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Copper-free and amine-free Sonogashira coupling in air in a mixed aqueous medium by palladium complexes of *N*/*O*-functionalized N-heterocyclic carbenes

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ABSTRACT

Highly convenient copper-free and amine-free Sonogashira coupling of aryl bromides and iodides with terminal acetylenes under amenable conditions in air and in a mixed aqueous medium are reported using several new, user friendly and robust palladium precatalysts (**1**–**5**) of *N*/*O*-functionalized N-heterocyclic carbenes (NHCs). In particular, the precatalysts, **1** and **2**, were synthesized from the imidazolium chloride salts by the treatment with $PdCl_2$ in pyridine in presence of K_2CO_3 as a base while the precatalysts, **3**–**5**, were synthesized from the respective silver complexes by the treatment with $(COD)PdCl_2$. The DFT studies carried out on the **1**–**5** complexes suggest the presence of strong NHC–Pd σ-interactions arising out of deeply buried NHC–Pd σ-bonding molecular orbitals (MOs) that account for the inert nature of the metal–carbene bonds and also provide insights into the exceptional stability of these precatalysts.

1. Introduction

The seemingly challenging C–C cross-coupling reaction, made easy by palladium, has inundated the literature in last two decades with several of its variants that mainly involve the coupling of aryl or alkyl halides with organometallic nucleophiles depending upon the requirement and the specificity of the cross-coupled products [1–3]. One such emerging name is the Sonogashira coupling that provide an easy pathway for the construction of all-important conjugate "enyne" and "arylalkyne" frameworks often encountered in the natural products, pharmaceuticals, biologically important molecules, molecular electronics as well as in molecules with materials related applications [4–7]. In particular, the Sonogashira reactions involve the coupling of aryl and alkenyl halide with terminal acetylenes and are catalyzed by palladium in a basic medium in presence of copper as a co-catalyst. The coupling of aryl and alkenyl halide with terminal acetylenes proceeds with the *in situ* generation of an extremely sensitive organometallic species, the Cu–acetylide, which renders the Sonogashira reactions air and moisture sensitive and potentially explosive. Furthermore, the Cu–acetylide species, under aerobic conditions yields the unwanted homo-coupled product, instead of the desired cross-coupled product, and thus restricts the Sonogashira reaction to stringent anaerobic conditions [8]. Hence, an important objective in this area lies in developing Cu-free Sonogashira [9–13] reactions as these would circumvent the formation of the air and moisture sensitive and also potentially explosive Cu–acetylide species, thereby providing a much needed answer for making the Sonogashira reaction more tolerant towards aerobic conditions.

The other limitation of Sonogashira coupling arises from the usage of not so environment friendly amines [14], which are frequently used as bases in many of the coupling reactions [4–7]. Thus, significant efforts are underway toward developing amine-free conditions for the Sonogashira couplings, in which traditional bases are used in place of the amines. Worth noting that against this backdrop, we decided to develop both Cu-free and amine-free Sonogashira couplings [15–20] as the Cu-free feature would facilitate the reaction to proceed under normal aerobic conditions without the requirement for the exclusion of air and moisture while the amine-free feature would make the reaction more environment friendly.

Our interest lies in developing the chemistry of *N*/*O*-functionalized N-heterocyclic carbenes [21–24] particularly with regard to their utility in biomedical applications [25,26] and in chemical catalysis [27–32], with special focus on the palladium mediated C–C cross-coupling reactions namely the Suzuki–Miyaura coupling [33,34], the Sonogashira and the Hiyama couplings [35,36]. In particular, we aim at designing efficient, robust and stable precatalysts of *N*/*O*-functionalized N-heterocyclic carbenes that would carry out the cross-coupling reactions under more amenable conditions. In this regard, worth mentioning that the utility of N-heterocyclic carbenes [37–44] in the Sonogashira coupling is relatively new with most of the existing reports are of the phosphine based systems [45–51]. Furthermore, on many occasions these catalyses were performed under "Ligand Assisted Catalysis" conditions

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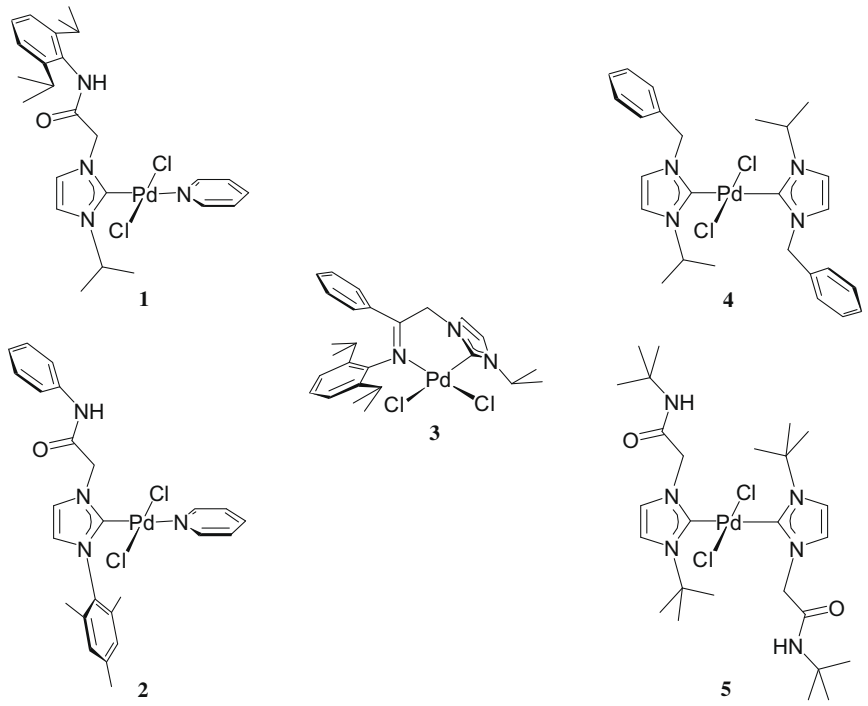


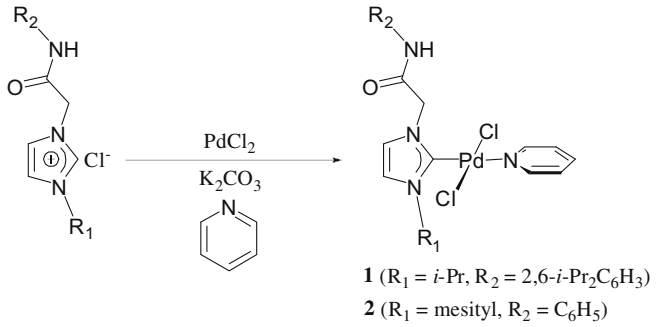
Fig. 1. Palladium complexes of *N/O*-functionalized and non-functionalized N-heterocyclic carbenes are shown.

(LAC), in which the catalytically active species were generated *in situ* and as a result only a handful of examples exist of the well-defined catalyst systems. Hence, in the light of these facts, we set out to design well-characterized precatalysts for the Sonogashira couplings under both Cu-free and amine-free conditions.

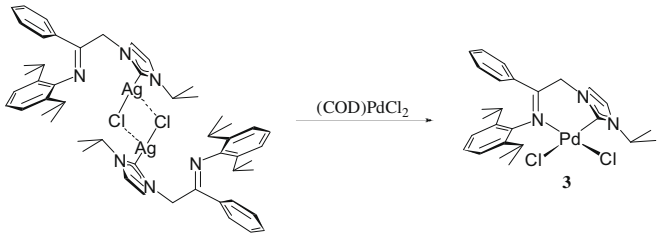
Here in this contribution, we report several new palladium precatalysts, **1**–**5** (Fig. 1), with improved attributes like high efficiency and enhanced stability for the Sonogashira coupling under the much desired Cu-free and amine-free conditions in air in a mixed aqueous medium. Specifically, we report the utility of three types of palladium precatalysts namely, the Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation (PEPPSI) [52–54] themed *trans*-(NHC)$PdCl_2$(pyridine) complexes, **1** and **2**, a [N and $C_{carbene}$] chelating complex, **3**, and the *trans*-$(NHC)_2PdCl_2$ type complexes, **4** and **5**, in the Sonogashira coupling reactions. Further insights on the influence of the *N*/*O*-functionalized N-heterocyclic carbene ligand (NHCs) in these **1**–**5** precatalysts were obtained from the density functional theory (DFT) studies, which revealed that the NHC−Pd σ-bonding molecular orbitals (MOs) were very deep seated thereby indicating the inertness of the NHC−Pd bond in these **1**–**5** complexes.

2. Results and discussion

The PEPPSI themed *trans*-(NHC)$PdCl_2$(pyridine) type complexes **1** and **2** were, respectively, synthesized from 1-(*i*-propyl)-3-(N-2,6-di-*i*-propylphenylacetamido)imidazolium chloride and [1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride by the reaction with $PdCl_2$ in pyridine in presence of K_2CO_3 as a base (Scheme 1). The [N and $C_{carbene}$] chelating complex, **3**, (Scheme 2) as well as the *trans*-$(NHC)_2PdCl_2$ type complexes, **4** and **5**, (Schemes 3 and 4) were prepared from the respective silver complexes by treatment with (COD)$PdCl_2$. Of foremost importance is the ^{13}C NMR spectrum which showed the appearances of the diagnostic Pd–$C_{carbene}$ resonance in the highly downfield shifted region [**1** (153.2 ppm), **2** (152.3 ppm), **3** (152.4 ppm), **4** (169.6 ppm) and **5** (166.5 ppm)], thus, confirming the formation of the palladium



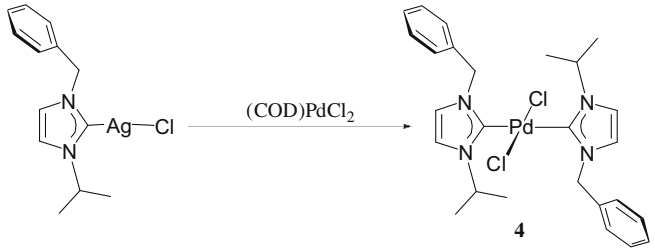
Scheme 1.



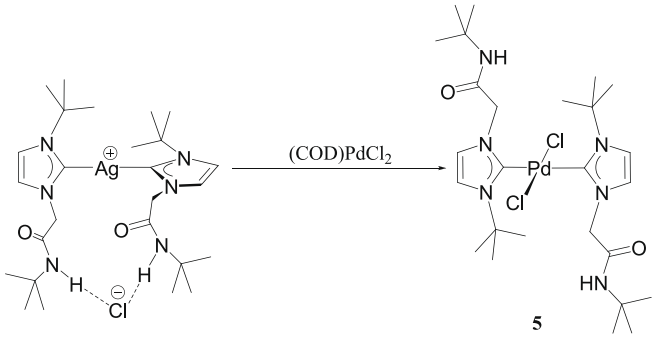
Scheme 2.

complexes. It is interesting to note that both the ^1H NMR and ^{13}C NMR spectrum of **3** showed two sets of resonances owing to *E*/*Z*-isomerization observed earlier by us [21], Coleman et al. [55–57], Bildstein et al. [58,59], and Tilset et al. [60–62] for the related ligand systems.

The molecular structures of the **1**–**5** complexes as determined by X-ray diffraction established the monomeric nature of these metal complexes with the palladium center being in expected square-planar geometry (Figs. 2–4 and Supporting information



Scheme 3.



Scheme 4.

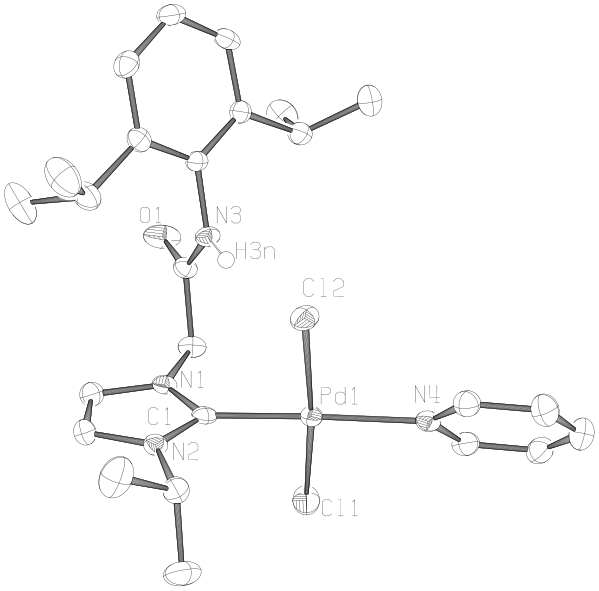


Fig. 2. ORTEP of **1** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N1–C1 1.348(3), N2–C1 1.348(3), Pd1–C1 1.959(2), Pd1–N4 2.1273(18), N1–C1–N2 105.66(17), and C1–Pd1–N4 177.11(7).

Figs. S1 and S2). The Pd–$C_{carbene}$ bond distances in **1** [1.959(2) Å], **2** [1.961(4) Å], **3** [1.952(5) Å], **4** [2.033(5) Å] and **5** [2.0530(17) Å] compare well with the other structurally characterized palladium N-heterocyclic carbene complexes, i.e. [1-(mesityl)-3-(pyrimidine)imidazole-2-ylidene]$PdCl_2$ [1.964(3) Å] [63], [(1-benzyl-1′-methyl-3,3′-ethylenediimidazolin-2,2′-diylidene)]$PdCl_2$ [1.967(5) Å and 1.982(6) Å] [64], [(1,3-dibenzhydrylbenzimidazolin-2-ylidene)CH_3CN]$PdBr_2$ [1.938(4) Å] [65], [N,N′-*bis*-(2,2-diethoxyethyl) imidazole-2-ylidene]$_2PdCl_2$ [2.013(7) Å] [66] and [1-(methyl)-3-(N-2,6-di-methylphenylimino-2-phenylmethyl)imidazol-2-ylid-ene] $PdCl_2$ [1.9677(18) Å] [67].

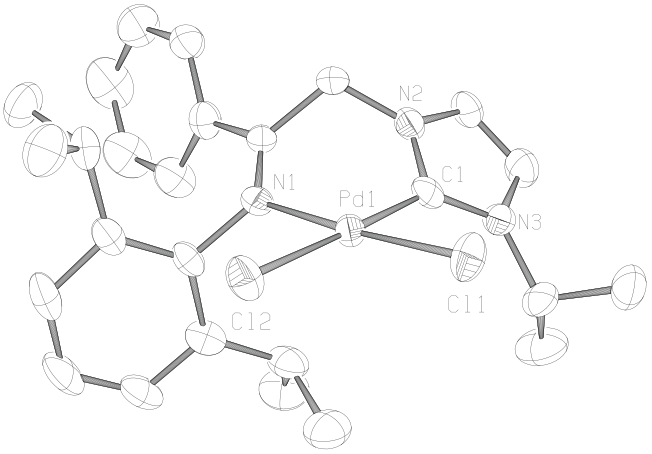


Fig. 3. ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N2–C1 1.354(7), N3–C1 1.346(7), Pd1–C1 1.952(5), Pd1–N1 2.072(4), N2–C1–N3 105.5(5), and C1–Pd1–N1 86.27(19).

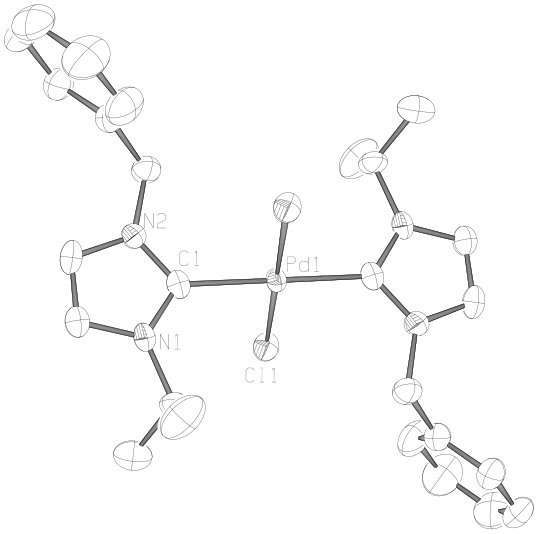


Fig. 4. ORTEP of **4** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N1–C1 1.341(6), N2–C1 1.348(6), Pd1–C1 2.033(5), Pd1–Cl1 2.3076(13), N1–C1–N2 105.0(4), and C1–Pd1–Cl1 88.05(14).

Of these, the PEPPSI themed **1** and **2** complexes, containing a "throwaway" pyridine moiety, exhibit an additional Pd–pyridine distance of 2.1273(18) Å (**1**) and 2.091(3) Å (**2**) similar to that observed in other related analogs like, the non-functionalized aryl substituted *trans*-[1,3-*bis*(2,6-di-*i*-propylphenyl)-imidazol-2-ylidene]$PdCl_2$(3-chloropyridine) [2.137(2) Å] [53], or the *N*/*O*-functionalized ones like, the *trans*-[1-(benzyl)-3-(N-*t*-butylaceta-mido) imidazol-2-ylidene]$PdCl_2$(pyridine) [2.089(3) Å] [33], *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]$PdCl_2$-(pyridine) [2.096(3) Å] [33] and *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]$PdBr_2$(pyridine) [2.100(8) Å] [33]. Furthermore, in concurrence with the "throwaway" nature of the pyridine moiety in **1** and **2**, slightly elongated Pd–pyridine distance is observed in **1** [2.1273(18) Å] and **2** [2.091(3) Å] as a consequence of strong *trans* influence of the NHC ligand in these **1** and **2** complexes. For example, fairly shorter Pd–pyridine distance is observed in the Pd-bound pyridine complexes of non-NHC ligands like, in [2,6-*bis*(2′-indolyl)pyridine]Pd(pyridine) [2.040(3) Å], [68] [*bis*(*bis*(2-pyridylmethyl)amine-N,N′,N″)]Pd(pyridine)]$(ClO_4)_2$ [2.037(3) Å]

[69] and [(2,2′:6′,2″-terpyridine)Pd(pyridine)]$(ClO_4)_2$ [2.038(4) Å] [70]. Lastly, consistent with the weakly bound pyridine moiety in the PEPPSI themed **1** and **2** complexes, the formation of free pyridine, as verified by GC and GCMS analysis, was indeed observed for a representative complex **1** under the Sonogashira catalysis conditions.

Quite interestingly, the complex **3** exhibits [N and $C_{carbene}$] chelation similar to that observed in a related [1-(methyl)-3-(N-2,6-di-*i*-propyl-phenylimino-2-propyl)imidazol-2-ylidene]$PdCl_2$ complex [62] but differs from another close analog, [1-(methyl)-3-(N-2,6-di-*i*-propyl-phenylimino-2-phenylethyl)imidazol-2-ylidene]$_2PdCl_2$ [61] which do not show such chelation.

Lastly, the complexes, **4** and **5**, that display coplanar imidazole rings, closely resemble other structurally characterized *trans*-$(NHC)_2PdX_2$ (X = halide) type examples like, [1-benzyl-3-*t*-butylimidazol-2-ylidene]$_2PdCl_2$ [26], [1-(*o*-methoxybenzyl)-3-(*t*-butyl)-imidazol-2-ylidene]$_2PdCl_2$ [34] and *trans*-[1-(benzyl)-3-(3,3-dimethyl-2-oxo-butyl)imidazol-2-ylidene]$_2PdBr_2$ [36].

Further insights on the nature of the NHC–Pd interaction in **1**–**5** were obtained from density functional theory (DFT) studies carried out on these complexes. Specifically, geometry optimizations followed by single-point calculations were performed at B3LYP/SDD, 6-31G(d) level of theory using atomic coordinates obtained from the X-ray analysis (Supporting information Tables S3–S5 and S7 & S8). The post wave function analysis using Natural Bond Orbital (NBO) method was performed to gain additional understanding of the nature of the NHC–Pd interaction.

The strong σ-donating ability of the N-heterocyclic carbene ligands was evident from both the Mulliken and Natural charge analyses, which clearly showed significant increase in the electron density on the palladium center upon binding of the NHC ligand fragment (see Supporting information Tables S9–S13). A closer scrutiny of the electronic configuration of the metal center in these complexes further revealed that the electron donation from the carbene lone pair occurred into the 5s orbital of palladium (Supporting information Tables S14 and S15). Specifically, the Natural Bond Orbital (NBO) analysis showed that the NHC–Pd bond is composed of the interaction between a $C_{carbene}$ (sp^2) orbital with a palladium based sd hybrid orbital (see Supporting information Table S20).

The Charge Decomposition Analysis (CDA) was performed on the **1**–**5** complexes to obtain a better understanding of the NHC–Pd interaction by cleaving the NHC–Pd bond into its associated free ligand and metal fragments and then looking into the extent of the NHC $\xrightarrow{\sigma}$ Pd forward donation, designated by *d*, and the NHC $\xleftarrow{\pi}$ Pd backward donation, designated by *b*, occurring in the NHC–Pd interaction. Worth noting that a significantly high *d*/*b* ratio (2.27–3.91) was estimated for the NHC–Pd interaction in all of the **1**–**5** complexes and is in accordance with the strong σ-donating nature of the N-heterocyclic carbene ligand (see Supporting information Tables S18 and S19).

The molecular orbital (MO) correlation diagram constructed from the interaction of the associated metal and ligand fragment molecular orbitals (FMOs) depict the NHC–Pd σ-interaction prevalent in these complexes, **1** (HOMO-18, HOMO-34), **2** (HOMO-18, HOMO-29), **3** (HOMO-8, HOMO-31), **4** (HOMO-16, HOMO-31) and **5** (HOMO-16, HOMO-45), (Figs. 5–7 and Supporting information Figs. S3–S9). The stable and hence inert nature of the NHC–Pd interaction is further evident from these deeply buried NHC–Pd σ-bonding molecular orbitals [**1** (HOMO-18, HOMO-34), **2** (HOMO-18, HOMO-29), **3** (HOMO-8, HOMO-31), **4** (HOMO-16, HOMO-31) and **5** (HOMO-16, HOMO-45)] that make the NHC–Pd interaction less vulnerable to electrophilic or nucleophilic attack. In this regard, it is worth noting that the metal–carbene interactions in N-heterocyclic carbene metal complexes are significantly more stable than what is observed in the Fischer or Schrock carbene complexes, which are susceptible to both nucleophilic or electrophilic attack [71–76]. Furthermore, a scrutiny of the molecular orbitals, HOMO-18 (**1**), HOMO-18 (**2**), HOMO-8 (**3**), HOMO-31 (**4**) and HOMO-45 (**5**), representing maximum σ-donation from

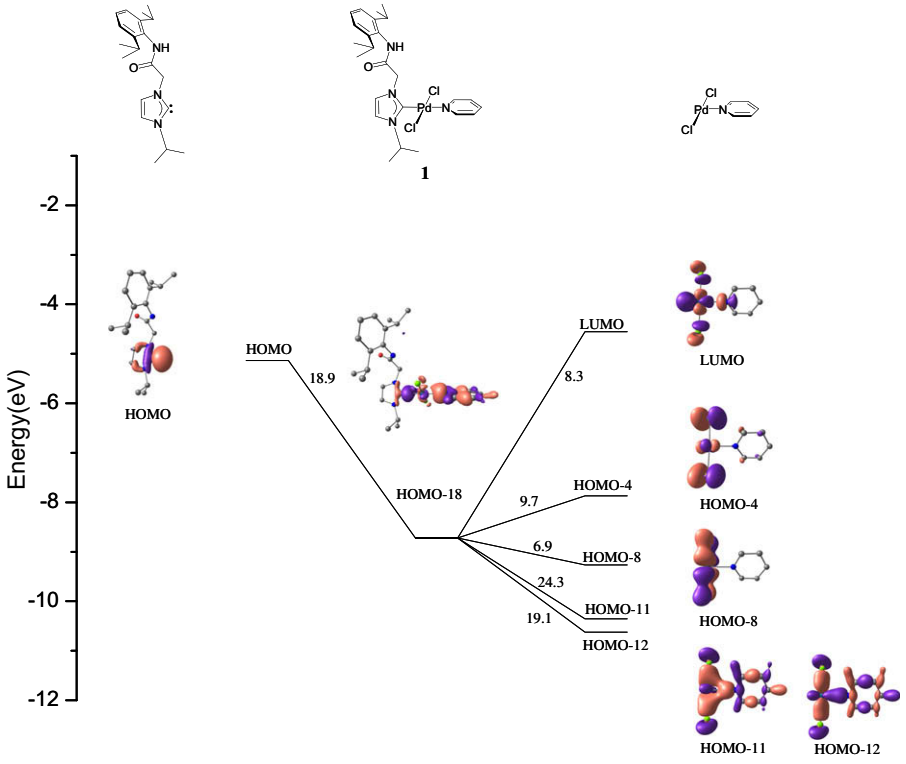


Fig. 5. Simplified orbital interaction diagram showing the major contributions of NHC–palladium bond in **1**.

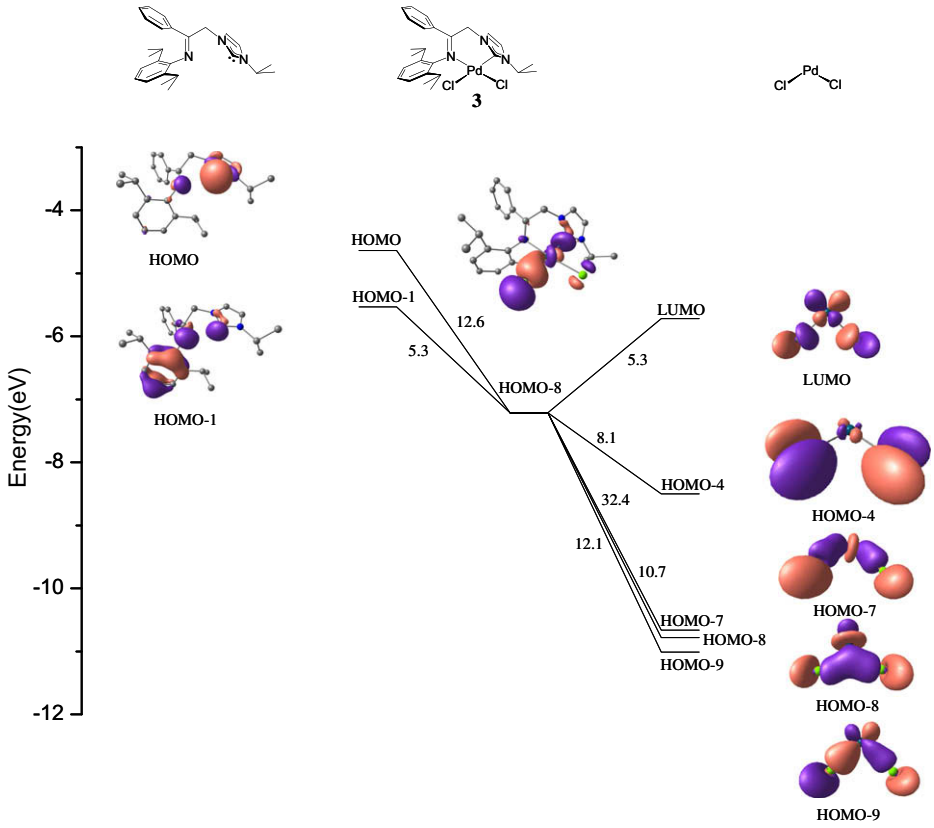
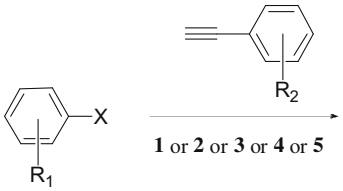


Fig. 6. Simplified orbital interaction diagram showing the major contributions of NHC–palladium bond in **3**.

the NHC ligand fragment to the Pd center in the **1**–**5** complexes, revealed significant interaction of the carbene lone pair of the NHC ligand fragment with the σ^*-orbital of the Pd–pyridine bond of the $PdCl_2(NC_5H_5)$ fragment in the **1** and **2** complexes and with the σ^*-orbital of the Pd–Cl bond of the $PdCl_2$ fragment in the **3**–**5** complexes.

An estimate of the strength of the NHC–Pd interaction can be obtained from the NHC–Pd bond dissociation energy D_e (NHC–Pd) computed at B3LYP/SDD, 6-31G(d) level of theory for **1** (81.7 kcal/mol), **2** (81.4 kcal/mol), **3** (78.5 kcal/mol), **4** (77.0 kcal/mol) and **5** (75.3 kcal/mol), (Supporting information Tables S16 and S17) which indicate that the NHC–Pd interaction is sufficiently strong and thus explains the superior stabilities of these palladium N-heterocyclic carbene complexes.

Significantly enough, all of the **1**–**5** complexes carried out the Sonogashira coupling of aryl bromides and iodides with terminal acetylenes (Eq. (1)) and that too under the much desired Cu-free and amine-free conditions in air in a mixed aqueous medium. Specifically, when the aryl bromides and iodides were treated with terminal acetylenes in presence of 3 mol% of the precatalyst loading, good to excellent conversions (Table 1) were observed in a relatively short period of time (1 h). It is noteworthy that Sonogashira reaction has been reported for a varying degree of reaction time that range from as low as 15 min to as long as 48 h [9–11,16,17,19]. Significant enhancement of up to 66% with regard to the formation of the desired Sonogashira products were observed when compared to the control experiments carried out using $PdCl_2$ for each of the substrates (Supporting information Table S21). Not surprisingly, consistent with the lower bond energy of the C–I bond (51–57 kcal/mol) relative to the C–Br bond (66–68 kcal/mol) [77,78], higher conversions were observed for the aryl iodides (47–99%) than for the aryl bromide (16–86%) substrates.



(1)

R_1 = H, $COCH_3$, OCH_3, CH_3, CHO, CN, NO_2
R_2 = H, NMe_2
X = Br, I

The most notable features of these **1**–**5** precatalysts are their air and moisture stability and their ability to carry out the Sonogashira coupling under the much desired Cu-free and amine-free conditions. Also, remarkable is the relatively short period of time of 1 h during which the coupling occurred.

Important is comparison of the **1**–**5** precatalysts with the other reported examples, particularly the N-heterocyclic carbene based systems, for the Sonogashira coupling. In this regard it is worth noting that most of the reports that exist of Sonogashira coupling are mainly of phosphine based precatalysts while those of N-heterocyclic carbene based ones are conspicuously fewer. Furthermore, many of the couplings have been tried under "Ligand Assisted Catalysis" (LAC) conditions, with only a handful of examples known for which well-defined palladium precatalysts have been used for the Sonogashira coupling. For the N-heterocyclic carbene based systems, we aware of only a few reports of the structurally characterized precatalysts like, [1,1′-dimethyl-3,

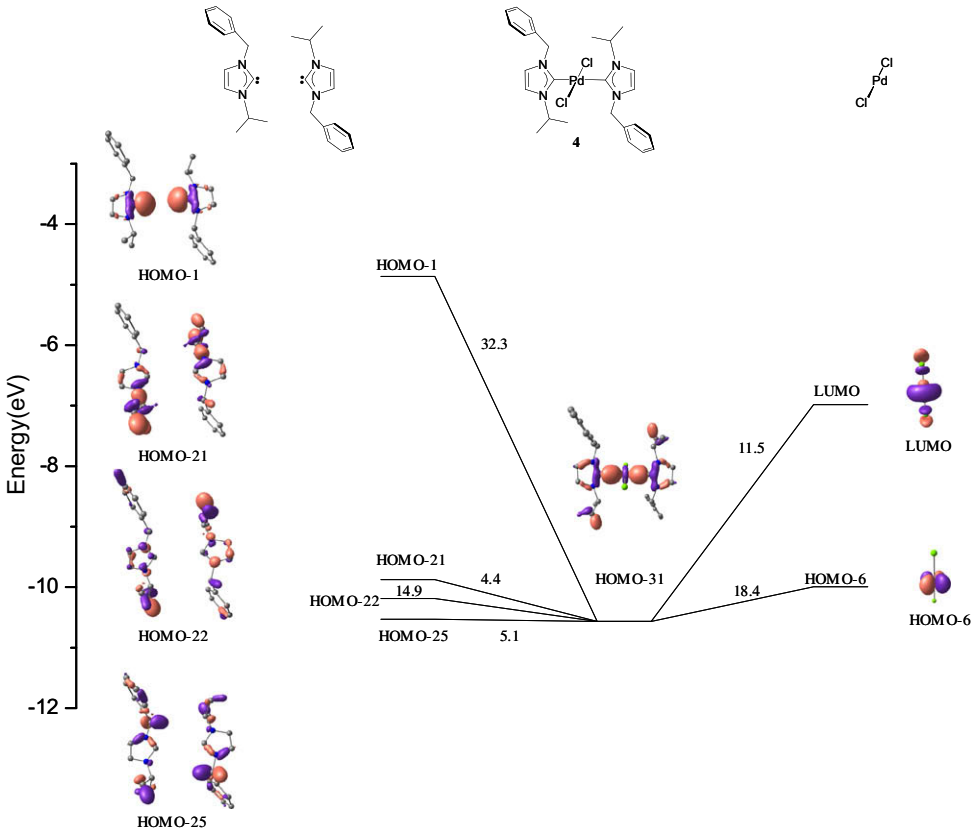
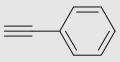
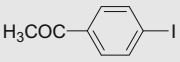
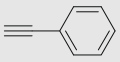
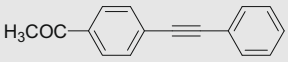
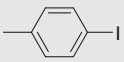
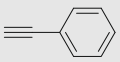
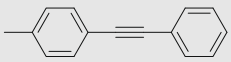
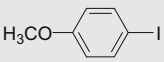
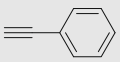
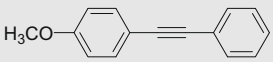
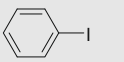
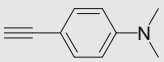
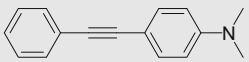
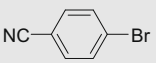
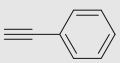
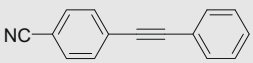
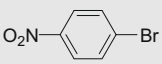
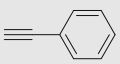
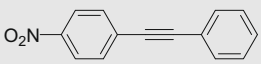
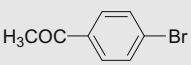
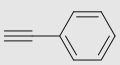
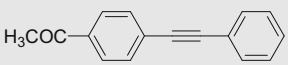
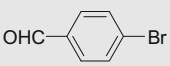
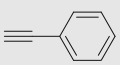
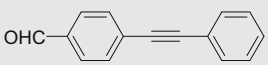


Fig. 7. Simplified orbital interaction diagram showing the major contributions of NHC–Palladium bond in **4**.

Table 1
Selected results of Sonogashira cross-coupling reaction of aryl halides (ArX, X = I, Br) catalyzed by **1**–**5**[a].

Entry	Reagent	Reagent	Product	Yield[b] **1**	Yield[b] **2**	Yield[b] **3**	Yield[b] **4**	Yield[b] **5**
1				96	99	99	99	99
2				80	59	78	99	87
3				93	99	85	70	75
4				50	47	61	46	72
5				53	74	64	56	65
6				38	36	64	58	40
7				67	86	52	63	34
8				23	25	32	43	21
9				69	46	72	66	69

[a] Reaction conditions: 0.50 mmol of aryl halide (ArX, X = I, Br), 1.00 mmol of phenylacetylene, 1 mmol of Cs_2CO_3, 3 mol% of catalyst **1** or **2** or **3** or **4** or **5** and 10 mL of DMF:H_2O (3:1), at 100 °C for 1 h.
[b] The yields (%) were determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

3′-methylene-4-diimidazolin-2,2′-diylidene]PdI_2 [79], which was used for Cu-free Sonogashira coupling of aryl bromides, while *trans*-[(3-pyrrolidincarbamoyl-1-methylimidazolin-2-ylidene)(N-methylimidazole)]PdI_2 [80], *trans*-[1-(benzyl)-3-(3,3-dimethyl-2-oxo-butyl)- imidazol-2-ylidene]$_2PdBr_2$ [36] and *cis*-[1-(benzyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]$_2PdCl_2$ [36] were used for amine-free Sonogashira coupling of aryl bromides and aryl iodides. Specifically, [1,1′-dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene]PdI_2 carried out the Sonogashira reaction in 1 mol% of the catalyst loading using aryl bromide as substrate. The *trans*-[(3-pyrrolidincarbamoyl-1-methylimidazolin-2-ylidene)(N-methylimida-zole)]PdI_2 complex was used for the Sonogashira coupling at 80 °C using 1 mol% of the catalyst and which displayed 74–99% conversion. The *trans*-[1-(benzyl)-3-(3,3-dimethyl-2-oxo-butyl)imidazol-2-ylidene]$_2PdBr_2$ complex was used at 100 °C for 2 h at 3 mol% of catalyst loading for Sonogashira coupling and the yield varied in the range 68–98%. The *cis*-[1-(benzyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]$_2PdCl_2$ complex was employed at 3 mol% of catalyst loading at 100 °C for 2 h. In this regard, the precatalysts **1**–**5** assumes significance as they carry out the Sonogashira coupling under both the Cu-free and amine-free conditions and that too, in air and in a mixed aqueous medium.

3. Conclusion

In summary, several new, highly efficient and robust precatalysts, **1**–**5**, that carried out the Sonogashira coupling under the much desired Cu-free and amine-free conditions in air in a mixed aqueous medium have been designed. The density functional theory studies performed on these complexes indicate stable NHC–Pd interaction that arise out of the deeply seated NHC–Pd σ-bonding molecular orbitals (MOs), which remain shielded from the electrophilic or nucleophilic attacks that usually occur on the peripheral valence molecular orbitals.

4. Experimental section

4.1. General procedures

All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 1-(*i*-Propyl)-3-(N-2,6-di-*i*-propylphenylacetamido)imidazolium chloride,[22] 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride [29], [1-(*i*-propyl)-3-(N-2,6-di-*i*-propyl-phenylimino-2-phenylethyl)-imidazol-2-ylidene]AgCl [21], [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl [29] and [1-(*t*-butyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]$_2Ag^+Cl^-$ [22], were synthesized according to literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian 400 and Varian 300 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. GC spectra were obtained on a Schimadzu gas chromatograph GC-15A equipped with a FID. GC–MS spectra were obtained on a Hewlett–Packard GCD-1800 A equipped with EI source. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer.

4.2. Synthesis of trans-[1-(i-propyl)-3-(N-2,6-di-i-propylphenyl-acetamido)imidazol-2-ylidene]$PdCl_2$(pyridine) (**1**)

A mixture of 1-(*i*-propyl)-3-(N-2,6-di-*i*-propylphenylacetamido)imidazolium chloride (0.207 g, 0.570 mmol), $PdCl_2$ (0.121 g, 0.684 mmol), and K_2CO_3 (0.393 g, 2.85 mmol) were refluxed in pyridine (ca. 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. The residue was washed with aqueous $CuSO_4$ solution and the aqueous solution was extracted in dichloromethane (ca. 3 × 10 mL). The organic layer was collected, and the solvent was removed under vacuum to obtain the product **1** as a yellow solid (0.146 g, 44%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 8.97 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-NC_5H_5), 8.62 (br, 1H, N*H*), 7.75 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-NC_5H_5), 7.34 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-NC_5H_5), 7.22 (s, 1H, NC*H*CHN), 7.14 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-C_6H_3\{2,6-*i*-Pr_2\}), 7.05 (s, 1H, NCHC*H*N), 7.01 (d, 2H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_3\{2,6-*i*-Pr_2\}), 5.80 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 5.41 (s, 2H, CH_2), 2.80 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 1.55 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 1.03 (br, 12H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C), δ 166.0 (*C*O), 153.2 (NCN), 151.0 (*o*-NC_5H_5), 146.1 (*ipso*-C_6H_3\{2,6-*i*-Pr_2\}), 138.3 (*p*-NC_5H_5), 128.4 (*o*-C_6H_3\{2,6-*i*-Pr_2\}), 124.9 (*m*-C_6H_3\{2,6-*i*-Pr_2\}), 124.5 (*p*-C_6H_3\{2,6-*i*-Pr_2\}), 123.3 (*m*-NC_5H_5), 122.3 (NCHCHN), 118.8 (NCHCHN), 54.9 (*C*H_2), 53.2 (*C*H$(CH_3)_2$), 28.5 (*C*H$(CH_3)_2$), 23.5 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$). IR (KBr pellet cm^{-1}): 1684 (s) ($\nu_{C=O}$). Anal. Calc. for $C_{25}H_{34}Cl_2N_4OPd$: C, 51.43; H, 5.87; N, 9.60. Found: C, 51.77; H, 5.45; N, 9.88%.

4.3. Synthesis of trans-[1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene]$PdCl_2$(pyridine) (**2**)

A mixture of 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride (0.206 g, 0.580 mmol), $PdCl_2$ (0.123 g, 0.695 mmol), and K_2CO_3 (0.401 g, 2.91 mmol) were refluxed in pyridine (ca. 5 mL) for 16 h. The reaction mixture was filtered and the solvent was removed under vacuum. The residue was washed with aqueous $CuSO_4$ solution and the aqueous solution was extracted in dichloromethane (ca. 3 × 10 mL). The organic layer was collected, and the solvent was removed under vacuum to obtain the product **2** as a brown solid (0.158 g, 47%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 8.51 (br, 1H, N*H*), 8.27 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-NC_5H_5), 7.41 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-NC_5H_5), 7.29 (d, 2H, $^3J_{HH}$ = 7 Hz, *m*-NC_5H_5), 7.16 (s, 1H, NC*H*CHN), 6.94 (br, 2H, *m*-C_6H_2\{2,4,6-Me_3\}), 6.93 (br, 2H, *o*-C_6H_5), 6.84 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 6.73 (s, 1H, NCHC*H*N), 6.65 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-C_6H_5), 5.22 (s, 2H, CH_2), 2.33 (s, 3H, *p*-C_6H_2\{2,4,6-*Me*$_3$\}), 2.22 (s, 6H, *o*-C_6H_2\{2,4,6-*Me*$_3$\}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C), δ 167.6 (*C*O), 152.3 (NCN), 150.2 (*o*-NC_5H_5), 147.2 (*ipso*-C_6H_5), 138.6 (*ipso*-C_6H_2\{2,4,6-Me_3\}), 137.2 (*p*-NC_5H_5), 135.1 (*o*-C_6H_5), 135.0 (*o*-C_6H_2\{2,4,6-Me_3\}), 128.7 (*m*-C_6H_5), 127.5 (*m*-C_6H_2\{2,4,6-Me_3\}), 126.2 (*p*-C_6H_5), 123.9 (*p*-C_6H_2\{2,4,6-Me_3\}), 123.3 (NCHCHN), 123.1 (*m*-NC_5H_5), 121.7 (NCHCHN), 57.7 (*C*H_2), 21.0 (*p*-C_6H_2\{2,4,6-*Me*$_3$\}), 18.5 (*o*-C_6H_2\{2,4,6-*Me*$_3$\}). IR (KBr pellet cm^{-1}): 1605 (s) ($\nu_{C=O}$). Anal. Calc. for $C_{25}H_{26}Cl_2N_4OPd{\cdot}0.5(C_5H_5N)$: C, 53.67; H, 4.67; N, 10.24. Found: C, 53.77; H, 5.47; N, 9.77%.

4.4. Synthesis of [1-(i-propyl)-3-(N-2,6-di-i-propyl-phenylimino-2-phenylethyl)imidazol-2-ylidene]$PdCl_2$ (**3**)

A solution of [1-(*i*-propyl)-3-(N-2,6-di-*i*-propyl-phenylimino-2-phenylethyl)imidazol-2-ylidene]AgCl (1.21 g, 2.28 mol) and (COD)$PdCl_2$ (0.651 g, 2.28 mmol) were taken in CH_3CN (ca. 30 mL) and was refluxed for 4 h, after filtration the solvent was removed under vacuum. The product was purified by recrystallization from CH_3CN to give **3** as a yellow solid (0.755 g, 59%). Isomer (*major*). ^1H NMR (CD_3CN, 300 MHz, 25 °C), δ 7.37–7.26 (m, 5H, C_6H_5), 7.22 (s, 1H, NCHC*H*N), 7.16 (s, 1H, NC*H*CHN), 6.96 (m, 3H, *m*-& *p*-C_6H_3\{2,6-*i*-Pr_2\}), 5.92 (s, 2H, CH_2), 5.68 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 2.91 (sept, 2H, $^3J_{HH}$ = 7 Hz C*H*$(CH_3)_2$), 1.50 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 1.49 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 0.95 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$, 0.87 (d, 3H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 25 °C), δ 162.2 (*C*=N), 152.4

(NCN), 140.5 (*ipso*-C_6H_3{2,6-*i*-Pr_2}), 135.8 (*ipso*-C_6H_5), 135.2 (*o*-C_6H_3{2,6-*i*-Pr_2}), 134.6 (*o*-C_6H_5), 129.7 (*m*-C_6H_5), 128.5 (*p*-C_6H_3{2,6-*i*-Pr_2}), 128.2 (*m*-C_6H_3{2,6-*i*-Pr_2}), 127.5 (*p*-C_6H_5), 120.0 (NCHCHN), 118.2 (NCHCHN), 56.6 (CH_2), 52.8 ($CH(CH_3)_2$), 27.3 ($CH(CH_3)_2$), 27.1 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 21.9 ($CH(CH_3)_2$). Isomer (*minor*). δ 7.37–7.26 (m, 5H, C_6H_5), 7.07 (s, 1H, NCHCHN), 7.05 (s, 1H, NCHCHN), 6.96 (m, 3H, *m*-& *p*-C_6H_3{2,6-*i*-Pr_2}), 5.47 (s, 2H, CH_2), 5.68 (sept, 1H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 2.91 (sept, 2H, $^3J_{HH}$ = 7 Hz $CH(CH_3)_2$), 1.41 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.26 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.14 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 25 °C), δ 162.1 (C=N), 152.4 (NCN), 141.2 (*ipso*-C_6H_3{2,6-*i*-Pr_2}), 135.4 (*ipso*-C_6H_5), 133.7 (*o*-C_6H_5), 134.8 (*o*-C_6H_3{2,6-*i*-Pr_2}), 129.7 (*m*-C_6H_5), 128.4 (*p*-C_6H_3{2,6-*i*-Pr_2}), 128.1 (*m*-C_6H_3{2,6-*i*-Pr_2}), 127.2 (*p*-C_6H_5), 119.7 (NCHCHN), 117.8 (NCHCHN), 56.9 (CH_2), 52.3 ($CH(CH_3)_2$), 27.8 ($CH(CH_3)_2$), 27.3 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 22.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 21.9 ($CH(CH_3)_2$), 21.8 ($CH(CH_3)_2$). IR (KBr pellet cm^{-1}): 1632 (s) ($\nu_{C=N}$). HRMS (ES): *m*/*z* 528.1392 [(NHC–Pd)-Cl]$^+$. Anal. Calc. for $C_{26}H_{33}Cl_2N_3Pd$: 528.1398: C, 55.28; H, 5.89; N, 7.44. Found: C, 55.39; H, 5.93; N, 7.63%.

4.5. Synthesis of [(1-i-propyl)-3-(benzyl)imidazol-2-ylidene]$_2$PdCl$_2$ (**4**)

A mixture of [(1-i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl (0.256 g, 0.748 mmol) and (COD)$PdCl_2$ (0.106 g, 0.371 mmol) were dissolved in CH_3CN (ca. 25 mL) and the mixture was refluxed for 4 h. The reaction mixture was filtered and the solvent was removed under vacuum. The product was purified by recrystallized from CH_3CN to give the product **4** as yellow solid (0.119 g, 55%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 7.56 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-C_6H_5), 7.42 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-C_6H_5), 7.39 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.35 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.28 (t, 2H, $^3J_{HH}$ = 7 Hz, 2 *p*-C_6H_5), 6.88 (s, 1H, NCHCHN), 6.86 (s, 1H, NCHCHN), 6.68 (s, 1H, NCHCHN), 6.65 (s, 1H, NCHCHN), 5.81 (s, 2H, CH_2), 5.75 (sept, 1H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 5.67 (s, 2H, CH_2), 5.61 (sept, 1H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.63 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.49 (d, 6H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C), δ 169.6 (2NCN), 136.4 (*ipso*-C_6H_5), 136.2 (*ipso*-C_6H_5), 128.7 (2*o*-C_6H_5), 128.6 (2*m*-C_6H_5), 128.0 (*p*-C_6H_5), 127.9 (*p*-C_6H_5), 120.3 (2NCHCHN), 116.8 (NCHCHN), 116.7 (NCHCHN), 54.2 (2CH_2), 52.1 ($CH(CH_3)_2$), 52.0 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$). IR (KBr pellet cm^{-1}): 3128 (m), 3099 (m), 2978 (s), 1457 (s), 1429 (s), 1371 (m), 1298 w), 1223 (s), 1189 (s), 720 (s), 700 (s). Anal. Calc. for $C_{26}H_{32}Cl_2N_4Pd$: C, 54.04; H, 5.58; N, 9.70. Found: C, 53.84; H, 5.46; N, 10.12%.

4.6. Synthesis of [(1-t-butyl)-3-(N-t-butylacetamido)imidazol-2-ylidene]$_2$PdCl$_2$ (**5**)

A mixture of [(1-*t*-butyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]$_2Ag^+Cl^-$ (0.319 g, 0.518 mmol) and (COD)$PdCl_2$ (0.157 g, 0.550 mmol) were dissolved in CH_2Cl_2 (ca. 35 mL) and the mixture was stirred at room temperature for 4 h. The reaction mixture was filtered and the solvent was removed under vacuum. The product was purified by column chromatography using $CHCl_3$/CH_3OH mixture (95:5 v/v) to give the product **5** as yellow solid (0.189 g, 56%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 8.10 (br, 2H, NH), 7.15 (s, 2H, NCHCHN), 7.00 (s, 2H, NCHCHN), 5.47 (s, 4H, CH_2), 2.04 (s, 18H, $C(CH_3)_3$), 1.31 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C), δ 167.4 (C=O), 166.5 (NCN), 120.8 (NCHCHN), 120.5 (NCHCHN), 59.2 (CH_2), 56.5 ($C(CH_3)_3$), 55.4 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 28.3 ($C(CH_3)_3$). IR (KBr pellet cm^{-1}): 1676 (s) ($\nu_{C=O}$). Anal. Calc. for $C_{26}H_{46}Cl_2N_6O_2Pd{\cdot}1/3(CHCl_3)$: C, 45.72; H, 6.75; N, 12.15. Found: C, 45.69; H, 7.28; N, 12.61%.

4.7. Computational methods

Density functional theory calculations were performed on the palladium complexes of N-heterocyclic carbenes, **1**–**5** using GAUSSIAN 03 [81] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee-Yang-Parr correlation functional (B3LYP) has been employed in this study [82,83]. Sttutgart-Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for palladium [84–86]. All other atoms are treated with 6-31G(d) basis set [87]. All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. Tight SCF convergence (10^{-8} a.u.) was used for all calculations. Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in the GAUSSIAN 03 package.

Inspection of the metal-ligand donor-acceptor interactions was carried out using the charge decomposition analysis (CDA) [88]. CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation [89,90]. The orbital contributions in the geometry optimized palladium complexes **1**, and **2** can be divided into three parts:

(i) σ-Donation from the [NHC → $PdCl_2(NC_5H_5)$] fragment.
(ii) π-Back donation from [NHC ← $PdCl_2(NC_5H_5)$] fragment.
(iii) Repulsive polarization (*r*).

The orbital contributions in the geometry optimized palladium complexes **3**–**5** can be divided into three parts:

(iv) σ-Donation from the [NHC → $PdCl_2$] fragment.
(v) π-Back donation from [NHC ← $PdCl_2$] fragment.
(vi) Repulsive polarization (*r*).

The CDA calculations are performed using the program AOMIX [91], using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMIX program [92]. 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 [93].

4.8. General procedure for the Sonogashira coupling reaction

In a typical run, performed in air, a 25 mL vial was charged with a mixture of aryl iodide or bromide, arylalkyne, Cs_2CO_3 and diethyleneglycol-di-n-butyl ether (internal standard) in a molar ratio of 0.5:1:1:0.5 and to it catalyst **1** or **2** or **3** or **4** or **5** was added at 3 mol% amount. Finally, 10 mL of a mixed-solvent (DMF:H_2O in 3:1 v/v) was added to the reaction mixture and heated at 100 °C for 1 h, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as an internal standard (Table 1).

4.9. Pyridine dissociation under Sonogashira conditions

Phenylacetylene (0.301 g, 2.95 mmol), Cs_2CO_3 (0.959 g, 2.95 mmol), diethyleneglycol-di-*n*-butyl ether (internal standard) (0.016 g, 0.073 mmol) and a representative catalyst, complex **1** (0.042 g, 0.073 mmol) in CH_3CN (6 mL) were taken in a 25 mL vial. The reaction mixture was heated at 70 °C for 1 h, after which it was filtered and the reaction mixture was analyzed by GC and GC–MS which showed formation of 7% pyridine under the reaction conditions.

4.10. X-ray structure determination

X-ray diffraction data for compounds **1**–**5** were collected on an Oxford Diffraction Excaliber-S diffractometer and crystal data collection and refinement parameters are summarized in Tables S1 and S2 (Supporting information). 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) [94,95].

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Appendix A. Supplementary material

CCDC 642034, 627574, 608263, 637160 and 648566 contain the supplementary crystallographic data for complexes **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.026.

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