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Abnormal NHC supported palladacycles: Regioselective arylation of heteroarenes *via* decarboxylation

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ABSTRACT

We report synthesis of two new palladium(II) complexes of abnormal *N*-heterocyclic carbene ligands. The catalytic activity of these palladium(II) complexes was examined for the decarboxylative arylation of *N*-methylindole-carboxylic acids. An exclusive regioselectivity and very good yields were obtained with a variety of aryl halide partners.

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1. Introduction

Heteroaromatic biaryls form an important class of organic compounds owing to their widespread applications in materials and biological sciences [1,2]. In medicinal chemistry for example; substituted indole nucleus has broad applications as biologically active natural and unnatural products [3]. In addition, indole derivatives can exhibit several photophysical properties [4,5]. Thus developing efficient methods for synthesis of compounds with indole nucleus is of great interest. Conventionally, biaryl motifs are synthesized by transition-metal catalyzed cross-coupling reactions or direct arylation *via* C-H bond activation [6,7]. An alternative approach is decarboxylative cross-coupling of aromatic carboxylic acid with aryl halides [8–10]. Over the past decade, carboxylic acids gained particular interest as coupling partners owing to their wide availability with variations in nature, ease of handling compared to highly sensitive organometallic reagents and high selectivity at carboxylic acid position compared to that of direct C-H functionalization [8–10].

Pioneering work in decarboxylation reaction was done in 1930 by Shepard [11] who reported that benzoic acid undergoes photodecarboxylation in the presence of stoichiometric amount of copper salts when heated at high temperature. Later Nilsson and co-workers [12–14] studied the decarboxylative coupling of nitrobenzoic acid derivatives with aryl halides as well as kinetics of decarboxylation in presence of stoichiometric amount of copper or silver salts at elevated temperatures. Further Cohen and co-workers [15,16] also studied the decarboxylation of aromatic carboxylic acids mediated by copper salts. The first catalytic decarboxylative coupling to form biaryls was reported by Forgione and co-workers in 2006 [17]. They have employed carboxylic acid functional group as a protecting group to functionalize or remove later during reaction. But arylation was observed at the carbon bearing carboxylic acid functional group after extrusion of carbon dioxide rather than C-H arylated product. Reports on decarboxylative C-C coupling of indole-carboxylic acid moieties are very scarce in literature. First report appeared in 2009, when Miura and co-workers [18] have reported decarboxylative cross-coupling of indole-carboxylic acid with aryl-bromide using $Pd(OAc)_2$ and phosphine ligand. However, it led to biarylated product and inaccessibility of mono-arylated product was the major drawback of Miura's reaction protocol (Scheme 1) and it works only with aryl bromide coupling partners. In 2012, Lee and co-workers [19] have reported synthesis of mono-arylated indoles at C2 position from 3-carboxyindoles and aryl bromides using a palladium(0)NHC based catalyst.

In several cases upon using 2-carboxyindole as indole partner C2-arylated product was obtained along with C3-arylated product

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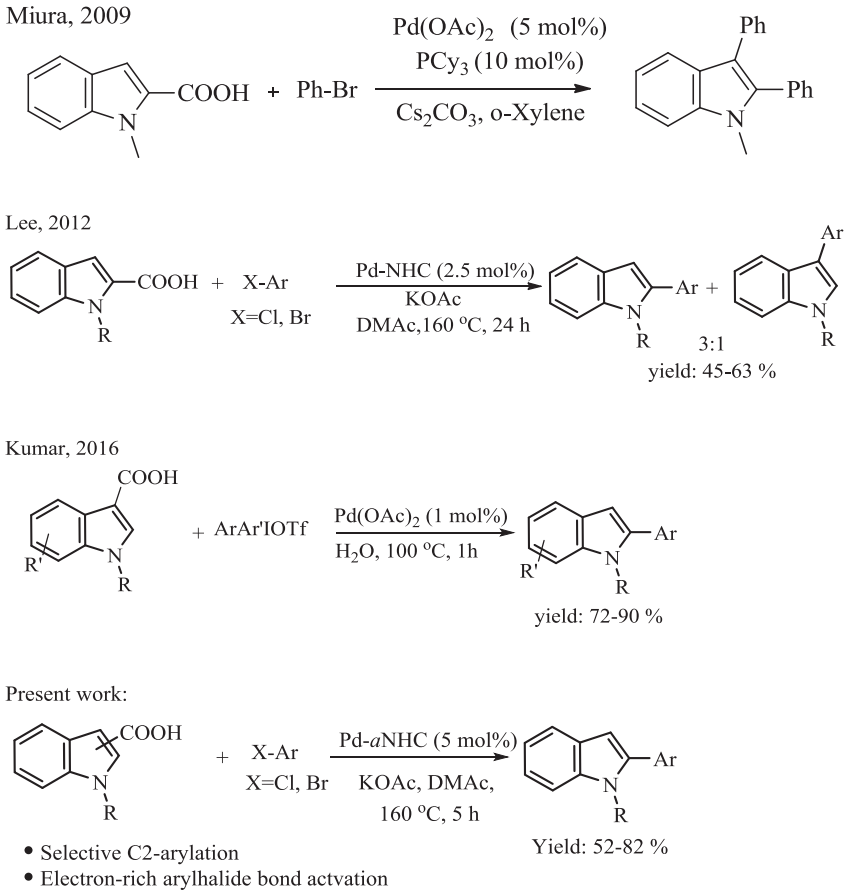


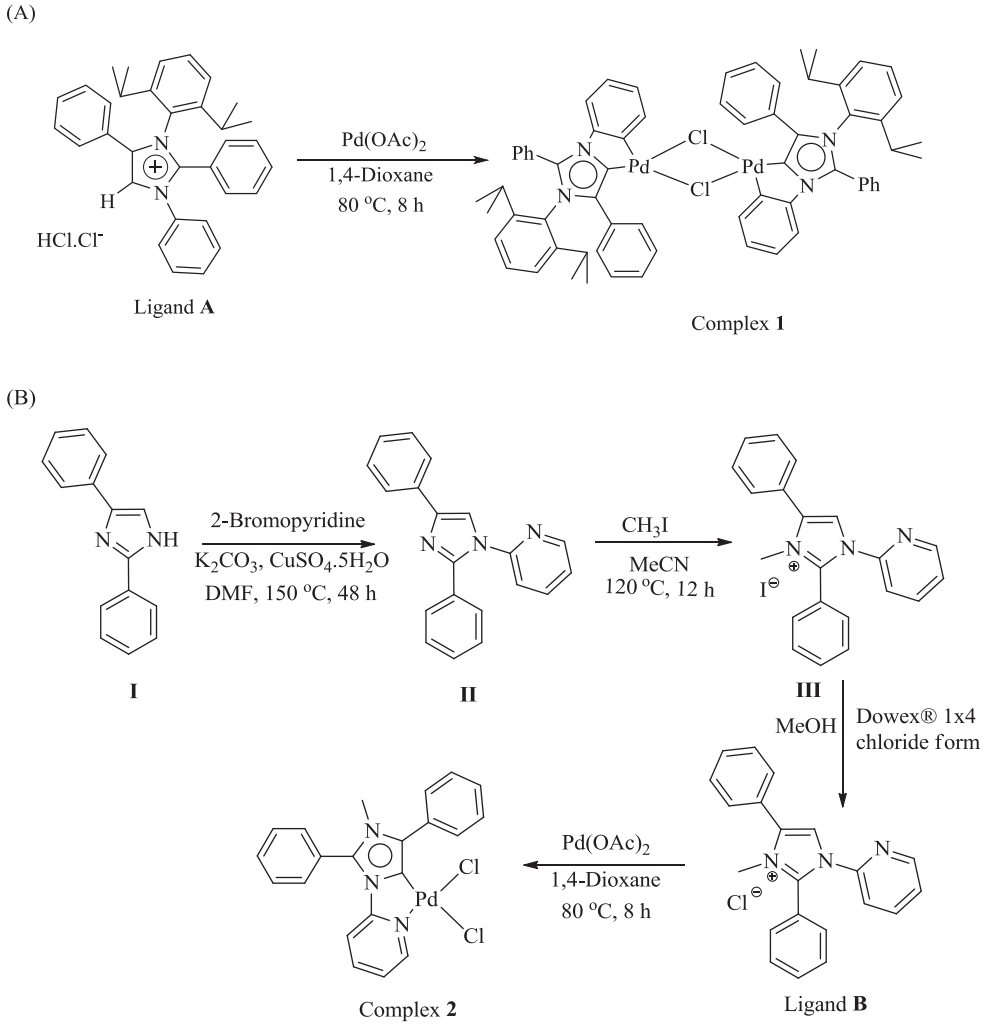
Scheme 1. Previous reports on decarboxylative C-C cross coupling of indole-carboxylic acid with different aryl partners and the present work.

with nearly 3:1 ratio (Scheme 1). In addition to this regioselectivity issue, Lee and co-workers failed to obtain higher yields. Later in 2016, Kumar and co-workers reported synthesis of 2-arylindoles *via* Pd-catalyzed decarboxylative strategy in water without base, oxidant and ligand (Scheme 1) [20]. Though a wide range of 2-arylindoles were synthesized in good yields, they have utilized diaryliodonium salts as aryl coupling partners instead of economically attractive aryl halide partners.

Thus, from the previous reports on decarboxylative coupling of *N*-methylindole-carboxylic acids with aryl halides, it clearly indicates important limitations such as lack of regioselective C2-arylation, poor yields using more abundant aryl halide coupling partners [18–20]. It may be noted that phosphine ligands used in the work of Miura was later replaced by NHC ligands [18,19], with anticipation that a stronger σ-donor ligand might improve the activity of the catalyst. As a part of our interest in developing abnormal NHC (*a*NHC) based catalysts [21–30], we herein report an efficient decarboxylative coupling protocol for arylation of indoles using *a*NHC bearing palladium catalysts. In this study, we report synthesis of two new *a*NHC ligand based palladium(II) complexes and their efficacy in catalytic decarboxylative coupling reaction of indole-carboxylic acids was tested. These *a*NHC supported palladium complexes afforded exclusive regioselectivity in C2 arylation with good yield even for unactivated aryl halide partners.

2. Results and discussion

Herein we report syntheses of two palladacycles, complex **1** and complex **2** using corresponding *a*NHC salts, 1-(2,6-diisopropylphenyl)-2,3,5-triphenyl-imidazolium chloride (ligand **A)** and 3-methyl-2,4-diphenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium chloride (ligand **B)**, respectively (Scheme 2). Ligand **A** was synthesized according to the literature procedure [31], and ligand **B** was synthesized by *N*-arylation of 2,4-diphenyl-1H-imidazole (**I**) through C-N coupling reaction with 2-bromopyridine using $CuSO_4 \cdot 5H_2O$ as catalyst followed by *N*-methylation using iodomethane to give 3-methyl-2,4-diphenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium iodide salt (**III**) (Scheme 2B). Corresponding chloro salt was obtained by using DOWEX chloride ion-exchange resin. A change in colour from brown to yellow was observed after the ion-exchange from iodide to chloride. Complexes **1** and **2** were synthesized using ligand **A** and ligand **B** by charging with palladium acetate in dioxane and heating at 80 °C for 8 h. It resulted in the formation of yellow coloured chloro-bridged, C-H activated palladium dimer **1** and monomeric complex **2**, respectively (Scheme 2). Complex **1** was characterized by spectroscopic methods (^{1}H and ^{13}C NMR spectroscopy) and elemental analysis. The C-5 resonance upon Pd(II) coordination resonates at δ 147.1 ppm, as observed in the ^{13}C NMR spectrum of complex **1**, which may be assigned to carbene-Pd resonance as also noted for similar palladium-*a*NHC complexes [27–29]. The NMR spectrum for complex **2** could not be recorded as the complex **2** is insoluble in common deuterated solvents ($CDCl_3$, Toluene-d_8, DMSO-d_6, THF-d_8, D_2O). Later, complexes **1** and **2** were characterized by single crystal X-ray crystallography. Analytically pure **1** and **2** were obtained by crystallization from DCM/hexane mixture and single crystal X-ray studies clearly established the molecular structures of **1** and **2**. The ORTEP diagrams of complexes **1** and **2** are displayed in Fig. 1. The crystal



Scheme 2. Syntheses of: (A) complex **1** and (B) complex **2**.

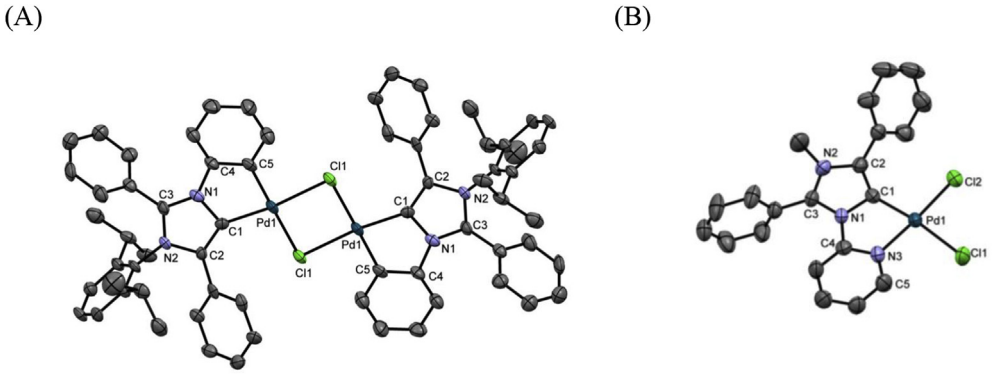


Fig. 1. (A) Molecular structure of complex **1** and (B) Molecular structure of complex **2**. Thermal ellipsoids represent 50% probability: hydrogen atoms and solvent (DCM) molecule for complex **2** were omitted for the sake of clarity. Selected bond distances (Å) and angles (°) are as follows: for complex **1**, Pd1-C1 1.979(5), Pd1-C5 1.977(5), Pd1-Cl1 2.3944(15), N1-C1 1.424(7); C1-Pd1-C5 80.4(2), Cl1-Pd1-C1 172.48(15), Cl1-Pd1-C5 94.23(14), Pd1-C1-N1 113.2(3), Pd1-C1-C2 141.5(4); for complex **2**, Pd1-C1 1.961(6), Pd1-Cl1 2.382(2), Pd1-Cl2 2.2827(18), Pd1-N3 2.033(5), N3-Pd1-C1 80.7(2), Cl1-Pd1-C1 172.74(18), Cl1-Pd1-N3 92.98(14), Cl2 -Pd -C1 96.17(17), Cl1-Pd1-Cl2 90.30(7).

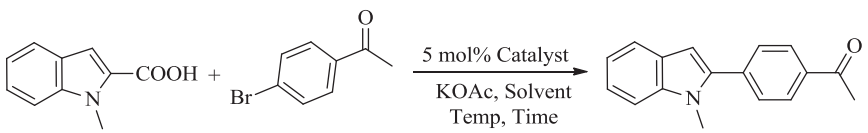
structure of complex **1** revealed that one of the *ortho* protons of the *N*-substituted phenyl groups had undergone activation *via* ortho-metallation process. A similar observation was also observed in previously reported palladium *a*NHC complex [28]. Fig. 1A clearly depicts the abnormal mode of binding of carbene *via* C1 and Pd(II) along with *ortho* aryl C-H bond activation at C5 forming Pd-C (aryl) bonds. Each palladium in complex **1** adopts a square planar geometry on coordination with two bridging chlorine atoms and two carbon atoms forming Pd-(aryl) and Pd-(carbene) bonds. The distance between two palladium atoms was found to be 3.555 Å which

is larger to describe a formal Pd-Pd bond. The crystal structure of **2** revealed the Pd-N bond *via* pyridine substituent along with the abnormal mode of bonding of carbene. Palladium in complex **2** adopts a square planar geometry on coordination with two chlorine atoms, a carbon atom Pd-(carbene) and nitrogen atom of pyridine (Fig. 1B). The Pd-C (carbene) bond distance in complex **2** is 1.960 Å which is slightly shorter than that in complex **1** (1.979(5) Å). The Pd-N (pyridine) bond distance was measured as 2.033(5) Å. The palladium-(carbene) bond distances were comparable with previously reported halo-bridged C-H activated palladium dimers of other *a*NHC ligands [27–29]. The Pd-C (aryl) bond distance was determined as 1.977 Å.

As a part of our ongoing interest to develop *a*NHC based homogeneous catalysts for different organic transformations [21–30], we evaluated the catalytic activity of *a*NHC palladium(II) complexes **1** and **2** for the decarboxylative C-C coupling reaction of indole-carboxylic acid and aryl halide. Optimization studies were performed with both palladium complexes. We started the optimization of reaction with complex **1**. To optimize the reaction method, *N*-methylindole-2-carboxylic acid and 4-bromoacetophenone were chosen and catalytic reactions were performed under different conditions as listed in Table 1. Initially, *N*-methylindole-2-carboxylic acid and 4-bromoacetophenone were charged with catalyst **1** using KOAc as the base, dioxane as solvent and heated at 160 °C for 24 h which yielded only 15% conversion (Table 1, entry 1). Changing the solvent to DMSO did not result any coupling product (Table 1, entry 2). However, using DMF as solvent yielded 60% conversion (Table 1, entry 3). Reaction in DMAc yielded 85% conversion (Table 1, entry 4). Thus, choosing DMAc as the solvent we proceeded with time optimization of this reaction. After 5 h of reaction at 160 °C, we obtained 82% conversion (Table 1, entry 5) whereas 85% conversion (Table 1, entry 4) was observed after 24 h. It is also worth noting that our protocol is efficient in performing reaction at 100 °C for 18 h to obtain 80% conversion (Table 1, entry 6). Similar optimization studies were performed to find the best reaction condition for catalyst **2**. Solvent optimizations were performed in dioxane, DMSO, DMF and no coupling product was observed (Table 1, entries 7–9). Only DMAc yielded the coupled product with 55% conversion (Table 1, entry 10). Thus, we concluded that complex **1** is a more efficient catalyst than complex **2** for decarboxylative C-C coupling of indole-carboxylic acids with aryl halides. It may be noted that using $PdCl_2$ as a catalyst yielded only 20% conversion (Table 1, entry 11) under the optimized conditions. A control reaction without any catalyst or base (KOAc) did not result in the formation of the desired coupling product (Table 1, entries 12 and 13). This observation unequivocally established the role of catalyst (**1** or **2**) in such reaction. Furthermore, to our delight, we found that only C2-arylated product was observed in the reaction mixture along with trace amount of decarboxylation product (*N*-methylindole) (<5%) but no C3-arylated product was obtained unlike previous report [19]. Thus, our reaction protocol is regioselective at C2 position of *N*-methylindole and does not promote any arylation at C3 position.

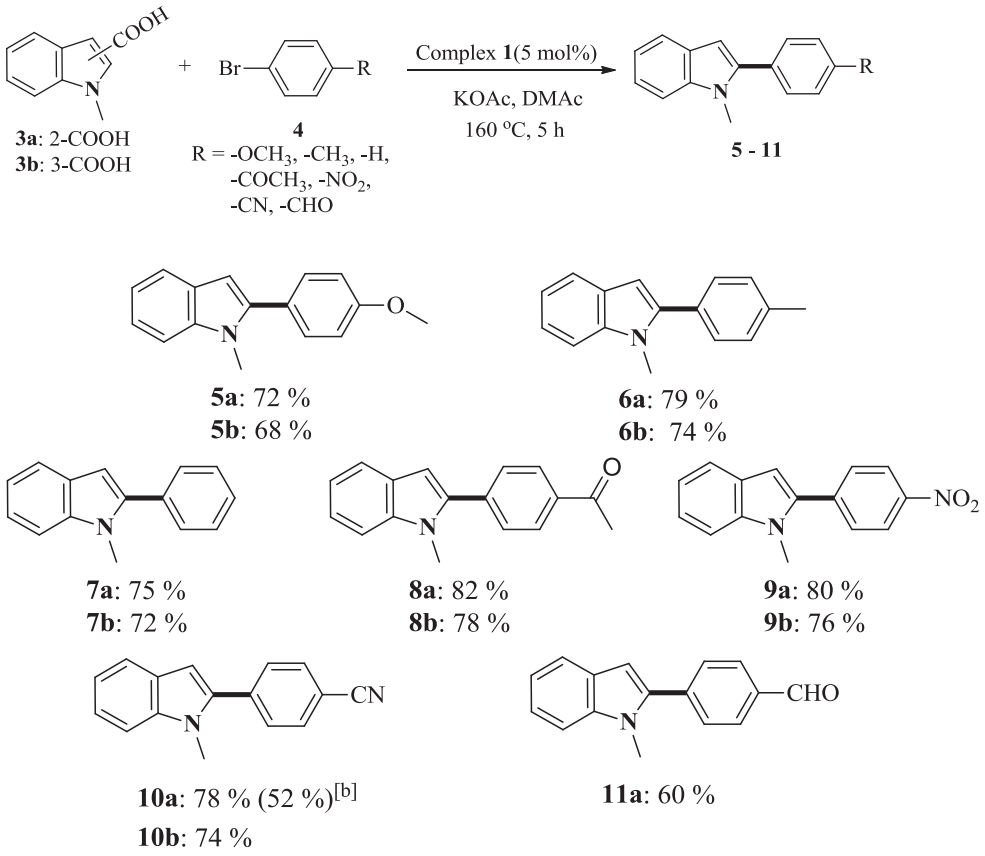
After optimizing the reaction conditions, further catalytic reactions were performed to explore the substrate scope of indole-carboxylic acids and aryl halide coupling partners (Scheme 3). *N*-methylindoles having carboxylic acid functionality at C2 and C3 position along with a variety of aryl halide coupling partners were chosen for the present study. Irrespective of position of acid functionality, exclusive arylation at C2 position of *N*-methylindole was observed. The formation of C2 arylated product from both C2- and C3-carboxylic acid substrates has also been observed in earlier study by Lee and coworkers [19], which has been explained in terms of higher nucleophilicity of the C2 position of *N*-methyl indole resulting in the migration of C3 palladation to C2 position leading to selective arylation at C2 position. It is interesting to note that electron-rich aryl bromides worked efficiently with our protocol giving good yield despite lower yield reported previously [19]. 4-Bromoanisole is generally considered to be a challenging substrate in coupling reactions owing to its highly electron-rich nature, and it delivered yields of 72% (**5a**) and 68% (**5b**) of coupled products with *N*-methylindole-2-carboxylic acid (**3a**) and *N*-methylindole-3-carboxylic acid (**3b**), respectively under our protocol (Scheme 3). Reaction with 4-bromotoluene gave corresponding coupling products **6a** and **6b** in 79% and 74% yields, respectively (Scheme 3). 4-Bromobenzene yielded corresponding coupling products **7a** in 75% and **7b** in 72%. Electronically poor aryl bromides like 4-bromoacetophenone, 1-bromo-4-nitrobenzene and 1-bromo-4-cyanobenzene afforded corresponding coupled products in good

Table 1
Evaluation of catalysts, solvents, time and temperature for decarboxylative C-C cross-coupling of *N*-methylindole-2-carboxylic acid with 4-bromoacetophenone.[a]



Entry	Catalyst	Solvent	Time (h)	Temp (°C)	Yield (%)[b]
1	**1**	Dioxane	24	160	15
2	**1**	DMSO	24	160	0
3	**1**	DMF	24	160	60
4	**1**	DMAc	24	160	85
5	**1**	DMAc	5	160	82
6	**1**	DMAc	18	100	80
7	**2**	Dioxane	24	160	–
8	**2**	DMSO	24	160	–
9	**2**	DMF	24	160	–
10	**2**	DMAc	24	160	55
11	$PdCl_2$	DMAc	24	160	20
12[c]	–	DMAc	24	160	–
13[d]	**1**	DMAc	24	160	–

[a] Reaction conditions: *N*-methylindole-2-carboxylic acid (0.1 mmol), aryl halide (0.15 mmol), KOAc (0.2 mmol) catalyst (0.005 mmol), solvent (1 mL).
[b] NMR conversion.
[c] Reaction without catalyst.
[d] Reaction without KOAc.



Scheme 3. Scope of Complex **1** Catalyzed Decarboxylative C-C Cross-Coupling of *N*-methylindole-(2 or 3)-carboxylic Acids with Aryl Halides.[a][a] Reaction conditions: *N*-methylindole-2-carboxylic acid (0.5 mmol), aryl halide (0.75) mmol, KOAc (1.0 mmol), catalyst **1** (30 mg, 0.025 mmol), DMAc (2 mL), All are isolated yields, for compounds **5**–**7** reaction time was 8 h[b] With aryl chloride partner in 8 h.

yields. 4-Bromoacetophenone as halide partner yielded corresponding coupling products **8a** and **8b** with yields of 82% and 78% respectively. With 1-bromo-4-nitrobenzene as halide partner, we obtained yields of 80% for **9a** and 76% for **9b**. Yields of 78% (**10a**) and 74% (**10b**) were obtained by using 1-bromo-4-cyanobenzene as the halide coupling partner with **3a** and **3b**, respectively. These results also indicate the improvement in decarboxylative coupling protocol for *N*-methylindoles in terms of yield and regioselectivity over previous reports [18,19]. Using 4-bromobenzaldehyde as halide partner, the decarboxylating reaction yielded 60% of the coupled product **11a** (Scheme 3). Noting encouraging catalytic activity of complex **1** towards the electron-rich aryl bromides, this reaction protocol was tested for activation of aryl chloride substrates which are even more challenging and attractive substrates owing to their inertness and low cost. Reaction with *N*-methylindole-2-carboxylic acid (**3a**) and 4-chlorobenzonitrile yielded 52% coupled product **10a** at C2 position within 8 h (Scheme 3). It is interesting that using aryl chloride as a coupling partner also did not affect the selectivity of the product obtained. However, reactions performed with unactivated aryl chlorides did not yield desired products.

3. Conclusions

In summary, two abnormal *N*-heterocyclic carbene supported palladacycles were synthesized. The complexes were characterized by X-ray crystallographic studies and elemental analyses. The catalytic activity of these palladacycles was tested in the decarboxylative C-C coupling of *N*-methylindole-carboxylic acids and aryl bromides. Very good yield and C2 selectivity of coupled products were obtained, irrespective of position of acid functionality. Our catalyst was also found to cleave C-Cl bond in activated aryl chloride with moderate yield and high regioselectivity.

4. Experimental section

4.1. General methods and instrumentation

Syntheses of catalysts were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk line techniques, utilizing glasswares those were oven dried (130 °C) after cooling it under reduced pressure. Dioxane was distilled from Na/benzophenone prior to use. All chemicals were purchased from Sigma-Aldrich and used as received. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed using Merck 60 silica gel (100–200 mesh). Elemental analyses were carried out using a PerkinElmer series 2 2400 CHN analyzer, and samples were prepared by keeping under reduced pressure (10^{-2} mbar) overnight. NMR spectra were recorded on a JEOL ECS 400 MHz or Bruker Avance 500 MHz NMR spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as the reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values.

4.2. Synthesis of complex *1*

Under inert atmosphere, a 50 mL Schlenk flask was charged

with $Pd(OAc)_2$ (112 mg, 0.5 mmol), 1-(2,6-diisopropylphenyl)-2,3,5-triphenyl-imidazolium chloride (ligand **A**) (264 mg, 0.5 mmol), and dry 1,4-dioxane (10 mL). The reaction mixture was heated to 80 °C for 8 h. After cooling to room temperature, the reaction mixture was filtered through a frit with fresh celite to obtain yellow solution. All volatiles were removed under reduced pressure. The yellow coloured solid was washed twice with dry hexane and crystals were obtained from DCM with hexane layering within one day. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.40–7.52 (m, 2H), 7.30 (dd, $J = 11.4$, 6.9 Hz, 4H), 7.25–7.30 (m, 8H), 7.10–7.20 (m, 8H), 7.00–7.10 (m, 4H), 6.78–6.80 (m, 2H), 6.63 (d, $J = 7.6$ Hz, 2H), 6.61 (d, $J = 7.6$ Hz, 2H), 6.24 (d, $J = 8.1$ Hz, 2H), 2.51–2.56 (m, 2H), 2.25–2.35 (m, 2H), 1.41 (d, $J = 6.4$ Hz, 6H), 1.05 (d, $J = 6.7$ Hz, 6H), 0.37 (d, $J = 6.6$ Hz, 6H), 0.06 (d, $J = 6.1$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 147.1, 146.1, 138.8, 138.5, 136.2, 132.2, 131.2, 130.6, 129.7, 128.9, 127.9, 127.5, 127.2, 124.6, 124.3, 123.2, 121.3, 114.4, 113.9, 28.1, 24.2, 24.0 ppm. Elemental analysis: Anal. Calcd for $C_{66}H_{62}Cl_2N_4Pd_2$: C, 66.34; H, 5.23; N, 4.69. Found: C, 66.38; H, 5.19; N, 4.75.

4.3. Synthesis of 3-methyl-2,4-diphenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium chloride (ligand *B*)

A mixture of 2,4-diphenyl-1H-imidazole (**I**) (1.26 g, 4.0 mmol), 2-bromopyridine (1.63 g, 24.0 mmol), K_2CO_3 (2.21 g, 16.0 mmol) and $CuSO_4 \cdot 5H_2O$ (0.025 g, 0.157 mmol) in DMF was heated to 150 °C for 48 h. The reaction mixture was then allowed to cool to ambient temperature. Reaction mixture was diluted with dichloromethane (50 mL) and the organic part was washed thrice (3×30 mL) with water. The organic part was dried over anhydrous Na_2SO_4 and filtered. Removal of the solvent gave a colorless solid. Analytically pure product 2-(2,4-diphenyl-1H-imidazol-1-yl)pyridine (**II**) was obtained by column chromatography using dichloromethane: methanol (95:5, v:v) as eluent. Yield: 37%. Compound **II** (4.284 g, 16.3 mmol) and iodomethane (3.1 mL, 50 mmol) were refluxed in acetonotrile (50 mL) for 16 h. Acetonitrile was then removed by distillation and washed with diethyl ether (3 X 30 mL) to give analytically pure 3-methyl-2,4-diphenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium iodide salt (**III**) with yield 97%. Compound **III** (0.5 g) was dissolved in methanol and passed through ion exchange resin DOWEX (2 g) packed in a column using methanol. Methanol was removed under reduced pressure to obtain ligand **B** as colorless solid compound with yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.56 (s, 1H), 7.87 (d, 1H), 7.78–7.82 (m, 5H), 7.58–7.68 (m, 6H), 7.40–7.49 (m, 2H), 3.85 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 149.1, 147.0, 144.4, 139.2, 135.6, 132.2, 130.8, 130.2, 129.8, 129.2, 128.8, 125.1, 124.6, 121.2, 120.5, 118.9, 34.7 ppm. Elemental analysis: Anal. Calcd for $C_{21}H_{18}ClN_3$: C, 72.51; H, 5.22; N, 12.08. Found: C, 72.59; H, 5.28; N, 12.15.

4.4. Synthesis of complex *2*

Under inert atmosphere, a 50 mL Schlenk flask was charged with $Pd(OAc)_2$ (112 mg, 0.5 mmol), 3-methyl-2,4-diphenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium chloride (ligand **B**) (173.92 mg, 1.15 mmol) and 10 mL dry 1,4-dioxane. The reaction mixture was heated to 80 °C for 8 h. After cooling to room temperature, all volatiles were removed under reduced pressure. The solid residue was dissolved in mixture of DCM and MeOH. The title compound was purified by column chromatography with DCM:MeOH (10:1 v:v) as eluent and crystals were obtained from DCM with hexane layering within two days. Yield: 70%. Elemental analysis: Anal. Calcd for $C_{21}H_{17}Cl_2N_3Pd$: C, 51.29; H, 4.10; N, 8.55. Found: C, 51.23; H, 4.16; N, 8.59.

4.5. General procedure for the decarboxylative C-C coupling

Complex **1** (30 mg, 5 mol%), *N*-methylindole-carboxylic acid (0.5 mmol), aryl halide (0.75 mmol), KOAc (1 mmol) and DMAc (2 mL) were added to a 5 mL pressure tube. Then catalytic reactions were performed at 160 °C for 5 h. After completion of reaction, the mixture was diluted with DCM and transferred to a separating funnel and added water. The organic part was washed thrice with water and dried over anhydrous Na_2SO_4. All the volatiles were removed under reduced pressure and pure compound was isolated by silica gel column chromatography with appropriate ratio of hexane and ethyl acetate.

4.6. X-ray crystallographic details

Suitable single crystals of complexes **1** and **2** were selected and an intensity data were collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal of complex **1** was kept at 100.00 K and the crystal of complex **2** was kept at 293 K during data collection. Using Olex2 [32], the structure was solved with the Superflip [33] structure solution program using Charge Flipping

Table 2
X-ray crystallographic details.

Crystal data	Complex **1**	Complex **2**
CCDC	1583942	1583943
Chemical formula	$C_{66}H_{62}Cl_2N_4Pd_2$	$C_{21}H_{17}Cl_2N_3Pd$
M_r	1194.90	488.71
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	100
a, b, c (Å)	13.5516 (13), 13.4772 (10), 15.8797 (10)	12.4936 (5), 13.3637 (5), 13.9093 (5)
β (°)	105.567 (8)	100.206 (4)
V (Å^3)	2793.8 (4)	2285.56 (15)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
ρ_{calc}g/cm^3	1.42	1.42
μ (mm^{-1})	0.784	1.00
T_{min}, T_{max}	0.374, 1.000	0.816, 1.000
$[I > 2\sigma(I)]$	7930, 4898, 3867	6544, 4013, 3364
R_{int}	0.051	0.022
$R[F^2 > 2\sigma(F^2)]$, w$R(F^2)$, S	0.061, 0.191, 1.133	0.0311, 0.1082, 0.78
No. of reflections	4898	4013
No. of parameters	338	246
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.78, −1.07	0.44, −0.46

and refined with the ShelXL [34] refinement package using Least Squares minimization. CCDC numbers 1583942 and 1583943 contains the supplementary crystallographic data for complexes **1** and **2**, respectively (See Table 2 for crystallographic data parameters for complexes **1** and **2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Appendix A. Supplementary data

CCDCs 1583942 and 1583943 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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