Synthesis of Palladium complexes derived from Amido linked N-Heterocyclic Carbenes and their use in Suzuki cross coupling reactions

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Abstract:

Treatment of 1-(*n*-butyl)-3-N-(2-Ar)acetamido-1, 3-imidazolium chloride (Ar = furylmethyl,phenylmethyl) with excess K_2CO_3 and $[PdCl_2(L\text{-}L)]$ (L-L = 2 PPh_3, dppf) afforded orange compounds of composition [(1-(n-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (Ar = furylmethyl; phenylmethyl). These complexes were characterized by NMR (^{1}H and ^{13}C{^{1}H} NMR), IR and micro-analysis data. Subsequently, the catalytic efficiency of these complexes for cross coupling reactions between 4-haloarenens (halo = Br, I) and phenylboronic acid was studied under different solvents (acetonitrile, THF and DMF), temperatures with different catalyst loadings. The molecular structure of [(1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazol-2-ylidene)]$_2$Pd was established by single crystal X-ray

diffraction analysis.

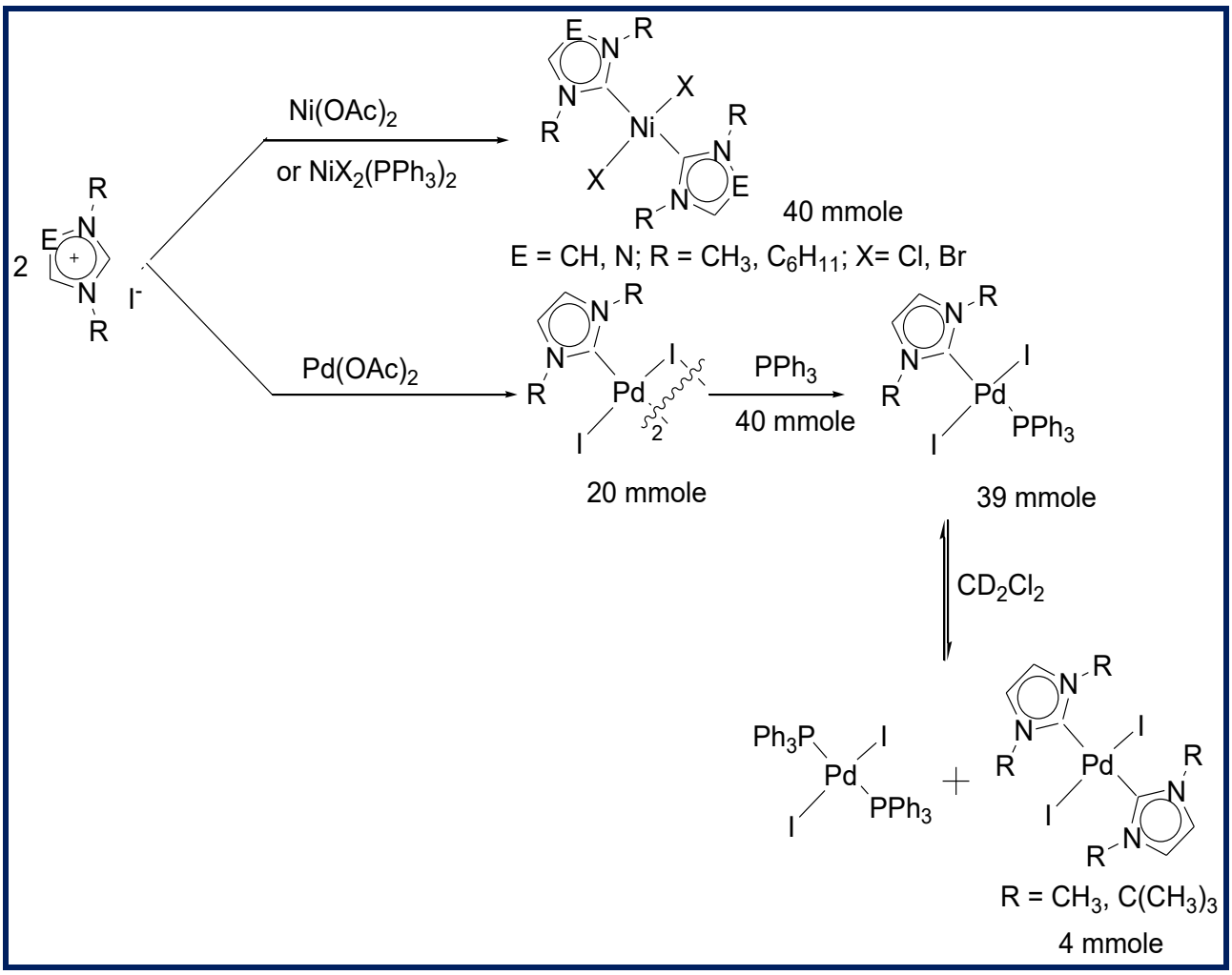
Key words: N-heterocyclic carbene, [$PdCl_2$(P-P)], NMR, Suzuki Cross coupling.

1. Introduction:

Internally functionalized amido linked N-heterocyclic carbenes (NHC) is an active area of research [1-4] The strong σ donor property of these carbenes[5] results in air stable compounds with strong metal carbon bonds.[6-9] NHC complexes of group 10 metals are highly efficient catalysts for C-C coupling reactions such as Suzuki–Miyaura,[2, 8, 10, 11] Sonogashira [12, 13] and the Hiyama couplings.[14]

The transmetalation reaction of {[1-R-3-{N-(benzylacetamido)imidazol-2-ylidene]$_2$Ag}Cl (R = ^{i}Pr, CH_2Ph) with [$PdCl_2$(COD)] resulted in a complex {[1-R-3-{N-(benzylacetamido)imidazol-2-ylidene]$_2PdCl_2$ (R = ^{i}Pr, CH_2Ph).[15] Several complexes of composition [1-(i-propyl)-3-(R)imidazol-2-ylidene]$PdCl_2$(R=2,6-di-i-propyl-phenylimino-2-phenylethyl, benzyl), *trans*-[{1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene}$_2PdBr_2$] and *cis*-[{1-benzyl-3-(*N-tert*-butylacetamido)imidazol-2-ylidene}$_2PdCl_2$], [1-(o-methoxybenzyl)-3-tert-butylimidazol-2-ylidene]$_2PdCl_2$ were also obtained by the above method.[11] However, the reaction of 1-(R)-3-(N-2,6-di-i-propylphenylacetamido)imidazolium chloride (R= 1-(2,4,6-trimethylphenyl, isopropyl) in pyridine with $PdCl_2$ and excess K_2CO_3 afforded *trans*-[1-(R)-3-(N-2,6-di-i-propylphenylacetamidol)imidazol-2-ylidene]$PdCl_2$(pyridine) (R= 1-(2,4,6-trimethylphenyl, isopropyl).[13] Meanwhile Hermann et.al. reported that [{(NHC)PdI_2}$_2$] on treatment with one equivalent of phosphine under ambient condition gives *trans* [(NHC)(PPh_3)PdI_2)]. NMR experiments revealed decomposition of [(NHC)(PPh_3)PdI_2)] to [(NHC)$_2PdI_2$)] and *trans* [Pd(PPh_3)$_2I_2$] over the course of several days (Scheme 1).[16] In contrast

to this result, the reaction of $[NiX_2(PPR_3)_2]$ (X = Cl, Br) with NHCs showed the substitution of the sterically demanding phosphine ligands by carbene ligands. [17, 18]



Scheme 1: Reaction of $[M(OAc)_2]$ (M= Ni, Pd) with dialkylimmidazolium salt with in presence of PPh_3 and their equilibrium existence (Adapted from reference 16-18)

We have recently reported the synthesis of 1-(*n*-butyl)-3-N-(2-Ar)acetamido-1, 3-imidazolium chloride (Ar = furylmethyl,phenylmethyl) and their reactivity towards $[NiCl_2(P\text{-}P)]$ (L-L = 2 PPh_3, dppf).[5] The interesting outcomes of our previous study prompted us to further

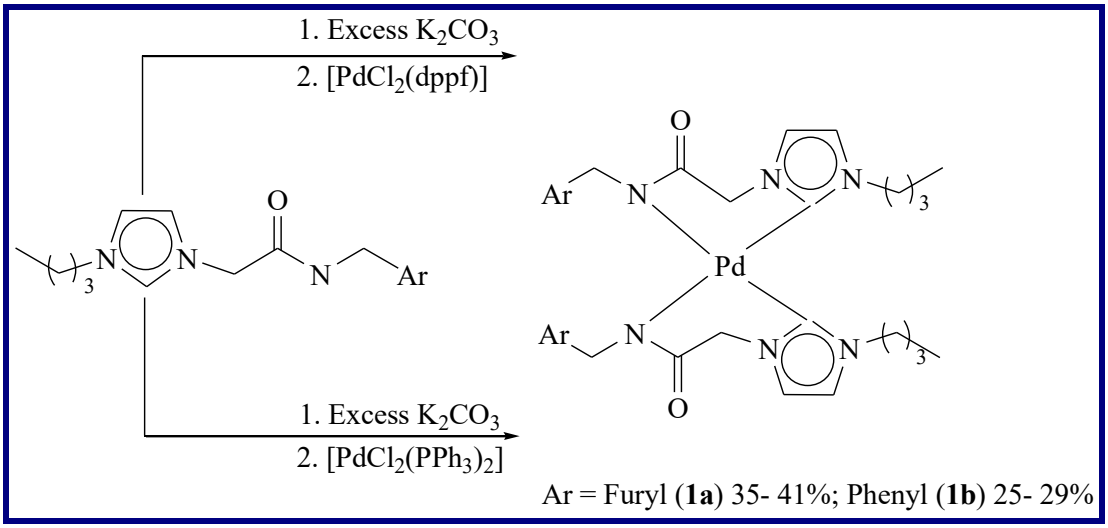
explore the chemistry of these imidazolium salts towards palladium metal precursors and study their promising catalytic activities for Suzuki coupling reactions.

2. **Result and Discussions:**

Refluxing an acetonitrile suspension (25 mL) of [1-(*n*-butyl)-3-N-(Ar)acetamido-1,3-imidazolium chloride (Ar = furyl methyl, phenyl methyl) with excess K_2CO_3 and one mole $[PdCl_2(L\text{-}L)]$ (L-L = $2PPh_3$, dppf) afforded a complex of composition [(1-(n-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (Ar = furylmethyl(**1a**), phenylmethyl (**1b**)) (**Scheme 2**). This result is different from the outcomes of transmetallation reaction between silver analogue [1-R-3-{N-(benzylacetamido)imidazol-2-ylidene]$_2$AgCl (R = ^{i}Pr, CH_2Ph) and $[PdCl_2(COD)]$ which resulted in the complex {[1-R-3-{N-(benzylacetamido)imidazol-2-ylidene]$_2PdCl_2$ (R = ^{i}Pr, CH_2Ph)[15] where the bond exists only between the metal and carbene carbon. These mentioned outcomes advocate strongly in favor of formation of the internally functionalized chelated ring where carbon and nitrogen are the donor atoms (complex **1**). This in turn facilitates the substitution of auxiliary phosphine ligands under basic conditions due to robust *trans* effect as well as harsh reaction conditions. Subsequently, theoretical studies about the electronic nature of amido-linked carbene reveals that σ donor nature of this carbene is ten time higher than its π acceptor properties.[14, 19] The rich charge density is further enhanced with prompt chelation of NHC ligand through carbon as well as nitrogen atoms to the metal center.[5, 19]

^{1}H NMRs of complexes **1a/1b** displayed resonances at 7.25/7.15 and 6.94/6.90 ppm of 4th and 5th position of imidazole ring respectively, supporting the complexation of palladium metal to carbene centre. Furthermore, the disappearance of the proton signal for 2nd position of imidazole ring as well as the amide proton also confirmed the coordination to the metal. The

$^{13}C\{^{1}H\}$ NMR displayed all the expected signals in the region ~13 to 169 ppm including the de-shielded resonance at 169 ppm which is regarded as the signature peak of a Pd-$C_{carbene}$ bond. [5, 9, 15] The IR spectra of complexes **1a** and **1b** displayed all possible vibrations ranging from 2966 to 536 cm^{-1}. The stretching frequency at 1588 cm^{-1} indicated the presence of carbonyl group. The somewhat lower frequency value can be attributed to the weak electron density around CO group as a result of the complexation.[19] Secondly, two prominent vibrations were observed at ~ 538 and 693 cm^{-1} which support the existence of Pd-$C_{carbene}$ and Pd-N bonds respectively. [5, 20-22]



Scheme 2: Reaction of [1-(*n*-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol chloride (Ar = Furyl methyl, phenyl methyl) with $[PdCl_2(L\text{-}L)]$ (L-L = $2PPh_3$, dppf)

We have also reported similar reactivity pattern of imidazolium salt with $[NiCl_2(L\text{-}L)]$ (L = PPh_3, dppf), where substitution of phosphine occurs through NHC.[5] We, however have not been able to confirm the phosphine-displacement step. However, the symmetrical NHC complex $[Pd(NHC)_2I_2]$ on stirring with one equivalent phosphine resulted in a compound $[Pd(NHC)(PPh_3)I_2]$ which on keeping in dichloromethane solution over several days gave $[Pd(NHC)_2]$ and a side product of $[PdI_2(PPh_3)_2]$.[16] The recent reports [23] about the values of ^{77}Se

chemical shift and coupling constants of ^{1}J(C-H) i.e. N-C*H*-N are fairly obliging to decide the donor property of carbene. The reported values of amido-linked carbene [5] (de-shielded ^{77}Se chemical shift and higher coupling constant) corresponds to their comparable σ donor nature with respect to the well-studied N, N-alkylimidazol-2-ylidenes e.g. IPr, IMes, ICy, I^{t}Bu.[23] However, comparisons with wider range of available carbenes confirm its weak σ donor nature. It appears that in [(1-(n-butyl)-3-N-(2-Ar)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (**1**) the substantial σ donor nature of the amido-linked carbine enabled the substitution of the phosphine ligand. In another example, the higher platinoids based carbene also demonstrated similar nature of reactivity, where ruthenium carbene complexes show the loss of phosphine under ambient conditions.[24]

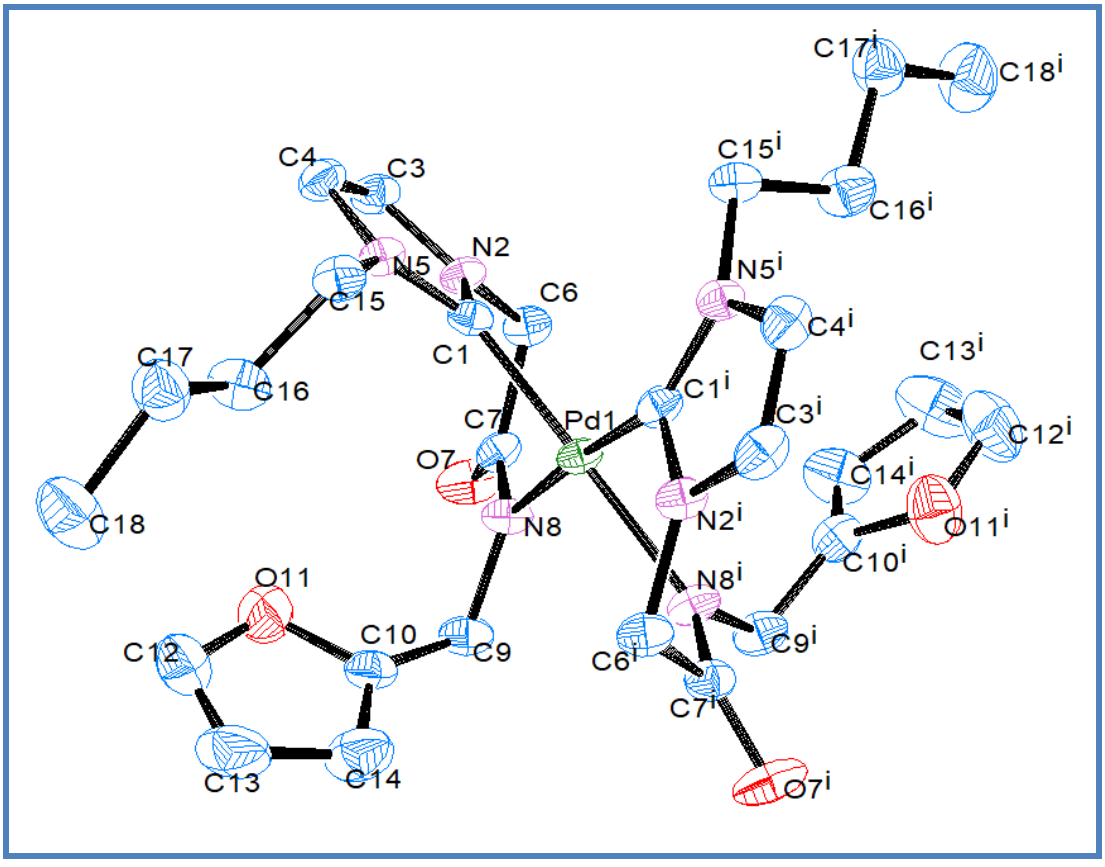


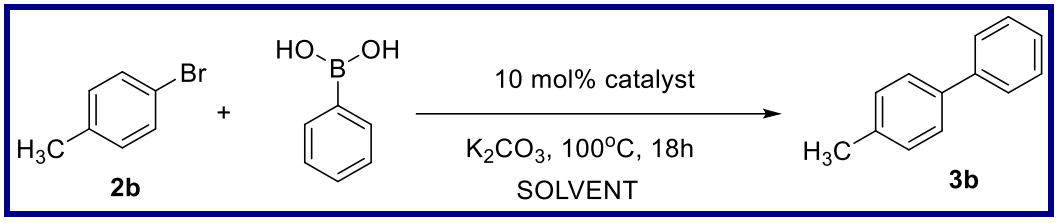
Figure 1. ORTEP drawing of [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd with atomic number scheme. The ellipsoids were drawn at the 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C11.9748 (17), Pd1-C1^{i}1.9749(17),Pd1-N82.0676(14), Pd1-N8^{i}2.0676(14); C1-Pd1-C1^{i}99.12(9), C(1)-Pd(1)-N(8)84.86(6), C(1)-Pd(1)-N(8)175.73(6), C(1)-Pd(1)-N(8)175.73(6), C(1)-Pd(1)-N(8)84.86(6), N(8)-Pd(1)-N(8)91.21(8).

The molecular structure of [(1-(n-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (**1a**) (Figure 1) consists of distorted square planar palladium center with *cis* ligands. The Pd-$C_{carbene}$ and Pd-N bond lengths (1.9748(17)/1.9749(17) Å, 2.0676 (14)Å) of complex **1a** are in good agreement with other palladium NHC complexes. [25-27] The C(1)-Pd(1)-C^i(1) bond angle is larger than the N(8)-Pd(1)-N^i(8) bond angle which may be due to steric repulsion of the butyl group.

Catalytic activity

Initially, we carried out the reaction of 4-bromotoluene (**2b**) with phenylboronic acid using 10 mol% of the catalyst **1a**/**1b** in presence of K_2CO_3 (3 equivalents) in different solvents like THF, N,N-dimethylacetamide, dioxane and isopropanol at 100 °C (**Scheme 3**, Table 1). In THF and isopropanol, the reactions were sluggish and afforded only 10-15% yields in 18 h. In N,N-dimethylacetamide, the yield was higher. In general, it is established fact that mostly palladium compounds form nanoparticles that catalyze these common substrates for coupling reactions whereas [Pd(OAc)$_2$] in water and polyethylene glycol mixture also act as proven catalyst for Suzuki reaction of aryl bromides under the mild conditions with quantitative yield of ~95%.[28] In our findings, the best result was obtained with dioxane where the product **3b** was

obtained in 75-79% yields. These results indicated that dioxane was the most suitable solvent amongst those chosen.



Scheme 3

Table 1. Solvent screening in Suzuki coupling of **2b** with phenylboronicacid.[a]

Substrate[a]	Product	Catalyst	Solvent	Yield[b](%)
2b	**3b**	**1a**	THF	8%
		1b	THF	9%
2b	**3b**	**1a**	Isopropanol	8%
		1b	Isopropanol	15%
2b	**3b**	**1a**	N,N-dimethylacetamide	42%
		1b	N,N-dimethylacetamide	39%
2b	**3b**	**1a**	Dioxane	76%
		1b	Dioxane	79%

[a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmolphenylboronic acid, 3 mmol K_2CO_3 in 5 mL solvent was heated at 100 °C with 10mol% catalyst for 18h. [b]Isolated yield.

Next, we attempted the reaction in dioxane solvent using different bases. It was observed that the coupling in presence of 3 equivalents of K_2CO_3 in dioxane solvent at 100 °C proceeded to give the best results where the product **3b** was obtained in 74-76% isolated yield, which was higher than when other bases were used (**Scheme 3**, Table 2). In all these reactions, 10 mol% of catalyst (**1a**/**1b**) was used.

Table 2. Screening of bases in Suzuki coupling of **2b** with phenylboronicacid.[a]

Substrate[a]	Product	Catalyst	Base	Yield[b](%)
2b	**3b**	**1a**	Et_3N	1%
		1b	Et_3N	1%
2b	**3b**	**1a**	KOAc	25%
		1b	KOAc	28%
2b	**3b**	**1a**	Cs_2CO_3	69%
		1b	Cs_2CO_3	61%
2b	**3b**	**1a**	K_2CO_3	74%
		1b	K_2CO_3	76%

[a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmolphenylboronic acid, 3 mmolbase in 5 mL dioxanewas heated at 100 ^oC with 10 mol% catalyst for 18h. [b]Isolated yield.

Further, to investigate the dependence of reaction yields on temperature of the reaction, the reactions were carried out at different temperatures (**Scheme 3**, Table 3). The reaction in dioxane using K_2CO_3 was not feasible at room temperature. Increasing the temperature gradually increased the yield. The optimum temperature for the reaction was 80^oC, beyond which the reaction did not show any beneficial effect. Hence the substrates were subjected to Suzuki cross coupling reaction at 80^oC.

Table 3. Screening of temperature in Suzuki coupling of **2b** with phenylboronicacid.[a]

Substrate[a]	Product	Catalyst	Temperature	Yield[b](%)
2b	**3b**	**1a**	25 °C	NR[c]
		1b	25 °C	NR[c]
2b	**3b**	**1a**	50°C	21%
		1b	50°C	19%
2b	**3b**	**1a**	80°C	73%
		1b	80°C	77%
2b	**3b**	**1a**	110°C	72%
		1b	110°C	75%

[a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmol phenylboronic acid, 3 mmol K_2CO_3 in 5 mL dioxane heated as specified with 10 mol% catalyst for 18h. [b]Isolated yield. [c]NR = No reaction

After the initial standardization of the solvent, base and temperature, Suzuki cross coupling reaction of **2b** was carried out in dioxane using K_2CO_3 as a base with different catalyst loadings. The reactions with 10 mol% of catalyst (**1a**/**1b**) were facile, and gave products in moderate yield. Lowering the catalyst concentration to 5 mol% and further to 2 mol% did not alter the reaction outcome (Table 4). However, when 1 mol% catalyst was used, the yields dropped to 41-46%. Further decrease in catalyst loading decreased the yields (data not shown). Hence 2 mol% was considered as the optimum amount of catalyst required for this reaction.

166 **Table 4**. Screening of catalyst loading in Suzuki coupling of **2b** with phenylboronicacid.[a]

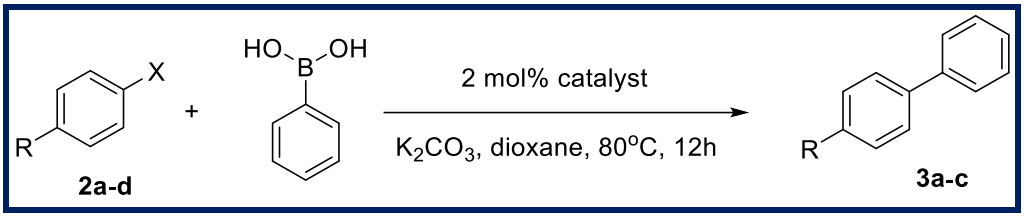
Substrate[a]	Product	Catalyst	Catalyst loading	Yield[b](%)
2b	**3b**	**1a**	10 mol%	73%
		1b	10 mol%	76%
2b	**3b**	**1a**	5 mol%	72%
		1b	5 mol%	74%
2b	**3b**	**1a**	2 mol%	73%
		1b	2 mol%	77%
2b	**3b**	**1a**	1 mol%	41%
		1b	1 mol%	46%

167 [a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmolphenylboronic acid, 3 mmol K_2CO_3 in 5
168 mL dioxane heated at 80ºC with catalyst for 18h. [b]Isolated yield.

169

170 Further the catalytic activities of the complexes **1a** and **1b** in a Suzuki cross coupling
171 reactions were evaluated using the standardized conditions (**Scheme 4**, Table 5). It was
172 gratifying to note that the reactions gave satisfactory yields (71%-85%) of the desired products.
173 Quite interestingly, these catalysts performed reasonably well in case of an aryl bromide
174 substrate with an electron donating group –OMe (**3b**) with 75-79% yield of the desired product,
175 which was otherwise not obtained with similar catalysts.[15] It is worth mentioning that the
176 marginal differences in yields of similar reactions during screening of different conditions were
177 due to the fact that all the calculated yields are isolated yields, and are amenable to human errors.
178 The discussed catalytic activities of complex **1** is considerably fair as compared to similar Pd(II)
179 catalysts derived from tridentate internally functionalized NHC ligands whereas it is in the range

of good agreement with monodentate NHC complex of composition [{1(R)-3N-(2-phenyl)acetamido-1, 3-imidazol-2-ylidene}{pyridine}]$PdCl_2$ (R = phenyl, naphthyl).[11c] However, the catalytic efficiency of complex **1a** and **1b** are inferior to neutral NHC ligands i.e. phosphine based NHC ligands [29] etc. This poor catalytic efficiency of these complex can easily be encountered due to unavailable vacant site and stable chelated ring formation in complex **1**.



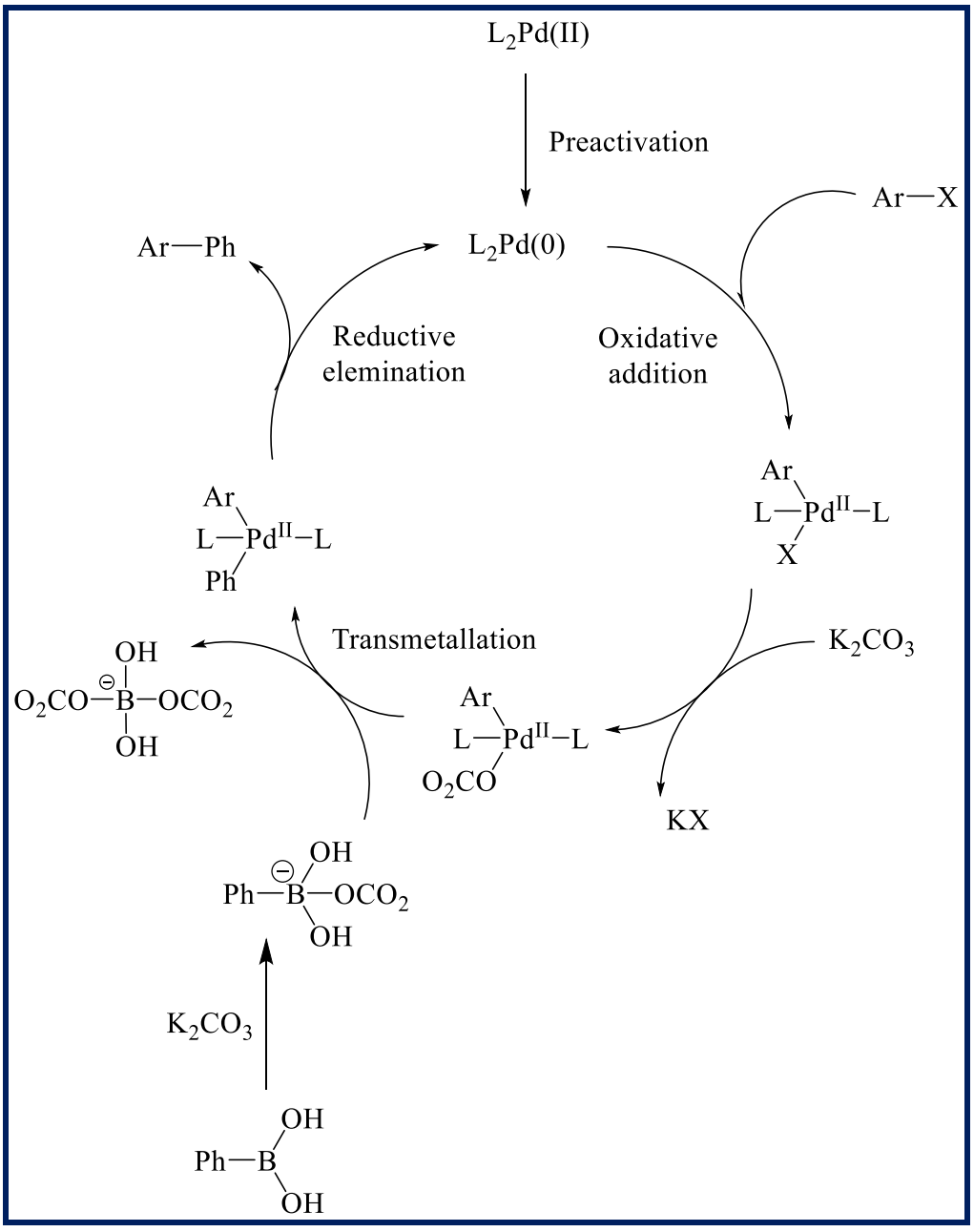
Scheme 4.

Table 5. Suzuki coupling of aryl bromides with phenylboronicacid.[a]

Substrate[a]	X	R	Product	Catalyst	Yield[b](%)
2a	I	H	**3a**	**1a**	82
	I			**1b**	85
2b	Br	H	**3a**	**1a**	73
	Br			**1b**	71
2c	Br	-OCH_3	**3b**	**1a**	79
	Br			**1b**	75
2d	Br	-CH_3	**3c**	**1a**	81
	Br			**1b**	82

[a]Reaction conditions: 1 mmol aryl bromide, 2.5 mmol phenylboronic acid, 3 mmol K_2CO_3 in 5 mL dioxane heated at 80°C with 2 mol% catalyst. [b]Isolated yield.

Based on the results, the possible mechanism of the Suzuki coupling reaction of aryl halide and phenylboronic acid using the catalysts can be summarized using the catalytic cycle (scheme 5). The reaction proceeds via the oxidative addition of substrate, transmetalation, and reductive elimination to finally produce the product.



Scheme 5:

3. Conclusion:

In summary, we have prepared a complex [1-(*n*-butyl)-3-N-(Ar)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (Ar = furylmethyl, phenylmethyl), by the substitution of phosphine ligand with an N heterocyclic carbene. The substantially strong σ donor nature of these amido linked carbene over π acceptor property accounts for the complexation of palladium metal center through carbon and nitrogen atom. The resulted complexes displayed promising catalytic activity for cross coupling reactions of haloarenes with phenyl boronic acid.

4. Experimental:

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk flasks. Solvents used in the reactions were distilled using standard procedures. The precursor compound N-benzyl, N-furyl 2-chloroacetamide,[19] 1-(*n*-butyl)-3-N-(2-Ar)acetamido-1, 3-imidazolium chloride (Ar = furylmethyl, phenylmethyl) [5, 30] and [$PdCl_2$(P-P)] (P-P = PPh_3, dppf),[31] were prepared according to literature methods. Triphenyl phosphine and 1, 1'-Bis(diphenylphosphino)ferrocene were procured from Sigma-Aldrich. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on a Varian spectrometer operating at 500 and 125 MHz respectively. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

Synthesis of complexes:

4.1. [(1-(n-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (1a)

(i) [$PdCl_2(PPh_3)_2$] (301 mg, 0.5 mmol) was added to an acetonitrile suspension (25 mL) of 1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazolium chloride (130 mg, 0.5 mmol) and K_2CO_3 (1.3 gm, 10 mmol). The resulting mixture was refluxed at 100^{o}C for 12 hours under an inert atmosphere. After filtration, the solvent was removed from the filtrate under reduced

pressure, the residue extracted with dichloromethane (5 mL) and kept for crystallization at -4ºC to afford yellow crystals of **1a** (yield: 140 mg, 41%; m.p.: 168ºC). Anal. Calcd. for $C_{28}H_{36}N_6O_4Pd$: C, 53.63; H, 5.78; N, 13.40%; Found: C, 53.66; H, 5.78; N, 13.41. ^{1}\{H\}NMR ($CDCl_3$): 7.25 (d, *J* = 2.0 Hz, 2H, NC(4)*H*C), 6.94 (d, *J* = 2Hz, 2H, NC(5)*H*C), 6.65 (d, *J* = 2Hz, 2H, C_4H_3O), 6.27 (dd, *J* = 4Hz, 2H, C_4H_3O), 6.05 (d, *J* = 4Hz, 2H, C_4H_3O), 5.22 (d, *J* = 14Hz, 2H, CH_2), 4.84 (d, *J* = 14Hz, 2H, CH_2), 4.35 (d, *J* = 14Hz, 2H, CH_2), 3.57 (d, *J* = 14Hz, 2H, CH_2), 3.24-3.09 (m, 4H, -$CH_2CH_2CH_2CH_3$). 2.80-2.66 (m, 4H, -$CH_2CH_2CH_2CH_3$), 1.16-1.09 (m, 4H, -$CH_2CH_2CH_2CH_3$), 0.84 (t, *J* = 7Hz, 6H, CH_2CH_3); ^{13}C\{^{1}H\}NMR ($CDCl_3$): 14.9, 24.9, 25.6, 38.5, 45.2, 53.0, 64.9, 68.6, 68.7, 69.2, 69.3, 101.4, 105.3, 114.9, 117.2, 120.8, 123.5, 123.6, 123.7, 123.8, 126.5, 126.9, 127.3, 128.6, 129.4, 135.9, 151.7, 161.0, 164.1. IR (KBr, cm^{-1}): 540 (s), 693 (s), 720 (s), 754 (w), 1116 (s), 1185 (s), 1439 (s), 1588 (b), 1678 (w), 2872 (w), 2935 (w), 2966 (w).

(ii) An acetonitrile solution (15 mL) of [$PdCl_2$(dppf)] (366 mg, 0.5 mmol) was added to a mixture of 1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazolium chloride (130mg, 0.5 mmol) and K_2CO_3 (1.3 gm, 10 mmol) in the same solvent. The resulting solution was refluxed at 100ºC for 14 hours and passed through a G-3 sintered crucible to remove the unreacted material. The collected filtrate was dried under reduced pressure and washed with ether (15mL) to remove phosphine. Yellow crystals of **1a** (yield: 120 mg, 35%) were obtained on crystallizing from dichloromethane-hexane solvent (5 mL) mixture. Anal. Calcd. for $C_{28}H_{36}N_6O_4Pd$: C, 53.63; H, 5.78; N, 13.40%; Found: C, 53.61; H, 5.71; N, 13.23%. ^{1}\{H\}NMR ($CDCl_3$): ^{1}HNMR signals are consistent with the above-mentioned values.

4.2. [(1-(n-butyl)-3-N-(2-phenylmethyl)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (1b)

(i) Treatment of an acetonitrile suspension (25 mL) of 1-(*n*-butyl)-3-N-(phenyl-methyl) acetamido-1, 3-imidazolium chloride (130 mg, 0.5 mmol) with K_2CO_3 (1.3 gm, 10 mmol), followed by the addition of [$PdCl_2(PPh_3)_2$] (301 mg, 0.5 mmol), and heating at 100ºC for 14 hours resulted in an orange solution. On passing through a celite column, a yellow solution was obtained which was dried under reduced pressure to afford an orange powder of **1b** (yield: 115 mg, 25%, m.p.: 175ºC). Anal. Calcd. for $C_{32}H_{40}N_6O_2Pd$: C, 59.39; H, 6.23; N, 12.99%; Found: C, 59.43; H, 5.99; N, 12.90%. ^{1}H}NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 7.7-7.4 (m, 10H, C_6H_5), 7.15 (d, *J* = 2Hz, 2H, NC_4HC), 6.90 (d, *J* = 2Hz, 2H, NC_5HC), 5.22 (d, *J* = 14Hz, 2H, CH_2), 4.99 (d, *J* = 14Hz, 2H, CH_2), 3.94 (d, *J* = 14Hz, 2H, CH_2), 3.22 (d, *J* = 14Hz, 2H, CH_2), 1.75 (br, 4H, $CH_2CH_2CH_2CH_3$), 1.41-1.34 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.00 (t, *J* = 7Hz, 4H, $CH_2CH_2CH_2CH_3$), 0.74 (t, *J* = 7Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C}NMR ($CDCl_3$): 13.3, 19.6, 29.7, 30.3, 33.0, 43.3, 49.9, 57.8, 69.7, 73.4, 73.5, 74.0, 106.1, 110.1, 119.6, 122.0, 125.5, 128.2, 128.3, 128.5, 131.2, 131.3, 131.5, 131.7, 132.0, 132.1, 140.7, 156.4, 165.7, 168.9. IR (KBr, cm^{-1}): 536 (s), 580 (w), 693 (s), 704 (s), 726 (s), 762 (w), 1120 (s), 1170 (b), 1448 (s), 1586 (b), 1681 (w), 2847 (s), 2928 (s).

(ii) Prepared in a manner similar to compound **1a**, using method (ii) with 1-(*n*-butyl)-3-N-(phenyl-methyl)acetamido-1,3-imidazolium chloride (137 mg, 0.5 mmol), K_2CO_3 (1.3 gm, 10 mmol) and [$PdCl_2$(dppf)] (366 mg, 0.5 mmol), gave a yellow powder, which was re-crystallized from dichloromethane-hexane (yield: 99 mg, 29%, m.p.: 175 ºC) (scheme **1**). Anal. Calcd. for $C_{32}H_{40}N_6O_2Pd$: C, 59.39; H, 6.23; N, 12.99%; Found: C, 59.02; H, 6.08; N, 13.13%. $^{13}C\{^1H\}$ NMR and FTIR signals are consistent with the above mentioned values.

4.3. Catalytic activities of 3a and 3b in Suzuki cross coupling reactions

Phenylboronic acid (305 mg, 2.5 mmol), K_2CO_3 (410 mg, 3 mmol) and **1a**/**1b** (2 mol%) was added to a solution of the substrate (1 mmol, Table 2) in dioxane (5 mL), and the suspension was refluxed for 16 h. After completion of the reaction (*cf*. TLC), the reaction mixture was concentrated in *vacuo*, followed by column chromatography (silica gel, 0-5% EtOAc/hexane) to obtain pure products. The yields of the products are summarized in Table 1.

4.3.1. Biphenyl (**2a**): White solid (m.p.71 ºC; lit. 70.5-72 ºC); [32] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34-7.49 (m, 6H), 7.58-7.63 (m, 4H).

4.3.2. 4-Methoxy-1,1'-biphenyl (**2b**): White solid (m.p.93 ºC; lit. 91.1-92.3 ºC); [32] ^{1}H NMR (500 MHz, CDCl3) δ 3.79 (d, *J* = 6.0 Hz, 3H), 6.81-7.04 (m, 2H), 7.12-7.25 (m, 3H), 7.39-7.50 (m, 3H), 7.57-7.66 (m, 1H).

4.3.3. 4-Methyl-1,1'-biphenyl (**2c**). White solid (m.p. 47ºC; lit. 45-50 ºC); [32] ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.25-7.27 (m, 2H), 7.31-7.34 (m, 1H), 7.431 (*t*, *J* = 5.5 Hz, 2H), 7.49-7.51 (m, 2H), 7.57-7.59 (m, 2H).

4.4. Crystal Structure determination:

The molecular structure of compound [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1, 3-imidazol-2-ylidene)]$_2$Pd(**1a**) was collected at 173K on using a Rigaku FR-XUltrahigh Brilliance Microfocus RA generator/confocal optics and XtaLAB P200 diffractometer [Mo-K_α radiation (λ = 0.71075 Å)]. Data were collected using Crystal Clear and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro.[33] The structures were solved dual-space methods (SHELXT),[34] and refined by full-matrix least-squares against F^2 (SHELXL-2018/3).[33]The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Molecular structures were drawn using ORTEP.[35] Selected

crystallographic data are listed in Table 6. Deposition number 2011024 contains the supplementary crystallographic data for this paper. These data was provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachin formations zentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table 6: Selected crystallographic data for [1-(*n*-butyl)-3-N-(2-furylmethyl)acetamido-1,3-imidazol-2-ylidene)]$_2$Pd (**1a**).

Complex	**1a**
Chemical formula	$C_{28}H_{36}N_6O_4Pd$
Formula wt.	627.05
Crystal size (mm^3)	0.150 ×0.090×0.030
Crystal system	orthorhombic
Space group	P_{ccn}
Unit cell dimensions	
a (Å)	16.9659(9)
b (Å)	10.0132(5)
c (Å)	16.6484(7)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	2828.3(2)
ρ_{cacld}, g cm^{-3}	1.047
Z	2
μ (mm^{-1})/F(000)	0.418/922

Limiting indices	-21 ≤h≤ 20
	-12 ≤k≤ 13
	-21 ≤l≤ 15
θ for data collection(°)	2.362< θ<29.013
No of reflections collected	22898
No of independent reflection (R_{int})	3361[R(int)-0.0364]
Data/restraints/parameters	3361/0/178
Final R_1, wR_2 indices ($I>2\sigma I$)	0.0244/0.0718
R_1, wR_2 (all data)	0.0419/0.0804
Goodness of fit on F^2	0.567

Acknowledgement:

One of the authors (RSC) is grateful to DST for the financial support under the DST young scientist scheme YSS/2014/000797. We thank Dr. Pradnya Prabhu for encouraging this work and his valuable suggestions for the preparation of this article.

Conflicts of interest

We confirm that there are no known conflicts of interest associated with this publication.

Supporting Information

CCDC2011024 for **1a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

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