Inorganica Chimica Acta 363 (2010) 831-840

Contents lists available at ScienceDirect

# Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# The C–N coupling reaction of pendant naphthyl group of palladium(II) complexes of 1-alkyl-2-(naphthyl-β-azo)imidazoles. Structural characterization, spectral and redox properties, and correlation with DFT computed data

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#### ARTICLE INFO

Article history: Received 16 November 2009 Accepted 23 December 2009 Available online 7 January 2010

Keywords: Pd-naphthylazoimidazoles C-N coupling reaction Electrochemistry Luminescence DFT computation

# 1. Introduction

Transition metal-catalyzed organic synthesis leading to the formation of C-C, C-N, C-O, and C-S bonds [1-5] has numerous industrial applications. Palladium-catalyzed coupling reactions have been extensively studied over the past three decades [6-11]. Extensive study in carbon-nitrogen bond formation has developed new synthetic methodologies. N-Arylation is achieved by copper [12-14], nickel [15,16], and palladium [17-19] catalysis. Among these three, palladium-based methods are most promising. Palladium-catalyzed C-N bond forming reactions have developed a versatile and efficient synthetic route [20,21,19,22]. The coordination of organic molecules to metal ions has affected the chemical nature of the molecules [23] and serves as effective template, and the suitable orientations and electronic requirement of ligands are responsible for chemical reactions [24-46]. For example, arylazoheterocycles do not show any nucleophilic reaction at free ligand state while metallated-arylazoheterocycles show easy reactions viz., hydroxylation [40,41], thiolation [42-44], aryl-amination [45,46] reaction. Azoheterocycles are  $\pi$ -acidic molecules and this property may be regulated by ring size, number of heteroatoms, substituents in the heterocyclic ring and side arm to azo function [47-52]. We have synthesised azoheterocycles such as azoimidazoles [53,54], naphthylazoimidazoles [55],

ABSTRACT

The reaction of Pd( $\beta$ -NaiR)Cl<sub>2</sub> (**2**) [ $\beta$ -NaiR (**1**) = 1-alkyl-2-(naphthyl- $\beta$ -azo)imidazoles)] with ArNH<sub>2</sub> in MeCN has yielded a C-N coupled product chloro[1-alkyl-2-{(7-imidoaryl)naphthyl- $\beta$ -azo}imidazole-N,N',N'']palladium(II), Pd( $\beta$ -NaiR-N-Ar)Cl (3-5) and coupling takes place at ortho-C-H position of pendant naphthyl group. The structural confirmation has been achieved by single crystal X-ray structure determination of the representative complexes,  $Pd(\beta-NaiEt)Cl_2$  (2b) and  $Pd(\beta-NaiEt-N-C_6H_4-Cl-p)Cl_2$ (5b). The electronic spectra of the products, 3-5, exhibit characteristic transition within 600-900 nm those are absent in  $Pd(\beta-NaiR)Cl_2(2)$ . Cyclic voltammogram shows one oxidative response and two ligand reductions. The products are emissive. The excited state decays via radiative and non-radiative biexponential routes. The electronic structure, spectra and redox properties are explained by DFT computation. © 2009 Elsevier B.V. All rights reserved.

> pyridylazoimidazoles [56], azopyridines [57], azopyrimidines [58], and azoantipyrine [59]. Pyridine- and pyrimidine-azo metallated complexes exhibit aryl-amination reaction at the pendant aryl ring [30-39,45,46,60]. In this work we account on the reaction of Pd( $\beta$ -NaiR)Cl<sub>2</sub> ( $\beta$ -NaiR = 1-alkyl-2-(naphthyl- $\beta$ -azo)imidazoles) with ArNH<sub>2</sub>. The structural characterization has been done by single crystal X-ray diffraction study. The electrochemical and luminescence properties of the complexes are examined.

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# 2. Results and discussion

## 2.1. Synthesis

Dichloro-(1-alkyl-2-(naphthyl-β-azo)imidazole)palladium(II) complexes,  $Pd(\beta-NaiR)Cl_2$  (2), are used in this work. The reaction between Pd( $\beta$ -NaiR)Cl<sub>2</sub> and ArNH<sub>2</sub> (1:1 molar ratio) in presence of Et<sub>3</sub>N in MeCN solution under stirring and refluxing for 12 h has yielded reddish-brown product (Scheme 1). This has been identified as amine coupled product abbreviated as Pd(β-NaiR–N–Ar)Cl (3-5) [where,  $R = CH_3$  (a),  $CH_2CH_3$  (b),  $CH_2Ph$  (c);  $Ar = X-C_6H_4$ where X = H (3), Me (4), Cl (5)].

The C–N coupling takes place via C–H activation of ortho C(6)–H bond to the azo function in the pendant naphthyl ring (B-ring) of  $\beta$ -NaiR and forms palladium(II) complex of tridentate N,N',N''-chelating ligand (N, N', N'' refer to N(imidazole), N(azo), and N(arylamine) respectively). Microanalytical data support the composition of the complexes (see Section 3). There are two  $\alpha$ -C-H groups, C(6)-H



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Scheme 1. C-N coupling reaction and atom numbering pattern.

and C(8)–H. The possibility of C(8)–H activation may be ruled out due to steric crowding of proximate C(9)–H.

The <sup>1</sup>H NMR spectra of  $\beta$ -NaiR (1), Pd( $\beta$ -NaiR)Cl<sub>2</sub> (2) and Pd( $\beta$ -NaiR–N–Ar)Cl (3–5) have been compared to determine the bonding and stereochemistry. The NMR signals were assigned to individual proton on the basis of chemical shifts, spin–spin interaction and their effect on substitution. The imidazole-H (4 and 5-H) (A-ring) and N-aryl-H (C-ring) appear in the up-field side (Table 1). Effect of substituent X (X–C<sub>6</sub>H<sub>4</sub>–N–) on the signal movement of C-ring, 15-H–19-H appear in accordance with the electromeric effect of the group. It is observed that the electron donating substituent (Me) moves the signal upfield  $\delta$  while electron withdrawing group, –Cl, moves them towards the downfield with reference to Pd( $\beta$ -NaiR–N–C<sub>6</sub>H<sub>5</sub>)Cl (3). N-Aryl ring (ring C) is a better electron donor and may assist efficient intramolecular charge transfer transition. This may be reason for large up-field shifting of ligand protons (8-H–13-H) in the fused compound.

### 2.2. Molecular structures

#### 2.2.1. Pd(β-NaiEt)Cl<sub>2</sub> (**2b**)

The spectral characterization of Pd( $\beta$ -NaiR)Cl<sub>2</sub> has been reported elsewhere [55]. The single crystal X-ray structure of Pd( $\beta$ -NaiEt)Cl<sub>2</sub> (**2b**) is shown in Fig. 1 and bond parameters are given in Table 2.  $\beta$ -NaiEt acts as a bidentate N, N' chelator (N, N(imidazole); N', N(azo)). The Pd–N(azo) (2.073(3)Å) is longer than Pd–N(imidazole) (1.979(3)Å) distance and follows general observation to the reported structures [40,41,55,61–64]. The Pd–Cl distances are also very close to each other (Pd(1)–Cl(1), 2.2692(11); Pd(1)–Cl(2), 2.2798(10)Å). The N=N distance is 1.272(4)Å which is slightly longer than free ligand value (1.250(2)Å) [56,65]. It may be due to  $d\pi$ (Pd)  $\rightarrow \pi^*$ (N=N) charge delocalization through chelated function. The chelate angle

Ta	bl	e	1

<sup>1</sup> H NMR spectral	data of	Pd(β-NaiR-N	-Ar)Cl	(3-5) in	CDCl <sub>3</sub> .
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N(1)–Pd–N(3), 78.20(13)° is comparable with Pd(azoheterocycle)Cl<sub>2</sub> system [40,41,55,61–63]. The pendant naphthyl is twisted by 42.9(6)° from the plane. A 1-D supramolecule is developed by Cl(2)–H(2)–C(2) interaction [d<sub>H–Cl</sub>, 2.76(1)Å; d<sub>C–Cl</sub>, 3.61(1)Å and C–H–Cl, 152.5(1)°].

# 2.2.2. $Pd(\beta - NaiEt - N - C_6H_4 - Cl - p)Cl \cdot C_6H_6$ (**5b**)

A molecular view of Pd( $\beta$ -NaiEt-N-C<sub>6</sub>H<sub>4</sub>-Cl-p)Cl·C<sub>6</sub>H<sub>6</sub> (**5b**) is shown in Fig. 2a and the selected bond parameters are listed in Table 2. The structure shows the C–N coupling of p-Cl–C<sub>6</sub>H<sub>4</sub>–NH<sub>2</sub> at C(6)-H bond of pendant naphthyl ring coordinated  $\beta$ -NaiEt in  $Pd(\beta-NaiEt)Cl_2(2b)$  (Fig. 1). Thus, the ligand is a tridentate N(imidazole) (N), N(azo) (N'), N(amine) (N'') donating agent. The chelate bite angles N(1)-Pd(1)-N(2) and N(2)-Pd(1)-N(4) are 81.16(10)° and 79.49(10)°, respectively. The Pd atom lies within the square plane defined by N<sub>3</sub>Cl donor centers (deviation, <0.01). The pendant *p*-chlorophenyl ring is inclined at an angle of 67.8(4)° with the principal plane. There are three types of Pd(1)-N bonds: Pd(1)–N(imidazole) [Pd(1)–N(4)], 2.015(3)Å]; Pd(1)–N(azo) [Pd(1)–N(2)], 1.946(3) Å] and longest Pd(1)–N(arylamine) [Pd(1)– N(1)], 2.027(2)Å]. The N=N bond length (1.326(3)Å) is 0.05Å elongated than the  $Pd(\beta$ -NaiEt)Cl<sub>2</sub> (Fig. 2a, Table 2). It may be due to better electronic movement from filled  $d\pi(Pd)$  to the lowlying  $\pi^*(N=N)$  of ligand which is enhanced via C–N fusion with electronically labile aromatic-amine. The immediate consequence of back bonding has been reflected in the shortened Pd-N(azo) distance, Pd(1)–N(2)], 1.946(3) Å compare to the Pd–N(imidazole) [Pd(1)–N(4)], 2.015(3)Å] and Pd–N(arylamine) [Pd(1)–N(1)], 2.027(2) Å] distances. The shorter N(azo)–C(naphthyl-B) distance, [N(2)-C(8)] 1.345(4) Å relative to N(azo)-C(imidazole-A), [N(3)-C(imidazole-A), [N(3)-C(imidazole-A)]C(17)] 1.383(4)Å may be due to backbone conjugation in the coordinated tridentate ligand. Both the N(azo)–C(imidazole-A). [N(3)-C(17)] 1.383(4) Å and N(imino)-C(naphthyl-B) distances,

Compound	δ/ppm (J/H	δ/ppm (J/Hz)										
	4-H <sup>a</sup>	5-H <sup>a</sup>	8-H <sup>a</sup>	9-H <sup>a</sup>	10-13-H <sup>c</sup>	15, 19-H <sup>a</sup>	16,18-H	17-H <sup>b</sup>	$N-CH_3^d$	N-CH <sub>2</sub>	(N-CH <sub>2</sub> )CH <sub>3</sub>	$17-CH_3^d$
( <b>3a</b> )	7.13 (7.0)	6.51 (7.0)	7.36 (7.0)	7.55 (7.0)	7.90-8.15	7.65 <sup>a</sup> (8.0)	7.54 <sup>b</sup> (8.0)	7.54 (8.0)	3.74			
( <b>3b</b> )	7.13 (7.0)	6.68 (7.0)	7.33 (7.0)	7.51 (7.0)	7.88-8.10	7.60 <sup>c</sup>	7.55 <sup>b</sup> (8.0)	7.55 (8.0)		4.55 <sup>e</sup> (10.0)	$1.48^{b}(8.0)$	
( <b>3c</b> ) <sup>f</sup>	7.16 (7.0)	6.78 (7.0)	7.33 (7.0)	7.52 (7.0)	7.91-8.18	7.57 <sup>c</sup>	7.42 <sup>b</sup> (8.0)	7.42 (8.0)		5.15 <sup>d</sup>		
( <b>4</b> a)	7.10 (7.0)	6.47 (7.0)	7.35 (7.0)	7.58 (7.0)	7.84-8.12	7.48 <sup>a</sup> (8.0)	$6.96^{a}(8.0)$		3.72			2.32
( <b>4b</b> )	7.05 (7.0)	6.48 (7.0)	7.31 (7.0)	7.50 (7.0)	7.90-8.15	$7.40^{a}(8.0)$	$6.82^{a}(8.0)$			3.97 <sup>e</sup> (10.0)	1.44 <sup>b</sup> (7.0)	2.34
( <b>4c</b> ) <sup>f</sup>	7.05 (7.0)	6.43 (7.0)	7.35 (7.0)	7.52 (7.0)	7.92-8.15	7.46	$6.80^{a}(8.0)$			5.70 <sup>d</sup>		2.27
( <b>5a</b> )	7.12 (7.0)	6.60 (7.0)	7.31 (7.0)	7.50 (7.0)	7.91-8.17	7.48 <sup>a</sup> (8.0)	7.50 <sup>a</sup> (8.0)		3.78			
( <b>5b</b> )	7.12 (7.0)	6.57 (7.0)	7.36 (7.0)	7.55 (7.0)	7.94-8.20	7.64 <sup>a</sup> (8.0)	7.55 <sup>a</sup> (8.0)			4.46 <sup>e</sup> (10.0)	1.54 <sup>b</sup> (8.0)	
( <b>5c</b> ) <sup>f</sup>	7.05 (7.0)	6.60 (7.0)	7.32 (7.0)	7.55 (7.0)	7.90-8.13	7.58 <sup>c</sup>	7.47 <sup>a</sup> (8.0)			5.08 <sup>d</sup>		



Fig. 1. Thermal ellipsoidal plot (30% probability) of Pd(β-NaiEt)Cl<sub>2</sub> (2b).

 Table 2

 Selected bond length (Å) and angles (°) of 2b and 5b.

	X-ray	Theoretical
2b		
Pd(1) - N(1)	2.073(3)	2.112
Pd(1)-N(3)	1.979(3)	2.013
Pd(1)-Cl(1)	2.2692(11)	2.321
Pd(1)-Cl(2)	2.2798(10)	2.332
N(1) - N(2)	1.272(4)	1.289
N(2)-C(1)	1.368(5)	1.362
N(2)-C(4)	1.354(5)	1.387
Cl(1)-Pd(1)-Cl(2)	90.72(4)	90.36
N(1)-Pd(1)-N(3)	78.20(13)	76.89
N(3)-Pd(1)-Cl(1)	91.41(10)	91.42
N(1)-Pd(1)-Cl(1)	169.61(9)	168.3
N(3)-Pd(1)-Cl(2)	177.86(10)	175.8
N(1)-Pd(1)-Cl(2)	99.66(9)	100.2
56		
N(1) - Pd(1)	2027(2)	2.065
N(2) - Pd(1)	1.946(3)	1.980
N(4) - Pd(1)	2.015(3)	2.053
N(2) - N(3)	1.326(3)	1.312
Cl(1)-Pd(1)	2.2973(10)	2.347
C(1) - N(1)	1.428(4)	1.416
C(7)-N(1)	1.330(4)	1.342
C(7) - C(8)	1.435(4)	1.451
C(8)-N(2)	1.345(4)	1.353
C(17)-N(3)	1.383(4)	1.367
C(17)–N(4)	1.327(4)	1.338
C(17)-N(5)	1.349(4)	1.358
C(18)–N(4)	1.374(4)	1.369
C(19)–N(5)	1.377(4)	1.388
C(7)-C(16)	1.464(4)	1.472
C(8)-C(9)	1.425(4)	1.427
C(9)-C(10)	1.341(5)	1.357
C(10)-C(11)	1.437(4)	1.441
C(18)-C(19)	1.350(5)	1.372
C(1)-N(1)-Pd(1)	121.36(19)	121.7
N(2)-Pd(1)-N(1)	81.16(10)	80.48
N(2)-Pd(1)-N(4)	79.49(10)	78.75
N(4)-Pd(1)-N(1)	160.63(11)	159.2
N(2)-Pd(1)-Cl(1)	173.70(7)	176.3
N(4) - Pd(1) - Cl(1)	98.51(8)	97.87
N(1)-Pd(1)-Cl(1)	100.66(8)	102.9

[N(1)–C(7)] 1.330(4) Å are noticeably shorter than that of N(imino)–C(phenyl-C) distance, [N(1)–C(1)] 1.428(4) Å. [Aromatic rings are abbreviated as: imidazole, A; naphthyl, B; phenyl, C]. Important feature is the ring C–C distance in B-ring: C(7)-C(8) has been elongated by 0.05 Å from that of ring-A and ring-C parameters. This concludes that the ring-B is more efficiently involved in conjugation than that of other rings (A and C). This is also supported by shortening of Pd(1)–N(2) distance (1.946(3) Å) with reference to Pd(1)–N(1), 2.027(2) and Pd(1)–N(4), 2.015(3) Å.

The packing view shows the presence of benzene of crystallization. A  $\pi$ - $\pi$  network is developed by Cg(3)–Cg(6), (3.268 Å, symmetry: -x, -y, 1-z), Cg(5)–Cg(5)\* (3.389 Å, symmetry: -x, y, 1/2-z), Cg(6)–Cg(5) (3.172 Å, symmetry: -x, y, 1/2-z) (where Cg(3) = N(4)  $\rightarrow$  C(17)  $\rightarrow$  N(5)  $\rightarrow$  C(19)  $\rightarrow$  C(18); Cg(5) = C(7)  $\rightarrow$  C(8)  $\rightarrow$  C(9)  $\rightarrow$  C(10)  $\rightarrow$  C(11)  $\rightarrow$  C(16); Cg(6) = C(11)  $\rightarrow$  C(12)  $\rightarrow$  C(13)  $\rightarrow$  C(14)  $\rightarrow$  C(15)  $\rightarrow$  C(16)) with C–H– $\pi$  interactions (C(2)–H(2)  $\rightarrow$  Cg(3): H– $\pi$ , 2.649 Å; C– $\pi$ , 3.551 Å, C–H– $\pi$ , 150°, symmetry: -x, y, 1/2 - z) and C(20)–H(20B)  $\rightarrow$  Cg(6): H… $\pi$ , 2.709 Å; C… $\pi$ , 3.491 Å, C–H– $\pi$ , 133°, symmetry: -x, -y, 1 - z) to hold C<sub>6</sub>H<sub>6</sub> in supramolecular cavity (Fig. 2b).

### 2.3. Spectral studies

# 2.3.1. IR spectra

The *cis*-PdCl<sub>2</sub> configuration of Pd( $\beta$ -NaiR)Cl<sub>2</sub> is supported [66] by two v(Pd-Cl) stretches at 330 and 310 cm<sup>-1</sup> while a single transmission at 310–320 cm<sup>-1</sup> is observed in the amine fusion products (**3–5**). The sharp single band at 1320–1345 cm<sup>-1</sup> in Pd( $\beta$ -NaiR–N–Ar)Cl (**3–5**) is referred to v(N=N) which has been shifted to lower frequency by 15–20 cm<sup>-1</sup> from that of Pd( $\beta$ -NaiR)Cl<sub>2</sub>. This supports the coordination of azo-N to Pd<sup>II</sup>. The significant reduction in azo frequency may be due to charge delocalization from N–Ar fragment (ring C) to the azo function intramolecularly [45,46].

### 2.3.2. Electronic spectra and singlet excited state

The absorption bands of Pd( $\beta$ -NaiR)Cl<sub>2</sub> are recorded in acetonitrile solution. The spectral pattern of Pd( $\beta$ -NaiR–N–Ar)Cl (**3–5**) (Fig. 3) exhibits multiple transitions in the visible to NIR region (500–850 nm). The spectral data are collected in Table 3. The electron donating substituent (X = Me) shifts the absorption maxima to longer wavelength region while an electron withdrawing group (X = Cl) shifts the band to shorter region relative to  $-C_6H_5$ (C-ring). The electron donating substituents destabilize the MOs and thus energy of HOMO is increased. The substituent X (at



**Fig. 2a.** Thermal ellipsoidal plot (30% probability) of Pd( $\beta$ -NaiEt-N-C<sub>6</sub>H<sub>4</sub>-Cl-*p*)Cl·C<sub>6</sub>H<sub>6</sub> (**5b**).



Fig. 2b.  $\pi$ - $\pi$  Network (C-H- $\pi$  network is not shown for clarity) holds C<sub>6</sub>H<sub>6</sub> in the cavity (5b).

C-ring) influences more prominently to the LUMOs (*vide infra*, DFT computation).

The photoluminescence properties of the complexes (**3–5**) are studied at room temperature (298 K) in MeCN solution. The ligands ( $\beta$ -NaiR) are photo-inactive. Pd( $\beta$ -NaiR)Cl<sub>2</sub> and amine coupled products Pd( $\beta$ -NaiR–N–Ar)Cl exhibit emission upon excitation at 300–450 nm (Fig. 3, Table 3). The chelation of ligand to the metal ion gives structural rigidity and inhibits vibrational loss [67]. This may be one of the reasons of showing emission property of metal complexes.

Life time data of the complexes are taken in acetonitrile solution when excited at 370 nm (Table 3). The fluorescence decay curve was deconvoluted with respect to the lamp profile. The observed florescence decay fits nicely with bi-exponential decay profile for the ligands and the complexes (Fig. 4) which is supported by goodness-of-fit ( $\chi^2$ ) (Table 3) data in the regression analyses. We have used mean fluorescence life time ( $\tau_f = a_1\tau_1 + a_2\tau_2$  where  $a_1$  and  $a_2$  are relative amplitudes of decay process). Radiative and non-radiative rate constants ( $k_r$  and  $k_{nr}$ ) are calculated and data show usual higher  $k_{nr}$  value than  $k_r$ .

# 2.4. Electrochemistry

The electrochemical properties of Pd( $\beta$ -NaiR–N–Ar)Cl (**3–5**) have been investigated by cyclic voltammetry. The results are given in Table 4 and a representative voltammogram is shown in



**Fig. 3.** Absorption spectra of (a)  $Pd(\beta$ -NaiBz $-N-C_6H_4-Me-p)Cl$  (**4c**) and fluorescence spectra of (c)  $Pd(\beta$ -NaiBz $-N-C_6H_4-Me-p)Cl$  (**4c**) in actionitrile solution at room temperature.

(2)

Fig. 5. Pd( $\beta$ -NaiR)Cl<sub>2</sub> exhibit two quasireversible ( $\Delta E_{\rm p} > 100 \text{ mV}$ ) reduction couples at negative to SCE and have been assigned to the reduction of azo group [30-39,57]. Pd(β-NaiR-N-Ar)Cl (3-5) show three successive redox couples. One redox couple appears at positive side to SCE in the potential range 0.9-1.1 V and is oxidative in nature. This redox response is quasireversible in nature which is supported from  $\Delta E_p \ge 80 \text{ mV} (\Delta E_p = [E_{pa} - E_{pc}], \text{ peak-}$ to-peak separation). One electron nature of the redox couple is supported from  $i_{pa}/i_{pc}$  ( $\approx$ 1.0) and differential pulse voltammetry (DPV). Palladium(II) is hardly oxidisable, so this oxidative response is referred to the ligand oxidation of azonaphthylarylamine (chelating ring 2), Eq. (1). Two redox responses those appear at negative to SCE are reductive in nature. The reduction is regarded as the electron accommodation in the LUMO characterized by azoamine function. There are four successive redox accessible levels in -N=N-C=N- group (Eqs. (2)-(5)). In this series of complexes we observe two negative couples and they may correspond to reductions Eqs. (2) and (3).



$$+ e \qquad (3)$$



# 2.5. DFT calculation and explanation of electronic spectra and redox properties

The full geometry optimization of the representative complexes **2b** and **5b** have been performed using density functional theory. Geometric parameters in the singlet ground-state configuration are summarized in Table 2. Bond lengths and angles are in good agreement with the X-ray values. Pd–N lengths are slightly overestimated (about 0.02–0.04 Å). The same trend is observed for Pd–Cl bonds, where the difference is ~0.05 Å. The N=N bond is longer (0.018 Å) in **2b**, whereas it is shorter (0.014 Å) in **5b** relative to the X-ray values. The formal charge of Pd atom is 0.659; azo-Ns are N(1), -0.198; N(2), -0.241 in **2b** and of Pd, 0.724, azo-Ns are N(1), -0.188; N(2), -0.328 in **5b**. The charge on the chloride ligands is also smaller than -1, and are -0.493, and -0.581 in **2b** and **5b**, respectively. This informs overlapping of ligand orbitals with metal orbitals.

The HOMO of **2b** has 30% Pd( $d\pi$ ) and 51% Cl( $p\pi$ ) contribution with reduced ligand(L) character (19%) whereas in 5b, 06% Pd, 68% chelated ligand (L) and 26% p-Cl-phenyl character (Fig. 6). The LUMO carries 81-92% ligand characteristics with major contribution from azo (N=N) function and energy gap with HOMOs  $(20.9 \times 10^3 \, \mathrm{cm}^{-1})$ 2.59 eV for and are 2b 2.14 eV  $(17.3 \times 10^3 \text{ cm}^{-1})$  for **5b**, respectively (Fig. 7). The HOMO-1 to HOMO-4 are composed of Cl( $p\pi$ ) orbital 50-80%, L 20-35%, and 10–15% Pd( $d\pi$ ) for **2b**. For **5b**, the HOMO–1 and HOMO–4 are dominated by chelated ligand (86-87%), HOMO-2 and HOMO-3 are characterized by  $Cl(p\pi)$  function with minor contribution from (15–25%) Pd( $d\pi$ ). The HOMO–5 in both the complexes has Pd(d $\pi$ ) character (75–76%). Similarly, the LUMO+1 has ~50%  $Pd(d\pi)$  character with reduced contribution from chelating ligand and  $Cl(p\pi)$ .

Pd(β-NaiEt)Cl<sub>2</sub> (**2b**) shows reasonably intense transition at 566 (oscillator strength *f*, 0.270 nm, Table 5) corresponding to HOMO → LUMO, Cl(pπ)/Pd(dπ) → N=N(π<sup>\*</sup>) which appears at shorter wavelength, 501 nm. The most intense transition at

UV-Vis, emission spectral	data and decay ra	tes of Pd( $\beta$ -NaiR)Cl <sub>2</sub>	and Pd(β-NaiR–N–	Ar)Cl in MeCN
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Compound	$\lambda_{\rm max}/{\rm nm}(10^{-3} \varepsilon [{\rm dm}^3 {\rm mol}^{-1} {\rm cm}^{-1}])$	$\lambda_{\rm ex}/{\rm nm}$	$\lambda_{\rm em}/{\rm nm}$	$\phi_{\mathrm{f}}$	$\tau_{\rm f}$	$\chi^2$	$k_{\rm r} \times 10^{-9}$	$k_{\rm nr} \times 10^{-9}$
(S <sup>-1</sup> )					(ns)		(s <sup>-1</sup> )	(S <sup>-1</sup> )
( <b>2</b> a)	273(10.63), 394(13.48), 496(6.24)	273	424	0.003	2.17	0.97	0.001	0.459
( <b>2b</b> )	245(14.81), 390(10.28), 501(5.69)	245	350	0.010	2.01	1.00	0.005	0.493
( <b>2c</b> )	272(16.78), 382(21.34), 395(19.50), 507(6.62)	272	382	0.044	2.12	0.98	0.021	0.451
( <b>3a</b> )	285(20.43), 354(10.54), 409(4.29), 487(1.72), 640(1.13), 700(2.29), 805(1.93), 881(1.39)	354	415	0.036	6.38	1.13	0.006	0.151
( <b>3b</b> )	278(13.92), 356(9.94), 410(3.65),482(1.75), 640(1.47), 700(3.38), 806(2.61), 879(1.92)	356	414	0.027	7.93	1.11	0.003	0.123
( <b>3c</b> )	274(18.84), 364(11.65), 523(2.43), 663(1.20), 728(1.75), 804(1.59), 879(1.15)	364	426	0.037	2.75	1.02	0.013	0.351
( <b>5a</b> )	278(15.21), 355(7.72), 415(2.68), 480(1.29), 643(0.67), 702(1.38), 805(1.72), 880(1.32)	355	412	0.036	7.88	1.21	0.005	0.122
( <b>5b</b> )	270(17.11), 286(15.43), 358(11.48), 415(4.30), 487(2.26), 643(1.37), 703(2.84), 805(3.07), 880(2.33)	358	416	0.021	7.42	1.10	0.003	0.132
( <b>5c</b> )	269(16.19), 295(12.81), 363(10.90), 402(7.17), 503(1.93), 649(0.94), 708(1.76), 805(2.03), 881(1.54)	363	424	0.039	2.91	1.00	0.013	0.331
( <b>4</b> a)	276(13.54), 352(7.46), 413(2.77), 479(1.36), 640(0.89), 699(1.81), 807(1.13), 879(0.84)	352	417	0.034	6.24	1.15	0.005	0.155
( <b>4b</b> )	283(17.52), 357(12.51), 406(5.41), 488(2.23), 638(1.40), 700(3.19), 805(3.00), 879(2.19)	357	414	0.033	7.49	1.12	0.004	0.129
( <b>4c</b> )	278(16.88), 353(8.99), 416(3.09), 476(1.26), 642(0.66), 702(1.85), 806(1.41), 879(0.91)	353	412	0.049	2.63	1.05	0.019	0.361

 $\lambda_{ex}$  - excitation wavelength;  $\lambda_{em}$  - emission wavelength;  $\Phi_{f}$  - fluorescence quantum yield,  $\tau_{f}$  - mean fluorescence life time,  $\chi^{2}$  - goodness of fit,  $k_{r}$  - radiative rate constant,  $k_{nr}$  - non-radiative rate constant.



Fig. 4. Bi-exponential decay profile () and fitting curve (--) in MeCN. Excitation is carried out at 370 nm.

Table 4	
Cyclic voltammetric data <sup>a</sup>	of Pd( $\beta$ -NaiR–N–Ar)Cl ( <b>3–5</b> ).

Compound	Oxidation E/V ( $\Delta E_p/mV$ )	Reduction E/V ( $\Delta E_{\rm p}/{\rm mV}$ )
( <b>3a</b> )	0.90 (180)	-0.44 (170), -0.93 (190)
( <b>3b</b> )	1.00 (200)	-0.50 (100), -1.17 (120)
( <b>3c</b> )	1.07 (170)	-0.51 (115), -1.00 (130)
( <b>4a</b> )	0.92 (180)	-0.49 (140), -1.28 (180)
( <b>4b</b> )	0.98 (170)	-0.55 (150), -1.18 (190)
( <b>4c</b> )	1.02 (180)	-0.45 (140), -1.22 (180)
( <b>5a</b> )	1.02 (180)	-0.41 (120), -1.00 (170)
( <b>5b</b> )	1.07 (160)	-0.36 (150), -1.07 (180)
( <b>5c</b> )	1.10 (180)	-0.35 (140), -0.96 (180)

<sup>a</sup> Solvent MeCN, supporting electrolyte [Bu<sub>4</sub>N](ClO<sub>4</sub>), Pt-disk milli working electrode, Pt-wire auxiliary electrode, reference electrode SCE, at 298 K, *E* = 0.5 (*E*<sub>pa</sub> + *E*<sub>pc</sub>) where *E*<sub>pa</sub> is anodic peak potential and *E*<sub>pc</sub> is cathodic peak potential,  $\Delta E_p = |E_{pa} - E_{pc}|$ ; scan rate – 100 mV/s.

435 nm (*f*, 0.494) corresponding to HOMO-1/HOMO $-2 \rightarrow$  LUMO, Cl(p $\pi$ )/L( $\pi$ )  $\rightarrow$  N=N( $\pi^*$ ) is also higher than experimental band,

390 nm. The introduction of the *p*-substituted anilines in **2** has dramatically changed the composition of MOs; the HOMO, which is principally palladium-localised in **2b**, shows mainly chelating ligand characteristics in **5b**. TD-DFT of Pd(β-NaiEt-N-C<sub>6</sub>H<sub>4</sub>-*p*-Cl)Cl·C<sub>6</sub>H<sub>6</sub> (**5b**) determines intense absorption at 725 nm (*f*, 0.192, Table 5), that signifies ligand centred transition and experimental spectrum shows transitions at 703, 805, and 880 nm. Transitions at 528 nm (*f*, 0.007) and 465 nm (*f*, 0.040) are LMCT and ILCT, respectively, these bands experimentally observed at 487 nm. Similarly transitions at 430 nm (*f*, 0.027) and 413 nm (*f*, 0.047) are the mixture of XLCT and MLCT. Transitions in UV region in both the complexes are all ligand centred transitions.

The complex **5b** shows emission on excitation at 358 nm. The TD-DFT calculation gives two intense transitions in this region: at 272 nm (*f*, 0.215) and 341 nm (*f*, 0.232) corresponding to HOMO–6  $\rightarrow$  LUMO, L( $\pi$ )/L'( $\pi$ )  $\rightarrow$  L( $\pi$ \*) and HOMO  $\rightarrow$  LUMO+2, L( $\pi$ )/L'( $\pi$ )  $\rightarrow$  L( $\pi$ \*), respectively. These are intra-ligand,  $\pi \rightarrow \pi$ \* transitions.



**Fig. 5.** Cyclic voltammogram of Pd(β-NaiMe–N–C<sub>6</sub>H<sub>5</sub>)Cl (**3a**) in MeCN.

# 3. Experimental

### 3.1. Materials

1-Alkyl-2-(naphthyl-β-azo)imidazoles (β-NaiR, 1;  $R = CH_3$  (a), CH<sub>2</sub>–CH<sub>3</sub> (b), CH<sub>2</sub>Ph (c)) were prepared by reported procedure [55]. PdCl<sub>2</sub> was purchased from Arrora Matthey, Kolkata, India. Pd(β-NaiR)Cl<sub>2</sub> (**2**) were prepared by reported procedure [55,60]. Aniline, *p*-toluidine, *p*-chloroaniline were received from Sisco Research Lab (SRL). The purification of acetonitrile and preparation of *n*-tetra butylammonium perchlorate [*n*Bu<sub>4</sub>N][ClO<sub>4</sub>] for electrochemical work were done as before [68]. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. Solvents used for solvatochromic study were purified by reported procedure [68]. Other chemicals and solvents were of reagent grade and were used without further purification. Commercially available SRL silica gel (60–120 mesh) was used for column chromatography.

#### 3.2. Physical measurements

Microanalytical data (C, H, N) were collected on Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra, Lambda 25, Perkin–Elmer L 120-000 A; IR spectra (KBr disk, 4000–200 cm<sup>-1</sup>), FTIR RX 1, Perkin–Elmer; <sup>1</sup>H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer. Emission was examined by LS 55 Perkin–Elmer spectrofluorimeter at room temperature (298 K) in MeCN under degassed condition. Electrochemical measurements were performed using computer-controlled PAR model 270 VERSASTAT electrochemical instruments with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to saturated calomel electrode (SCE) in acetonitrile using [ $nBu_4N$ ][ClO<sub>4</sub>] as supporting electrolyte. The reported potentials are uncorrected for junction potential.

Luminescence property was measured using LS-55 Perkin–Elmer fluorescence spectrophotometer at room temperature (298 K) in CH<sub>3</sub>CN solution by 1 cm path length quartz cell. The fluorescence quantum yield of the complexes was determined using carbazole laser dye as a reference with a known  $\phi_R$  (fluorescence quantum yield of reference) of 0.42 in MeCN [60]. The complex and the reference dye were excited at 270–285 for Pd( $\beta$ -NaiR)Cl<sub>2</sub> and 340–355 nm for Pd( $\beta$ -NaiR-N–C<sub>6</sub>H<sub>4</sub>–X)Cl, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded from 300 to 500 nm for **2** and 360– 650 nm for **3–5**. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yields were calculated according to the following equation:

$$\phi_{\rm S}/\phi_{\rm R} = [A_{\rm S}/A_{\rm R}] \times [({\rm Abs})_{\rm R}/({\rm Abs})_{\rm S}] \times [\eta_{\rm S}^2/\eta_{\rm R}^2]$$

Here  $\phi_{\rm S}$  and  $\phi_{\rm R}$  are the fluorescence quantum yield of the sample and the reference, respectively;  $A_{\rm S}$  and  $A_{\rm R}$  are the area under the fluorescence spectra of the sample and the reference, respectively,  $(Abs)_{\rm S}$  and  $(Abs)_{\rm R}$  are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and  $\eta_{\rm S}$ 

		C C C C	C - S - S - S - S - S - S - S - S - S -
HOMO	HOMO-1	LUMO	LUMO+1
E, -6.16 eV; Pd, 30%;	E, -6.26 eV; Pd, 11%;	E, -3.57 eV; Pd, 06%;	E, -2.41 eV; Pd, 49%;
L, 19%; Cl, 51%	L, 34%; Cl, 55%	L, 92%	L, 18%; Cl, 33%
(a)			

	-		And A
HOMO	HOMO-1	LUMO	LUMO+1
E, -5.16 eV; Pd, 06%;	E, -6.17 eV; Pd, 10%;	E, -3.02 eV; Pd, 07%;	E, -1.92 eV; Pd, 48%;
L, 68%; L <sup>/</sup> , 26%	L, 24%; L <sup>/</sup> , 63%	L, 81%; L <sup>/</sup> , 11%	L, 25%; L <sup>/</sup> , 14%; Cl,
( <b>b</b> )			13%

Fig. 6. Contour plots of the selective frontier molecular orbitals of (a) Pd(β-NaiEt)Cl<sub>2</sub> (2b) and (b) Pd(β-NaiEt-N-C<sub>6</sub>H<sub>4</sub>-Cl-p)Cl (5b).



Fig. 7. Energy level correlation of MOs of Pd(β-NaiEt)Cl<sub>2</sub> (2b) and Pd(β-NaiEt-N-C<sub>6</sub>H<sub>4</sub>-Cl-p)Cl (5b) in gas phase.

 Table 5

 Selected list of excitation for 2b and 5b at TD-DFT/B3LYP/6-31G(d) level calculation.

Excitation energy(eV)	Wavelength $\lambda$ , nm	Osc. strength (f)	Major contribution	Character
2b				
2.191	565.8	0.270	(67%)HOMO → LUMO	$Cl(p\pi)/Pd(d\pi) \rightarrow N=N(\pi^*)$ , (XLCT, MLCT)
2.847	435.3	0.494	$(38\%)$ HOMO $-2 \rightarrow$ LUMO	$Cl(p\pi)/L(\pi) \rightarrow N=N(\pi^*)$ , (XLCT, ILCT)
			$(24\%)$ HOMO $-1 \rightarrow$ LUMO	$Cl(p\pi)/L(\pi) \rightarrow N=N(\pi^*)$ , (XLCT, ILCT)
3.247	381.7	0.095	$(64\%)$ HOMO $-5 \rightarrow$ LUMO	$Pd(d\pi) \rightarrow N=N(\pi^*)$ , MLCT
4.963	249.7	0.152	$(53\%)$ HOMO $-15 \rightarrow$ LUMO	$L(\pi) \rightarrow L(\pi^*)$ , ILCT
5.006	247.6	0.222	$(25\%)$ HOMO $-16 \rightarrow$ LUMO	$L(\pi) \rightarrow L(\pi^*)$ , ILCT
			$(19\%)$ HOMO $-9 \rightarrow$ LUMO+1	$Cl(p\pi)/L(\pi) \rightarrow Pd(d\pi)$ , (LMCT, XMCT)
			$(17\%)$ HOMO $-15 \rightarrow$ LUMO	$L(\pi) \rightarrow L(\pi^*)$ , ILCT
5b				
1.711	724.8	0.192	$(72\%)$ HOMO $\rightarrow$ LUMO	$L(\pi)/L'(\pi) \rightarrow L(\pi^*)$ , ILCT
2.346	528.4	0.007	$(90\%)$ HOMO $\rightarrow$ LUMO+1	$L(\pi)/L'(\pi) \rightarrow Pd(d\pi)$ , LMCT
2.666	465.0	0.040	$(64\%)$ HOMO $-1 \rightarrow$ LUMO	$L'(\pi)/L(\pi) \rightarrow L(\pi^*)$ , ILCT
2.885	429.8	0.027	$(82\%)$ HOMO $-2 \rightarrow$ LUMO	$Cl(p\pi)/Pd(d\pi) \rightarrow L(\pi^*)$ , (XLCT, MLCT)
2.999	413.3	0.047	$(56\%)$ HOMO $-3 \rightarrow$ LUMO	$Cl(p\pi) \rightarrow L(\pi^*)$ , XLCT
3.328	372.5	0.215	$(54\%)$ HOMO $-6 \rightarrow$ LUMO	$L(\pi)/L'(\pi)/Pd(d\pi) \rightarrow L(\pi^*)$ , (ILCT, MLCT)
3.631	341.4	0.232	$(59\%)$ HOMO $\rightarrow$ LUMO+2	$L(\pi)/L'(\pi) \rightarrow L(\pi^*)$ , ILCT
4.352	284.9	0.176	(52%)HOMO $\rightarrow$ LUMO+3	$L(\pi)/L'(\pi) \rightarrow L(\pi^*)$ , ILCT

and  $\eta_{\rm R}$  are the values of refractive index for the respective solvent used for the sample and the reference. Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH. UK. The instrument uses a picosecond diode laser (NanoLed-07, 408 nm) as the excitation source and works on the principle of time-correlated single photon counting [67,69,70]. The instrument responses function is ~230 ps at FWHM. To eliminate depolarization effects on the fluorescence decays, measurements were done with magic angle geometry (54.7°) for the excitation and emission polarizers. The observed decays palladium(II) complexes fitted well with a bi-exponential function as in Eq. (7), where  $\tau$ 's are the fluorescence lifetime and  $\alpha$  is the pre-exponential factor. For the fits, the reduced  $\chi^2$  values were within 0.9–1.3 and the distribution of the weighted residuals were random among the data channels.  $\tau_{\rm f}$  is mean fluorescence life time (meaning of the symbols are usual) [67].

$$I(t) = [a_1 \exp(-t/\tau_1) - a_2 \exp(-t/\tau_2)]$$
(6)

$$\tau_{\rm f} = a_1 \tau_1 + a_2 \tau_2 \tag{7}$$

3.3. Preparation of chloro[1-methyl-2-{(7-imidophenyl)naphthyl- $\beta$ -azo}imidazole-N,N',N'']palladium(II), Pd( $\beta$ -NaiMe-N-C<sub>6</sub>H<sub>5</sub>)Cl, (**3a**)

To an acetonitrile solution (20 ml) of Pd( $\beta$ -NaiMe)Cl<sub>2</sub> (0.08 mg, 0.20 mmol) was added slowly aniline (0.04 mg, 0.43 mmol) in the same solvent (10 ml). And 0.2 ml triethylamine was added to this solution. The reaction mixture was stirred and refluxed for 12 h. The colour of the solution changed gradually from orange-red to reddish-brown. The solution was evaporated in air, and the residue was washed thoroughly first with water  $(2 \times 5 \text{ ml})$  and then with 50% aqueous-ethanol  $(3 \times 5 \text{ ml})$ . The residue was dissolved in dichloromethane (10 ml) and the solution was chromatographed over silica gel column (60-120 mesh). A reddish-brown band was eluted by MeCN. The eluted solution on evaporation in vacuo gave pure compound. Reddish-brown compound was isolated in 52% yield. This product is the coupled product, Pd(β-NaiMe-N- $C_6H_5$ )Cl, (**3a**). A red band was also eluted by acetonitrile and had remained uncharacterized till date. Anal. Calc. for C20H16N5ClPd (3a): C, 51.34; H, 3.42; N, 14.97. Found: C, 51.29; H, 3.32; N,

14.88%. M.p. 280–282 °C. IR data (cm<sup>-1</sup>) v(Pd–Cl) 310, v(N=N) 1320, v(C=N) 1564 cm<sup>-1</sup>. Anal. Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>5</sub>ClPd (**3b**): C, 52.34; H, 3.74; N, 14.54. Found: C, 52.31; H, 3.72; N, 14.52%. M.p. 240–243 °C, yield 50%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 325, v(N=N) 1335, v(C=N) 1552 cm<sup>-1</sup>. Anal. Calc. for C<sub>26</sub>H<sub>20</sub>N<sub>5</sub>ClPd (**3c**): C, 57.41; H, 3.68; N, 12.88. Found: C, 57.43; H, 3.64; N, 12.81%. Compound (**3c**), M.p. 285–290 °C, yield 55%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 311, v(N=N) 1325, v(C=N) 1555 cm<sup>-1</sup>. Anal. Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>5</sub>ClPd (4a): C, 52.34; H, 3.74; N, 14.54. Found: C, 52.30; H, 3.71; N, 14.51%. M.p. 281–284 °C, yield 48%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 315, v(N=N) 1332, v(C=N) 1545 cm<sup>-1</sup>. Anal. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>5</sub>ClPd (4b): C, 53.28; H, 4.04; N, 14.13. Found: C, 53.25; H, 4.01; N, 14.11%. M.p. 244–248 °C, yield 51%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 310, v(N=N) 1343, v(C=N) 1560 cm<sup>-1</sup>. Anal. Calc. for C<sub>27</sub>H<sub>22</sub>N<sub>5</sub>ClPd (4c): C, 58.12; H, 3.95; N, 12.56. Found: C, 58.09; H, 3.91; N, 12.49%. M.p. 252–255 °C, yield 50%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 325, v(N=N) 1344, v(C=N) 1562 cm<sup>-1</sup>. Anal. Calc. for C<sub>20</sub>H<sub>15</sub>N<sub>5</sub>Cl<sub>2</sub>Pd (5a): C, 47.81; H, 2.99; N, 13.94. Found: C, 47.82; H, 2.91; N, 13.81%. M.p. 260–262 °C, yield 46%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 333, v(N=N) 1351, v(C=N) 1572 cm<sup>-1</sup>. Anal. Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>5</sub>Cl<sub>2</sub>Pd (5b): C, 48.84; H, 3.29; N, 13.57. Found: C, 48.81; H, 3.22; N, 13.49%. M.p. 251–255 °C, yield 49%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 311, v(N=N) 1342, v(C=N) 1550 cm<sup>-1</sup>. Anal. Calc. for C<sub>26</sub>H<sub>19</sub>N<sub>5</sub>Cl<sub>2</sub>Pd (5c): C, 53.98; H, 3.29; N, 12.11. Found: C, 53.85; H, 3.21; N, 12.01%. M.p. 278–280 °C, yield 47%, IR data (cm<sup>-1</sup>) v(Pd–Cl) 313, *v*(N=N) 1337, *v*(C=N) 1551 cm<sup>-1</sup>.

#### 3.4. X-ray structure determination

The X-ray quality single crystals of  $Pd(\beta-NaiEt)Cl_2$  (**2b**) and  $Pd(\beta-NaiEt-N-C_6H_4-Cl-p)Cl \cdot C_6H_6$  (**5b**) were grown by slow diffusion of benzene into dichloromethane solution of the complex at 298 K. A summary of the crystallographic data and structure refinement parameters are given in Table 6. Data were collected with the Bruker SMART CCD using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Unit cell parameters were determined from least-squares refinement of setting angles with  $2\theta$  in the range  $3.52 \le 2\theta \le 52.04$  for **2b** and  $3.26-52.02^{\circ}$  for **5b**. Data were corrected for  $L_p$  effects and for linear decay. Semi-empirical absorption corrections based on multi-scans were applied. The structure was solved by direct method using SHELXL-97 [71] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using riding model. All calculations were carried out using shelxl-97 [72], ORTEP-32 [73], PLATON-99 [74] programs.

#### 3.5. Computational methods

Full geometry optimizations were carried out using the density functional theory method at the (R)B3LYP [75]. All elements except palladium were assigned the 6-31G(d) basis set. The SDD basis set with effective core potential was employed for the palladium atom [76,77]. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigen values. All calculations were performed with GAUSSIAN03 program package [78]. Vertical electronic excitations based on B3LYP optimized geometries were computed using the time-dependent density functional theory (TD-DFT) formalism [79-81] in acetonitrile using conductor-like polarizable continuum model (CPCM) [82-84]. GaussSum [85] was used to calculate the fractional contributions of various groups to each molecular orbital.

#### Table 6

Crystallographic data of  $Pd(\beta-NaiEt)Cl_2$  (2b) and  $Pd(\beta-NaiEt-N-C_6H_4-Cl-p)Cl\cdot C_6H_6$ (5b).

	Pd(β-NaiEt)Cl <sub>2</sub> ( <b>2b</b> )	$Pd(\beta-NaiEt-N-C_6H_4-Cl-p)Cl\cdot C_6H_6$ (5b)
Chemical formula Formula weight	C <sub>15</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>4</sub> Pd 427.60	C <sub>21</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>5</sub> Pd, 0.5(C <sub>6</sub> H <sub>6</sub> ) 555.75
Crystal colour	Brown	Brown
Crystal size (mm <sup>3</sup> )	$0.42 \times 0.32 \times 0.18$	$0.42 \times 0.24 \times 0.22$
Crystal system	Triclinic	Orthorhombic
Space group	ΡĪ	Pbcn
a (Å)	7.2498(5)	15.8106(8)
h (Å)	10.0632(7)	20.4401(11)
c (Å)	12.4475(9)	14.0167(8)
α (°)	68.4470(10)	90.00
β (°)	83.6770(10)	90.00
γ(°)	73.7870(10)	90.00
$V(\dot{A}^3)$	811.01(10)	4529.8(4)
Z	2	8
T (K)	293(2)	298(2)
$\lambda$ (Å)	0.71073	0.71073
2θ Range (°)	$3.52 \leqslant 2\theta \leqslant 52.04$	$3.26 \leqslant 2\theta \leqslant 52.02$
hkl Range	$-8\leqslant h\leqslant 8$	$-19 \leqslant h \leqslant 16$
	$-12 \leqslant k \leqslant 12$	$-19 \leqslant k \leqslant 25$
	$-15 \leqslant l \leqslant 15$	$-17 \leq l \leq 17$
$ ho_{\rm calc}  ({ m g}  { m cm}^{-3})$	1.751	1.630
μ (Mo Kα) (mm <sup>-1</sup> )	1.474	1.078
Reflection collected	8510	24310
Unique reflections	3174	3369
R <sup>a</sup>	0.0386	0.0349
wR <sup>b</sup>	0.0869	0.0847
Goodness -of-fit	1.035	1.036

<sup>a</sup>  $R_1 = \Sigma |F_o - F_c| / \Sigma F_o.$ <sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2) / \Sigma w F_o^4]^{1/2}, w = 1/[\sigma^2(F^2) + (0.0433P)^2 + 0.0000P] \text{ for } (2b);$  $w = 1/[\sigma^2(F^2) + (0.0485P)^2 + 1.4923P]$  for (**5b**).

# 4. Conclusion

Palladium assisted C–N coupling reaction of arylamine (ArNH<sub>2</sub>) with coordinated  $\beta$ -NaiR (1-alkyl-2-(naphthyl- $\beta$ -azo)imidazoles)) in  $Pd(\beta-NaiR)Cl_2$  is examined in this work. The coupled products have been characterized by spectroscopic and electrochemical studies. The complexes are potentially fluorescent in solution and the excited state decay follows bi-exponential decay process. The absorption and emission processes are dependent on polarity of the solvent. The electronic and redox properties are explained by theoretical calculation of optimized geometry of the ligand and complexes.

#### Acknowledgments

Financial support from the University Grants Commission, New Delhi and CAS-UGC (New Delhi) sanctioned to the Department of Chemistry, Jadavpur University are gratefully acknowledged.

### **Appendix A. Supplementary material**

DFT calculated orbital energies, orbital compositions (Table S4) and selected list of excited energies (Table S5) are given as Supplementary data.

CCDC 723282 and 723283 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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.ica.2009.12.050.

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