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Phosphonate functionalized N-heterocyclic carbene Pd(II) complexes as efficient catalysts for Suzuki-Miyaura cross coupling reaction[☆]

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ABSTRACT

A N-heterocyclic carbene (NHC) ligand, L_1 bearing a pendant phosphonate ester group is used to prepare two new NHC-Pd(II) complexes, $[Pd(L_1)_2I_2]$ (**1**) and $[Pd(L_1)(py)I_2]$ (**2**) (py = pyridine). Hydrolysis of phosphonate ester group in **2** results another Pd(II)-NHC complex, $[Pd(L_2)(py)I_2]$ (**3**) where a phosphonic acid group is attached to the NHC ligand L_2. All the three complexes are characterized by analytical and spectroscopic studies while the molecular structures of **1**-**2** are also determined by single crystal X-ray diffraction measurement. The catalytic efficacies of **1-3** in Suzuki-Miyaura cross coupling reactions of aryl halides and aryl boronic acid are investigated. DFT calculations were performed to decipher the role phosphonate ester or phosphonic acid substituents on the catalytic efficacy.

1. Introduction

Carbon-carbon bond formation reactions remains highly relevant in fine chemical as well as pharmaceutical industry and continuous efforts are being focused to address emerging challenges in this area [1]. In this regard, the advent of palladium catalyzed Suzuki-Miyaura cross coupling reaction of aryl halides with aryl boronic acid is a major breakthrough with diverse synthetic utility [2]. Comparatively mild and environmentally safer reaction conditions, easy access to diverse boronic acids, broad reaction scope and high selectivity of Suzuki-Miyaura cross coupling reaction favored wide proliferation of this reaction [3]. Initial studies established the superior catalytic efficacy of phosphine based palladium complexes in Suzuki-Miyaura cross coupling reaction [4]. Phosphine being a strong σ-donor imposes large electron density to the active metal centre and thus increases its reactivity [5]. However, in recent times N-heterocyclic carbene (NHC) based palladium catalysts have gained attention due to several advantages of these catalysts over the conventional palladium phosphine catalysts [6]. Strong σ-donating nature along with ability to easily tune the steric bulk promote both the oxidative addition as well as reductive elimination and thereby enhance catalytic efficacy. Apart from that, by modulating electronic characteristics of the N-pendant group linked to the NHC, the efficacy of Pd(II)-NHC based catalyst in cross coupling reactions can be drastically enhanced [7,8]. In particular, employing well-defined air and moisture stable Pd(II)-NHC complexes as pre-catalyst has emerged as an elegant strategy for Suzuki-Miyaura cross coupling reaction involving challenging substrates. In this context, the NHC-Pd-PEPPSI (pyridine enhanced pre-catalyst preparation stabilization and initiation) complexes developed by the Organ group [9] and the $[PdCl(\eta^3\text{-R-allyl})(NHC)]$ complexes developed by the Nolan group [10,11] are notable due to their easy handling and considerably high catalytic efficacy. Systematic variation of the N-pendant group or the allyl moiety in respective complexes allowed optimization of catalytic efficacy as well as provided crucial insight into the mechanism involved [12,13].

Functionalization of NHC by incorporating side chains bearing donor groups has emerged as an efficient strategy to design hemilabile ligands [14,15]. Complexes of such donor functionalized NHC ligands are expected to show superior catalytic efficacy as the hemilabile arm is capable of reversible dissociation from the metal center. Apart from that, another advantage associated with donor functionalized NHC complexes is their improved water solubility when hydrophilic substituents are present [16,17]. In view of the above, plethora of donor functionalized NHC-Pd(II) complexes have been so far reported and many of these complexes show good catalytic efficacy [18]. In this regard it is surprising to note that phosphonate ester or phosphonic acid functionalized NHC or their complexes are yet to be reported. Due to the presence of three donor oxygen atoms in phosphonate group, it can show diverse coordination modes with a wide range of metal ions. Thus, phosphonate

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[☆] Dedicated to Prof. Pradeep Mathur on the occasion of his 65th birth anniversary.

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ester or phosphonic acid functionalized NHC complexes offer significant potential in devising efficient catalytic systems.

During this study, NHC-Pd(II)-PEPPSI and bis(NHC)-Pd(II) type complexes are prepared by employing a precursor imidazolium ligand containing N-pendant phosphonate group and their catalytic efficacies in Suzuki-Miyaura cross coupling reaction were explored. Starting from diethy-4-aminobenzylphosphonate, the precursor 4-imidazol-1-yl-benzyl-phosphonic acid diethyl ester was prepared. A bis(NHC)-Pd(II) complex and two NHC-Pd(II)-PEPPSI type complexes were prepared by the reaction of the precursor phosphonate functionalized imidazolium salt with $Pd(OAc)_2$ and $PdCl_2$ respectively. To the best of our knowledge, this set of complexes are the only examples of NHC-Pd(II) complexes having N-pendant phosphonate groups reported so far. The effect of the phosphonate group in the catalytic activity was also investigated during this study. The activities of the catalysts were explored in Suzuki coupling reaction of aryl chlorides and bromides with boronic acid.

2. Experimental section

2.1. Materials and methods

Starting materials were purchased from commercial sources and used without further purification. Ligand 4-imidazol-1-yl-benzyl-phosphonic acid diethyl ester and 3-[4-(diethoxy-phosphorylmethyl)-phenyl]-1-methyl-3H-imidazol-1-ium iodide $[HL_1]I$, used for the synthesis of the three reported NHC-Pd(II) complexes were synthesised by following an unpublished procedure designed by our group with the help of a reported procedure [19]. Solvents were purified by conventional techniques and distilled prior to use. Fourier transformed infrared spectra from 400 to 4000 cm^{-1} were recorded on Perkin Elmer Frontier MIR-FIR FT-IR spectrophotometer. Elemental analyses were performed on a Perkin Elmer Model PR 2400 series II elemental analyzer. NMR spectra were recorded on a JEOL JNM-ECS 400 NMR spectrometer operating at 400 MHz and Bruker ASCEND 600 NMR spectrometer operating at 600 MHz and samples were dissolved in deuterated solvents. Chemical shifts were reported in parts per million downfield of Me_4Si (TMS) as internal standard.

Single crystals of the complexes suitable for diffraction measurements were used directly from the reaction mixtures. The diffraction data for the compounds were collected on a Bruker APEX-II CCD Diffractometer using MoK_α radiation (λ=0.71073 Å) using φ and ω scans of narrow (0.5°) frames at 296 K. The structures were solved by direct methods using SHELXL-97 as implemented in the WinGX program system [20]. Anisotropic refinement was executed on non-hydrogen atoms. The aliphatic and aromatic hydrogen atoms were placed on calculated positions but were allowed to ride on their parent atoms during subsequent cycles of refinements. Positions of O-H hydrogen atoms were located on a different Fourier map and allowed to ride on their parent atoms during subsequent cycles of refinements. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 2096459 (**1**) and CCDC 2096460 (**2**) (E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

2.2. Computational details

The structures were fully optimized without any symmetry constraints in the gas phase and at 298 K using M06-2X/def2-TZVP level of theory [21]. Harmonic frequency calculations were also performed at the same level of theory to understand the nature of the stationary states. Intermediates and products were found to be at their local minima with real frequencies while the transition state was found to have one imaginary value of the frequency. Further, the transition state was verified with intrinsic reaction coordinate analysis. Energies are zero point and thermally corrected. Electronic structures were analyzed using natural bond orbital (NBO) analysis. Calculations were performed using GAUSSIAN16 suite of program [22].

2.3. Synthesis of $[Pd(L_1)_2I_2](1)$

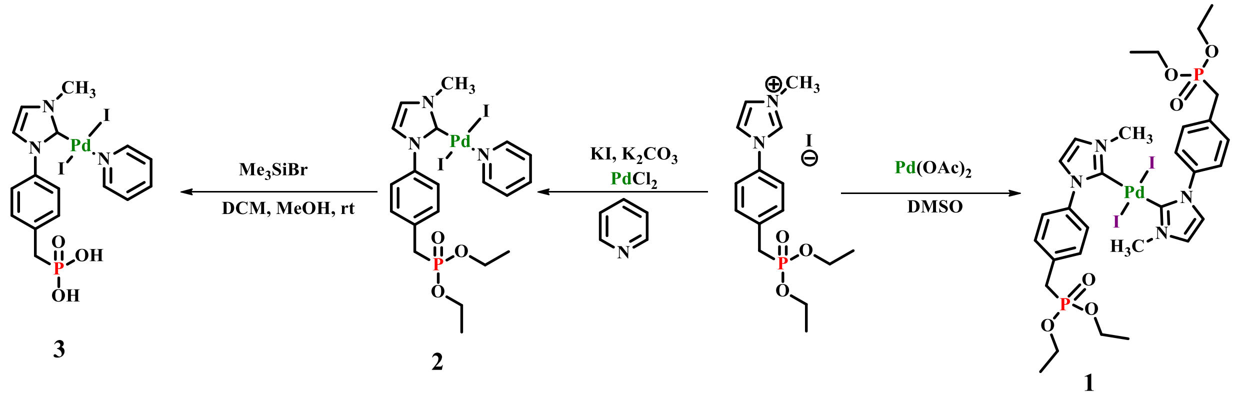
3-[4-(Diethoxy-phosphorylmethyl)-phenyl]-1-methyl-3H-imidazol-1-ium iodide $[HL_1]I$ (0.5 mmol, 218 mg) was added to a solution of $Pd(OAc)_2$ (0.25 mmol, 56 mg) in dimethylsulphoxide (DMSO) and the resulting mixture was stirred for 6 hours at ambient temperature. Thereafter, the reaction mixture was heated at 130 °C under continuous stirring for another 4 hours. The resultant mixture was added drop wise to a mixture of diethyl ether (Et_2O) and dichloromethane (4:1 v/v) under vigorous stirring. The precipitate thus obtained was filtered and washed with Et_2O and dried at room temperature to isolate the product $[Pd(L_1)_2I_2]$ (**1**) as yellow solid. Yield: 145 mg (58%), Elemental analysis % found (calculated for $C_{30}H_{42}I_2N_4O_6P_2Pd$): C: 36.72 % (36.89 %) H: 4.62 % (4.33 %) N: 5.66 % (5.74 %), FT-IR (KBr, cm^{-1}): υ 3417 (br), 2983 (m), 2907 (w), 1573 (w), 1520 (m), 1384 (m), 1226 (s), 1052 (vs), 1022 (vs), 962 (s), 856 (m), 570 (m). ^1H NMR (400 MHz, DMSO-d_6, δ/ppm): 8.06 (1H, ImH), 7.69 (1H, ImH), 7.56 (2H, ArH), 7.45 (2H, ArH), 3.94 (4H, $-CH_2$), 3.78 (3H, $-CH_3$), 3.35-3.32 (2H, $-P-CH_2$), 1.19 (6H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 133.08, 131.72, 130.83, 125.50, 124.07, 62.85, 33.14-31.80, 29.62, 16.85. ^{31}P NMR (DMSO-d_6, δ/ppm): 26.48.

2.4. Synthesis of $[Pd(L_1)(py)I_2]$ (2)

A mixture of ligand 3-[4-(diethoxy-phosphorylmethyl)-phenyl]-1-methyl-3H-imidazol-1-ium iodide $[HL_1]I$ (218 mg, 0.5 mmol), $PdCl_2$ (97 mg, 0.55 mmol), KI (1 mmol, 166 mg) and K_2CO_3 (345 mg, 2.5 mmol) are dissolved in 10 mL of pyridine. The resultant solution was heated to reflux and stirred overnight under N_2 atmosphere. After cooling the mixture to room temperature, all volatiles were evaporated under reduced pressure. The obtained residue was dissolved in $CHCl_3$ (50 mL) and H_2O (50 mL) was added. The separated organic layer was washed with 5% $CuSO_4$ solution, followed by 5% brine solution and then dried over Na_2SO_4. The extracted organic layer was further filtered over short pad of silica and washed thoroughly with hexane/acetone (2:1). The combined organic solution was evaporated to give the product $[Pd(L_1)(py)I_2]$ (**2**) as orange powder. The complex thus obtained was dissolved in $CHCl_3$, and upon slow evaporation yellow block shape crystal of the complex was obtained. Yield: 245 mg (65%), Elemental analysis % found (calculated for $C_{20}H_{26}I_2N_3O_3PPd$): C: 31.80 % (32.13 %) H: 3.52% (3.51%) N: 5.20% (5.62%). FT-IR (KBr, cm^{-1}): υ 3436(br), 2924(s), 2853(w), 1603(m), 1512(m), 1450(s), 1387(m), 1237(s), 1237(s), 1017(s), 935(s), 866(w), 759(s), 693(s), 568(s), 482(w). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.90 (1H, PyH), 8.81 (2H, PyH), 7.96 (2H, ImH), 7.66-7.09 (4H, ArH), 7.50 (2H, PyH), 4.08 (3H, $-CH_3$), 4.02 (4H, m, $-CH_2$), 3.26-3.21 (2H, $-P-CH_2$), 1.24-1.22 (6H, $-CH_3$).^{13}C NMR (150 MHz, DMSO-d_6, δ/ppm): 178.57, 158.21, 150.87, 143.73, 137.64, 135.49, 135.44, 130.17, 129.98, 128.51, 66.88, 36.73-35.03, 34.23, 21.53. ^{31}P NMR ($CDCl_3$, δ/ppm): 26.27.

2.5. Synthesis of $[Pd(L_2)(py)I_2](3)$

To $[Pd(L_1)(py)I_2]$ (**2**) (0.24 mmol, 180 mg), 10 mL dry dichloromethane was added. After complete dissolution of **2** in dichloromethane, 10 equivalents of $(CH_3)_3SiBr$ (312 mL, 2.36 mmol) was added and stirred for 4 hours at room temperature



Scheme 1. Synthesis of NHC-Pd(II) complexes [Pd(L$_1$)$_2$I$_2$] (**1**), [Pd(L$_1$)(py)I$_2$] (**2**) and [Pd(L$_2$)(py)I$_2$] (**3**).

under N_2 atmosphere. To the resultant reddish brown solution, 10 mL of dry CH_3OH was added and stirring continuously for another one hour to ensure complete quenching of excess$(CH_3)_3SiBr$. Thereafter, volatiles were evaporated under reduced pressure and the residue was washed with dichloromethane (2 mL). The crude product was dissolved in minimum amount of CH_3OH. Slow addition of diethyl ether to the above methanol solution gives the product [Pd(L$_2$)(py)I$_2$] (**3**) as yellow solid. Yield: 115 mg (69%), Elemental analysis % found (calculated for $C_{16}H_{18}I_2N_3O_3PPd$): C: 27.50% (27.79%) H: 2.65% (2.62%) N: 5.85% (6.08%), FT-IR (KBr, cm^{-1}): υ 3430(br), 3092(s), 2941(w), 1629(s), 1516(m), 1481(s), 1384(w), 1232(s), 994(s), 932(s), 748(s), 677(s), 556(m), 510(m). ^{1}H NMR (400MHz, DMSO-$d_6\delta$/ppm): 8.81 (1H, PyH), 8.73-8.58 (2H, PyH), 8.06-7.46 (8H,ArH, PyH), 4.49 (2H, O-H), 4.00 (3H, -CH_3), 3.07-3.02 (2H, -P-CH_2). ^{13}C NMR (100 MHz, DMSO-d$_6$, δ/ppm): 153.18, 152.45, 130.82, 129.30, 128.40, 127.55, 125.50, 125.13, 124.86, 36.10-34.79, 30.59. ^{31}P NMR (DMSO-d$_6$, δ/ppm): 21.15.

2.6. Typical procedure for Suzuki-Miyaura cross-coupling reaction

0.24 mmol of the aryl boronic acid and 0.2 mmol of aryl bromide were dissolved in 4 mL isopropanol-water (3:1) solution. To the above solution, 0.4 mmol of potassium carbonate and 0.001 mmol of catalyst (0.5 mol%) were added and the reaction mixture was stirred under heating condition in a preheated oil bath at 60 °C for variable time as mentioned in the Table 2. The progress of the reaction was monitored by using thin layer chromatography. After completion of the reaction, all solvent were removed under reduced pressure. The product was extracted by using hexane and dried over Na_2SO_4. Yields were determined from GC-MS. To investigate the role of the solvents and the base used in the reaction mixture, test has been carried out using different solvents and bases. It has been found that the use of isopropanol-water (3:1) as solvent and K_2CO_3 as base at 60 °C condition gives the maximum yield under N_2 atmosphere.

3. Result and discussion

Phosphonate ester functionalized imidazolium salt, 3-[4-(diethoxy-phosphorylmethyl)-phenyl]-1-methyl-3H-imidazol-1-ium iodide, [HL$_1$]I was prepared by a multistep synthetic route recently developed in our laboratory [19]. Initially, a phosphonate ester functionalized imidazole was prepared by reaction of diethyl 4-aminobenzylphosphonate with glyoxal, NH_4Cl and formaldehyde. Treatment of the imidazole with methyl iodide resulted the NHC precursor imidazolium salt [HL$_1$]I in good yield. Reaction of [HL$_1$]I with Pd(OAc)$_2$ in DMSO medium led to the formation of a bis(NHC)-Pd(II) type complex [Pd(L$_1$)$_2$I$_2$] (**1**) (Scheme 1). However, when the same reaction was carried out in presence of KI and K_2CO_3 using pyridine as solvent, a PEPPSI type Pd(II)-NHC complex, [Pd(L$_1$)(py)I$_2$] (**2**) is isolated. The N-pendant phosphonate group attached to the NHC ligand L$_1$ in **2** can be hydrolyzed into phosphonic acid functionality and thereby resulting in a related complex, [Pd(L$_2$)(py)I$_2$] (**3**). Analytical and spectroscopic data of **1**-**3** conform well to the proposed formulations. Further, the molecular structures of compound **1** & **2** are also established unambiguously using single crystal X-ray structure analysis.

Sharp peaks observed within 1226-1237 cm^{-1} in the FT-IR spectra of compound **1**-**3** can be attributed to P=O stretching vibration (Figs. S2–S4). The symmetric and anti-symmetric P-O stretching vibrations appeared between 1017-1022 cm^{-1} and 935-962 cm^{-1} respectively in complex **1**-**2**. However, in case of **3** the symmetric and anti-symmetric P-O stretching vibrations are observed at considerably lower frequency of 994 and 932 cm^{-1} respectively [23]. A broad peak observed at 2139 cm^{-1} in the FT-IR spectrum of **3** can be assigned to P-OH stretching vibration and therefore establish the presence of phosphonic acid functionality [24]. The Pd-C stretching vibrations in **1**-**3** appear as medium intensity peaks between 556-570 cm^{-1} while the Pd-N stretching vibrations in **1**-**2** are observed at 482 and 510 cm^{-1} respectively [25].

^{1}H NMR spectra of **1**-**3** show peaks for all constituent protons in expected regions and consistent with the proposed formulations. Disappearance of ^{1}H NMR resonance corresponding to the imidazolium proton (NC*H*N) upon complexation of the ligand with Pd(II) to form **1**-**3** support formation of Pd(II)-NHC complexes **1**-**3**. Resonances corresponding to the ethyl group of phosphonate ester functionality are observed in ^{1}H NMR spectra of **1**-**2** in the same region as in case of the parent ligand [HL$_1$]I. Absence of these resonances in the ^{1}H NMR spectrum of **3** confirm the hydrolysis of phosphonate ester functionality to result in phosphonic acid group. The benzylic CH_2 protons in **1**-**3** appear as doublets centered between 3.2, 3.3 and 3.0 ppm respectively due to coupling with phosphorus atom of the phosphonate group. Protons of N–CH_3 group in **1**-**2** are observed as singlet at δ 4.0 ppm and δ 3.8 ppm respectively, whereas in case of **3**, a multiplet rather than a singlet was observed at δ 4.0ppm. H-bonding interaction of the N-CH_3 protons with the P-OH groups of phosphonic acid functionality in DMSO-d$_6$ medium can be possibly attributed to the splitting of the peak into a multiplet in case of **3** (Figs. S4–S6) [26]. Such H-bonding interactions can be ruled on in case of **1**-**2** due to the presence of aliphatic substituents on the phosphonate ester functionalities and therefore supports appearance of N–CH_3 protons group in **1**-**2** as singlets. ^{13}C NMR spectra of **1**-**3** are in good agreement with the proposed formulations (Figs. S7–S9). Resonances corresponding to the carbene carbon atom in **2** is observed at 178.5 ppm in and compare well with those observed in case of other reported Pd(II)-NHC complexes [27,28]. Methyl and

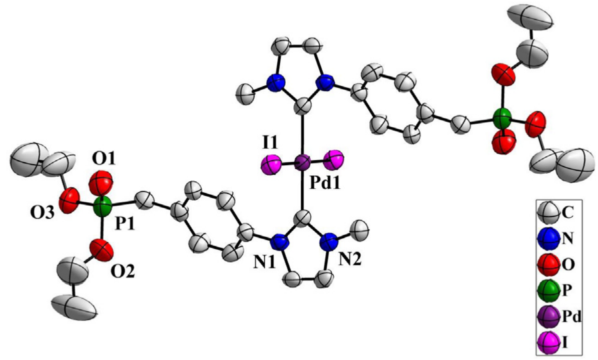


Fig. 1. Thermal ellipsoid plot (50% probability) of molecular structure of $[Pd(L_1)_2I_2]$ (**1**). H atoms are omitted for clarity.

methylene carbon atoms of ethyl phosphonate ester substituent in **1**-**2** resonate between 16.8-21.5 and 62.2-66.8 ppm respectively. Absence of these peaks in ^{13}C NMR spectrum of **3** gives credence to the hydrolysis of phosphonate ester group in to **2** into phosphonic acid functionality. Resonances observed between 29.6-34.2 ppm can be assigned to carbon atom of N-pendant methyl substituent in **1**-**3**. The benzylic carbon atoms in **1**-**3** resonate as a doublet centered between 32.4-35.8 ppm due to coupling with adjacent phosphorous atom. ^{31}P NMR spectra of **1**-**3** showed single resonances at 26.4, 26.2 and 21.1 ppm respectively and further establish presence of phosphonate ester groups in **1**-**2** and while phosphonic acid moiety in **3** (Figs. S10–S12).

3.1. Molecular structures of 1-2

The molecular structures of **1**-**2** are unambiguously established by single crystal X-ray diffraction analysis. Both the compounds crystallize in triclinic P-1 space group and their crystal data along with refinement parameters are listed in Table S1. The selected bond length and bond angles **1**-**2** are listed in Tables S2 and S3. A perspective view of the molecular structure of **1** is depicted in the Fig. 1 and formation of a (bis-NHC)-Pd(II) complex is established.

The palladium centre in **1** is coordinated to carbene carbon atoms of two NHC ligands which are positioned trans to each other. Apart from that, two iodo groups are also coordinated to the palladium centre in trans fashion and thus overall coordination geometry around the Pd(II) center is therefore square planar. The square planar geometry around the Pd(II) centre in **1** is highly symmetrical having perfectly 180.0° bond angle between C(8)#1-Pd(1)-C(8) and I(1)#1-Pd(1)-I(1). The Pd(1)-C(8) bond length measure 2.016 Å while the Pd(1)-I(1) is 2.6213 Å which are also comparable to the similar reported (bis-NHC)-Pd complex (Fig. 1) [29–31].

A prospective view of the molecular structure of $[Pd(L_1)(py)I_2]$ (**2**) is depicted in Fig. 2 and formation of a NHC-Pd-PEPPSI type complex is established. Apart from the NHC carbon atom, two iodo groups and a pyridine N-atom are also coordinated to the palladium centre. Thus, the geometry around the palladium atom in **2** is square planar. The benzene ring and the imidazole ring of the L_1 ligand lie on the different plane making an angle of 44.09°. The O(1)-P(6) bond length is 1.462 Å, which is shorter than the other two O(2)-P(6) and O(3)-P(6) bond length of 1.577 Å and 1.578 Å, and therefore associated with the P=O group. The molecular plane of the imidazole ring makes an angle of 25.64° with the pyridine ring coordinated to the Pd-atom. The observed bond length of Pd(1)-C(1) is 1.970 Å, shorter than the Pd(1)-N(3) 2.110 Å, which are comparable to the other reported NHC-Pd(II)-PEPPSI complexes [32,33]. Moreover, the Pd(1)-I(1) and Pd(1)-I(2) bond lengths measure 2.6105 Å and 2.6195 Å, which are similar to the typically reported Pd-I bond lengths in such complexes [33,34]. The I(1)-Pd(1)-I(2) and C(1)-Pd(1)-N(3) bond angles measure 174.9° and 177° respectively whereas the C(1)-Pd(1)-I(1) and N(3)-Pd(1)-I(1) angles are 88.27° and 91.56° respectively. Thus, the geometry around the Pd(II) atom in **2** is distorted square planer (Fig. 2).

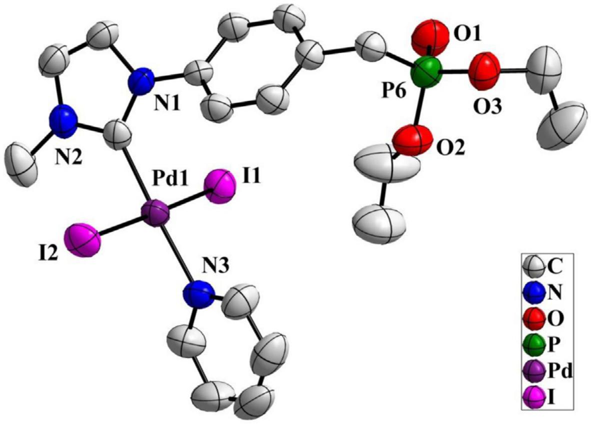


Fig. 2. Thermal ellipsoid plot of molecular structure of $[Pd(L_1)(py)I_2]$ (**2**). H atoms are omitted for clarity.

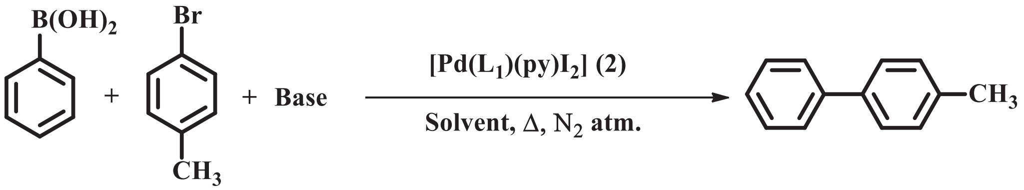
3.2. Catalytic application of 1-3

NHC-Pd(II) complexes typically show superior catalytic activity in various C-C coupling reactions as compared to conventional catalysts. In order to probe the influence of N-pendent phosphonate groups on catalytic efficiency of NHC-Pd(II) complexes, catalytic activity of **1**-**3** in Suzuki-Miyaura cross coupling reaction of aryl halides with aryl boronic acid were investigated. Initially investigations to optimize the temperature, solvent and base used in the Suzuki-Miyaura cross coupling reaction of 4-bromo toluene with phenyl boronic acid were carried out by employing **2** as catalyst. The efficacies of the catalyst in presence of various bases e.g. Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOH, KOH etc. and in different solvent systems are explored and the results are listed in Table 1. Further, it was observed that 60 °C is an ideal temperature for carrying out the cross coupling reaction. While poor yields are obtained at lower temperatures, heating above 60 °C leads to decomposition of the catalyst due to formation of metallic palladium. Thus, the reaction is best carried out by employing 0.5 mol% of the catalyst in presence of K_2CO_3 as a base and in ^{i}PrOH/H_2O (3:1) solvent system at 60 °C under N_2 atmosphere.

Under the optimized conditions, a series of reactions were performed by using **1**-**3** as catalyst with various substituted aryl halides and boronic acid. In all cases, better yields of the cross coupling products are obtained when compound **3** is used as catalyst. Moreover, presence of electron donating substituents on the boronic acid results improved yield of the coupling products in case of all three catalysts. Interestingly, all three compounds **1**-**3** acted as efficient catalyst in Suzuki-Miyaura cross coupling of aryl chlorides with arylboronic acids and upto 98% yield of the cross coupling product could be achieved within 3 hours reaction time. It is pertinent to note here that formation of homo coupling products are observed in the reactions involving **1** as catalyst, while the same are not observed when Pd-PEPPSI catalytic systems **2** and **3** are employed.

NHC-Pd complexes bearing less bulky N-pendent substituents typically show poor catalytic efficacy in cross-coupling reactions involving aryl chlorides [30,31,35–41]. Catalytic efficacy of **1**-**3** in Suzuki-Miyaura cross coupling reaction of aryl boronic acid with aryl chlorides are compared with catalytic efficacies of other reported Pd(II)-NHC complexes (Table 3) [11,30,37,40,42–45]. Surpris-

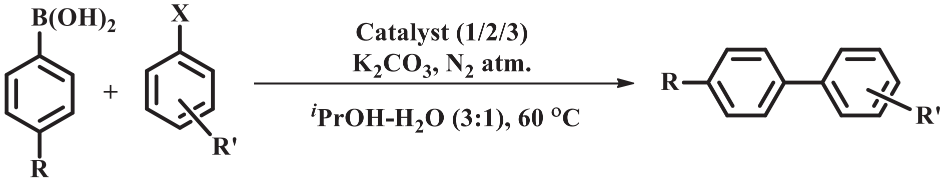
Table 1
Optimization of reaction condition for Suzuki-Miyaura reaction in presence of $[Pd(L_1)(py)I_2]$ **(2)** as catalyst.



Entry	Solvent	Base	Temp (°C)	Yield %
1.	$^iPrOH/H_2O$(3:1)	K_2CO_3	RT	0
2.	$^iPrOH/H_2O$(3:1)	K_2CO_3	40	48
3.	$^iPrOH/H_2O$(3:1)	K_2CO_3	60	74
4.	$^iPrOH/H_2O$(3:1)	Cs_2CO_3	60	63
5.	$^iPrOH/H_2O$(3:1)	KOH	60	72
6.	$^iPrOH/H_2O$(3:1)	NaOH	60	55
7.	$^iPrOH/H_2O$(3:1)	Na_2CO_3	60	65
8.	n-PrOH	K_2CO_3	60	59
9.	DMF	K_2CO_3	60	40
10.	DMF/TBAB	K_2CO_3	60	50
11.	^iPrOH	K_2CO_3	60	65
12.	1,4-Dioxane	K_2CO_3	60	56
13.	THF	K_2CO_3	60	16

Reaction condition: 0.24 mmol phenyl boronic acid; 0.2 mmol 4-bromo toluene; 0.4 mmol base, catalyst 0.5 mol%

Table 2
Suzuki-Miyaura cross coupling reaction with different substrates under optimized reaction conditions using complex **1-3** as catalyst.



Sl. No.	-R	-R′	-X	Time (Hour)	Yield (%)		
					Catalyst**1**	Catalyst**2**	Catalyst**3**
1.	-H	$-CH_3$ (*p*)	-Br	1	54	74	77
2.	-H	$-CH_3$ (*m*)	-Br	1	35	69	92
3.	-H	$-OCH_3$ (*p*)	-Br	6	86	52	93
4.	-H	fx	-Br	6	99	91	80
5.	$-CH_3$	$-CH_3$(*p*)	-Br	1	99	81	99
6.	$-CH_3$	$-CH_3$(*m*)	-Br	1	99	86	99
7.	$-CH_3$	$-CH_3$(*p*)	-Cl	3	95	90	98
8.	$-CH_3$	$-CH_3$(*m*)	-Cl	3	98	74	98
9.	-H	$-CH_3$ (*p*)	-Cl	3	65	80	90
10.	-H	$-CH_3$ (*m*)	-Cl	3	72	85	92

Reaction condition: 0.24 mmol aryl boronic acid; 0.2 mmol aryl halide; 0.4 mmol K_2CO_3; catalyst 0.5 mol%

ingly, catalytic efficacy of **1**-**3** in Suzuki-Miyaura cross coupling reactions involving aryl chlorides are comparable to those reported for Pd(II)-NHC complexes bearing bulky substituents. The superior catalytic efficacy of **1**-**3** as compared to other Pd(II)-NHC complexes bearing sterically less bulky substituents can be attributed to the dangling phosphonate ester or phosphonic acid functionality. We anticipate that the phosphonate ester or phosphonic acid groups play an important role in the catalytic cycle and thereby enhance the catalytic activity of these systems.

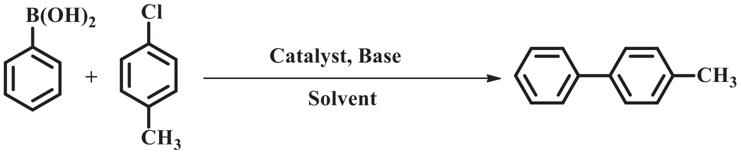
3.3. Computational results

As NHCs are known to be good σ donors and π acceptors, we therefore, calculated the energies of the HOMO and LUMO which corresponds to the donor and acceptor orbital, respectively, of three NHCs. The first one is the parent with H atom as the substituent, the second one is a modified one where one of the H atom is replaced by $PhCH_3$ group and the last one is similar to the second with an additional phosphonate group. Fig. 3 shows the frontier Kohn-Sham orbitals with their respective energies in eV. It is evident from Fig. 3 that introduction of $PhCH_3$ group increases the π-accepting ability of the NHCs. Introduction of phosphonic acid group makes it the best π-acceptor among the chosen molecules. As the NHC become more π-accepting, the Pd centre becomes electron poor which facilitates the addition para-chloro toluene and helps in providing suitable reaction energetics.

Fig. 4 shows the reaction energies (ΔG^{298}, kcal/mol) of the Pd(0)-NHC catalyzed coupling reaction or para-chloro toluene with phenyl boronic acid . The addition of para-chloro toluene to the activated Pd(0)-NHC complex **I**, is exergonic by 2.3 kcal/mol to generate **II**. The isomeric complex **III** is slightly higher in energy than **II**. The addition of $PhB(OH)_3$ to **III** is again exergonic by 5.4 kcal/mol. **IV** then rearranges to **V** via the transition state $TS_{IV\text{-}V}$. The activation barrier involved in this process is 9.2 kcal/mol. The Pd-B and Pd-C distances in $TS_{IV\text{-}V}$ are 3.847 and 3.439 Å respectively. Formation of Pd-C and cleavage of Pd-B bonds take place at the transition state $TS_{V\text{-}VI}$. The activation barrier for this process is 8.4 kcal/mol. The Pd centre forms a bond with the carbon atom of $PhB(OH)_3$

Table 3

Comparison of the catalytic efficacy of **1-3** with catalytic efficacies of reported Pd(II)-NHC catalysts in Suzuki-Miyaura cross coupling reaction of 4-chloro toluene and phenyl boronic acid.



Catalyst	Catalyst mol%	Solvent	Temperature (°C)	Time (hour)	Base	Yield (%)	Reference
[Pd(bmim-y)$_2$Br$_2$]	1	Ethylene glycol	110	1	NaHCO$_3$	5	30
[Pd(NHC$_{sulphonate}$)I$_2$]	1	H$_2$O: ^{i}PrOH	110	12	K$_2$CO$_3$	12-34	42
[Pd(NHC′)$_2$Cl$_2$]	0.25	Toluene	80	3	*t*-BuOK	20-50	40
[PdCl$_2$(X)(NHC′)]	0.25	Toluene	80	3	*t*-BuOK	24-41	
[(IMes)Pd(allyl)Cl]	1	1,4-dioxane	80	0.33	NaO^{t}Bu	80	11
[(SIMes)Pd(allyl)Cl]	1	1,4-dioxane	80	0.33	NaO^{t}Bu	70	
[(IPr)Pd(allyl)Cl]	1	1,4-dioxane	80	0.33	NaO^{t}Bu	80	
[(SIPr)Pd(allyl)Cl]	1	1,4-dioxane	80	0.33	NaO^{t}Bu	62	
[(I^{t}Bu)Pd(allyl)Cl]	1	1,4-dioxane	80	0.33	NaO^{t}Bu	68	
[Pd(μ-Cl)Cl(NHC″)]$_2$	0.1	EtOH	RT	24	NaOMe	86	43
trans-[PdBr$_2$(NHC‴)(X′)]	1	H$_2$O	100	4	KOH	88	37
[PdBr$_2$(NHC⁗)Py′]	1	H$_2$O	100	4	KOH	89	
[(IPr-SO$_3$)PdCl$_3$]$^{3-}$	0.1	H$_2$O: ^{i}PrOH	60	6	NaOH	98	44
[Pd(NHC″‴)(cin)Cl]	1	EtOH	40	20	K$_2$CO$_3$	99	45
[Pd(L$_1$)$_2$I$_2$]	0.5	H$_2$O: ^{i}PrOH	60	3	K$_2$CO$_3$	65	This work
[Pd(L$_1$)(py)I$_2$]	0.5	H$_2$O: ^{i}PrOH	60	3	K$_2$CO$_3$	80	
[Pd(L$_2$)(py)I$_2$]	0.5	H$_2$O: ^{i}PrOH	60	3	K$_2$CO$_3$	90	

bmim-y= 1-butyl-3-methylimidazol-2-ylidene; NHC$_{sulphonate}$ = 3-(1-methyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate, 3,3′-(1,1′-(ethane-1,2-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate) and 3,3′-(1,1′-(pyridine-2,6-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate); NHC= 3-(1-methyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate, 3,3′-(1,1′-(ethane-1,2-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate), 3,3′-(1,1′-(pyridine-2,6-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate); NHC′= 1,3-bis-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene, 1,3-bis-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene, 1,3-bis-(2,3,4,5,6-pentamethylbenzyl)benzimidazole-2-ylidene, X=Pyridine; IMes= *N,N′*-bis(2,4,6-trimethylphenyl)imidazol)-2-ylidene), SIMes= *N,N′*-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol)-2-ylidene); IPr= *N,N′*-bis(2,6-diisopropylphenyl)imidazol)-2-ylidene; SIPr= *N,N′*-bis(2,6 diisopropylphenyl)-4,5-dihydroimidazol)-2-ylidene); I^{t}Bu= *N,N′*-bis(2,6-*tert*-butyl)imidazol)-2-ylidene; NHC″= IMes, IPr; NHC‴= N-(2,4,6-trimethylbenzyl)-N′-(2-metoxyethyl)benzimidazoline-2-ylidene, N-(2,3,5,6-tetramethylbenzyl)-N′-(2-metoxyethyl)benzimidazoline-2-ylidene, N-(pentamethylbenzyl)-N′-(2-metoxyethyl)benzimidazoline-2-ylidene; X′ = pyridine carboxylic acid; NHC⁗ = 1,3-diisopropylbenzimidazolylidene Py′ = pyridine, 4,4′-bipyridine, 4,4′-bipridylethane, 4,4′-bipridylethylene; H(IPr-SO$_3$)=1,3-(4-sulfonate-2,6-diisopropylphenyl)imidazolium; NHC″‴ = bis(2,6-diisopropylphenyl)imidazol-2-ylidene; cin= cinnamyl

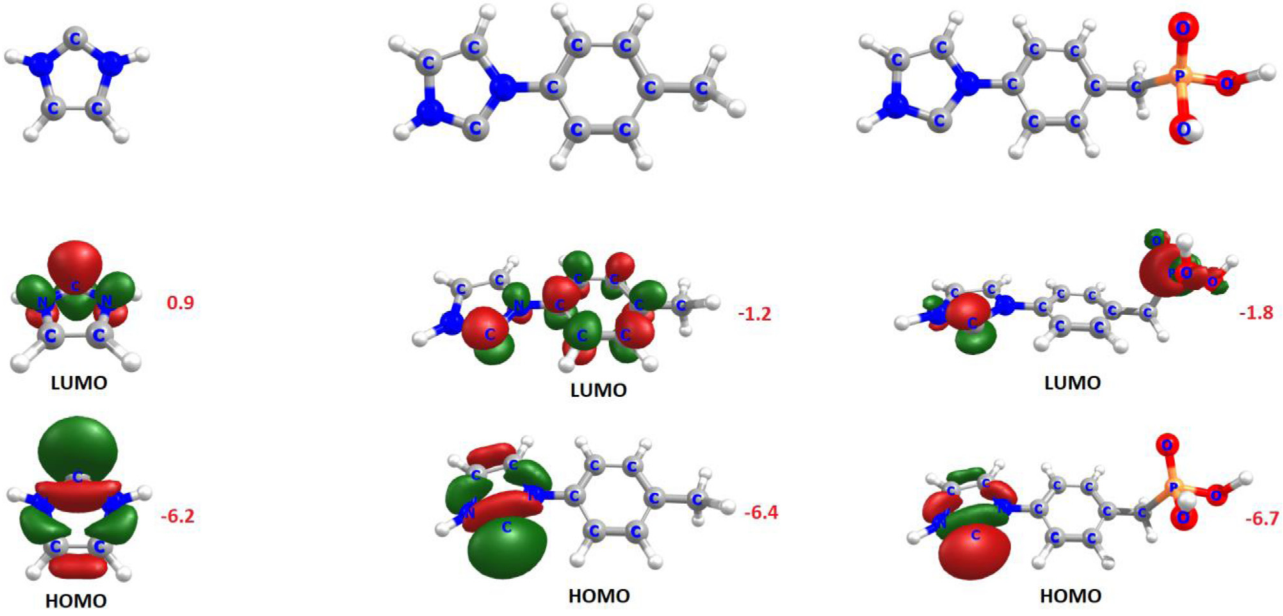


Fig. 3. Frontier Kohn-Sham orbitals along with their energies in eV.

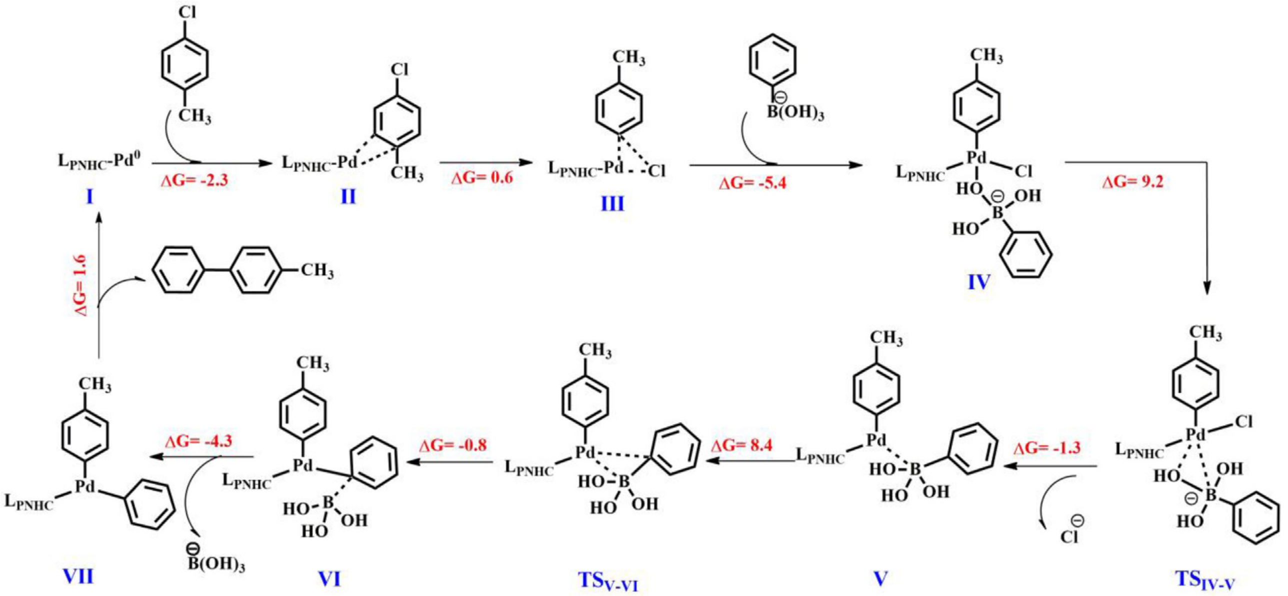


Fig. 4. Reactions energies of the proposed mechanism. Relative energies are in kcal/mol.

in the transition state with Pd-C distance of 3.465 Å. Conversion of **VI** to **VII** is exergonic by 4.3 kcal/mol while the regeneration of the active complex, Pd(0)-NHC, is slightly endergonic. The steps of the proposed mechanism showed that the reaction is thermodynamically favorable. Having low to moderate reaction barriers; prepared Pd-NHC catalyst bearing phosphonate ester/acid groups are suitable for the cross coupling reaction of aryl chlorides with phenyl boronic acid.

4. Conclusion

Thus, three new NHC-Pd(II) complexes, **1**-**3** are prepared by employing NHC ligand bearing N-pendent phosphonate ester or phosphonic acid functionality. Complexes, **1**-**3** are characterized using elemental analysis, FT-IR and ^{1}H & ^{13}C NMR studies while molecular structures of **1**-**2** are unambiguously established by single crystal X-ray diffraction technique. Structural analysis establish that the phosphonate ester groups in **1**-**2** are dangling and do not coordinate with Pd(II) centers. Complexes, **1**-**3** act as efficient catalyst in Suzuki-Miyaura cross coupling reactions of aryl boronic acid with both aryl bromides and aryl chlorides. Further, it was observed that the catalytic efficiency of NHC-Pd(II) complex bearing free phosphonic acid functionality is better than those containing N-pendant phosphonate ester functionality. The easy preparation method along with the high activity of the catalysts even in cross coupling reaction involving unactivated aryl chlorides highlights the importance of N-pendent phosphonate substituents on NHC ligand.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.122067.

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