

Green Chemistry Letters and Reviews

ISSN: 1751-8253 (Print) 1751-7192 (Online) Journal homepage: www.tandfonline.com/journals/tgcl20

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To cite this article: Sarah Alnasser, Nedra Touj, Suliman Alomar, Lamjed Mansour, Mathieu Sauthier, Nevin Gurbuz, Ismail Özdemir & Naceur Hamdi (2024) Pd–PEPPSI-type expanded ring N-heterocyclic carbene complexes: synthesis, characterization, and catalytic activity in Suzuki–Miyaura cross coupling, Green Chemistry Letters and Reviews, 17:1, 2370268, DOI: 10.1080/17518253.2024.2370268

To link to this article: https://doi.org/10.1080/17518253.2024.2370268

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GREEN CHEMISTRY LETTERS AND REVIEWS
2024, VOL. 17, NO. 1, 2370268
https://doi.org/10.1080/17518253.2024.2370268

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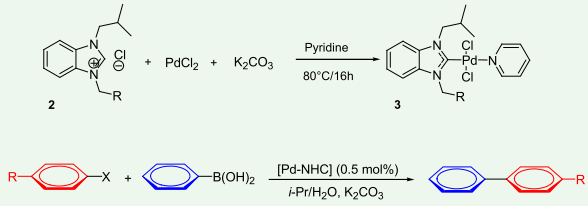
Pd–PEPPSI-type expanded ring N-heterocyclic carbene complexes: synthesis, characterization, and catalytic activity in Suzuki–Miyaura cross coupling

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ABSTRACT

In this work, we synthesized a series of six unsymmetrical benzimidazolium salts 2 and their pyridine-enhanced precatalyst preparation stabilization and initiation (PEPPSI)-themed palladium N-heterocyclic carbene complexes [$PdCl_2$(NHC)(Py)]. All the products were isolated in satisfactory yields (75-85%). The synthesis of these novel palladium PEPPSI complexes involved in reacting NHC precursors with $PdCl_2$ in pyridine at 60°C in the presence of excess K_2CO_3. The structures of all compounds have been characterized by ^{1}H NMR, ^{13}C NMR, HRMS and IR spectroscopy, as well as elemental analysis techniques, which support the proposed structures. The catalytic activity of the six complexes was assessed in the Suzuki-Miyaura cross-coupling of phenylboronic acid and aryl halides. The reactions required only a low catalyst loading (0.1 mol %) and were carried out under mild aerobic conditions in a green, water-based solvent mixture.



ARTICLE HISTORY
Received 22 February 2024
Accepted 16 June 2024

KEYWORDS
Palladium *N*-heterocyclic carben complex; benzimidazole; Suzuki–Miyaura cross coupling; C–C bond formation; water

1. Introduction

Over the past few decades, the chemical industry has developed growing interest in inexpensive and environmentally friendly reaction media such as water based on considerations of safety, availability and environmental impact (1). With palladium-catalyzed cross-coupling reactions being widely applied for the synthesis of fine chemicals, functional materials and industrial starting materials (2), the development of water soluble Pd compounds as highly efficient catalysts for crosscoupling reactions in aqueous reaction media has become an important field of research (3). Since the first example was described by Calabrese and co-workers in 1990 (4), considerable efforts have been undertaken to develop water-soluble Pd catalysts for cross-coupling reactions, especially by modifying traditional Pd phosphine catalysts (5). However, most of the phosphine ligands are air and moisture sensitive, restricting the reuse of the catalyst and leading to undesirable residues under aqueous reaction conditions (6). In addition, the syntheses of phosphine ligands are generally demanding and toxic intermediates are involved (7). Therefore, introducing more stable and less toxic ligands is desirable. N-heterocyclic carbenes (NHCs) have recently gained a strong foothold as ancillary ligands for homogeneous catalysis, sometimes displacing phosphine ligands (8,9). NHCs are advantageous due to their high thermal stability and non-toxic chemical properties. Oxidative stability (10,11), strong σ-donor ability (12) and weak π-acceptor ability, tunable electronic and steric properties, and easy process handling (6). Commonly used transition metal NHC ligands are generated from

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Supplemental data for this article can be accessed online at https://doi.org/10.1080/17518253.2024.2370268

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imidazolium, imidazolinium, and benzimidazolium salts in the presence of strong bases. NHC-Pd complexes have been successfully used as efficient catalysts for C–C bond formation (13–16). In particular, the work of Organ and colleagues plays an important role in the cross-coupling reaction (17). They synthesized a series of Pd-PEPPSI complexes with different NHC ligands. The catalytic properties of these substances resulted in their ability to react efficiently with a diverse range of substrates. According to theoretical analyses, the N-heterocyclic carbene (NHC) ligands are responsible for the origin of the Pd-PEPPSI complex's reactivity (18–22). Principally, the properties of NHC ligands in transition-metalcatalysis can be effectively described by three factors: (1) r-donation from the carbene to the metal center; (2) p-backbonding from the metal to the empty p-orbitals of the NHC; and (3) steric impact (23,24). Since the first report of Pd-NHC systems in C–C bond forming reaction by Hermann and coworkers (25); several research groups such as of Nolan (26–28), Organ (29–31), Szostak (32,33) etc. have developed a plethora of well-defined Pd-NHC-based catalytic systems for Suzuki–Miyaura reactions. Although majority of these NHC complexes were very stable in air and moisture, the catalytic cross-coupling reactions were mainly performed in an oxygen free environment, as the actual catalytic species Pd (0) was highly air sensitive (29). In recent years, a new type of Pd-NHC systems, known as Pd-PEPPSI (PEPPSI: Pyridine enhanced pre-catalyst preparation, stabilization and initiation) has surfaced in literature that showed remarkable activity as catalysts in many cross-coupling reactions including Suzuki–Miyaura reaction (34,35). Unlike conventional Pd-NHC systems, these Pd-PEPPSI complexes are air and water stable and can promote cross-coupling reactions in water or mixed aqueous environment (36,37). Moreover, due to the presence of a weakly bound pyridine moiety makes the Pd-PEPPSI system more efficient as the labile pyridine moiety can act as a 'through-away ligand' and can create a vacant coordination site for the substrate binding and are thus expected to enhance catalytic activities. In fact, in 2006, Organs' group for the first time introduced PdPEPPSI system in Suzuki–Miyaura reactions (38). Since then, a number of highly efficient Pd-PEPPSI complexes have been reported for Suzuki–Miyaura reactions, however majority of the systems suffered from limitations like narrow substrate scope, harsh reaction conditions, high metal loadings (39–41), etc. Until now, only a couple of examples are known that remained successful in activating Suzuki reaction at room temperature in an aqueous environment (42). Thus, there is a need to develop high performance Pd-PEPPSI-based catalytic systems for Suzuki–Miyaura reaction in room temperature in an aqueous environment. In 1990, Casalnuovo et al., reported the Suzuki reaction between aryl halides and boron reagents in water (43). This reaction has been crucial in the advancements of aqueous phase cross-coupling reactions (44). As a consequence, numerous catalysts capable of promoting Suzuki coupling under mild conditions in pure water or in combination with co-solvents are currently known (45).

Catalytic tests performed by Szostak *et al.* (46) and in our group (47) showed that complexes **1**–**3** displayed a high catalytic activity in various palladium-catalyzed cross-coupling reactions. In particular, both studies highlighted that they efficiently promoted the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acids. To minimize its environmental impact, we optimized the experimental procedure for these reactions by working with a low catalyst loading (0.25 mol%) at 40°C in a green, water-based solvent mixture using K_2CO_3 as an innocuous base in the presence of air. Under these mild, aerobic conditions, aryl bromides and iodides bearing either electron-donating or withdrawing substituents afforded a wide range of biaryl derivatives. Although less reactive, aryl chlorides were also successfully activated under more forcing conditions, provided that an electron-withdrawing group was present on their aromatic ring. Encouraged by the good results obtained in Suzuki–Miyaura cross-coupling reactions, we decided to investigate more challenging catalytic applications that could take advantage of the environmental-friendly Pd-NHC PEPPSI complexes **3**. Herein, we describe the synthesis and characterization of the benzimidazoles **2** and their palladium PEPPSI complexes **3**. Thus, the aim of this study is to synthesize novel benzimidazoles **2** and their palladium PEPPSI complexes **3** featuring unsymmetrical ligands with various combinations on their nitrogen atoms. The catalytic activity of these novel complexes will be assessed in the Suzuki–Miyaura cross-coupling of phenylboronic acid with aryl halides in aqueous media, even at room temperature. Using water as a solvent for such reactions is not only cost-effective, but also beneficial for the environment, since it is widely available, inexpensive, and easily separable from organic compounds.

2. Experimental section

2.1. Materials

All reactions for the preparation benzimidazolium salts **2** and palladium-(NHC)-PEPPSI complexes **3** were carried out under air. $PdCl_2$, pyridine and solvents were purchased from Sigma-Aldrich and used as obtained.

Elemental analyses were performed by Elementar Vario EL III Carlo Erba 1108. The melting points of the complexes and NHC precursors were determined using Stuart automatic melting point apparatus (SMP-40). IR spectra were recorded with a PerkinElmer Spectrum 100 GladiATR FT/IR spectrophotometer. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d^6 solutions operating on a Bruker Advance 400 MHz NMR spectrometer and chemical shifts were reported relative to tetramethylsilane for ^{1}H, ^{13}C NMR spectra as standard. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. The HRMS (ESI) electrospray ionization mass spectra were recorded on a Shimadzu LCMS-IT-Toff spectrometer in CH_3CN/$CHCl_3$. All reactions were monitored on a Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratio is given as v/v.

2.2. General procedure for the synthesis of NHC precursors, 2a-f

Compounds **1** (1.1 mmol) and aryl chloride (1 mmol) were dissolved in 5 mL DMF in a pre-dried Schlenck tube. The temperature of the medium is brought to 80°C. with stirring and the reaction is monitored by ^{1} H-NMR for 24 h. At the end of the reaction, the reaction mixture was diluted with ether to precipitate the product. After filtration, the white solid obtained was washed with diethyl ether, dried in vacuo, and then recrystallized from DCM/DE (1:3).

2.2.1. 1-(Isobutyl)-3-(benzyl)benzimidazolium chloride 2a

Yield: 89%, m.p. = 128.3°C, IR $\nu_{(CN)}$: 1650.9 cm^{-1}, ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 12.07 (s, 1H, H_2); 7.71–7.30 (m, 9H, $H_{4,\ 5,\ 6,\ 7,\ 3'',\ 4'',\ 5'',\ 6'',\ 7''}$); 5.95 (s, 2H, $H_{1''}$); 4.44 (d, 2H, $H_{1'}$); 2.44 (sept, 1H, $H_{2'}$); 1.06 (d, 6H, $CH_{3\ (a,b)}$). ^{13}CNMR($CDCl_3$, 101MHz) δ (ppm) = 144.05 (C_2); 132.94 ($C_{2''}$); 131.73 (C_8); 131.12 (C_9); 129.36 ($C_{4'';6''}$); 129.18 ($C_{5''}$); 128.30 ($C_{3'';7'')}$; 127.11 (C_5); 127.08 (C_6); 113.88 (C_7); 113.15 (C_4); 54.44 ($C_{1'}$); 51.38 ($C_{1''}$); 28.89 ($C_{2'}$); 19.86 ($C_{a,b}$). Anal. Calc. for $C_{18}H_{21}ClN_2$ (%):C, 71.86%; H, 7.03%; N, 9.31%. found (%): C, 71.9%; H, 7.1%; N, 9.2%.

2.2.2. 1-(Isobutyl)-3-(4-methylbenzyl)benzimidazolium chloride 2b

Yield: 87%, m.p. = 176.1°C, $C_{19}H_{23}ClN_2$, M = 314,85g mol^{-1}. IR $\nu_{(CN)}$:1550 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 11.81 (s, 1H, H_2); 7.30–7.49 (m, 7H, $H_{4,\ 7,\ 3'',\ 4'',\ 5'',\ 6'',\ 7''}$); 5.86 (s, 2H, $H_{1''}$); 4.36 (d, 2H, $H_{1'}$, *J* = 8 Hz); 2.44 (sept, 1H, $H_{2'}$, *J* = 8 Hz); 2.42 (s, 3H, $CH_{3(d)}$); 2.38 (s, 3H, CH_3(c)); 1.04 (d, 6H, $CH_{3(a,b),}$ *J* = 8 Hz). ^{13}CNMR ($CDCl_3$, 101MHz) δ (ppm) = 143.96 (C_2); 139.16 ($C_{2''}$); 131.75 (C_9); 131.09 (C_8); 129.99 ($C_{4'';6''}$); 129.91 ($C_{5''}$); 128.31 ($C_{3'';7''}$); 127.05 ($C_{5;6}$); 113.97 (C_7); 113.12 (C_4); 54.39 ($C_{1'}$); 51.24 ($C_{1''}$); 28.90 ($C_{2'}$); 21.19 (C_c); 19.86 ($C_{a,b}$). Anal. Calc. for $C_{19}H_{23}ClN_2$ (%):C, 72.48%; H, 7.36%; N, 8.89% . found (%): C, 72.5; H, 7.4; N, 8.9%. DART-TOF-MS: m/z = 340, 267.

2.2.3. 1-(isobutyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium Chloride 2c

Yield: 94%, m.p. = 218.3°C, $C_{21}H_{27}ClN_2$, M = 342.90g mol^{-1}. IR $\nu_{(CN)}$:1469cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 11.61 (s, 1H, H_2); 7.64 (d, 1H, H_7, *J* = 8 Hz); 7.51 (t, 1H, H_6, *J* = 8 Hz); 7.37 (t, 1H, H_5, *J* = 8 Hz); 7.10 (d, 1H, H_4, *J* = 8 Hz); 6.88 (s, 2H, $H_{4'',6''}$); 5.90 (s, 2H, $H_{1''}$); 4.42 (d, 2H, $H_{1'}$, *J* = 8 Hz); 2.37 (sept, 1H, $H_{2'}$, *J* = 8 Hz); 2.28 (s, 6H, $CH_{3(c,e)}$); 2.25 (s, 3H, $CH_{3(d)}$); 1.00 (d, 6H, $CH_{3\ (a,b)}$, *J* = 8 Hz), ^{13}CNMR($CDCl_3$, 101MHz) δ (ppm) = 144.2 (C_2); 130.2 (C_8); 139.6 ($C_{2''}$); 137.9 ($C_{5'',7'');}$ 131.8 ($C_{3''}$); 131.3 (C_9); 127.1 ($C_{6''}$); 126.9 ($C_{4''}$); 125.2 ($C_{5,6}$); 114.0 (C_7); 113.1 (C_4); 54.3 ($C_{1'}$); 47.5 ($C_{1''}$); 28.9 ($C_{2'}$); 21.1 (C_d); 20.3 ($C_{a,b}$); 19.8 ($C_{c,e}$). Anal. Calc. for $C_{21}H_{27}ClN_2$ (%):73.56%; H, 7.94%; N, 8.17%. found (%): C, 73.5; H, 7.9; N, 8.1%.

2.2.4. 1-(Isobutyl)-3-(2.3.5.6-tetramethylbenzyl)benzimidazolium chloride 2d

Yield: 89%, m.p. = 176.3°C, $C_{22}H_{29}ClN_2$, M = 491.51 g mol^{-1}. IR $\nu_{(CN)}$ = 1660.1 cm−^{1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 11.44 (s, 1H, H_2); 7.07–7.69 (m, 5H, $H_{4,\ 5,\ 6,\ 7,\ 5''}$), 5.97 (s, 2H, $H_{1''}$); 4.49 (d, 2H, $H_{1'}$, *J* = 8 Hz); 2.38 (sept, 1H, $H_{2'}$, *J* = 8 Hz); 2.25 (s, 12H, $CH_{3(c,d,e,f)}$); 1.02 (d, 6H, $CH_{3\ (a,b)}$, *J* = 8 Hz). ^{13}CNMR($CDCl_3$, 101MHz) δ (ppm) = 143.9 (C_2); 135.0 ($C_{2''}$); 134.0 ($C_{4'',6''}$); 133.5 ($C_{3'',\ 7''}$); 131.8 (C_9); 131.3 (C_8), 127.9 ($C_{5''}$); 127.0 (C_5); 126.8 (C_6); 113.8 (C_7); 113.0 (C_4); 54.2 ($C_{1'}$); 48.0 ($C_{1''}$); 28.8 ($C_{2'}$); 20.5 ($C_{a,b}$); 19.7 ($C_{d,e}$); 16.12 ($C_{c,f}$). Anal. Calc. for $C_{22}H_{29}ClN_2$ (%):74.03%; H, 8.18%; N, 7.84%. Found (%): C, 8.2; H, 7.2; N, 7.9%.

2.2.5. 1-(Isobutyl)-3-(2.3.4.5.6-pentamethylbenzyl)benzimidazolium chloride 2e

Yield: 92%, m.p. = 198.2°C, $C_{23}H_{31}ClN_2$, M = 370,95g mol^{-1}. IR $\nu_{(CN)}$ = 1546 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 11.29 (s, 1H, H_2); 7.22–7.70 (m, 4H, $H_{4,\ 5,\ 6,\ 7}$); 5.94 (s, 2H, $H_{1''}$); 4.51 (d, 2H, $H_{1'}$); 2.38 (sept, 1H, H20); 2.28 (s, 3H, CH_3(e)); 2.28 (s, 6H, CH_3(d,f)); 2.24 (s, 6H, CH_3(c,g)); 1.05 (d, 6H, CH3 (a,b), J = 4 Hz), ^{13}CNMR($CDCl_3$, 101MHz) δ (ppm) = 143.78 (C_2); 137.21 ($C_{2''}$); 133.87 ($C_{8;9}$);

133.54 ($C_{3'';7''}$); 131.87 ($C_{6''}$); 131.39 ($C_{4''}$); 127.00 (C_6); 126.84 (C5); 125.15 ($C_{5''}$);113.98 (C_7); 113.06 (C_4); 54.27 ($C_{1'}$); 48.50 ($C_{1''}$); 28.88 ($C_{2'}$); 19.79 ($C_{a,b}$); 17.34 (C_e); 17.12 ($C_{d,f}$); 16.98 ($C_{c,g}$). Anal. Calc. for $C_{23}H_{31}ClN_2$ (%):C, 74.46; H, 8.42; N, 7.55 . found (%): C, 74.5; H, 8.5; N, 7.4%.

2.2.6. 1-(Isobutyl)-3-(3,4,5 trimethoxylbenzyl)benzimidazolium chloride 2f

Yield: 97%, m.*p* = 250.9°C, $C_{27}H_{31}N_2Br$, M = 463.45 g mol-1. IR ν(CN) = 1562.47 cm-1. ^{1}H NMR ($CDCl_3$, 400MHz) δ (ppm) = 12.02 (s, 1H, H2); 7.57–7.74 (m, 4H, H4,5,6,7); 6.88 (s, 2H, H3″,7″); 5.81 (s, 2H, H1″); 4.40 (d, 2H, H1′, J = 4 Hz); 3.84 (s, 3H, CH3(d)); 3.78 (s, 6H, CH3(c,e)); 2.39 (sept, 1H, H2′, J = 4 Hz); 1.01 (d, 6H, CH3(a,b)). ^{13}CNMR ($CDCl_3$, 101MHz) δ (ppm) = 153.9 (C4″,6″); 144.1 (C2,2″); 138.6 (C5″); 131.7 (C9); 131.2 (C8); 128.6 (C6); 127.2 (C5); 113.8 (C7); 113.2 (C4); 106.1 (C3″,7″); 60.9 (Cd); 56.7 (Cc, e); 54.5 (C1′); 51.6 (C1″); 28.9 (C2′); 19.9 (Ca,b). DART-TOF-MS: m/z = 267, 225. Anal. Calc. for $C_{27}H_{31}N_2Br$ (%):C, 69.97; H, 6.74; N, 6.04 . Found (%): C, 69.9; H, 6.7; N, 6.1%.

2.3. General procedure for the preparation of the palladium-PEPPSI complexes, (3a-f)

A solution of benzimidazolium salt **2** (1 mmol), palladium(II) chloride (1.05 mmol, 0.18 g), potassium carbonate (5 mmol, 0.69 g) in pyridine (1 mmol, 3 mL) was prepared at 80 °C Stir at 4pm. Thin layer chromatography (eluent dichloromethane) showed formation of a new, more polar product **3** after 16 h. After the reaction was complete, the mixture was cooled to room temperature and filtered through celite. The filtrate solvent was removed in vacuo. The resulting product was washed with n-pentane (3×5 mL) and dried in vacuo. Pure complex 3 was isolated by column chromatography on silica gel (eluting with dichloromethane) or by recrystallization from DCM/DE (1:3).

2.3.1. Dichloro[1-(methoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazole-2-ylidene]pyridinepalladium(II), 3a

Yield: 78% (0.4 g); m.p. = 243.9°C.$\nu_{(CN)}$ = 1447.16 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.25 [s, 6H, $CH_2C_6(CH_3)_5$-2,6], 2.32 [s, 6H, $CH_2C_6(CH_3)_5$-3,5], 2.34 [s, 3H, $CH_2C_6(CH_3)_5$-4], 3.38 [s, 3H, $CH_2CH_2OCH_3$], 4.23 [t, *J* = 4 Hz, 2H, $CH_2CH_2OCH_3$], 5.13 [t, *J* = 4 Hz, 2H, $CH_2CH_2OCH_3$], 6.26 [s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6], 6.44, 6.97 and 7.18 [t, 3H, NC_6H_4N], 7.54 [d, *J* = 8 Hz, 1H, NC_6H_4N], 7.39 [t, *J* = 8 Hz, 2H,, NC_5H_5-$H_{3,5}$], 7.81 [t, *J* = 8 Hz, 1H, NC_5H_5-H_4], 8.98 [d, *J* = 8 Hz, 2H, NC_5H_5-$H_{2,6}$]. ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 16.9, 17.3 and 17.5 [$CH_2C_6(CH_3)_5$-2,3,4,5,6], 48.6 [$CH_2CH_2OCH_3$], 51.2 [$CH_2C_6(CH_3)_5$-2,3,4,5,6], 59.2, 72.0 [$CH_2CH_2OCH_3$], 111.3 [NC_6H_4N-*o*], 122.7 [NC_5H_5, $C_{3,5}$], 123.0 [NC_6H_4N-*m*], 124.5 [$CH_2C_6(CH_3)_5$-2,3,4,5,6;$C_{3,5}$], 127.8 [$CH_2C_6(CH_3)_5$-2,3,4,5,6;C_4], 133.1 [NC_6H_4N-*i*], 134.7 [$CH_2C_6(CH_3)_5$-2,3,4,5,6;$C_{2,6}$], 135.9 [NC_5H_5,C_4], 138.1 [$CH_2C_6(CH_3)_5$-2,3,4,5,6;C_1], 151.2 [NC_5H_5, $C_{2,6}$], 163.27 [Pd-*C*carb]. Anal. Calc. for $C_{27}H_{33}N_3OCl_2Pd$ (%): C, 54.70; H, 5.61; N, 7.09. Found (%): C, 54.78; H, 5.73; N, 7.21. HR-MS(ESI), m/z = 468,1243 $[M+Na+H]^+$ (calcd for $C_{22}H_{28}N_2OPdNa$:468,1217).

2.3.2. Dichloro[1-(methoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazole-2-ylidene]pyridinepalladium(II), 3b

Yield: 75% (0.35 g); m.p. = 215.5°C. $\nu_{(CN)}$ = 1448.80 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.26 [s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 3.28 [s, 3H, $CH_2CH_2OCH_3$], 4.14 [t, *J* = 4 Hz, 2H, $CH_2CH_2OCH_3$], 5.04 [t, *J* = 4 Hz, 2H, $CH_2CH_2OCH_3$], 6.11 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 6.39 and 7.47 [d, *J* = 8 Hz, 2H, NC_6H_4N], 6.86 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 6.89 and 7.10 [t, *J* = 8 Hz, 2H, NC_6H_4N], 7.31 [t, *J* = 8 Hz, 2H,, NC_5H_5-$H_{3,5}$], 7.72 [t, *J* = 8 Hz, 1H, NC_5H_5-H_4], 8.91 [d, *J* = 8 Hz, 2H, NC_5H_5-$H_{2,6}$]. ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): = 20.8 and 21.1 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 48.6 [$CH_2CH_2OCH_3$], 50.0 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 59.2, 72.0 [$CH_2CH_2OCH_3$], 111.1 and 111.4 [NC_6H_4N-*o*], 122.8 [NC_5H_5, $C_{3,5}$], 123.1 [NC_6H_4N-*m*], 124.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6;$C_{3,5}$], 127.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6;C_4], 134.7 [$CH_2C_6H_2(CH_3)_3$-2,4,6;$C_{2,6}$], 134.4 and 135.6 [NC_6H_4N-*i*], 138.2 [NC_5H_5,C_4], 138.8 [$CH_2C_6H_2(CH_3)_3$-2,4,6;C_1], 151.3 [NC_5H_5, $C_{2,6}$], 163.5 [Pd-*C*carb]. Anal. Calc. for $C_{25}H_{29}N_3OCl_2Pd$ (%): C, 53.16; H, 5.17; N, 7.44. Found (%): C, 53.22; H, 5.24; N, 7.56. HR-MS(ESI), m/z = 440,0914 $[M+Na+H]^+$ (calcd for $C_{20}H_{24}N_2OPdNa$:440,0904); m/z = 413,0680 $[M-H]^+$ (calcd for $C_{20}H_{24}N_2OPd$:413,0845).

2.2.3. Dichloro[1-(methoxyethyl)-3-(3,5-dimethylbenzyl)benzimidazole-2-ylidene]pyridinepalladium(II), 3c

Yield: 82% (0.32); m.p. = 205.5°C. $\nu_{(CN)}$ = 1445.58 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm):2.21 [s, 6H, $CH_2C_6H_3(CH_3)_2$-3,5], 3.30 [s, 3H, $CH_2CH_2OCH_3$], 4.23 [m, 2H, $CH_2CH_2OCH_3$], 5.10 [d, *J* = 6 Hz, 2H, $CH_2CH_2OCH_3$], 6.07 [m, 2H, $CH_2C_6H_3(CH_3)_2$-3,5], 6.86 [s, 1H, NC_6H_4N], 7.05[m, 2H, NC_6H_4N], 7.48 [d, *J* = 8 Hz, 1H, NC_6H_4N], 7.15 and 7.19 [s, 3H, $CH_2C_6H_3(CH_3)_2$-3,5], 7.28 [m, 2H, NC_5H_5-$H_{3,5}$], 7.48 [d, *J* = 8 Hz, 1H, C_6H_4–H_4], 7.67–6.72 [m, 1H, NC_5H_5-H_4], 8.95 [m, 2H, NC_5H_5-$H_{2,6}$]. ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 21.3 [$CH_2C_6H_3(CH_3)_2$-3,5], 48.8 [$CH_2CH_2OCH_3$], 53.3 [$CH_2C_6H_3(CH_3)_2$-3,5], 59.2 [$CH_2CH_2OCH_3$], 71.7 [$CH_2CH_2OCH_3$], 111.2 and 111.5 [NC_6H_4N-*o*], 123.1 [NC_5H_5, $C_{3,5}$], 124.6 [NC_6H_4N-*m*], 125.9 [$CH_2C_6H_3(CH_3)_2$-3,5;$C_{2,6}$], 129.8 [$CH_2C_6H_3(CH_3)_2$-3,5;C_4], 134.8 and 134.3 [NC_6H_4N-*i*], 135.9 [$CH_2C_6H_3(CH_3)_2$-3,5;C_1], 138.1 [NC_5H_5, C_4], 138.4 [$CH_2C_6H_3(CH_3)_2$-3,5;$C_{3,5}$], 152.7 [NC_5H_5, $C_{2,6}$], 163.4 [Pd-*C*carb]. Anal. Calc. for $C_{24}H_{29}N_3OCl_2Pd$ (%): C, 52.33; H, 4.94; N, 7.63. Found (%): C, 52.39; H, 5.01; N, 7.95. HR-MS(ESI), m/z = 571,6105 $[M+Na-H]^+$ (calcd for

$C_{24}H_{27}N_3OCl_2PdNa$:571,0385); m/z = 426,0798 $[M+Na+H]^+$ (calcd for $C_{19}H_{22}N_2OPdNa$:426,0786).

2.2.4. Dichloro-[1-(isobutyl)-3-(methoxyethyl)-5,6-dimethylbenzimidazole-2-ylidene](pyridine)palladium(II)3d

Yield: 81%, m.p. = 242.5°C, $C_{21}H_{29}Cl_2N_3OPd$, M = 516,81. $gmol^{-1}$, IR ν_{CN}, cm^{-1}: 1400, ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 0.91 (d, 6H, $CH_{3(a,b)}$, $J = 4$ Hz), 1.28 (sept, 1H, $H_{2'}$, $J = 8$ Hz), 1.57 (s, 3H, $CH_{3(e)}$), 2.20 (s, 6H, $CH_{3(c,d)}$), 3.97 (m, 2H, $H_{2''}$), 5.07 (m, 2H, $H_{1''}$), 6.57 (s, 2H, $H_{1'}$), 6.88 (s, 2H, $H_{4,7}$), 7.68–7.72(m, 2H, $H_{3''', 5'''}$), 8.84–8.86 (m, 3H, $H_{2''',6''', 4'''}$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 20.0 ($C_{c,d}$), 20.3($C_{a,b}$), 20.6 ($C_{2'}$), 21.1($C_{1''}$), 29.1 (C_c), 53.6 ($C_{1',2''}$), 109.9 (C_4), 114.3(C_7), 124.8 ($C_{3''';5'''}$), 129.2 (C_5), 129.4 (C_6), 133.8 (C_8), 137.9 (C_9), 140.3 ($C_{4'''}$), 151.5 ($C_{2''';6'''}$), 161.7 (C_2). Anal.Calcd. pour $C_{19}H_{25}Cl_2N_3OPd$ (%):C, 48.806; H, 5.656; N, 8.131; Trouvé (%): C, 48.9; H, 5.7; N, 8.3. DART-TOF-MS (m/z) = 516,81

2.2.5. Dichloro-[1-(isobutyl)-3-(2.4.6 trimethylbenzyl)benzimidazol-2-ylidene](pyridine) palladium(II)3e

Yield: 85%, m.p. = 220.2°C, $C_{26}H_{31}Cl_2N_3Pd$, M = 562.87. $gmol^{-1}$, IR ν_{CN}, cm^{-1}: 1458, ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 1.15 (d, 6H, $CH_{3\ (a,b)}$, $J = 8$ Hz), 2.33 (s, 9H, $CH_{3(c,d,e)}$), 3.11 (sept, 1H, $H_{2'}$, $J = 8$ Hz), 4.65 (d, 2H, $H_{1'}$, $J = 8$ Hz), 6.24 (s, 2H, $H_{1''}$), 6.93 (s, 2H, $H_{4'',6''}$) 6.95–7.36 (m, 4H, $H_{4, 5, 6, 7}$), 7.38 (m, 2H, $H_{3''',4'''}$), 7.79 (t, 1H, $H_{4'''}$, $J = 8$ Hz), 8.99 (d, 2H, $H_{2''',6'''}$, $J = 4$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 20.9 ($C_{(c,e)}$), 21.0 ($C_{(a,b)}$), 21.2 (C_d), 29.7 ($C_{2'}$), 50.4 ($C_{1''}$), 55.5 ($C_{1'}$), 110.6 (C_4), 111.6 (C_7), 122.8 ($C_{3'''}$), 123.1 ($C_{5'''}$), 124.6 ($C_{5;6}$), 129.7 ($C_{4'';6''}$), 134.4 (C_8), 135.5 (C_9), 138.2 ($C_{5'';4'''}$), 138.6 ($C_{2''}$), 138.8 ($C_{3'';7''}$), 151.4 ($C_{2''';6'''}$), 163.6 (C_2). Anal.Calcd. pour $C_{26}H_{31}Cl_2N_3Pd$ (%): C, 55.48; H, 5.55; N, 7.47; Trouvé (%):C, 55.60; H, 5.40; N, 7.60.

2.2.6. Dichloro-[1-(isobutyl)-3-(3.4.5 trimethoxylbenzyl)benzimidazol-2-ylidene](pyridine) palladium(II) 3f

Yield: 87%, m.p. = 158.4°C, $C_{26}H_{31}Cl_2N_3O_3Pd$, M = 610.86 $gmol^{-1}$, IR ν_{CN}, cm^{-1}: 1431, ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 1.14 (d, 6H, $CH_{3\ (a,b)}$, $J = 8$ Hz), 3.09 (sept, 1H, $H_{2'}$, $J = 8$ Hz), 3.81 (s, 3H, $CH_{3(d)}$), 3.82 (s, 6H, $CH_{3(c,e)}$), 4.68 (d, 2H, $H_{1'}$, $J = 8$ Hz), 6.14(s, 2H, $H_{1''}$), 6.86 (s, 2H, $H_{3'',7''}$), 7.14–7.23 (m, 2H, $H_{3''',5'''}$), 7.32–7.38 (m, 4H, $H_{4, 5, 6, 7}$), 7.78 (t, 1H, $H_{4'''}$, $J = 8$ Hz), 9.00(d, 2H, $H_{2''',6'''}$, $J = 4$ Hz), ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 20.8 ($C_{a,b}$), 29.5 ($C_{2'}$), 53.4 ($C_{1''}$), 55.7 ($C_{1'}$), 56.6 ($C_{c;e}$), 60.9 (C_d), 105.1 ($C_{3'';7''}$), 110.8 (C_4), 111.5 (C_7), 123.3 ($C_{3'''}$), 124.7 ($C_{5'''}$), 125.1 ($C_{5;6}$), 130.89, ($C_{2''}$), 131.0 (C_8), 134.0 (C_9), 135.6 ($C_{5''}$), 138.7 ($C_{4'''}$), 151.3 ($C_{2''';6'''}$), 153.5 ($C_{4'',6''}$), 163.9 (C_2). Anal.Calcd. pour C28H35Cl2N3Pd (%): C, 51.12; H, 5.12; N, 6.88; Trouvé (%):C, 51.20; H, 5.10; N, 3.90.

2.4. General procedure for Suzuki–Miyaura reactions

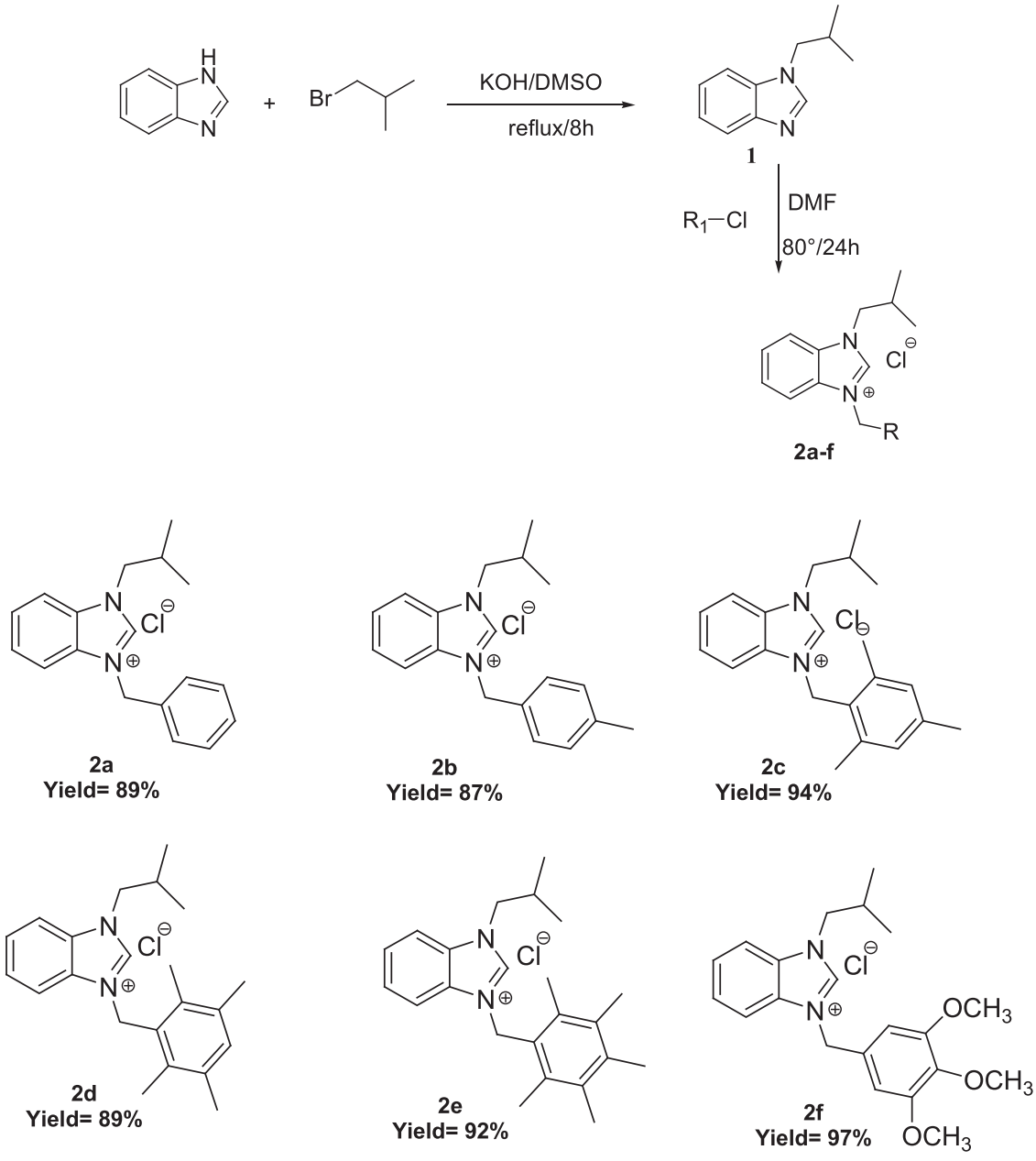
To initiate the reaction, a small round bottom flask was used to introduce air, Pd-PEPPSI complex (0.1 mol %), aryl bromide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1 mmol), and 4 mL of water/i-PrOH (3:1 v/v). The mixture was then stirred for an appropriate amount of time. Following this, the reaction mixture was extracted with Et_2O, and the extract was filtered through a pad of silica with copious washing of diethyl ether. To ensure the purity of the compounds, GC was used to check yields based on aryl chloride and calibrated internal standard (undecane).

3. Results and discussion

3.1. Preparation of benzimidazolium salts 2

New benzimidazolium salts **2**, which are carbene precursors, were synthesized firstly by N-alkylation reaction using benzimidazole (1 mmol) with isobutyl bromide (1 mmol) in the presence of KOH for 8h at reflux to prepare the starting material 1-Isobutyl-1H-benzoimidazole (**1**). The precursor (**2**) was then synthesized by the quaternization of the intermediate (**1**) with same benzyl chloride in DMF for 24h in degassed dimethylformamide at 80°C (Scheme 1). The new benzmidazolium salts were obtained and isolated as air- and moisture-stable white solid in high yield (>87%). The structures of the salts were determined by their characteristic spectroscopic data and elemental analyses. The benzimidazolium salts include an acidic NC*H*N proton, which can be deprotonated easily to form an NHC, at the C_2 position of the benzimidazole ring. The sharp salt peak indicating the synthesis of a benzimidazolium salt came quite downfield at δ 12.07, 11.81, 11.61,11.44,11.29 and 12 ppm, in the ^1H NMR spectra for **2**, respectively. The NCHN peaks of the carbene precursors were observed at δ 144.05, 143.96, 144.2, 143.9, 143.87 and 143.7ppm in the 13C{1H} NMR spectra for **2**, respectively. The formation of the benzimidazolium salts was also evident through their IR spectra, which showed peaks at 1650.9,1550,1469,1660.1,1546 and 1542cm^{-1} for the ν(CN) bond of **2**, respectively.

The one-bond CH J-coupling value (1 JCH) is related to the hybridization of the carbon atom involved (48). There is an empirical correlation between the carbon s-fraction 's' and the coupling constant J as follows: 1 JCH = 500 s, with 's' ranging from 0.25 to 0.33 to 0.5 as the hybridization changes from sp3 to sp2 to sp, respectively (49). Higher one-bond CH J-coupling constants correspond to poorer r-donating properties of NHC ligands due to increased s-orbital character of the CAH bond.



Scheme 1. Synthesis of NHC precursors **2a-f**.

The one-bond CH J-coupling value can in principle be obtained either from the ^{1}H-coupled ^{13}C NMR spectrum or from the ^{13}C satellites of the ^{1} H NMR spectrum. If the main ^{1} H peaks are well resolved, the latter represents a much more efficient approach given the higher sensitivity of ^{1}H vs ^{13}C NMR spectroscopy (50). The one-bond *J*CH coupling constant value can be obtained either from the 1Hcoupled ^{13}C-NMR spectrum or from the 13C satellites of the ^{1}H NMR spectrum. In a simple ^{13}C-NMR spectrum, the carbene carbon appears as a singlet. But it displays two peaks in proton-coupled ^{13}C-NMR. From this, we can calculate the ^{1}*J*CH coupling constant which is related to the sigma donating properties of the ligands. The value of one-bond *J*CH coupling is inversely related to the sigma-donating properties. The *J*CH values of all ligands were listed in Table 1.

The ^{1}*J*CH coupling constant values for **2b** and **2c** were 165.44 and 162.29 Hz, respectively. On the other hand, the ^{1}*J*CH coupling constant values of **2d** and **2e** were 225.19 and 220.16 Hz, respectively. The ligands **2b** and **2c** exhibited strong sigma donating properties, and **2d-f** exhibited weak sigma donating properties.

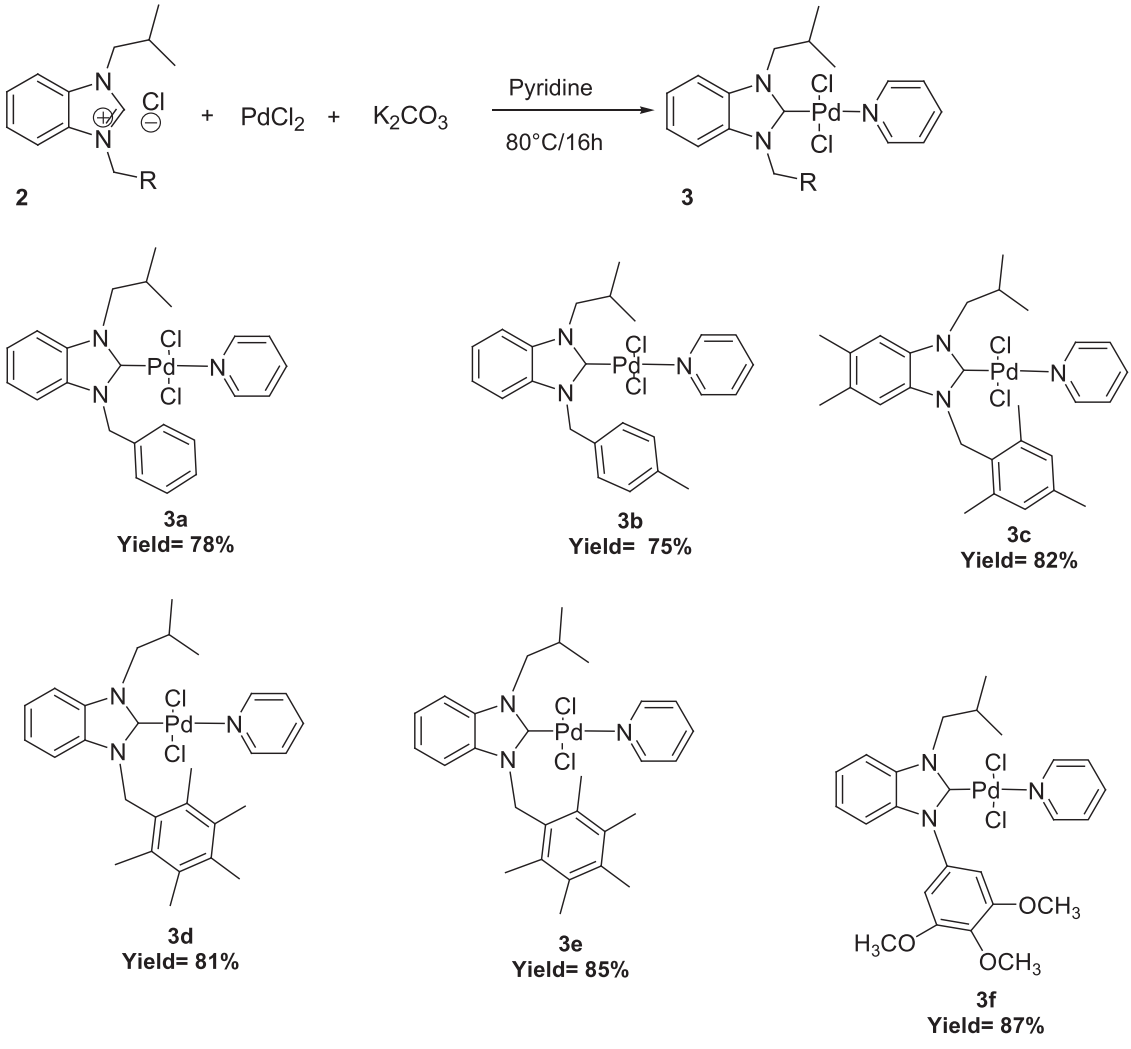
3.2. Synthesis of PEPPSI Pd–NHC complexes 3

Our aim was to synthesize novel Pd–NHC complexes containing a PEPPSI skeleton. The target PEPPSI Pd–NHC complexes **3** were successfully synthesized by

Table 1. ^{1}JCH coupling values of NHC Ligands **2a-f** in Hz.

S. No	Ligands	^{1}JCH (Hz)
1.	**2a**	165.44
2.	**2b**	162.29
3.	**2c**	164.35
4.	**2d**	225.19
5.	**2e**	220.16
6.	**2f**	226.18

using carbene precursors **2**, $PdCl_2$ and K_2CO_3 as a base in pyridine at 60 °C in the presence of excess K_2CO_3 (Scheme 2). The colors of the obtained solid complexes were either yellow or white. These complexes, which are stable both in solution and in solid states against air, light and moisture, were obtained in low yields of 75–85%. All complexes with a benzimidazolium moiety display characteristic signals for the pyridine ligand in the ^{1}H and $^{13}C\{1H\}$ NMR spectra. For the ^{1}H NMR spectra of the metal complexes, sharp peaks in the lower field belonging to the benzimidazolium salts (NC*H*N) were not observed between δ 10 and 12 ppm. The FTIR data clearly indicated the presence of ν(CN) at 1447.16, 1448.80, 1445.58,1400,14459 and 1431. for the PEPPSI Pd–NHC complexes **3**, respectively. Unfortunately, we were unable to yield a proper single crystal from these complexes for X-ray diffraction. The signal of benzylic proton (N–CH_2–Ar) belonging to Pd-NHC complexes **3a-f** complexes was observed as a sharp singlet signal at around *δ* 6.26 ppm, 6.11 ppm,6.07 ppm,6.57 and 6.24 ppm respectively. While signals for the pyridine ring, protons are found downfield. The signals for aromatic protons appear between 7.10 and 7.68 ppm. The presence of pyridine in the coordination sphere was confirmed by characteristics 1 H NMR signals at 8.98, 7.71 and 7.29 ppm. These signals suggest that the pyridine ring coordinated to the palladium center to form a PEPPSI-type palladium complexes **3**. In ^{13}C NMR the signals of the aromatic carbons of the pyridine ring were detected at δ = 152.8, 152.2, 128.1 ppm. The characteristic Pd-C_2-carbene signals of Pd-complex (**3i**) appear as a



Scheme 2. Synthesis of Pd-PEPPSI complexes **3**.

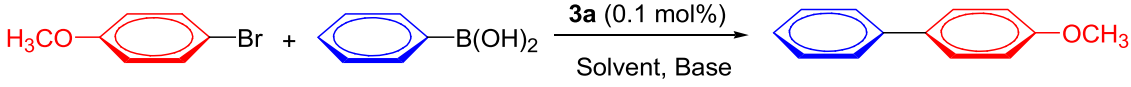
singlet at δ = 163.5 ppm in ^{13}C NMR spectra. The aromatic carbons of the benzene ring resonate between 112.03 and 152.6 ppm. These results are in agreement with the data of other such complexes (51–53). The contents of C, H, and N in palladium PEPPSI-type complexes **3a–f** were determined by elemental analysis. The results agreed well with the theoretical formula of the complexes. The obtained fragments are typical for each palladium PEPPSI-type complexes **3a–f** and can provide further evidence for the characterization of the examined compounds.

After the characterization of these complexes, their catalytic behavior was studied in the Suzuki coupling reaction of aryl boronic acids with aryl halides in water

3.3. Suzuki–Miyaura cross-coupling reaction

Compared to conventional phosphine-based catalysts, the NHC-PdPEPPSI complexes typically show very good activity for a diverse range of cross-coupling reactions including Suzuki–Miyaura reactions. However, the activity and selectivity of such PEPPSI complexes largely depends on the combined effects of backbone and N-substituents of the NHC (54). To check the catalytic performance of our PEPPSI complex, the Suzuki–Miyaura cross coupling reaction of aryl bromides / chlorides with arylboronic acid was explored. The initial optimization study was conducted using p-bromoanisole (1mmol) and phenyl boronic acid (1.1 mol) as model substrates in presence of K_2CO_3 (1mmol) as base taking i-PrOH/H_2O (1:3) (4 mL) as solvent at room temperature with 0.1 mol% catalyst. When a single type of solvent, such as water, EtOH, MeOH, DMF, or i-PrOH, was used, low coupling product was observed (Table 2, entries 1–10). However, increasing the volume ratio of water to any solvent, such as EtOH, DMF and i-PrOH, from 1:1 to 3:1 (v/v) and changing the solvent type, led to a significant increase in coupling product (Table 2, entries 1–14). The control experiments showed that without the Pd-PEPPSI complex **3a**, only a trace amount of the product was obtained (Table 2, entry 15). As shown in Table 2, the heterocoupling of boronic acid derivatives with various aryl bromides gave the corresponding biaryl compounds in good to excellent yields, and only o-methyl bromobenzene gave a low yield (entries 4, 9, and 14). We think this is due to steric hinderance. Through the experiments performed, we were able to achieve a quantitative yield (97%) using the i-PrOH-water solvent system at ratios of 1:3 and 1:1 v/v, as indicated in Table 2, entry 11. However, when the ratio of i-PrOH or water was increased, it resulted in a decrease in the coupled product due to the solubility of the base in i-PrOH or the solubility of the complex in water. Therefore, we opted for a 1:3 ratio to achieve quantitative yields and also implemented a green chemistry procedure that utilizes more water. By screening different bases, in i-PrOH-water (1:3 and 1:1 v/v) during the Suzuki reaction including K_2CO_3, Na_2CO_3, Cs_2CO_3, K_3PO_4, KOH and K_2CO_3 (Table 2), Results showed that different bases produced varying levels of activity in the reaction (Table 2, entries 1–14), we found that K_2CO_3 was the best when using the Pd-PEPPSI complex **3a** (0.1 mol %) for 1 h in water giving a 97% yield when isolated within an hour. For KOH, the yield was not satisfactory. We are quite satisfied to report that trace amount of undesired homo-coupling product

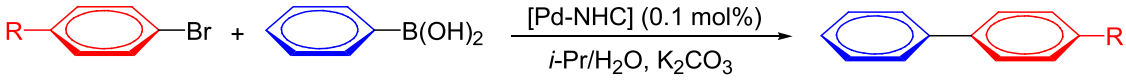
Table 2. The optimization for the Suzuki-Miyaura reaction of 4-bromoanisole[a].

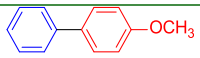
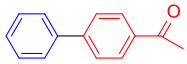
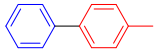
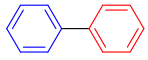
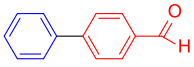
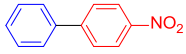


Entry[a]	Solvent	Base	Yield(%)[b]
1	i-PrOH	K_2CO_3	75
2	i-PrOH	Na_2CO_3	58
3	i-PrOH	Cs_2CO_3	48
4	i-PrOH	K_3PO_4	59
5	i-PrOH	KOH	49
6	H_2O	K_2CO_3	45
7	DMF	K_2CO_3	53
8	EtOH	K_2CO_3	69
9	MeOH	K_2CO_3	68
10	Acetone	K_2CO_3	45
11	i-PrOH/H_2O(1:3)	K_2CO_3	97
12	i-PrOH/H_2O(1:1)	K_2CO_3	94
13	DMF/H_2O(1:3)	K_2CO_3	79
14	EtOH/H_2O(1:3)	K_2CO_3	87
15[c]	i-PrOH/H_2O(1:3)	K_2CO_3	0.3

[a]Reaction Condition:1 mmol of 4-bromoanisole, 1.1 mmol of phenylboronic acid, 1 mmol of base, 0,1 mol% complex 3**a**, 4 mL solvent, room temperature, 1 h.
[b]Isolated yield.
[c]The reaction was conducted under ligandless conditions and with a trace amount of palladium chloride.

Table 3. Catalytic activities of **3a-f** complexes in the Suzuki coupling reactions under optimized conditions.[a]



Entry	Product	[Pd-NHC]/yield (%)[b] 3a	3b	3c	3d	3e	3f
1		80	82	75	54	72	93
2[c]		96	88	91	87	89	95
3		80	67	52	51	57	59
4		66	71	74	54	65	76
5[c]		94	96	85	88	91	96
6[c]		90	81	83	74	90	92

[a]Reaction condition: 0.1 mol % [Pd], 1 mmol *p*-R-C_6H_4Br, 1.1 mmol phenylboronic acid, 1.0 mmol K_2CO_3, rt, 1h.
[b]Isolated product.
[c]10 min.

was observed in optimization of Suzuki coupling reaction proceed at room temperature in air.

Under these optimum conditions, a range of aryl bromides/chlorides containing different types of electrons donating or withdrawing substituents were screened as coupling partners with phenylboronic acid (Table 3). As shown in Table 3, the either electron-donating or electron-withdrawing groups bearing aryl bromides effectively to afford the corresponding products in good yields (51–96%) in *i*-PrOH/H_2O mixture in 1h at rt (Table 2, entries 1–6). For example, 4-bromoacetophenone afforded a good yield in 10 min, resulting in a TOF of 1000 h^{-1} (Table 3, entry 2). However, -CH_3 and -OCH_3 substituted aryl bromides showed slightly lower activity than –NO_2, -$COCH_3$ and -CHO substituted aryl bromides due to the high nuclophilicity of the electron donating aryl bromides (Table 3, entries 1,2,5,6). Trace amount homo-coupled by-product was observed although cross-coupling reactions were carried out on air. Overall, these results direct that this PEPPSI-Pd-NHC complex efficient for the coupling of aryl bromides/chlorides with phenylboronic acid. Based on literature support we can conclude that our catalyst follow Organ-type (55–59) mechanism where the Pd-NHC-PEPPSI is reduced to Pd (0) followed by pyridine dissociation. The dissociation of pyridine generate the Pd (0) active species which subsequently undergo oxidative addition of aryl halide, transmetallation of phenyl boronic acid and reductive elimination of cross-coupling product complete the reaction cycle.

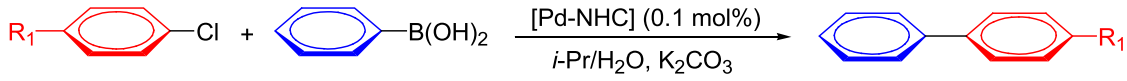
When the efficiency of catalysts is compared, the complex **3a** has performed slightly higher catalytic activity then rest of complexes. Also, this catalytic system is almost equally effective for electronically rich and poor aryl bromides. For the coupling reaction of 1-chloro aryl derivatives with phenylboronic acid (Table 4, entries 1–4), the catalytic activity of the Pd-PEPPSI complex **3a** at 0.01 mol % loading was not satisfactory and only 71% of the coupling product was obtained using p-nitrochlorobenzene (Table 4, entry 3) as the substrate.

The yields with other substrates were very low under the same conditions. Thus, our study is pretty significant for produce coupled product at room temperature in very short time using green solvents with low catalyst loading (0.1 mol%) without need to any additives.

4. Conclusion

In this work, we have demonstrated synthesis of benzimidazolium salts (**2**) and PEPPSI Pd–NHC complexes and explored its potential as catalyst for the Suzuki-Miyaura Cross coupling reactions of aryl halides with phenyl boronic acid. Good-to-excellent yields of cross-coupling products were obtained with a range of substrates in aqueous-isopropanol under mild reaction

Table 4. Catalytic activities of **3a** complex in the Suzuki coupling reactions under optimized conditions.[a]



Entry	R_1	Time (h)	Yield[b]
1	4-CH_3	12 h	4
2	2-CH_3	12 h	3
3	4-NO_2	12 h	71
4	4-OCH_3	12 h	1

[a]Reaction condition: 0.1 mol % [Pd], 1 mmol *p*-R_1-C_6H_4Cl, 1.1 mmol phenylboronic acid, 1.0 mmol K_2CO_3, rt, 1h.
[b]Isolated product.

conditions. The structures of the obtained compounds were confirmed via ^1H and $^{13}C\{1H\}$ NMR and elemental analysis. Among these complexes, complexes **3a** and **3b** showed good +--catalytic performance towards various types of aryl bromides, while the other complexes showed lower catalytic activity. Ultimately, the catalyst system described here has several advantages: low catalyst loading, substrate tolerance, quantitative yield, room temperature, environmentally friendly solvent, short reaction time, and very simple procedure. The use of green solvents such as water and i-PrOH, the low catalyst loading and the fact that the reaction takes place in air at room temperature are the main advantages of this catalytic system.

Acknowledgements

The authors extended their appreciation to the Researchers Supporting Project number (RSP2024R75), King Saud University, Riyadh, Saudi Arabia.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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