

N, N'-Olefin functionalized *Bis*-Imidazolium Pd(II) chloride N-Heterocyclic carbene complex builds a supramolecular framework and shows catalytic efficacy for 'C–C' coupling reactions

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Abstract. The ligand 3,3'-(*p*-phenylenedimethylene)*bis*{1-(2-methylallyl)} imidazolium bromide (**1**) and its Palladium(II) N-heterocyclic carbene (NHC) complex (**3**) has been synthesized and characterized by several spectroscopic techniques and the solid-state structure of **3** has been determined by single crystal X-ray diffraction studies. The Pd(II) complex possesses ring head to tail Π – Π stacking interactions (3.767 Å^o) through imidazole rings. Complex **3** catalyzes Suzuki–Miyaura 'C–C' coupling reaction. DFT calculations have been used to understand the HOMO/LUMO energy and hence the stability and reactivity of Pd(II) complex in *syn* and *anti*-configuration.

Keywords. N-heterocyclic carbene (NHC); Pd(II)–NHC complex; supramolecular framework; catalysis; DFT

1. Introduction

Subsequent to the isolation of free carbene by Arduengo *et al.*¹ in the early 1990s, the N-heterocyclic carbene (NHC) ligands have attracted the attention of scientific community in terms of both academic curiosity and applications in industry.^{2–24} Over the past few years, the metal complexes of NHC (M–NHC) have become a prime focus of intense research due to their ability to generate robust and versatile catalyst precursors that offer complementary properties to phosphine ligands, in some cases showing pre-eminent efficacy^{25–27} as well. Electronically, the NHC, a neutral two-electron donor is considered to be a better σ donor and a weak Π acceptor than the corresponding phosphine ligand,²⁸ although it is still under debate.²⁹ The unique electronic properties of the NHCs, such as high σ -basicity and low Π -acidity, enhance the catalytic activities of the NHC-bound transition metal complexes in various organic transformation processes.

Palladium(II)–NHC complexes have been found to be highly active in 'C–C' cross-coupling reactions, such as Heck, Suzuki–Miyaura,^{11,12,30–33} Kumada–Tamao–Corriu type coupling,³⁴ Mizoroki–Heck reaction,³⁵ amination of aryl halide,^{36,37} Sonogashira coupling³⁸ and also in polymerization reactions.³⁹ In this regard, many M–NHC complexes have been reported. The N-functionalized NHCs bearing various functional groups such as pyridine,⁴⁰ pyrimidine,⁴¹ pyrazine,^{11,12,42,43,92} pyridazine⁴⁴ thiazole^{45,46} and naphthyl^{47,93} have also attracted considerable attention among the experimental chemists.

Various *bis*-NHC ligands have been reported, which are usually linked by alkene chains^{48–51} and tend to form chelating complexes with metals. NHC ligands containing a xylene bridge^{52,53} are surprisingly rare. There are very few reports of *bis*-NHC complexes in which the carbene moieties are linked by arene^{54,55} group devoid of an 'N' donor. The hemi-labile nature of allylic^{56–59} substituent at the 'N' centre of imidazole changes the metal–organic coordination mode during complex formation, which encourages us to design

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the Pd complexes of the allylic ligand. In the recent years, silver(I) complexes of NHCs as carbene transfer reagents^{55,60} have been the subject of intense study due to their superior stability compared with many free carbenes. This paper reports the synthesis of a new palladium complex containing *bis*-NHC ligand, via Ag(I)-NHC. The new Pd(II)-NHC complex shows distinct catalytic behaviour in different solvents. DFT calculations duly complement the findings.

2. Experimental

2.1 Chemicals and reagents

All the reagents – imidazole, α,α -dibromo-*p*-xylene, 3-chloro-2-methylpropene, Ag₂O and NH₄PF₆, were purchased from Sigma-Aldrich, UK, and were used without further purification. All manipulations were carried out in an open atmosphere, unless otherwise stated. Solvents Et₂O, DMSO, and CH₃CN of analytical-grade type were purchased from Qualigen, Kolkata, India. Solvents were distilled and dried over appropriate drying agents and nitrogen before use. ¹H NMR spectra were recorded on a Bruker ARX 400 (400MHz) in d⁶-DMSO as the solvent and ¹³C NMR data were recorded on a 75 MHz instrument, respectively, using the same solvent.

2.2 Synthesis of ligand 3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)} imidazolium bromide, **1** and Ag-NHC complex [3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)}imidazoline] silver(I) bromide, **2**

The ligand 3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)} imidazolium bromide, **1** and Ag-NHC complex [3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)} imidazoline] silver(I) bromide, **2** were synthesized and characterized as reported in Samanta *et al.*,²³ and used for the preparation of Pd(II)-NHC complex through carbene transfer process.^{28,55,60}

2.3 [3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)}imidazoline] palladium(II) chloride, **3**

A solution of PdCl₂ (18 mg, 0.1 mmol) in 10 mL CH₃CN was taken in a 50 mL round-bottomed flask and the solution was refluxed at 120°C for 2 h to produce Pd(CH₃CN)₂Cl₂, then 36 mg (0.05 mmol) Ag(I)-NHC (complex **2**) was added to the reaction mixture and refluxed for 12 h at 140°C temperature, which produced a yellow-colored solution of the complex. After removing the solvent, it gives a yellow-colored solid mass (complex **3**). Yield was 36 mg, (78%) ¹H NMR (400

MHz, d⁶-DMSO): δ 7.63 (s,1H,b), 7.45 (s,1H,c), 7.30 (s,2H,h), 5.69 (s,2H,g), 5.12 (s,1H,e), 4.88 (s,1H,e), 4.88 (s,2H,d), 2.1 (s,3H,CH₃CN), 1.68, (s,3H,f). ¹³C NMR (75MHz, DMSO-d₆): 163.4(a), 137.1(b), 136.1(c), 129.0(h), 119.5(i), 119.3(g), 113.1(d), 54.5(j), 51.1(e), 41.9 (CH₃CN), 18.5(f), 2.0 (CH₃CN). MALDI Mass: (m/z) values are 783.1 (**3**), 742.6 (**3**-CH₃CN), 701.2, 645.8, 590.7, 523.1 and 346.6. Anal. Calcd. for C₂₆H₃₂Cl₄Pd₂N₆, (Mw=783.18): C,39.87; H,4.12; N,10.73%. Found: C,39.84; H,4.11; N,10.71%.

2.4 Crystallographic study

Single-crystal X-ray diffraction intensity data of the title complex were collected at 296(2)K using a Bruker APEXII CCD diffractometer equipped with graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was carried out using the program Bruker SAINT.⁶¹ An empirical absorption correction SADABS⁶² was applied. The structure of the title complex was solved by direct method and refined by the full-matrix least-square technique on F2 with anisotropic thermal parameters to describe the thermal motions of all non-hydrogen atoms using the programs SHELXS97 and SHELXL97,⁶³ respectively. All calculations were carried out using PLATON⁶⁴ and WinGX system Ver-1.64.⁶⁵ All hydrogen atoms were located from difference Fourier map and refined isotropically. CCDC 947088 contains the supplementary crystallographic data for this paper. A summary of crystal data and relevant refinement parameters are given in table 3.

2.5 DFT study

Full geometry optimizations were carried out using the density functional theory (DFT) method at the B3LYP level of theory and LANL2DZ basis set⁶⁶ with G03-E01 software.⁶⁷ For complex **3**, *anti*-configuration was drawn using Gause View program taking dihedral angle of N(2)-C(3)-C(15)-N(3) = 179.973° as per the crystallographic structure and *syn*-configuration was drawn taking the dihedral angle of N(2)-C(3)-C(15)-N(3) = 0°. Frontier molecular orbitals (FMOs) were generated with Gause-View-4.1.2 software package⁶⁷ using the same level of theory.

2.6 Suzuki-Miyaura coupling reaction

The synthesized Pd(II)-NHC complex **3** was tested for its catalytic activity in the Suzuki-Miyaura coupling reaction.^{11,12,68-75} The coupling of activated 4-substituted bromobenzene with phenylboronic acid

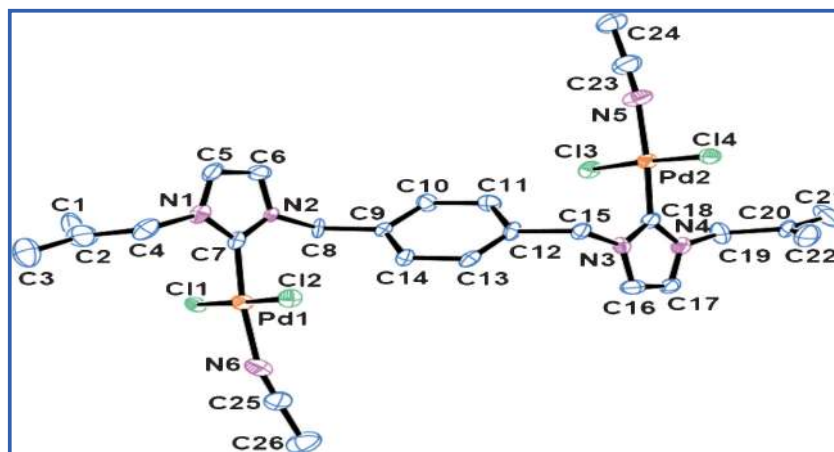


Figure 1. ORTEP view of X-ray crystallographic structure of Pd(II)-NHC complex **3**, 60% probability) [H atoms and two CH₃CN solvent molecules are removed for clarity].

with 0.5 mol% catalyst loading, 1.5 mol% external bases, and a reaction time of 10–12 h at 80–85°C were chosen as a standard test reaction to study the effect of various electron-poor and electron-rich substituents in two different solvents – acetonitrile and toluene. Quantitative yields of cross-coupling products were measured based on ¹H NMR spectra and LC mass data. The results are summarized in table 2.

3. Results and Discussion

3.1 Synthesis and structure

Ligand 3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)imidazolium} bromide (**1**) and Ag(I)-NHC complex

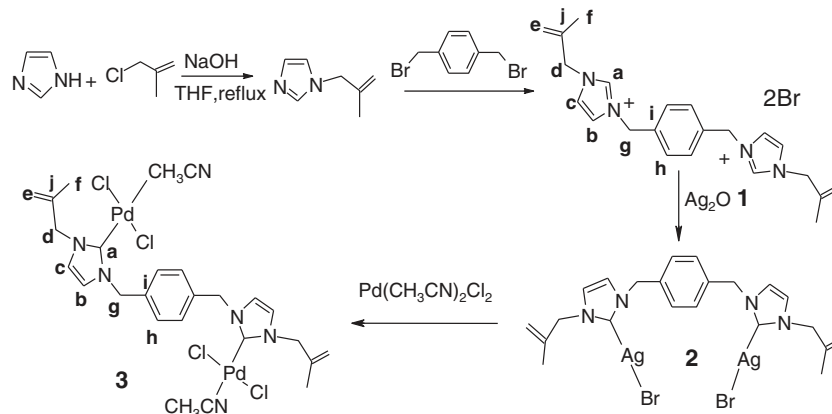
[3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)imidazole} silver(I) bromide (**2**) were obtained following the procedure reported by Samanta *et al.*,²³ A convenient method of synthesizing the NHCs involves deprotonation of the imidazolium proton from the ligand precursor.^{23,24} To obtain the desired Pd(II)-NHC complex, first the PdCl₂ was taken in an acetonitrile solvent and refluxed at 120°C for 2 h to produce a red-yellow solution of Pd(CH₃CN)₂Cl₂. Ag(I)-NHC complex (**2**) was added to the reaction mixture in stoichiometric ratio and refluxed for 12 h at 140°C temperature, which produced a yellow-coloured solution of Pd(II)-NHC complex, [3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)imidazole} palladium(II)] chloride (**3**). On removing the solvent in vacuum, a yellow

Table 1. Some selected bond parameters of complex **3**.

Bond Lengths (Å)		Bond Angles (°)	
N(1)-C(7)	1.347(10)	N(1)-C(7)-N(2)	104.5(7)
N(2)-C(7)	1.343(11)	C(7)-Pd(1)-N(6)	173.9(3)
C(7)-Pd(1)	1.940(9)	C(7)-Pd(1)-Cl(1)	89.9(2)
N(6)-Pd(1)	2.069(8)	C(7)-Pd(1)-Cl(2)	88.8(2)
Pd(1)-Cl(1)	2.3309(18)	Cl(1)-Pd(1)-Cl(2)	177.98(7)
Pd(1)-Cl(2)	2.3414(18)	N(6)-Pd(1)-Cl(1)	91.2(2)
		N(6)-Pd(1)-Cl(2)	90.3(2)
		C(9)-C(8)-N(2)	114.4(7)
N(3)-C(18)	1.363(11)	N(3)-C(18)-N(4)	105.0(7)
N(4)-C(18)	1.342(11)	C(18)-Pd(2)-N(5)	176.5(4)
C(18)-Pd(2)	1.941(9)	C(18)-Pd(2)-Cl(3)	87.6(3)
N(5)-Pd(2)	2.086(8)	C(18)-Pd(2)-Cl(4)	89.3(2)
Pd(2)-Cl(3)	2.3261(19)	Cl(3)-Pd(2)-Cl(4)	176.87(9)
Pd(2)-Cl(4)	2.313(2)	N(5)-Pd(2)-Cl(3)	89.7(2)
		N(5)-Pd(2)-Cl(4)	93.4(2)
		C(12)-C(15)-N(3)	113.5(7)

solid mass (**3**) was obtained. The downfield shift of ^1H NMR from complex **2** ($\delta = 7.54$ ppm) to complex **3** ($\delta = 7.63$ ppm) and proton signal at $\delta = 2.0$ ppm for CH_3CN indicate the formation of the complex. It was further confirmed by the downfield shift of ^{13}C NMR signal of carbenic carbon from 178.2 ppm [for complex **2**] to 163.4 ppm for Pd(II)-NHC complex **3**. The ^{13}C NMR signal of CH_3CN came at 41.9 ppm and that of $\text{C}(\text{H}_3)\text{CN}$ at 2.0 ppm, which is similar to that of other reported Pd-NHC complexes.⁷⁶ MALDI Mass (m/z) value at 783.1 indicates that the two CH_3CN molecules are attached to the Pd(II) centre to satisfy the coordination. This was further confirmed by the X-ray crystallographic studies. The ORTEP view⁷⁷ is shown in figure 1. Light yellow crystals of the formula $[\{\text{PdCl}_2(\text{CH}_3\text{CN})\}_2(\mu\text{-}1\text{-}2\text{H})]$ were grown via diffusion of diethyl ether into the acetonitrile solution of the complex **3**. The Pd ions are in distorted square-planar

coordination. For Pd1, the mean deviation from the coordination plane is 0.029 Å, with the chlorine atom (Cl2) 0.060 Å and the carbon atom (C7) 0.078 Å out of this plane and, for Pd2, the mean deviation from the coordination plane is 0.010 Å, with the chlorine atom (Cl3) 0.025 Å and the carbon atom (C18) 0.031 Å out of this plane. Structural analysis reveals the geometrical coordination at the metal centre, with an *anti*-configuration of imidazolium moieties with respect to one another with the Pd-C_{carbene} bond length 1.940 ~ 1.941 Å, which is relatively shorter than other chelating *bis*-NHC-Pd(II) complexes.^{7,78-80} The Pd-C_{carbene} bond is however comparable to the Pd-NHC complex having the same type of geometry⁵⁸ or those in which Pd(II) centre is connected to one NHC.^{81,82} Solvent acetonitrile, coordinated through 'N', is *trans* to carbene carbon of the ligand and the other two coordination hands of Pd(II) centre are occupied by the



Scheme 1. Synthesis of ligand **1**, Ag(I)-NHC complex **2** and Pd(II)-NHC complex **3**.

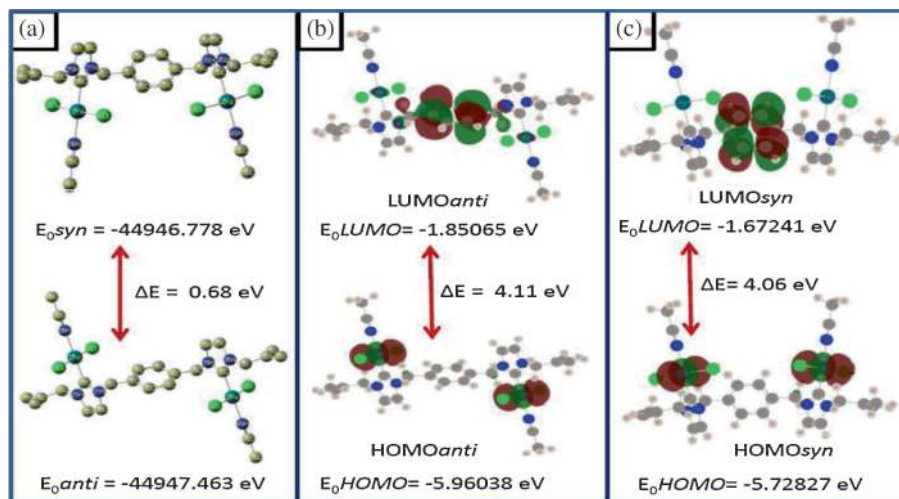


Figure 2. (a) Groundstate energy of syn and anti-configuration of complex **3**; (b) HOMO-LUMO energy gap of anti-configuration of complex **3**; (c) HOMO-LUMO energy gap of syn-configuration of complex **3**.

two Cl moieties, resulting in a square-planar geometry. Pd–Cl bond lengths are in the range of 2.31~2.34Å and that of Pd–N(CH₃CN) are in the range of 2.069–2.086Å. A few selected bond lengths and bond angles of complex **3** are summarized in table 1.

The data are comparable with the Pd–NHC complexes⁵⁸ reported earlier (scheme 1).

The larger the HOMO/LUMO energy gap (LUMO–HOMO), the more stable/less reactive is the molecule.^{83,84}

Thus, the *anti*-configuration (LUMO–HOMO energy gap = 4.11 eV) is more stable than the *syn*-configuration (LUMO–HOMO energy gap = 4.06 eV) of complex **3** (figure 2), which corroborates the ground-state energy of the theoretically optimized geometries of complex **3**. Figure 2 shows that the *anti*-configuration is energetically more stable than *syn*-configuration ($\Delta E_0 = 0.68$ eV).

3.2 Supramolecular framework

The solid-state structure of **3** is stabilized through C–H···N, C–H···Cl hydrogen bonds along with

C–H··· π and face-to-face π – π stacking interactions (tables TS1 and TS2). It is convenient to consider the substructures generated by each type of interactions acting individually, and then the combination of substructures to build a supramolecular framework. The methyl carbon atom C(26) of metal coordinated acetonitrile molecule acts as a double donor to the Cl atoms, Cl(3) and Cl(4), to extend the network. The C(26) atom at (x, y, z) acts as a donor through H26B to the Cl(3) atom of the partner molecule at $(1-x, 1/2+y, 1-z)$ and again methyl carbon C(26) is acting as a donor to Cl(4) atom in the molecule at $(2-x, 1/2+y, 1-z)$ (table TS1). The combination of these two intermolecular hydrogen bonding interactions leads the molecules to form a tetrameric unit in complex **3**. Repetition of this tetrameric ring motif leads the molecules to form an extended supramolecular framework in $(1\ 1\ 0)$ plane (figure 3). In another substructure, the carbon atom C(4) in the molecule at (x, y, z) acts as donor to the centroid of the aryl ring (C9–C14) in the molecule at $(x, y, 1+z)$ with a separation distance of 2.98Å (table TS2). Again the carbon atom C(19) of the partner molecule acts as donor to that aryl ring in the molecule at $(x, y,$

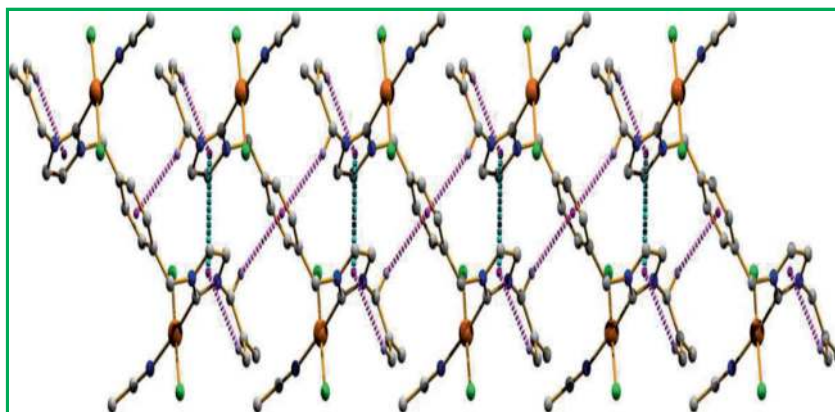


Figure 3. Perspective view of cooperative effect of weak C–H··· π and π – π forces in complex **3**.

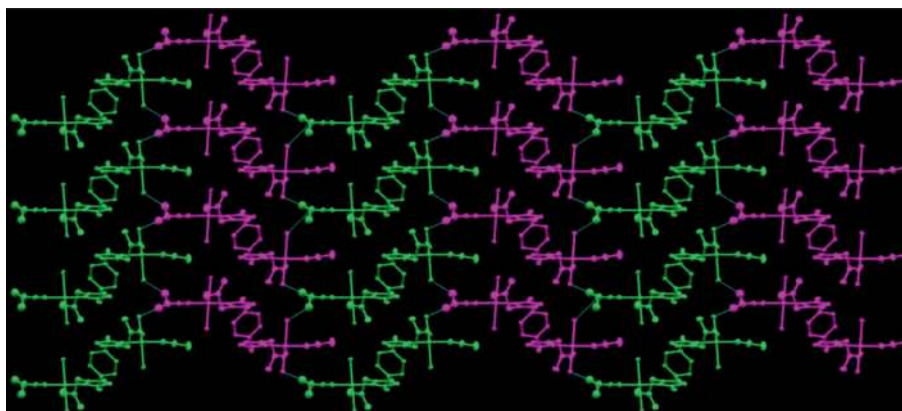


Figure 4. Formation of supramolecular 2D network through C–H···Cl hydrogen bonds of complex **3**.

$1+z$) with the same separation distance. Thus, an associative very rare C–H $\cdots\pi/\pi\cdots$ H–C network is generated in complex **3** (figure 4). The possible cooperative effects for these interactions have been described in the literature reported earlier.⁸⁵

In another substructure, the carbon atom C(1) acts as donor to the centroid of the (N1/C5/C6/N2/C7) ring where on either side of that ring, another ring (N3/C16/C17/N4/C18) is in contact with the carbon atom C(22) through C–H $\cdots\pi$ interactions (figure 4). Interestingly, these two adjacent rings are in contact

through π – π stacking interactions. The rings at (x, y, z) and $(x, y, -1+z)$ are parallel, with an inter-planar spacing of 3.357(4)Å corresponding to a ring centroid separation of 3.767(6)Å. Thus, the overall supramolecular build-up of the molecular moiety is the result of the self-assembly of the co-operative self-recognition through these weak forces. So, by utilizing both types of weak forces in a co-operative manner, a very rare C–H $\cdots\pi/\pi$ – $\pi/\pi\cdots$ H–C type extended network has been observed in the title complex (figure 4). The associative extended networks of several weak non-covalent

Table 2. Suzuki–Miyaura cross-coupling reaction catalyzed by complex **3** using acetonitrile (1) and toluene (2) as solvent.

R = -H, -CH₃, -OCH₃, -COCH₃, -NO₂

Entry	–R	Time (h)	Temp (°C)	Yield (%) ¹	Yield (%) ²
1	–CH ₃	12	85	86	91
2	–OCH ₃	12	85	87	91
3	–H	10	80	89	95
4	–COCH ₃	10	80	92	98
5	–NO ₂	10	80	92	98

Product based on ¹HNMR spectra and LC mass data for catalyst **3** using solvent acetonitrile (1) and toluene (2)

Table 3. Crystal data and structure refinement for complex **3**.

Empirical formula	C ₃₀ H ₃₈ Cl ₄ N ₈ Pd ₂
Formula weight	865.28
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁
Unit cell dimensions	$a = 8.9571(13)$ Å; $\alpha = 90^\circ$ $b = 25.792(4)$ Å; $\beta = 118.814(3)^\circ$ $c = 9.0154(13)$ Å; $\gamma = 90^\circ$
Volume	1824.9(5) Å ³
Z, Calculated density	2, 1.575 Mg/m ³
Absorption coefficient	1.310 mm ⁻¹
F(000)	868
Crystal size	0.21 × 0.16 × 0.09 mm
θ range for data collection	1.58 to 25.00 deg.
Limiting indices	-10 < h < 10, -30 < k < 30, -10 < l < 10
Reflections collected/unique	16769/6431 [R(int)=0.0629]
Completeness to θ	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.89 and 0.78
Refinement method	Full-matrix least-squares on F ²
Data/parameters	6431/404
Goodness-of-fit on F ²	1.035
Final R indices [I > 2 σ (I)]	R1=0.0520, wR2=0.1311
R indices (all data)	R1=0.0598, wR2=0.1359
Largest diff. peak and hole	2.476 and -1.037 e.Å ⁻³

forces are described in the recent literature.^{86–89} On either side of the extended network, the molecules are juxtaposed through hydrogen bonding interactions and are propagated in the (0 1 1) plane (figure S1).

3.3 Suzuki–Miyaura coupling reaction catalyzed by complex 3

In a preliminary study, the Pd(II)-NHC complex **3** was tested for its catalytic activity in the Suzuki–Miyaura coupling reaction.^{11,12,68–75} The results summarized in table 2 indicate an excellent catalytic activity of complex **3** in both the solvents, acetonitrile and toluene, giving virtually quantitative yields of cross-coupling products. The catalytic efficiency of **3** is slightly more in toluene than in acetonitrile as a solvent. The nature of the initial pre-catalyst, solvent, base, the counter anion, and the structure of the catalyst is crucial for the success of the C–C coupling reactions. The assumed catalytic cycle of Pd–NHC-mediated cross-coupling reactions occurs via NHC–Pd(0) intermediate species.⁹⁰ It is believed that in toluene, the NHC–Pd(0) is formed easily than in polar acetonitrile, which favours the catalysis. This phenomenon is very common in the Suzuki–Miyaura coupling reaction and reported by several groups.^{90,91} At the same time, efficiency of **3** is slightly better than the previously reported pyrazine functionalized Pd(II)-NHC complexes¹¹ in toluene; this may be due to two coordinated acetonitrile which during catalysis open the space around Pd. The results of catalysis (table 2) indicate the higher yield obtained in case of electron withdrawing group (*i.e.*, –NO₂ and –COCH₃) at 4-position of bromobenzene and less yield obtained in case of electron-donating group. Detailed studies are required in future on different effects (solvent effect, effect of counter anion of complexes) to understand the mechanism of the reaction and to find out the effective catalysts for application (Table 3).

4. Conclusions

Olefin functionalized Pd(II)-NHC complex **3** of the ligand 3,3'-(*p*-phenylenedimethylene)-bis{1-(2-methylallyl)imidazolium bromide has been synthesized by silver carbene transfer method and fully characterized by different spectroscopic techniques. The solid-state crystal structure of complex **3** has been determined by X-ray diffraction studies. Complex **3** shows a square planar geometry. DFT findings show that *anti*-configuration of complex **3** is energetically more stable than the *syn*-configuration. The solid-state structure of **3** is stabilized through different types of H-bond interface

along with C–H— π and π – π interactions and build a supramolecular framework. Complex **3** shows good catalytic activity in Suzuki–Miyaura ‘C–C’ coupling reaction in acetonitrile and toluene as solvent.

Supplementary Information

Tables S1 and S2 and figure S1 are available at www.ias.ac.in/chemsci.

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