

A new air-stable Pd-PEPPSI N-heterocyclic carbene complex: Synthesis, structure, computational and catalytical studies

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ABSTRACT

In this work, we have synthesized a new, air and moisture stable, Pd-PEPPSI (pyridine enhanced pre-catalyst preparation, stabilization and initiation) complex, [PdBr₂(NHC)Py] (NHC is 3-benzyl-1-(4-methoxyphenyl)-1H-imidazolone-2-ylidene) and successfully employed as catalyst under mild conditions (35 °C, 0.5 mol% Pd loading) Suzuki-Miyaura cross-coupling reactions of aryl halides with aryl boronic acids in aqueous isopropanol. A wide range of aryl bromides / iodides were effectively utilized as coupling partners with arylboronic acids to afford corresponding biaryls in moderate-to-excellent yields. The complex was characterized by ESI-MS, ¹H and ¹³C NMR spectroscopy and the molecular structure was determined by X-ray single crystal analysis. In order to gain more insight about structure, bonding and electronic properties, density functional theory (DFT) studies were performed. Moreover, TDDFT calculations were also performed to interpret the observed electronic absorption bands in the UV-VIS spectra. A good agreement between experimental and theoretical data was observed.

1. Introduction

With N-heterocyclic carbenes (NHCs) being one of the most successful ligand systems in homogeneous catalysis, and palladium being one of the most exploited noble metals in coordination chemistry, in the past few years, there has been considerable interests in designing novel Pd-NHC complexes for multifunctional catalysis [1–4]. By virtue of the non-toxic chemistry, resistance to air and moisture, tunable electronic/sterical properties; the NHC ligands has emerged as highly successful alternative to conventional phosphines in many palladium-mediated carbon-carbon bond forming reactions like Suzuki-Miyaura [5–8], Heck [9–12], Sonogashira [13–15], etc. Among the wide range of carbon-carbon cross-coupling methods, the Suzuki-Miyaura reaction between aryl halides and arylboronic acids has got particular attention from industrial perspective because of its simple reaction conditions, high-functional group tolerance, nontoxic reagents, handling convenience [16–18], etc. Indeed, according to a recent literature it is one of the second most frequently used reactions exploited in medicinal chemistry [19].

Since the first report of Pd-NHC systems in C-C bond forming reaction by Hermann and coworkers [20]; several research groups such as of

Nolan [21–23], Organ [24–26], Szostak [27,28] etc. have developed a plethora of well-defined Pd-NHC-based catalytic systems for Suzuki-Miyaura reactions. Although majority of these NHC complexes were very stable in air and moisture, the catalytic cross-coupling reactions were mainly performed in an oxygen free environment, as the actual catalytic species Pd (0) was highly air sensitive [29]. In recent years, a new type of Pd-NHC systems, known as Pd-PEPPSI (PEPPSI: Pyridine enhanced pre-catalyst preparation, stabilization and initiation) has surfaced in literature that showed remarkable activity as catalysts in many cross-coupling reactions including Suzuki-Miyaura reaction [30, 31]. Unlike conventional Pd-NHC systems, these Pd-PEPPSI complexes are air and water stable and can promote cross-coupling reactions in water or mixed aqueous environment [32–34]. Moreover, due to the presence of a weakly bound pyridine moiety makes the Pd-PEPPSI system more efficient as the labile pyridine moiety can act as a ‘through-away ligand’ and can create a vacant coordination site for the substrate binding and are thus expected to enhance catalytic activities.

In fact, in 2006, Organs’ group for the first time introduced Pd-PEPPSI system in Suzuki-Miyaura reactions [35]. Since then, a number of highly efficient Pd-PEPPSI complexes have been reported for Suzuki-Miyaura reactions, however majority of the systems suffered

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from limitations like narrow substrate scope, harsh reaction conditions, high metal loadings [36–38], etc. Until now, only a couple of examples are known that remained successful in activating Suzuki reaction at room temperature in an aqueous environment [39,40]. Thus, there is a need to develop high performance Pd-PEPPSI-based catalytic systems for Suzuki-Miyaura reaction in room temperature in an aqueous environment. In line with this, herein, we have reported synthesis of a new Pd-PEPPSI complex which exhibited excellent activity as catalysts for the Suzuki-Miyaura cross coupling reactions with a diverse range of aryl bromides or iodides at room temperature in aqueous isopropanol as reaction media. The complex was crystallographically characterized and DFT studies were also performed to have a better understanding about electronic structure and transition.

2. Experimental section

2.1. General section

All reactions were carried out in the air unless otherwise stated. Imidazolium precursors 1-(4-methoxyphenyl)-1H-imidazole and PdCl₂ were purchased from sigma Aldrich and TCI respectively. All solvents, substrates and other necessary chemicals were purchased from various commercial manufacturers like TCI, Acros Organics, Spectrochem and Merck. The NMR spectra for the NHC ligand was recorded in DMSO, while for the complex, the spectra were recorded in CDCl₃ on a Bruker Avance 500 MHz NMR spectrometer. ESI-mass spectra were recorded with a Thermo Fisher Scientific TSQ Endura MS system. The conversion was determined with a Perkin Elmer Clarus 480 GC system. The UV-Vis spectra of the complex recorded with a Shimadzu UV-1700 spectrophotometer system.

2.2. Synthesis

2.2.1. Synthesis of 3-benzyl-1-(4-methoxyphenyl)-1H-imidazolium-bromide

The imidazolium salt is synthesized by arylation of 1 mmol of 1-(4-methoxyphenyl)-1H-imidazole treated with 5 mmol benzyl bromide and refluxed at 80 °C in acetonitrile for 48 h. Following the completion of the reaction, the solvent was withdrawn under reduced pressure and the oily residue was washed three times with 30 ml diethyl ether, resulted white precipitate. The ether solution was filtered out, and the white residue was collected and dried. Yield: 70 %, *Analytical data*: ¹H NMR (DMSO, 500 MHz, ppm): 10.03 (s, 1H, NCHN), 8.25 (d, J = 1.6 Hz, 1H, CH=CH, imidazole), 8.04 (d, CH=CH, imidazole), 7.75–7.73 (m, 2H, Ar), 7.56–7.46 (m, 2H, Ar), 7.44–7.39 (m, 3H, Ar), 7.19–7.18 (m, 2H, Ar), 5.54 (s, 2H, benzyl -CH₂), 3.84 (s, 3H, -OCH₃), ¹³C (DMSO, 126 MHz, ppm) 160.36, 135.54, 129.34, 129.19, 128.90, 128.14, 123.91, 123.36, 122.24, 122.15, 115.46, 56.12, 52.59.

2.2.2. Synthesis of dibromo [3-benzyl-1-(4-methoxyphenyl)-1H-imidazolium] pyridine-palladium(II)

In a 100 ml round bottom flask, Imidazolium salts (1 mmol), PdCl₂ (1 mmol), K₂CO₃ (5 mmol), KBr (5 mmol), pyridine (5 ml) was added and the reaction mixture was allowed to stir at 80 °C for 16 h [35]. After completion, the reaction mixture was allowed to cool at room temperature and then the pyridine was removed under vacuum. The residue was dissolved in dichloromethane and purified by column chromatography, eluting with DCM/hexane (9:1). Yield 60 %; yellow powder; *Analytical data*: ¹H NMR (CDCl₃, 500 MHz, d, ppm) δ 8.89 (d, Py, 2H), 7.96 (d, Py, 2H), 7.70 (s, Py, 1H), 7.61 (d, Ar, 2H), 7.46–7.39 (m, 3H), 7.31–7.29 (m, 3H), 7.18 (d, J = 2.2 Hz, 1H), 7.13–7.08 (m, Ar, 3H), 6.83 (d, 1H), 5.90 (s, -CH₂, 2H), 3.91 (s, -OMe 3H). ¹³C NMR (126 MHz, CDCl₃) δ 159.62, 152.44, 149.01, 137.84, 135.00, 132.60, 129.37, 128.97, 128.62, 127.41, 124.49, 123.84, 121.56, 116.51, 114.26, 60.36, 55.54, 55.22 ESI-MS[M]⁺: 609.15.

2.3. General procedure for Suzuki-Miyaura reaction

The aryl halides (1 mmol), phenyl boronic acid (1.25 mmol), K₂CO₃ (1.5 mmol), [PdBr₂(NHC)Py] (0.5 mol%) were added to 1:1 aqueous isopropanol mixture in a 50 ml round bottom flask. The sealed flask was set to stirrer for four hours at 35 °C. After the completion of reaction, 30 ml of distilled water and brine solution were added to the reaction mixture. The organic part was extracted with ethyl acetate (3 times × 10 ml). The crude product was obtained by evaporating ethyl acetate under reduced pressure. The crude product was purified by column chromatography by eluting hexane: ethyl acetate (9:1) mixture. The products were characterised by NMR and ESI-MS.

2.4. X-ray crystallography

The single crystal of the complex was grown in DCM solution through slow evaporation technique for five days at 4 °C under refrigeration. Several needle-like yellow crystals were grown in this condition. The size of the crystal is 0.36 × 0.30 × 0.23 mm³. X-ray reflections were collected on a Bruker APEX-II, CCD diffractometer using Mo Kα (λ = 0.71073 Å) radiation. Data reduction was performed using Bruker SAINT Software [41]. Intensities for absorption were corrected using SADABS. Structures were solved and refined using SHELXL-2014 with anisotropic displacement parameters for non-H atoms. Hydrogen atom on Oxygen was experimentally located in the crystal structure. All C–H atoms were fixed geometrically using the HFIX command in SHELX-TL [42]. A check of the final CIF file using PLATON did not show any missed symmetry [43].

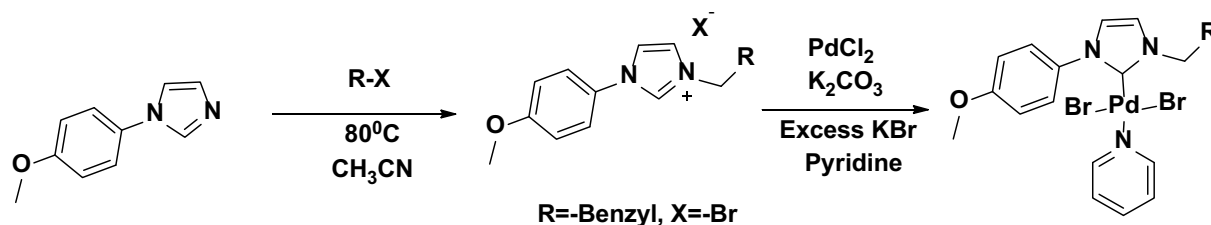
2.5. Computational details

All the theoretical calculations are done using Gaussian 16 program package [44]. Initially, the geometrical optimization is done using meta-GGA functional M06-2X [45] along with def2-TZVP basis set in the gas phase. The optimized geometries are then confirmed through a frequency calculation at the same level of theory. Further, the time-dependent DFT calculation is done on the gas phase optimized geometry of the catalyst. Later, in order to mimic the experimental environment, calculations of bond dissociation enthalpies (BDE) in the 2-propanol solvent medium are done. For this, the geometries of the catalyst, NHC-Pd-Br₂, Py, NHC, and Pd-Br₂-Py are optimized again with def2-TZVP basis and M06-2X functional in the PCM [46] solvent model. The minimum energy geometries were confirmed by the positive value of frequencies. The BDE includes thermal and zero-point corrections.

3. Results and discussion

3.1. Synthesis and characterization of Pd-PEPPSI complex

The synthesis of Pd-PEPPSI complex was schematically shown in Scheme 1. At first the NHC salt 3-benzyl-1-(4-methoxyphenyl)-1H-imidazolium-2-ylidene was synthesized by reacting commercially available (4-methoxyphenyl)-1H-imidazole with benzyl bromide by following a previously reported procedure [11]. The NHC ligand and its Pd-complex were characterised by ESI-MS, ¹H, and ¹³C NMR spectroscopy. The ESI-MS spectra of the ligand (Fig. S3) shows a peak at m/z = 265.1 corresponds to [M-Br]⁺ ion. In the ¹H NMR (Fig. S1), the signal due to NCHN appeared as a singlet at 10.03 ppm which is related reported literature [11,47,48]. In addition, the characteristic peaks for the -OMe and benzylic -CH₂ groups appears at 3.84 ppm and 5.54 ppm, respectively. The Pd-PEPPSI complex was synthesized by a one pot reaction between the NHC salt and PdCl₂ in pyridine in presence of excess of KBr and K₂CO₃. The resulting Pd-complex was purified by column chromatography taking hexane and DCM (7:3) as eluting solvent. The NHC-Pd-PEPPSI complex was isolated as yellow solid. Alongside, a small amount of bis-pyridine complex, trans-[PdX₂(Py)₂] was also isolated



Scheme 1. Synthesis of NHC salt and PEPPSI-Pd-NHC complex.

through column chromatography. The formation of Pd-C_{carbene} bond was confirmed by the disappearance of imidazole proton (NCHN) at around 10.03 ppm in the ¹H NMR (Fig. S4). The characteristic ¹³C NMR peak of Pd-NHC carbon was appeared at 152 ppm (Fig. S5). The presence of pyridine in the coordination sphere was confirmed by characteristics ¹H NMR signals at 8.89, 7.96 and 7.70 ppm. The ESI-MS spectra of the complex showed a peak m/z 609.15 corresponds to the molecular ion [M]⁺ (Fig. S6).

3.2. Structural description of the complex

Single crystal of the Pd-PEPPSI complex was grown in the DCM/hexane mixture by slow diffusion technique and the structure of the complex is displayed in Fig. 1. The complex crystallizes in monoclinic space group P21/n. The crystallographic parameters are displayed in the supplementary section in Table S1. As expected, the Pd centre in the complex occupies a slightly distorted square planar geometry with NHC and pyridine occupies two mutually *trans* positions. The other two positions are occupied by the two Br atoms *trans* to each other. The C_{carbene}-Pd-N_{py} and Br(1)-Pd-Br(2) bond angles measures 176.3 and

177.63, respectively, while the Br(1)-Pd-N and Br(2)-Pd-C bond angles measures at 89.28 and 90.96, respectively, are in agreement with distorted square planar geometry of the complex. The Pd-C_{carbene} (1.968) and Pd-N_{py} (2.094) bond lengths (Å) are more or less similar with and other related Pd-PEPPSI complexes where the Py ligand is loosely bound to Pd-center [39,49]. The two Pd-Br bond lengths (Å) of 2.431 and 2.434, which are also very much comparable to the Pd-Br bond lengths reported in similar complexes [11,50–52], and also with the individual covalent radii of Pd-Br (2.423 Å).

From the crystal analysis, it is observed that crystal packing of the complex involves different type of intermolecular and intramolecular H-bonding interactions. The intermolecular H-bonding between two molecules of the complex namely [C(10)-H(10B)...O#2], d_{C-O} = 3.476 (Å)

Table 1
Weak interaction.

Donor(D)-H...Acceptor (A)	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (deg)
C(10)-H(10B)...O#2	0.96	2.64	3.476(12)	146.5

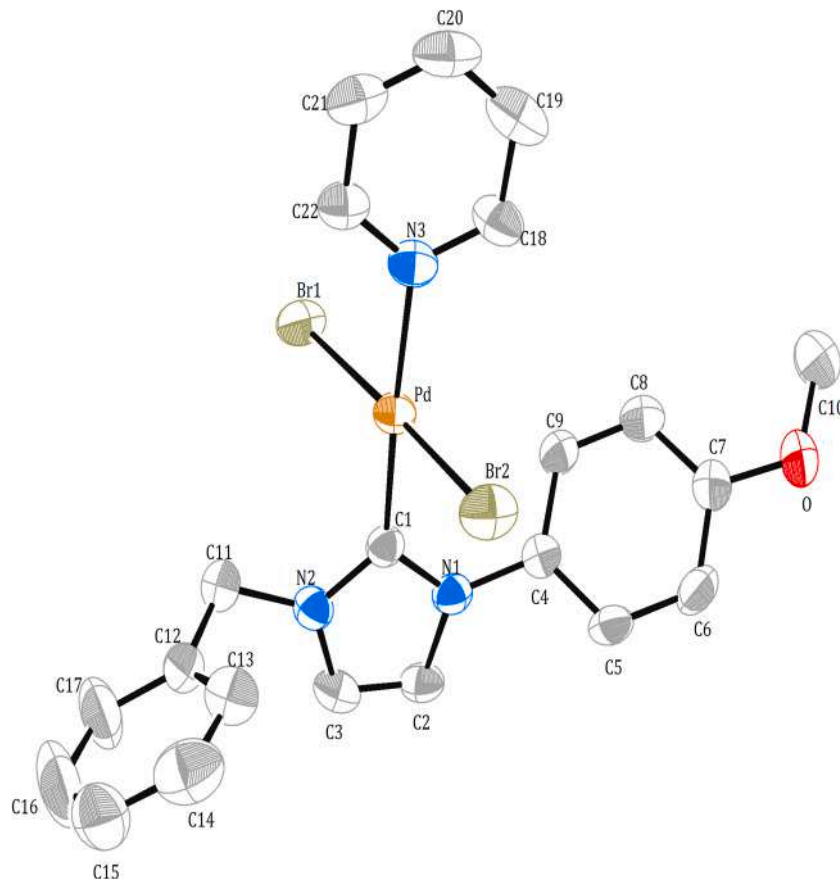


Fig. 1. ORTEP diagram of Pd-PEPPSI complex with 40 % probability ellipsoid. Hydrogen atoms are omitted for clarity (CCDC no. 2233171 †).

(Table 1) arise due to involvement of 4 methoxy phenyl substituent (Fig. 2). Moreover, the intramolecular H-bonding involves the interaction of H atom of -CH_2 benzyl group and Br i.e [C(11)-H(11B)....Br(1)=3.607(8)]. The another intramolecular H-Bonding involves [C(19)-H(19)...Br(1)#1]H19=3.888(8) of Pyridine and Br. These H-bonding observe along the “c” axis direction (Fig. 2).

3.3. Theoretical investigation

The calculated bond length and bond angles of the optimized structure correlate with the experimental X-ray results with minor deviations. For instance, the experimental bond length of the Pd-C_{Carbene} and Pd-N_{Pyridine} are 1.968 and 2.094 Å, respectively, whereas the computed values are 1.942 and 2.190 Å. In addition, the experimental values of bond angles Br(1)-Pd-Br(2) and C(1)-Pd-N(3) are 177.63 and 176.3°, respectively, as compared to the computed values of 172.68 and 179.55°. It is observed that the computational values are in close agreement with the experimental values, this indicates that the optimization of the molecular structure through the DFT approach is accurate and relevant (Table 2).

To explain the bond strength of Pd-C_{carbene} and Pd-N_{Py}, the bond dissociation enthalpy (BDE) values are calculated. It is seen that the bond strength between the Pd-C_{carbene} is stronger (58.49 kcal/mol) than the Pd-N_{Py} bond (22.52 kcal/mol). This indicates that NHC is strongly coordinated with the Pd while a weaker Pd-N_{Py} bond indicates that pyridine moiety may easily get dissociated from Pd.

The frontier molecular orbitals are important tools to describe the nature of electronic distribution in a molecule. The electronic distribution of the complex in the gas phase using M06-2X/ def2-TZVP level of theory can be found in Fig. 3.

From Fig. 3, it may be observed that HOMO is mostly distributed on the Br-Pd-Br while HOMO-1 is localized along the Br-Pd-Br as well as on the imidazole moiety of the ligand. It can also be seen that the HOMO-1 is significantly distributed on Br-Pd-Br than the imidazole part of the ligand. On the other hand, LUMO is localized more over the Pd atom than Br (with different symmetry than HOMO). The distribution of HOMO-2 is primarily observed over the imidazole and 4 methoxy phenyl

Table 2

Bond length and bond angles obtained from both Single Crystal XRD Data and M06-2X/def2-TZVP method in the gas phase.

Bond Length	Experimental data	Computational Data
Pd-C(1)	1.968(6)	1.942
Pd-N(3)	2.094(5)	2.190
Pd-Br(1)	2.4318(10)	2.509
Pd-Br(2)	2.4346(10)	2.503
Bond Angle		
Br(1)-Pd-Br(2)	177.63	172.68
C(1)-Pd-N(3)	176.30	179.55
C(1)-Pd-Br(1)	90.96	86.837
N(3)-Pd-Br(1)	89.28	93.581
C(1)-Pd-Br(2)	89.03	85.984
N(3)-Pd-Br(2)	90.88	93.598

moieties of the ligand. However, HOMO-3 is mostly localized around the Pd and Br atoms. Further, the LUMO+1 and LUMO+2 are mainly localized over the pyridine moiety.

3.4. UV visible spectrum and TD DFT calculation

The UV-Vis investigation of the complex in dichloromethane solution reveals prominent peaks at 244 as well as one hump at 370 nm (Fig. S34). In addition, a shoulder peak at around 285 nm was observed. The initial peak is due to the NHC-Pd²⁺ compound to the characteristics band (about 244 nm), and the large hump formed around 370 nm due to the presence of the Pd (II) d-d transition [53,54]. The shoulder peak at 285 nm could be attributed to intra ligand π - π^* and n - π^* transition [55]. A similar type of peak was also observed in other PEPPSI type Pd-NHC complex [56].

To comprehend the electronic transitions in the complex, time-dependent DFT calculations have been performed in the gas phase using M06-2X/def2-TZVP. The vertical electronic excitation energy (eV) and oscillator strength (f) have been computed. There are mostly two peaks observed at 272 nm and 417.86 nm (Fig. S35) with oscillating strengths of 0.0051 and 0.0041, respectively. For the peak at 272 nm,

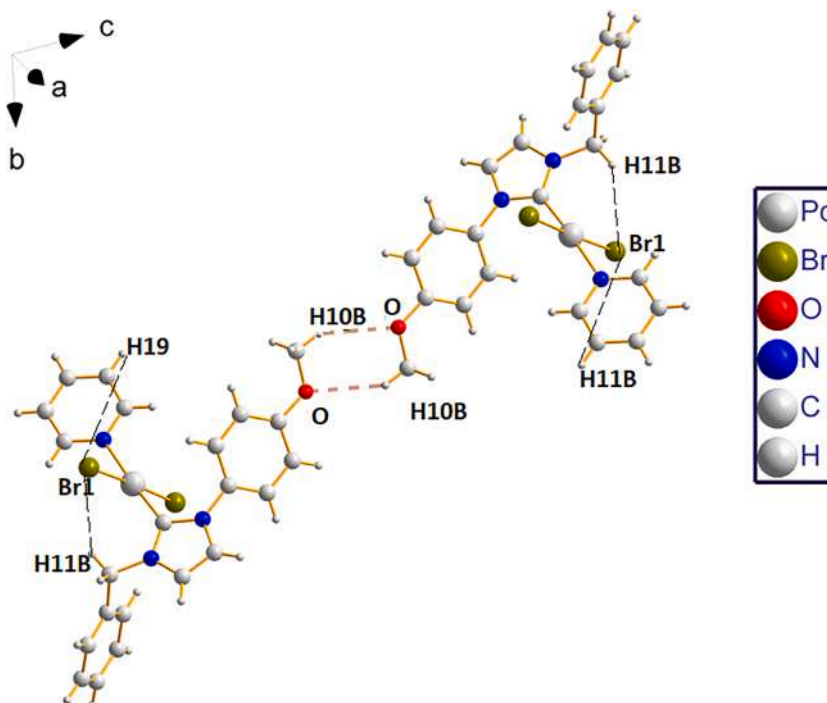


Fig. 2. Inter molecular hydrogen bonding interaction C(10)-H(10B)....O#2 and Intramolecular hydrogen bonding interaction.

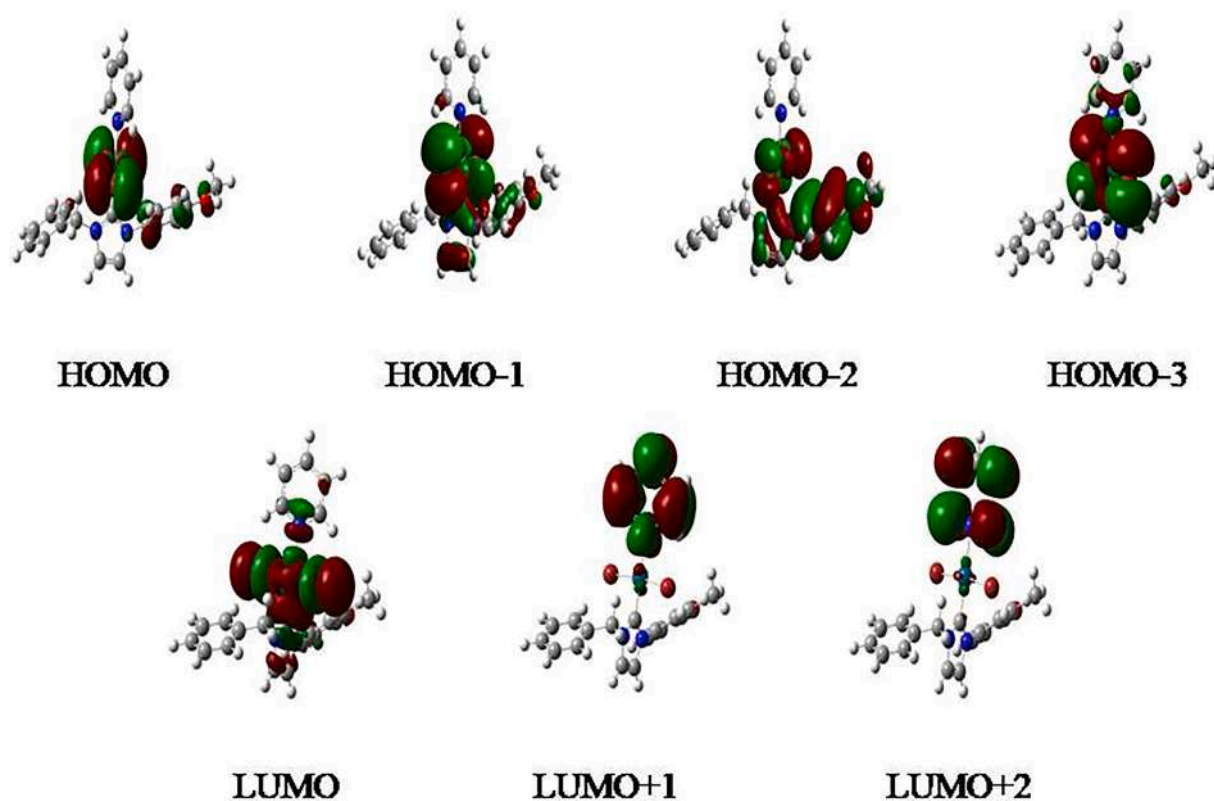


Fig. 3. FMOs of the complex in the gas phase.

the major orbital contribution is observed from HOMO-3 to LUMO. However, the major orbital contribution from HOMO-1 to LUMO is assigned to the peak at 417.86 nm. In addition, the peak at 272 nm and the broad peak at 417.86 nm may be ascribed to the d-d transition. However, the shoulder peak at around 285 nm was not visible in the gas phase TDDFT spectra. Conclusively, the computational results are in acceptable agreement with the experimental observations (Table 3).

3.5. Catalytic activity

Compared to conventional phosphine-based catalysts, the NHC-Pd-PEPPSI complexes typically show very good activity for a diverse range of cross-coupling reactions including Suzuki-Miyaura reactions. However, the activity and selectivity of such PEPPSI complexes largely depends on the combined effects of backbone and N-substituents of the NHC [57]. To check the catalytic performance of our PEPPSI complex, the Suzuki-Miyaura cross coupling reaction of aryl bromides / iodides with arylboronic acids was explored. The initial optimization study was conducted using p-bromoanisole and phenyl boronic acid as model substrates in presence of K_2CO_3 as base taking water as solvent at 50 °C with 1 mol% catalyst. Only moderate yield (36 %) of biphenyl was observed after 4 h of reaction time. After a brief optimization study, it was observed that the yield can be significantly improved to 95 % under optimum condition (*i*-PrOH- H_2O ; K_2CO_3 , 35 °C, 0.5 mol% catalyst) (Table 4).

Under these optimum conditions, a range of aryl bromides/iodides containing different types of electrons donating or withdrawing substituents were screened as coupling partners with phenylboronic acid. Good-to-excellent yields of biaryl were obtained in most of the cases (Table 5 entries 1a-1l). It is observed that the system shows good catalytic activity towards electron withdrawing/ donating o-, m- and p-substituted aryl bromides/iodides (Isolated yield 70–90 %, Entries 1a-1c, 1e-1f). The conversion obtained for substrates with o- and m- electron donating substituents were decreased due to electronic parameters

Table 3
UV spectrum and TD-DFT calculated electronic excitations of the catalyst.

Excitation (eV)	Major orbital contribution	λ experimental (nm)	λ calculated (nm)	Oscillating Strength
4.5582	HOMO-3 → LUMO	244	272.00	0.0051
2.9671	HOMO-1 → LUMO	370	417.86	0.0041

of the substituents (entries 1a-1c, 1e, 1f). The conversion for the electron withdrawing group containing substituents were excellent (entries 1h, 1i, 1j). The heterocyclic iodide, 2-iodo thiophene was converted to corresponding products 1g with 70 % yield. The catalytic activity of the system was also explored with aryl boronic acid containing electron withdrawing and donating functional groups. The corresponding products 1j-1l resulted moderate yields. One of the possible reasons of the outcome was the electronic parameters of the aryl boronic acid.

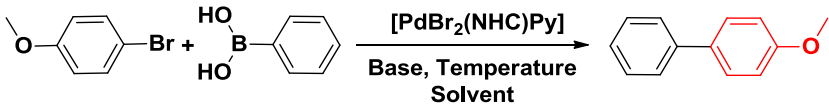
Overall, these results direct that this PEPPSI-Pd-NHC complex efficient for the coupling of aryl bromides/iodides, heteroaromatic iodides with aryl boronic acid.

Based on literature support we can conclude that our catalyst follow Organ-type [35] mechanism where the Pd-NHC-PEPPSI is reduced to Pd(0) followed by pyridine dissociation. The dissociation of pyridine generate the Pd(0) active species which subsequently undergo oxidative addition of aryl halide, transmetalation of phenyl boronic acid and reductive elimination of cross-coupling product complete the reaction cycle.

4. Conclusion

In this work, we have demonstrated synthesis of a new PEPPSI type Pd-NHC complex and explored its potential as catalyst for the Suzuki-Miyaura Cross coupling reactions of aryl halides with aryl boronic

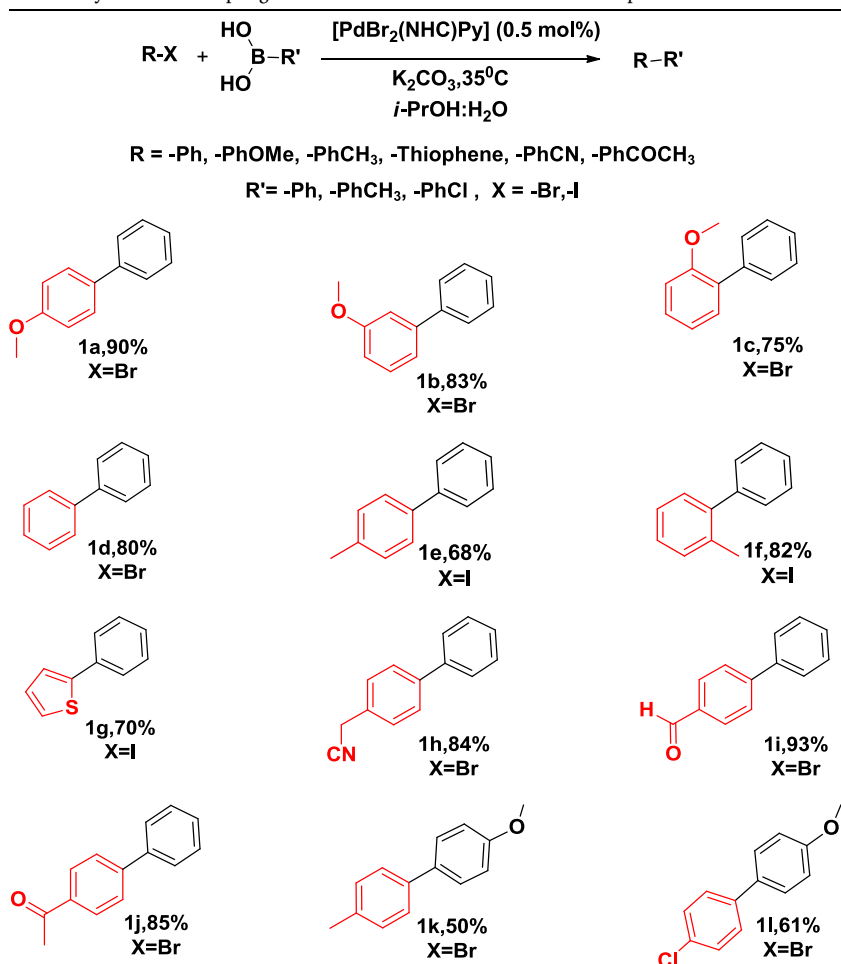
Table 4
Optimization table of Suzuki-Miyaura Cross coupling reaction¹.



Entry	Solvent	Cat. loading	Base	Temp.	Time	Yield
1	H ₂ O	1 mol%	K ₂ CO ₃	50	4	36 %
2	<i>i</i> -PrOH	1 mol%	K ₂ CO ₃	50	4	57 %
3	Et-OH	1 mol%	K ₂ CO ₃	50	4	50 %
4	DMF	1 mol%	K ₂ CO ₃	50	4	60 %
5	<i>i</i> -PrOH: H ₂ O(3:1)	1 mol%	K ₂ CO ₃	50	4	82 %
6	<i>i</i> -PrOH: H ₂ O(2:1)	1 mol%	K ₂ CO ₃	50	4	85 %
7	<i>i</i> -PrOH: H ₂ O(1:1)	1 mol%	K ₂ CO ₃	50	4	91 %
8	EtOH:H ₂ O(3:1))	1 mol%	K ₂ CO ₃	50	4	77 %
9	EtOH:H ₂ O(2:1))	1 mol%	K ₂ CO ₃	50	4	77 %
10	EtOH:H ₂ O(1:1))	1 mol%	K ₂ CO ₃	50	4	84 %
11	<i>i</i> -PrOH: H ₂ O(1:1)	0.5 mol%	K ₂ CO ₃	35	4	95 %
12	<i>i</i> -PrOH: H ₂ O(1:1)	0.25 mol%	K ₂ CO ₃	35	4	89 %
13	<i>i</i> -PrOH: H ₂ O(1:1)	0.1 mol%	K ₂ CO ₃	35	4	77 %
14	<i>i</i> -PrOH: H ₂ O(1:1)	0.05 mol%	K ₂ CO ₃	35	4	58 %
15	<i>i</i> -PrOH: H ₂ O(1:1)	0.01 mol%	K ₂ CO ₃	35	4	38 %
16	<i>i</i> -PrOH: H ₂ O(1:1)	0.5 mol%	Cs ₂ CO ₃	35	4	50 %
17	<i>i</i> -PrOH: H ₂ O(1:1)	0.5 mol%	Na ₂ CO ₃	35	4	82 %
18	<i>i</i> -PrOH: H ₂ O(1:1)	0.5 mol%	KOH	35	4	–
19	<i>i</i> -PrOH: H ₂ O(1:1)	0.5 mol%	NaOH	35	4	78 %

¹Reaction Condition: Solvent: 4 ml, phenyl boronic acid (1.25 mmol), 4-bromo anisole (1 mmol), Base (1.5 mmol), *GC yield with respect to Aryl Bromide.

Table 5
Suzuki-Miyaura cross coupling reaction with different substrates under optimized reaction condition using [PdBr₂(NHC)Py]¹.



¹Reaction Condition: 1.25 mmol phenyl boronic acid, 1 mmol 4-bromo anisole, 1.5 mmol base, catalyst 0.5 mol% Pd-NHC-PEPPSI.

acids. Good-to-excellent yields of cross-coupling products were obtained with a range of substrates in aqueous-isopropanol under mild reaction conditions. The complex was crystallographically characterized. The DFT calculations were also performed in order to gain more insight about structure and bonding and a good correlation has been observed between theoretical and experimental observations.

†The crystallographic data of the complex as cif file was submitted at the Cambridge Crystallographic Data center having CCDC no. 2233171 and are available at <https://www.ccdc.cam.ac.uk/structures> and conveniently can be accessed without any charge.

CRedit authorship contribution statement

Bibekananda Gogoi: Investigation, Data curation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Sangeeta Khargharia:** Data curation, Formal analysis, Investigation, Validation. **Rahul Kar:** Conceptualization, Resources, Validation. **Biraj Jyoti Borah:** Resources, Data curation, Investigation, Validation. **Pankaj Das:** Conceptualization, Supervision, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2023.136678](https://doi.org/10.1016/j.molstruc.2023.136678).

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