclopalladated complexes with 2-(*m*-nitrophenyl)imidazolines. These complexes have been successfully used in room temperature Suzuki reactions of arylbromides with phenylboronic acid in aqueous media under air, giving the coupled products in satisfactory to excellent yields in most cases.

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