Air-stable, convenient to handle Pd based PEPPSI (pyridine enhanced precatalyst preparation, stabilization and initiation) themed precatalysts of *N*/*O*-functionalized N-heterocyclic carbenes and its utility in Suzuki–Miyaura cross-coupling reaction†‡

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Several new air-stable, convenient to handle and easily synthesized Pd based PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation) type precatalysts supported over *N*/*O*-functionalized N-heterocyclic carbenes (NHC) namely, *trans*-[1-(benzyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl_2 (**2**), *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]Pd(pyridine)Cl_2 (**3**) and *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br_2 (**4**), have been designed. Specifically, the Pd–NHC complexes, **2**, **3** and **4**, were conveniently synthesized from their respective imidazolium halide salts by the reaction with $PdCl_2$ in pyridine in presence of K_2CO_3 as a base. A new imidazolium chloride salt, 1-(benzyl)-3-(N-*t*-butyl-acetamido)imidazolium chloride (**1**) was synthesized by the alkylation reaction of benzyl imidazole with *N*-*t*-butyl-2-chloroacetamide. The molecular structures of the imidazolium chloride salt, **1**, and the Pd–NHC complexes, **2**, **3** and **4**, have been determined by X-ray diffraction studies. The density functional theory studies of the **2**, **3** and **4** complexes were carried out to in order to gain insight about their structure, bonding and the electronic properties. The nature of the NHC–metal bond in these complexes was examined using Charge Decomposition Analysis (CDA), which revealed that the N-heterocyclic carbene ligands are effective σ-donors. In addition, the catalysis studies revealed that the Pd–NHC complexes, **2**, **3** and **4**, are effective catalysts for the Suzuki–Miyaura type C–C cross-coupling reactions.

Introduction

With N-heterocyclic carbenes (NHCs) being extremely successful in homogeneous catalysis[1] and with Pd emerging as an undisputed leader in the catalysis of many important C–C bond forming reactions[2] namely, the Hiyama,[3] Kumada,[4] Negishi,[5] Suzuki,[6] and Stille[7] reactions, rational catalyst designing involving Pd–NHC complexes has thus taken center stage and has brought forth significant advancements in the area of catalyst development in recent years. The focus has mainly been on developing a universal catalyst that would be highly efficient, robust, user-friendly and convenient to synthesize and could be employed for various Pd-mediated cross-coupling reactions.[2] The key to a rational catalyst designing exercise lies in the successful realization of important fundamental concepts[8] and one such instance has been in the introduction of a "throwaway ligand," intended to give way to the incoming substrate, in the Grubbs catalyst for olefin metathesis.[9] Specifically, when loosely bound pyridine and its substituted derivatives, acting as the "throwaway" ligands, replaced a more tightly bound tricyclohexylphosphane (PCy_3) in the Grubbs second-generation catalyst, [$(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh], higher activities were observed even for the more challenging acetonitrile Cross-Metathesis (CM) reactions.[9] Along a similar theme, PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation), a term recently coined and demonstrated by Organ and coworkers,[10,11] also resulted in highly active catalysts for various Pd-mediated C–C cross-coupling reactions.

Our interest lies in designing high performance Pd catalysts stabilized by *N*/*O*-functionalized N-heterocyclic carbenes (NHCs) for a variety of C–C bond forming reactions particularly, the Suzuki–Miyaura cross-coupling reaction.[12] The growing popularity of the Suzuki–Miyaura cross-coupling reaction can be ascribed to mild reaction conditions (ambient temperature *ca.* 80–100° C in air), commercial availability of diverse boronic acids that are also environmentally safer than many organometallic reagents, the ease of handling and removal of boron by-products and functional group tolerance.[13] The extent of the importance of the Suzuki–Miyaura cross-coupling reaction can be gauged from the diverse range of its applications that span from materials to pharmaceuticals to polymers to ligands in organometallic chemistry to natural product synthesis.[13] For example, many important natural products and pharmaceuticals possessing complex

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‡ Electronic supplementary information (ESI) available: B3LYP coordinates for geometry optimized calculations and CDA of **2′**, **3′** and **4′**. See DOI: 10.1039/b706607d

architectures like, kendamycin,[14] myxovirescin,[15] marinomycin A,[16] vancomycin[17] *etc.* have been synthesized employing the Suzuki–Miyaura cross-coupling reaction.

Our intention in using *N*/*O*-functionalized N-heterocyclic carbenes for designing these precatalysts was in enhancing the stability of these precatalysts as the incorporation of polar groups often leads to greater stability of metal–NHC complexes through a variety of intermolecular interactions,[18] chelation to the metal center,[19] *etc.* For example, higher decomposition temperatures (*ca.* > 180 °C) were observed for the two cationic Ag–NHC complexes, [(1-*i*-propyl-3-{*N*-phenylacetamido}imidazol-2-ylidene)$_2$Ag]$^+$Cl$^-$[18] and {[1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazol-2-ylidene]$_2$Ag}$^+$Cl$^-$,[20] bearing *N*/*O*-functionalized sidearms as N-substituents.

Here in this contribution, we report the syntheses and structural characterizations of a series of air-stable, convenient to handle and easily accessible PEPPSI styled precatalysts, *trans*-(NHC)Pd(pyridine)X$_2$ (X = Cl, Br) (Fig. 1), **2**, **3** and **4**, stabilized over *N*/*O*-functionalized N-heterocyclic carbene ligands and containing a "throwaway" pyridine ligand. These **2**, **3** and **4** precatalysts are effective for the Suzuki–Miyaura cross-coupling reactions of phenylboronic acids and aryl halides (X = Br, I). In addition, the synthesis and the structural characterization of a new imidazolium chloride salt, 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** is also described.

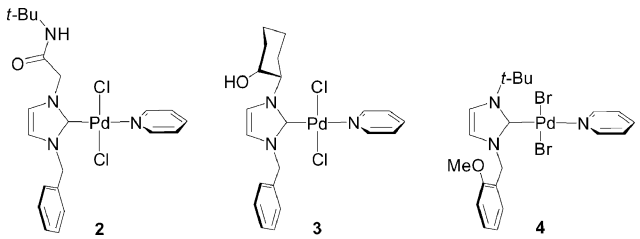
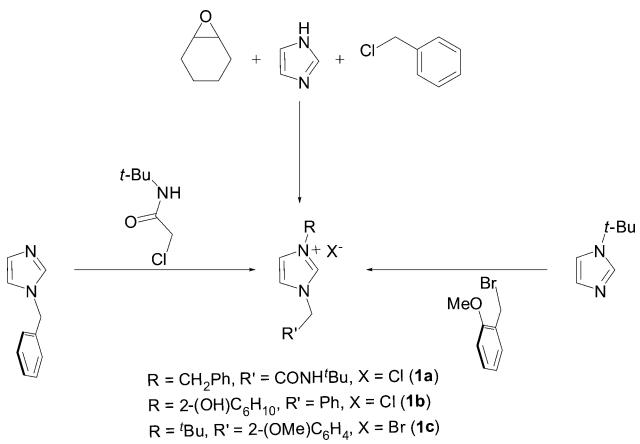


Fig. 1 *trans*-(NHC)Pd(pyridine)X$_2$ (X = Cl, Br) **2**, **3** and **4**.

Results and discussion

The *N*/*O*-functionalized imidazolium halide salts were synthesized as outlined in Scheme 1. While the 1-(2-hydroxycyclohexyl)-3-(benzyl)imidazolium chloride[21] was synthesized by following a ring-opening reaction of the cyclohexene oxide with imidazole and benzyl chloride reported earlier by us,[22] the 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide[12] and 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** were synthesized by the direct alkylation reaction of the respective imidazoles with the corresponding alkyl halides. Specifically, the new imidazolium chloride salt, **1**, was synthesized by the alkylation reaction of benzyl imidazole with *N*-*t*-butyl-2-chloroacetamide in 70% yield. The formation of **1** was verified by the appearance of the diagnostic NC*H*N peak at 10.1 ppm in the ^{1}H NMR spectrum. The two bridging methylene peaks of the benzyl and the N-*t*-butylacetamido moieties appeared at 5.45 ppm and 5.31 ppm in the ^{1}H NMR spectrum and at 53.0 ppm and 51.8 ppm in the ^{13}C NMR spectrum. The amide proton of the –CON*H*–moiety appeared downfield shifted at 8.66 ppm in the ^{1}H NMR spectrum while the carbonyl band of the –*CO*NH– moiety appeared at 1685 cm^{-1} in the infrared spectrum.

The molecular structure of the imidazolium chloride salt, **1**, has been determined by X-ray diffraction studies (Table 1 and Fig. 2). The N–C bond distances of 1.329(3) Å and 1.330(3) Å in the imidazolium ring are consistent with its aromatic nature and are in concurrence with the values reported for other structurally characterized imidazolium halide salts. For example, in closely related imidazolium halide salts the corresponding N–C distances are, 1-(2-hydroxycyclohexyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride[22] [1.326(6) Å, 1.314(6) Å], 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride[23] [1.320(2) Å, 1.323(2) Å] and 1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride[20] [1.324(3) Å, 1.322(3) Å]. Similarly, the ∠N–C–N angle of 108.60(17)° of the imidazolium ring in **1** is similar to that of other related imidazolium halide salts.



Scheme 1

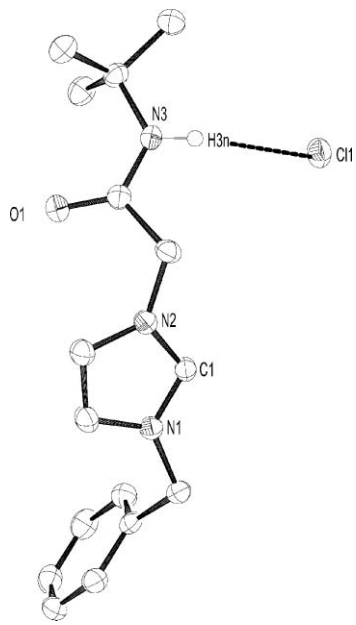


Fig. 2 ORTEP of **1** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.329(3), N(2)–C(1) 1.330(3), N(1)–C(1)–N(2) 108.41(17).

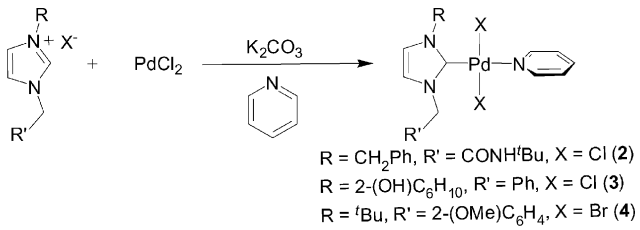
The most important aspect of the imidazolium chloride **1** structure is the presence of [Cl···H–N] type H-bonding interaction

Table 1 X-Ray crystallographic data for **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
Lattice	Triclinic	Triclinic	Triclinic	Monoclinic
Formula	$C_{16}H_{22}ClN_3O$	$C_{21}H_{26}Cl_2N_4OPd$	$C_{21}H_{25}Cl_2N_3OPd$	$C_{20}H_{25}Br_2N_3OPd$
Formula weight	307.82	527.76	512.74	589.65
Space group	*P*-1	*P*-1	*P*-1	$P2_1/c$
a/Å	6.0741(3)	10.829(2)	8.9556(10)	12.9252(3)
b/Å	10.996(3)	11.2668(15)	9.830(2)	10.8313(3)
c/Å	12.313(4)	11.429(2)	14.552(2)	16.0613(4)
α/°	82.75(2)	107.068(14)	71.923(17)	90.00
β/°	83.452(14)	111.852(19)	75.819(10)	102.569(2)
γ/°	81.642(13)	100.997(14)	64.689(16)	90.00
V/Å^3	803.3(3)	1164.3(4)	1091.5(3)	2194.64(10)
Z	2	2	2	4
Temperature/K	150(2)	150(2)	150(2)	150(2)
Radiation (*λ*/Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.)/g cm^{-3}	1.273	1.505	1.560	1.785
μ(Mo-K*α*), mm^{-1}	0.241	1.045	1.111	4.501
θ/°	25.00–3.35	32.50–3.05	32.17–3.09	32.19–3.20
No. of data	2819	4090	3827	3840
No. of parameters	197	269	253	248
R_1	0.0411	0.0374	0.0365	0.0682
wR_2	0.1049	0.0963	0.0834	0.2190
GOF	1.207	1.009	1.088	1.169

between the Cl$^-$ anion and the amide proton of the –CONH– substituent of the imidazole ring. The [Cl···N] distance of 3.267 Å is comparable to the sum of the individual van der Waals radii (Cl–N = 3.30 Å).[24] Quite interestingly, the Cl$^-$ anion was found to interact with the amide proton of the –CONH– substituent and not with the acidic NC*H*N proton of the imidazole ring. In this regard, it is worth mentioning that the H-bonding interaction of the halide counter anion with the acidic proton of the functional sidearm (*H*X– ; X = O, NR) as well as with that of the acidic NC*H*N proton have been observed for various imidazolium halide salts. Indeed, examples of imidazolium halide salts exhibiting all three [Cl···H–O] [$d_{(Cl\cdots O)}$ = 3.091 Å],[22] [Cl···H–N] [$d_{(Cl\cdots N)}$ = 3.244 Å, 3.236 Å][20] and [Cl···H–C] [$d_{(Cl\cdots C)}$ = 3.373 Å][23] types of H-bonding interactions have been recently reported by us. It is worth mentioning that the H-bonding interaction in imidazolium halide salts has been extensively studied by NMR[25] and X-ray diffraction techniques.[26]

The **2**, **3** and **4** precatalysts were conveniently synthesized by direct reaction of the imidazolium halide salt with $PdCl_2$ in pyridine (Scheme 2).[11] The $^{13}C\{^1H\}$ NMR of **2**, **3** and **4** showed the metal bound carbene N*C*N–Pd resonances appearing at 157–153 ppm and are comparable to that observed in other reported Pd–NHC complexes (175–145 ppm).[27] The **2**, **3** and **4** complexes have been structurally characterized and, as expected, the geometries around the Pd centers were found to be square planar (Table 1 and Fig. 3–5) with the $C_{carbene}$–Pd–Cl angles in



Scheme 2

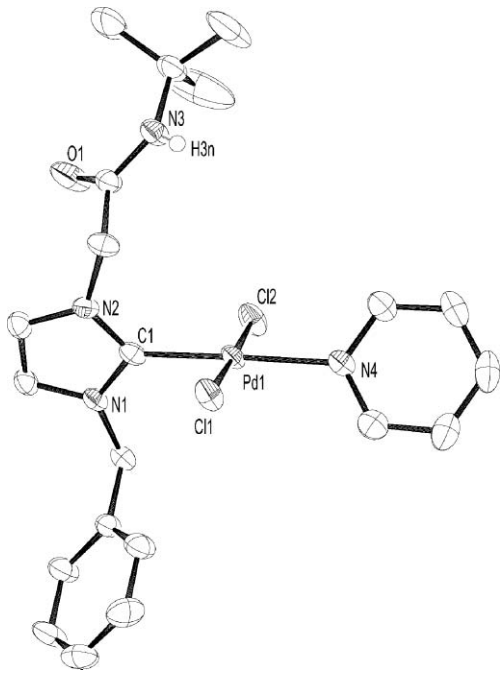


Fig. 3 ORTEP of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.356(4), N(2)–C(1) 1.337(4), Pd(1)–C(1) 1.957(3), Pd(1)–Cl(1) 2.3026(9), Pd(1)–N(4) 2.089(3), C(1)–Pd(1)–N(4) 178.63(11), C(1)–Pd(1)–Cl(1) 87.62(9).

2 [C1–Pd1–Cl2 = 91.24(9)°], **3** [C1–Pd1–Cl2 = 88.70(11)°] and **4** [C1–Pd1–Br2 = 86.3(2)°] being closer to *ca.* 90°. While the $C_{carbene}$–Pd–$N_{pyridine}$ angles in **2** [C1–Pd1–N4 = 178.63(11)°], **3** [C1–Pd1–N3 = 179.66(14)°] and **4** [C1–Pd1–N3 = 176.0(3)°] are nearly linear. The Pd-$C_{carbene}$ bond distances [1.953(8)–1.967(4) Å] in these complexes, **2** [Pd1–C1 = 1.957(3) Å], **3** [Pd1–C1 = 1.967(4) Å] and **4** [Pd1–C1 = 1.953(8) Å], are comparable to that reported for other Pd–NHC complexes.[19,28,29] The two Pd–Cl bond distances in **2** [Pd1–Cl1 = 2.3026(9) Å, Pd1–Cl2 = 2.2913(9) Å] and **3**

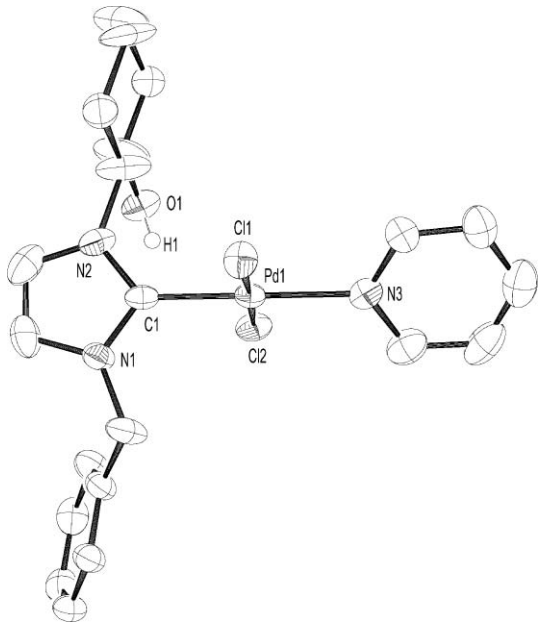


Fig. 4 ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.345(5), N(2)–C(1) 1.343(5), Pd(1)–C(1) 1.967(4), Pd(1)–Cl(1) 2.3071(10), Pd(1)–N(3) 2.096(3), C(1)–Pd(1)–N(3) 179.66(14), C(1)–Pd(1)–Cl(1) 89.07(11).

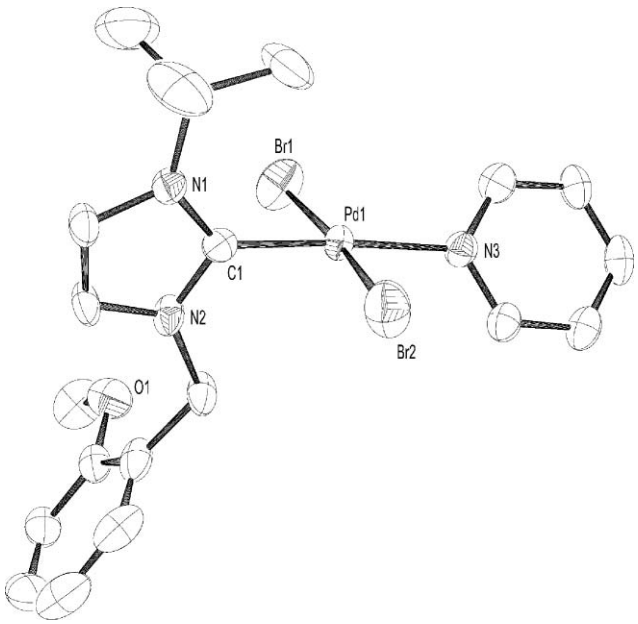


Fig. 5 ORTEP of **4** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.359(11), N(2)–C(1) 1.341(12), Pd(1)–C(1) 1.953(9), Pd(1)–Br(1) 2.3993(13), Pd(1)–N(3) 2.100(8), C(1)–Pd(1)–N(3) 176.0(3), C(1)–Pd(1)–Br(1) 87.6(2).

[Pd1–Cl1 = 2.3071(10) Å, Pd1–Cl2 = 2.3068(10) Å] and the two Pd–Br bond distances in **4** [Pd1–Br1 = 2.399(2) Å, Pd1–Br2 = 2.393(2) Å] are comparable to the sum of the individual covalent radii (Pd–Cl = 2.273 Å and Pd–Br = 2.423 Å).[30] Quite interestingly, though no chelation of the functionalized sidearms to Pd was observed in any of the **2**, **3** and **4** complexes, a variety of both intermolecular as well as intramolecular H-bonding interactions involving the functional sidearm substituents were observed in these complexes *e.g.*, **2** (intermolecular [Cl···H–N] interaction, $d_{(Cl\cdots N)}$ = 3.306 Å), **3** (intramolecular [Cl···H–O] interaction, $d_{(Cl\cdots O)}$ = 3.316 Å, intermolecular [Cl···H–C] interaction, $d_{(Cl\cdots C)}$ = 3.695 Å) and **4** (intermolecular [Br···H–C] interaction, $d_{(Br\cdots C)}$ = 3.666 Å, intermolecular [Br···H–C] interaction, $d_{(Br\cdots C)}$ = 3.583 Å).

The role of the metal bound pyridine is vital to the observed high activities of the PEPPSI based precatalysts and thus merits discussion. For the **2**, **3** and **4** complexes, the Pd-bound pyridine appeared as distinct resonances in comparison to the free pyridine in the ^{1}H NMR spectra of these complexes.[31] However, the definitive proof came from the X-ray diffraction studies that showed the pyridine was, indeed, coordinated to Pd and was tilted by *ca.* 39°–46° relative to the plane containing the imidazolium ring of the NHC ligand.[32] Interestingly, the Pd–N (pyridine) bond distances [2.100(8)–2.089(3) Å] in **2**, **3** and **4** are closer to that in a related complex, [1,3-bis-2,6-di-*i*-propylphenyl-imidazol-2-ylidene]$PdCl_2$(3-chloropyridine) [2.137(2) Å],[11] bearing a similar *trans* pyridine ligand, but are longer than that observed [2.017(4) Å] in [{CNC}Pd(pyridine)][BF_4]$_2$, [CNC = (2,6-bis{[*N*-methyl-*N*′-methylene]imidazol-2-ylidene}pyridine],[33] in which the metal bound pyridine was not *trans* to the NHC ligand. It is worth noting that owing to the strong *trans*-effect[34] of the N-heterocyclic carbene ligand, the Pd–N (pyridine) bond distance of the *trans*-pyridine is expected to be longer, thereby, resulting in weaker binding of the pyridine and subsequent triggering of the "throwaway" pyridine ligand dissociation in the initiation step of the catalytic cycle.[10,11] Indeed, when the precatalyst **4** was heated at 85 °C with 3 equivalents of phenylboronic acid in the absence of aryl halides, simultaneous formations of pyridine and biphenyl, as verified independently by gas chromatography, were observed. Further support for the relatively weaker Pd–pyridine bond came from the density functional theory studies as the Pd–pyridine bond dissociation energy [D_e (Pd-pyridine)], computed for the geometry optimized structures of **2**, **3** and **4** respectively designated by **2**′, (32.9 kcal mol^{-1}), **3**′ (32.7 kcal mol^{-1}), and **4**′ (30.8 kcal mol^{-1}) using B3LYP/SDD, 6-31G(d) level of theory, were found to be significantly lower than the (NHC)–Pd bond dissociation energy [D_e (Pd–$C_{carbene}$)] in these complexes, **2**′ (81.9 kcal mol^{-1}), **3**′ (82.4 kcal mol^{-1}) and **4**′ (77.6 kcal mol^{-1}) and thus the pyridine moiety in these palladium complexes are more amenable to dissociation.

Detailed bonding studies on the geometry optimized structures **2**′, **3**′ and **4**′ were performed using Charge Decomposition Analysis (CDA) that involved breaking the molecule into two fragments, *i.e.* N-heterocyclic carbene (NHC) (fragment 1) and Pd(pyridine)X_2 (fragment 2) (Table 2). The optimized geometries were obtained from the crystallographic co-ordinates using B3LYP/SDD, 6-31G* level of theory for the complexes **2**, **3** and **4**. The electron donation from the carbene fragment to the metal center [NHC $\xrightarrow{\sigma}$ Pd(pyridine)X_2] is denoted as *d* while the electron back donation from the metal center to the carbene moiety [NHC $\xleftarrow{\pi}$ Pd(pyridine)X_2] is represented by *b* and the (*d*/*b*) ratio gives a measure of the forward [NHC $\xrightarrow{\sigma}$ Pd(pyridine)X_2] and backward [NHC $\xleftarrow{\pi}$ Pd(pyridine)X_2] donations occurring in these complexes. Thus high (*d*/*b*) ratio in **2**′ (2.59), **3**′ (2.79) and **4**′ (3.99) complexes are indicative of the predominantly

Table 2 Charge decomposition analysis (CDA) results showing the [NHC $\xrightarrow{\sigma}$ Pd(pyridine)X_2] donation (*d*), the [NHC $\xleftarrow{\pi}$ Pd(pyridine)X_2] donation (*b*) and the *d*/*b* ratio for the geometry optimized structures, **2′**, **3′** and **4′** are shown

Complexes	[NHC $\xrightarrow{\sigma}$ Pd(pyridine)X_2]	[NHC $\xleftarrow{\pi}$ Pd(pyridine)X_2]	*d*/*b* ratio
2′	0.559	0.216	2.59
3′	0.570	0.204	2.79
4′	0.603	0.151	3.99

σ-donating nature of the N-heterocyclic carbene ligands. In this regard, it is worth noting that theoretical studies earlier carried out by us[18,23] on Ag–NHC complexes and also by others[35] suggest that N-heterocyclic carbenes as ligands, in general, are strong σ-donors with minimal π-accepting abilities and, thus would be conducive to the stabilization of the Pd center after the pyridine dissociation.[10,11]

In order to gain insight about the NHC–palladium bonding, a detailed molecular orbital analysis was carried out using the AOMix-CDA software,[36] in which the orbital contributions to the frontier molecular orbitals of the geometry optimized (NHC)Pd(pyridine)X_2 type complexes, **2′** (X = Cl), **3′** (X = Cl) and **4′** (X = Br), from the individual NHC and the Pd(pyridine)X_2 fragments (X = Cl, Br) were considered. Interestingly, the molecular orbitals signifying the NHC–palladium interactions were found buried deep inside the surface *i.e.* in **2′** (HOMO-16 and HOMO-29, Fig. 6), **3′** (HOMO-16 and HOMO-28, Fig. 7) and **4′** (HOMO-14 and HOMO-25, Fig. 8) and were consistent with the inert character of the NHC–palladium bond that are often attributed to the "spectator" nature of the NHC ligand in general.[1a] Specifically, the contributions of the NHC and the Pd(pyridine)X_2 fragments to these molecular orbitals were, **2′** [HOMO-16 {20% NHC fragment, 71% from Pd(pyridine)Cl_2}, HOMO-29 {29% NHC fragment, 52% from Pd(pyridine)Cl_2}] (Fig. 6), **3′** [HOMO-16 {31% NHC fragment, 58% from Pd(pyridine)Cl_2}, HOMO-28 {29% NHC fragment, 54% from Pd(pyridine)Cl_2}] (Fig. 7) and **4′** [HOMO-14 {24% NHC fragment, 64% from Pd(pyridine)Br_2}, HOMO-25 {39% NHC fragment, 35% from Pd(pyridine)Br_2}] (Fig. 8). However, detailed orbital interactions are more intricate due to the contributions from various other fragment molecular orbitals (FMO) in the palladium complexes. It is interesting to note that

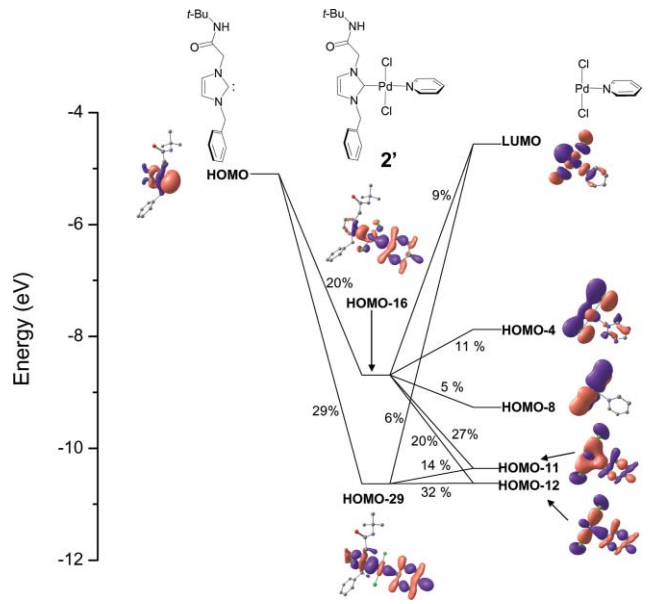


Fig. 6 Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **2′**.

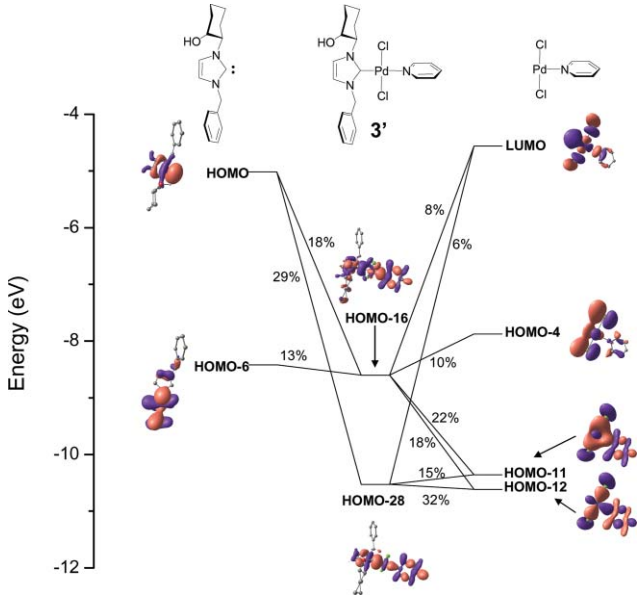


Fig. 7 Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **3′**.

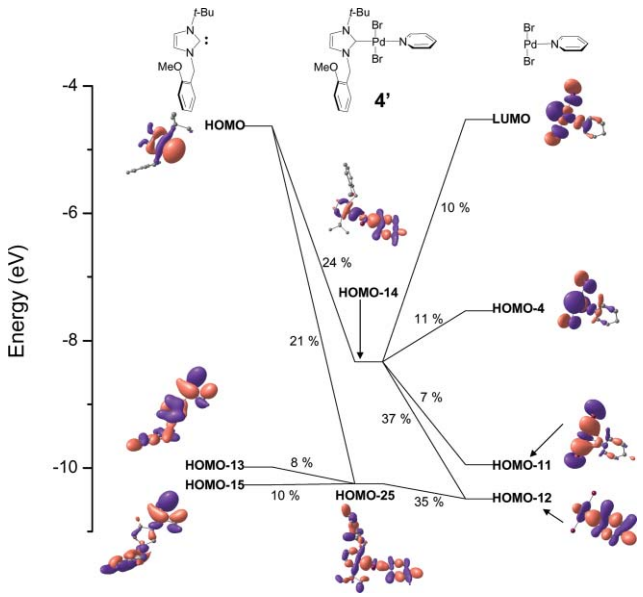
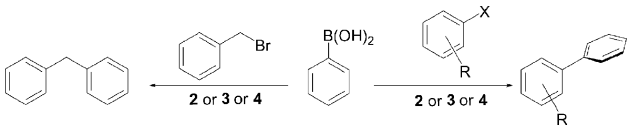


Fig. 8 Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **4′**.

donation of the carbene lone pair partially occurs to the Pd–pyridine σ* orbital as can be seen in Fig. 6, 7 and 8 thereby weakening the Pd–pyridine bond.

A comparison of the solid state crystal structures of **2**, **3** and **4** with that of the geometry optimized structures **2′**, **3′** and **4′** revealed good agreement between the X-ray and computed structures (See Tables S4, S5 and S6‡).

The Pd complexes **2**, **3** and **4** efficiently catalyzed the Suzuki–Miyaura cross-coupling (eqn (1)) of a wide variety of aryl halide substrates with phenyl boronic acid at a low catalyst loading (0.35 mol%). It is interesting to note that high modulations of the yields (> 99–7%) of the cross-coupled products were seen, with higher yields observed for aryl halides containing activating substituents while lower conversions were observed for the ones with less electron withdrawing substituents (Table 3). For example, phenyl bromides having electron-withdrawing substituents like, –CHO, –COMe and –NO_2 moieties in the *o*/*p*-positions gave higher product yields for **2** (52–79%), **3** (64–85%) and **4** (59–> 99%) while those with electron-donating substituents like, –Me and –OMe moieties in the *o*/*p*-positions, gave comparatively much-lower product yields for **2** (37–48%), **3** (34–45%) and **4** (31–47%). The yields observed for iodobenzene is, however, lower than the activated bromo derivatives.



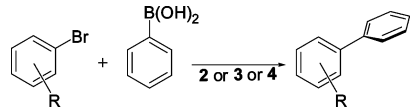
(1)

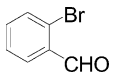
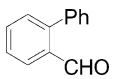
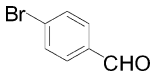
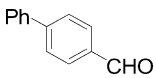
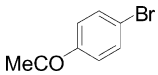
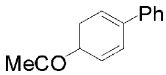
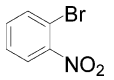
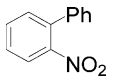
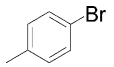
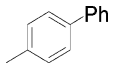
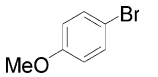
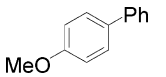
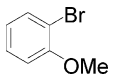
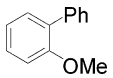
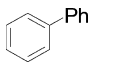
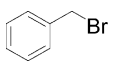
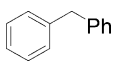
Quite interestingly, the commonly observed C_{sp2}–C_{sp2} cross-coupling (Table 3, entries 1–8) between the two C_{sp2} centers of aryl halide and phenyl boronic acid can even be extended to a relatively more challenging C_{sp3}–C_{sp2} coupling (Table 3, entry 9) in which a C_{sp3} carbon of benzyl bromide was coupled with the C_{sp2} carbon of phenyl boronic acid, albeit in lower yields.

Though all the three **2**, **3** and **4** precatalysts displayed similar trends, quantitative conversions were observed in the case of **4** for the coupling of *o*- and *p*-bromobenzaldehydes. Hence, concentration dependence studies of the precatalyst **4** were carried out in order to gauge the maximum turnover efficiency of the catalyst (Table 4) and, indeed, high turnover numbers as high as 9700 at 8.6×10^{-3} mol% was observed for the *o*-bromobenzaldehyde (Table 4). Interestingly, the pyridine tilt as defined by the torsion angle between pyridine and the imidazolium ring[32] is the lowest for **4**, which coincidently showed the highest conversion for *o*-bromobenzaldehyde. However, detailed theoretical studies are needed to elucidate the exact role of the catalyst structure in its mode of action.

Important is the comparison of the precatalysts **2**, **3** and **4** containing *N*/*O*-functionalized N-heterocyclic carbenes, with the other related PEPPSI precatalysts, *trans*-[1,3-bis-2,6-di-*i*-propylphenyl-imidazol-2-ylidene]$PdCl_2$(3-chloropyridine),[11] *trans*-[1,3-bis-2,6-di-ethylphenyl-imidazol-2-ylidene]$PdCl_2$(3-chloropyridine),[11] and *trans*-[1,3-bis-2,4,6-tri-methylphenyl-imidazol-2-ylidene]$PdCl_2$(3-chloropyridine),[11] containing non-functionalized Arduengo type N-heterocyclic carbenes reported by Organ and coworkers.[10,11] Though the Organ's PEPPSI

Table 3 Selected results of Suzuki–Miyaura cross-coupling reaction of aryl halides (ArX, X = Br, I) catalyzed by **2**, **3** and **4**.[a]



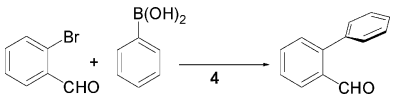
Entry	Reagent	Product	**2**[b]	**3**[b]	**4**[b]
1			79	85	99
2			72	82	99
3			66	67	73
4			52	64	59
5			48	43	47
6			43	45	38
7			37	34	31
8			36	32	30
9			7	11	22

[a] Reaction conditions: 2.16 mmol of aryl halide (ArX, X = Br, I), 2.64 mmol of phenyl boronic acid, 3.24 mmol of K_2CO_3, 7.5×10^{-3} mmol of catalyst, 30 mL of CH_3CN, 12 h at 85 °C. [b] The yields (%) were determined by GC using diethyleneglycol–di-n-butyl ether as an internal standard.

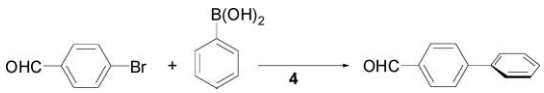
percatalysts[11] successfully carried out Suzuki–Miyaura cross-coupling of the more challenging aryl chlorides along with the frequently encountered aryl bromide substrates but at comparatively higher catalyst loadings (1–2 mol%) than the **2**, **3** and **4** precatalysts (3.5×10^{-1}–8.6×10^{-3} mol%) showed activity toward the aryl bromide and iodide substrates.

Also worthwhile is the comparison of the activity of a *trans*-(NHC)Pd(pyridine)X_2 (X = halide) type PEPPSI precatalyst with a similar *trans*-$(NHC)_2PdX_2$ precatalyst supported over the same N-heterocyclic carbene (NHC) ligand. Interestingly, the activity of **4**, containing a *N*/*O*-functionalized N-heterocyclic carbene and a "throwaway" pyridine ligand, was found to be significantly lower than a *trans*-$(NHC)_2PdX_2$ (X = halide) complex,[12] containing two of the same *N*/*O*-functionalized N-heterocyclic carbene ligand. For example, for the Suzuki–Miyaura cross-coupling of *o*-bromobenzaldehyde with phenyl boronic acid, the maximum TON (9700) (Table 4 entry 5) obtained for *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br_2

Table 4 Selected results of Suzuki coupling of *o*/*p*-bromobenzaldehyde with phenyl boronic acid catalyzed by **4**[a]



Entry	**4** (mol%)	Yield[b](%)	TON
1	3.5×10^{-1}	>99	288
2	8.6×10^{-2}	>99	1160
3	3.5×10^{-2}	>99	2900
4	1.7×10^{-2}	>99	5500
5	8.6×10^{-3}	83	9700



Entry	**4** (mmol)	Yield[b](%)	TON
6	3.5×10^{-1}	>99	288
7	8.6×10^{-2}	>99	1160
8	3.5×10^{-2}	58	1700

[a] Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenyl boronic acid, 3.24 mmol of K_2CO_3, complex **4**, 30 mL of CH_3CN, 12 h at 85 °C. [b] Determined by GC using diethyleneglycol–di-n-butyl ether as an internal standard.

(**4**) is significantly lower (TON = 49 700, after 12 h at 85 °C) than its bis-NHC analog, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$_2$PdCl$_2$[12] also obtained under the same conditions (after 12 h at 85 °C). The greater activity of *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$_2$PdCl$_2$ may be due to the formation of a more electron-rich active species, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$_2$Pd^0, containing two electron-donating NHC ligands, as opposed to the active species, *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd^0 (solvent),[10,11] formed from the precatalyst **4** containing only one NHC ligand, and thereby greatly enhancing the oxidative addition of the aryl halide, often the rate-determining step in the catalytic cycle, in the case of the former.[37]

Experimental

General procedures

All manipulations were carried out using a combination of glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. The synthetic procedures of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride[21] and 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide[12] were reported by us. Benzyl imidazole[38] and *N*-*t*-butyl-2-chloroacetamide[39] were synthesized according to literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ on a Varian 400 MHz NMR spectrometer. ^{1}H NMR peaks are labeled as singlet (s), doublet (d) and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were performed on a Micromass Q-Tof spectrometer. GC spectra were measured on a Shimadzu gas chromatograph GC-15A equipped with a FID. X-Ray diffraction data for **1**, **2**, **3** and **4** were collected on an Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).

Synthesis of 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride 1. A mixture of benzyl imidazole (1.06 g, 6.71 mmol) and *N*-*t*-butyl-2-chloroacetamide (1.00 g, 6.71 mmol) was dissolved in toluene (*ca.* 40 mL) and the reaction mixture was refluxed at 110 °C for 12 h when a sticky solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × *ca.*10 mL) to obtain the product **1** as a light yellow solid (1.45 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 10.1 (s, 1H, NC*H*N), 8.66 (br, 1H, N*H*), 7.59 (br, 1H, NC*H*CHN), 7.41–7.39 (m, 5H, C_6H_4), 7.09 (br, 1H, NCHC*H*N), 5.45 (s, 2H, CH_2), 5.31 (s, 2H, CH_2), 1.37 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.5 (*C*O), 136.8 (N*C*HN), 132.6 (*ipso*-C_6H_5), 129.1 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 128.6 (*p*-C_6H_5), 123.6 (NCH*C*HN), 120.9 (N*C*HCHN), 53.0 (CH_2), 51.8 (CH_2), 51.7 (*C*(CH$_3$)$_3$), 28.2 (C(*C*H$_3$)$_3$). IR data (KBr) cm^{-1} 3441 (m), 3212 (s), 3047 (m), 3011 (m), 2969 (m), 2928 (w), 2905 (w), 1685 (s), 1544 (s), 1497 (w), 1456 (m), 1396 (m), 1367 (m), 1283 (m), 1225 (m), 1162 (s), 1097 (w), 1032 (w), 1018 (w), 950 (w), 920 (w), 872 (w), 829 (w), 796 (w), 776 (w), 729 (m), 713 (s), 674 (w), 621 (m), 578 (m), 458 (w). Anal. Calcd. for $C_{16}H_{22}ClN_3O$: C, 62.43; H, 7.20; N, 13.65. Found: C, 61.76; H, 8.02; N, 13.96%.

Synthesis of *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl$_2$ 2. A mixture of 1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride **1** (0.167 g, 0.543 mmol), $PdCl_2$ (0.105 g, 0.592 mmol) and K_2CO_3 (0.375 g, 2.71 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous $CuSO_4$ solution and the aqueous layer was extracted with dichloromethane (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **2** as a yellow solid (0.116 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.93 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-NC_5H_5), 7.74 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-NC_5H_5), 7.40 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-NC_5H_5), 7.31 (m, 5H, C_6H_5), 7.04 (br, 1H, NCHC*H*N), 6.71 (br, 1H, NC*H*CHN), 5.77 (s, 2H, CH_2), 5.15 (s, 2H, CH_2), 1.27 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 165.8 (*C*O), 153.3 (N*C*N–Pd), 151.1 (*o*-NC_5H_5), 138.5 (*ipso*-C_6H_5), 138.2 (*p*-NC_5H_5), 128.9 (*o*-C_6H_5), 128.8 (*m*-C_6H_5), 128.6 (*p*-C_6H_5), 124.6 (*m*-NC_5H_5), 122.5 (NCH*C*HN), 122.1 (N*C*HCHN), 55.6 (CH_2), 54.7 (CH_2), 51.9 (*C*(CH$_3$)$_3$), 28.3 (C(*C*H$_3$)$_3$). IR data (KBr) cm^{-1} 3416 (s), 3306 (m), 3130 (m), 1682 (m), 1638 (m), 1618 (m), 1543 (w), 1450 (m), 1400 (s), 1262 (w), 1246 (w), 1165 (w), 1071 (w), 1017 (w), 804 (w), 761 (w), 722 (w), 691 (m), 617 (w), 481 (w). Anal. Calcd. for $C_{21}H_{27}Cl_2N_4OPd \cdot 1/2(CH_2Cl_2)$: C, 45.20; H, 4.94; N, 9.81. Found: C, 45.59; H, 5.42; N, 8.99%.

Synthesis of *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]Pd(pyridine)Cl$_2$ 3. A mixture of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride (0.440 g, 1.51 mmol), $PdCl_2$ (0.294 g, 1.66 mmol) and K_2CO_3 (1.04 g, 7.54 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture

was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous $CuSO_4$ solution and the aqueous layer was extracted with dichloromethane (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **3** as a yellow crystalline solid (0.364 g, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.03 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-NC_5H_5), 7.79 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-NC_5H_5), 7.47 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-NC_5H_5), 7.40–7.34 (m, 5H, C_6H_5), 6.95 (br, 1H, NCHC*H*N), 6.76 (br, 1H, NC*H*CHN), 5.89 (d, 1H, $^2J_{HH}$ = 15 Hz, CH_2), 5.82 (d, 1H, $^2J_{HH}$ = 15 Hz, CH_2), 5.09–5.03 (m, 1H, C_6H_{10}), 3.30–3.27 (m, 1H, C_6H_{10}), 2.32–2.24 (m, 2H, C_6H_{10}), 1.92–1.85 (m, 3H, C_6H_{10}), 1.63–1.53 (m, 3H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 153.2 (N*C*N-Pd), 151.2 (*o*-NC_5H_5), 147.9 (*ipso*-C_6H_5), 138.1 (*p*-NC_5H_5), 135.0 (*o*-C_6H_5), 129.0 (*m*-C_6H_5), 128.9 (*p*-C_6H_5), 124.5 (*m*-NC_5H_5), 122.0 (NCH*C*HN), 119.7 (N*C*HCHN), 72.7 (C_6H_{10}), 66.9 (C_6H_{10}), 54.9 (CH_2), 34.9 (C_6H_{10}), 32.9 (C_6H_{10}), 25.0 (C_6H_{10}), 24.3 (C_6H_{10}). IR Data (KBr) cm^1 3118 (m), 2937 (w), 2849 (w), 1619 (m), 1605 (m), 1559 (w), 1448 (m), 1400 (s), 1278 (w), 1241 (w), 1215 (w), 1163 (w), 1069 (m), 1047 (w), 1032 (w), 955 (w), 868 (w), 761 (w), 732 (w), 691 (m), 615 (w), 472 (w). Anal. Calcd. for $C_{21}H_{26}Cl_2N_3OPd$: C, 49.19; H, 4.91; N, 8.19. Found: C, 48.83; H, 4.60; N, 8.04%.

Synthesis of *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br$_2$ 4. A mixture of 1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazolium bromide (0.381 g, 1.17 mmol), $PdCl_2$ (0.229 g, 1.29 mmol) and K_2CO_3 (0.809 g, 5.85 mmol) were refluxed in pyridine (*ca.* 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. Then the residue was washed with aqueous $CuSO_4$ solution and the aqueous layer was extracted with ethyl acetate (*ca.* 3 × 10 mL). Then the organic layer was collected and the solvent was removed under vacuum to obtain the product **4** as a yellow crystalline solid (0.291 g, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.07 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-NC_5H_5), 7.74 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-NC_5H_5), 7.61 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-NC_5H_5), 7.34 (d, 1H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_4), 7.29 (br, 1H, NCHC*H*N), 7.02 (br, 1H, NC*H*CHN), 6.95 (t, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.89 (d, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.78 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_4), 6.09 (d, 1H, $^2J_{HH}$ = 15 Hz, CH_2), 6.03 (d, 1H, $^2J_{HH}$ = 15 Hz, CH_2), 3.89 (s, 3H, OCH_3), 2.10 (s, 9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 157.4 (N*C*N-Pd), 152.6 (*o*-NC_5H_5), 137.7 (*p*-NC_5H_5), 137.6 (OC_6H_4), 131.8 (*ipso*-C_6H_4), 129.8 (*o*-C_6H_4), 124.4 (*p*-C_6H_4), 124.3 (*m*-C_6H_4), 120.9 (NCH*C*HN), 120.8 (*m*-NC_5H_5), 120.3 (N*C*HCHN), 110.4 (*m*-C_6H_4), 58.6 (CH_2), 55.3 (OCH_3), 50.6 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$). IR data (KBr) cm^{-1} 3416 (s), 3137 (m), 2974 (m), 1603 (s), 1496 (m), 1463 (m), 1445 (m), 1400 (s), 1372 (m), 1348 (w), 1283 (w), 1253 (s), 1154 (w), 1118 (m), 1064 (w), 1047 (m), 1027 (s), 913 (w), 819 (w), 754 (s), 730 (m), 700 (m), 687 (s), 623 (m). Anal. Calcd. for $C_{20}H_{26}Br_2N_3OPd{\cdot}1/2(NC_5H_5)$: C, 42.95; H, 4.41; N, 7.79. Found: C, 43.50; H, 4.43; N, 8.54%.

Computational methods

The density functional theory calculations were performed on the **2**, **3** and **4** complexes using GAUSSIAN 03[40] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) have been employed in this study.[41,42] Stuttgart-Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for palladium.[43] All other atoms are treated with 6-31G(d) basis set.[44] All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA).[45] CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.[46] The orbital contributions in the geometry optimized NHC-Pd(pyridine)X_2 type complexes, **2′** (X = Cl), **3′** (X = Cl) and **4′** (X = Br), can be divided into three parts:

(i) σ-donation from the [NHC $\xrightarrow{\sigma}$ Pd(pyridine)X_2] fragment

(ii) π-back donation from [NHC $\xleftarrow{\pi}$ Pd(pyridine)X_2] fragment and

(iii) repulsive polarization (*r*)

The CDA calculations are performed using the program AOMix,[36] using the B3LYP/SDD, 6-31G* wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the *AOMix* program.[36,47] The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, the charge decomposition analysis (CDA) was performed using the *AOMix-CDA*.[48]

General procedure for the Suzuki coupling reaction

In a typical run, a round bottom flask was charged with a mixture of aryl halides (ArX, X = Br, I), phenylboronic acid and K_2CO_3 and diethyleneglycol–di-n-butyl ether (internal standard) in a molar ratio of 1 : 1.2 : 1.5: 1 and to this mixture was added precatalysts **2**, **3** or **4** at varying mol% amounts (Tables 3 and 4). Acetonitrile (30 mL) was added to the reaction mixture and refluxed for an appropriate period of time after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol–di-n-butyl ether as an internal standard.

Conclusion

In summary, a series of air stable, user-friendly and conveniently synthesized Pd precatalysts **2**, **3** and **4** *trans*-(NHC)Pd(pyridine)X_2 (X = Cl, Br), stabilized over *N*/*O*-functionalized N-heterocyclic carbenes and containing "throwaway" pyridine ligand have been synthesized and structurally characterized. The weakly bound nature of the pyridine moiety was further supported by density functional theory studies as the estimated Pd–pyridine bond dissociation energy [D_e (Pd–pyridine)] in the geometry optimized complexes **2′** (32.9 kcal mol^{-1}), **3′** (32.7 kcal mol^{-1}) and **4′** (30.8 kcal mol^{-1}) were found to be significantly lower than the (NHC)–Pd bond dissociation energy [D_e (Pd–$C_{carbene}$)] in the same **2′** (81.9 kcal mol^{-1}), **3′** (82.4 kcal mol^{-1}) and **4′** (77.6 kcal mol^{-1}) complexes. Furthermore, the NHCs were found to behave as strong σ-donor ligands with very little component of π-back-bonding from the metal center to NHC in the palladium complexes. The catalysis studies revealed that the **2**, **3** and **4** complexes are excellent precatalysts for Suzuki–Miyaura cross-coupling reactions at low catalyst loadings (0.35 mol%) and exhibit not only the commonly observed C_{sp2}–C_{sp2} coupling but also the more challenging C_{sp3}–C_{sp2} cross-coupling reactions.

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