

Coupling of arylamine with coordinated naphthylazoimidazole in palladium(II) complexes. Spectroscopic and electrochemical studies

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Abstract : 1-Alkyl-2-(naphthyl- α -azo)imidazoles (α -NaiR) are bidentate N,N' -chelator and form $\text{Pd}(\alpha\text{-NaiR})\text{Cl}_2$ complexes. The reaction of $\text{Pd}(\alpha\text{-NaiR})\text{Cl}_2$ (2) with ArNH_2 in MeCN has synthesized C-N coupled product, $\text{Pd}(\alpha\text{-NaiR-N-Ar})\text{Cl}$ (3-5). The stereochemistry and the bonding are described by ^1H NMR data. The solution electronic spectra of the amine coupled products exhibit multiple transition within 600–850 nm which are absent in the precursor complex, $\text{Pd}(\alpha\text{-NaiR})\text{Cl}_2$. Cyclic voltammogram shows azo reductions exhibit four successive redox couples, one of them (positive to SCE) is oxidative in nature and other (negative to SCE) are ligand reductions.

Keywords : Pd-naphthylazoimidazoles, C-N coupling reaction, LLCT, electrochemistry.

The π -deficient nitrogenous molecules are efficient starting system to design varieties of organic, inorganic and hybrid systems of important material properties. The efficacy is primarily dependent on the functional group. For example, polypyridines having diimine function, $-\text{N}=\text{C}-\text{C}=\text{N}-$, are most studied molecules and have inspired to design new molecules. Azoimine, $-\text{N}=\text{N}-\text{C}=\text{N}-$, isoelectronic to diimine function in arylazoheterocycle draws immense attention in the present day chemical research¹. These classes of molecules are π -deficient and can stabilize low valent metal redox state and induce MLCT transitions^{2,3}. Ring size, number of heteroatoms, substituents in the heterocyclic ring and side arm to azo function can significantly modify the physical and chemical properties of the complexes; much greater effect can be observed from the change in heterocyclic part. Significant changes have been received by replacing six-membered to five-membered N-heterocycle. Six-membered N-heterocycles being π -deficient are excellent π -acceptors while five-membered N-heterocycles are much poorer π -acceptor and hence better π -donor⁴.

The electronic property of the coordinated arylazoheterocycles in the metal complex shows substantial different and even sometimes just unpredictable to that of free ligand data. For example, free ligands do not show nucleophilic substitution reaction while metallated-arylazoheterocycles show hydroxylation⁵, thiolation⁶, aryl-amination⁷ reactions. We have been designing different series of azoheterocycles such as azoimidazoles⁸,

naphthylazoimidazoles⁹, pyridylazoimidazoles¹⁰, azopyridines¹¹, and azopyrimidines¹², azoantipyrine¹³. Pyridine- and pyrimidine-azo metallated complexes exhibit aryl-amination reaction at the pendant aryl ring^{7,12}. No such reaction has been studied with aryl or naphthylazoimidazole complexes. In this work we will report hitherto unknown amine fusion reaction of palladium(II)-naphthylazoimidazole complexes. The complexes have been characterized by the spectral and electrochemical data.

Experimental

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; IR spectra (KBr disk, 4000–450 cm^{-1}), FTIR RX 1, Perkin-Elmer; ^1H 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 $[\text{nBu}_4\text{N}][\text{ClO}_4]$ as supporting electrolyte. The reported potentials are uncorrected for junction potential.

Materials :

1-Alkyl-2-(naphthyl- α -azo)imidazoles (α -NaiR, **1**; R = CH₃ (**a**), CH₂CH₃ (**b**), CH₂Ph (**c**)) were prepared by reported procedure⁹. PdCl₂ was purchased from Arrora Matthey, Kolkata, India. Pd(α -NaiR)Cl₂ (**2**) were prepared following reported procedure from our laboratory¹⁴. Aniline, *p*-toluidine, *p*-chloroaniline were received from Sisco Research Lab (SRL). The purification of acetonitrile and preparation of *n*-tetra butylammonium perchlorate [nBu₄N][ClO₄] for electrochemical work were done as before⁹. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All 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.

Preparation of complexes :

*Chloro[1-methyl-2-{(7-imidophenyl)naphthyl- α -azo}imidazole-N,N',N'']palladium(II), Pd(α -NaiMe-N-C₆H₅)Cl (**3a**) :*

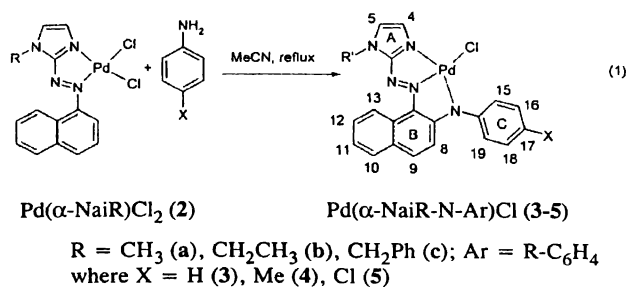
To an acetonitrile solution (20 ml) of Pd(α -NaiMe)Cl₂ (82 mg, 0.20 mmol) was added slowly aniline (40 mg, 0.43 mmol) in the same solvent (10 ml). The reaction mixture was stirred and refluxed for 12 h. The colour of the solution changed gradually from orange-red to reddish-brown. The solution was evaporated in air, and the residue was washed thoroughly first with water (2 \times 5 ml) and then with 50% aqueous-ethanol (3 \times 5 ml). The residue was dissolved in dichloromethane (10 ml) and the solution was chromatographed over silica gel column (60–120 mesh). As greenish-brown band was eluted by MeCN. The eluted solution on evaporation in vacuo gave pure compound. Orange-brown compound was isolated in 45% yield. This product is the coupled product, Pd(α -NaiMe-N-C₆H₅)Cl, (**3a**). A red band was also eluted by acetonitrile and had remained uncharacterized till date.

All other complexes were prepared similarly; yield 40–55%. Calcd. for C₂₀H₁₆N₅ClPd (**3a**) : C, 51.34; H, 3.42; N, 14.97. Found : C, 51.18; H, 3.35; N, 14.83%. Calcd. for C₂₁H₁₈N₅ClPd (**3b**) : C, 52.34; H, 3.74; N, 14.54. Found : C, 52.23; H, 3.67; N, 14.48%. Calcd. for C₂₆H₂₀N₅ClPd (**3c**) : C, 57.41; H, 3.68; N, 12.88. Found : C, 57.48; H, 3.62; N, 12.96%. Calcd. for C₂₁H₁₈N₅ClPd (**4a**) : C, 52.34; H, 3.74; N, 14.54. Found : C, 52.22; H, 3.65; N, 14.46%. Calcd. for C₂₂H₂₀N₅ClPd (**4b**) : C, 53.28; H, 4.04; N, 14.13. Found : C, 53.33; H, 4.07; N, 14.18%. Calcd. for C₂₇H₂₂N₅ClPd (**4c**) : C, 58.12; H, 3.95; N, 12.56. Found : C, 58.05; H, 3.90; N, 12.47%. Calcd. for C₂₀H₁₅N₅Cl₂Pd (**5a**) : C, 47.81; H, 2.99; N, 13.94. Found : C, 47.92; H, 3.06; N,

13.83%. Calcd. for C₂₁H₁₇N₅Cl₂Pd (**5b**) : C, 48.84; H, 3.29; N, 13.57. Found : C, 48.75; H, 3.22; N, 13.48%. Calcd. for C₂₆H₁₉N₅Cl₂Pd (**5c**) : C, 53.98; H, 3.29; N, 12.11. Found : C, 53.80; H, 3.42; N, 12.00%.

Results and discussion*Synthesis and formulation :*

The reaction between Pd(α -NaiR)Cl₂ and ArNH₂ in 1 : 1 ratio in MeCN solution under stirring and refluxing for 12 h has yielded brown product (eq. (1)). This has been identified as amine coupled product abbreviated Pd(α -NaiR-N-Ar)Cl (**3-5**) [where, R = CH₃ (**a**), CH₂CH₃ (**b**), CH₂Ph (**c**); Ar = R-C₆H₄ where R = H (**3**), Me (**4**), Cl (**5**)]. Red product is isolated in low yield which has remained uncharacterized. The arylation takes place by the C-H activation of *ortho* C(7)-H bond to the azo function^{7,12} in the pendant naphthyl ring (B-ring) of α -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 Experimental section).

*Spectra and bonding :*

The presence of two ν (Pd-Cl) stretches at 330 and 310 cm⁻¹ in Pd(α -NaiR)Cl₂ is in agreement with *cis*-PdCl₂ configuration¹² while a single transmission at 310–320 cm⁻¹ is observed in the amine coupled products (**3-5**). The sharp single band at 1320–1345 cm⁻¹ in Pd(α -NaiR-N-Ar)Cl (**3-5**) is referred to ν (N=N) which has been shifted to lower frequency by 25–30 cm⁻¹ compared to free ligand data and by 15–20 cm⁻¹ from that of Pd(α -NaiR)Cl₂. This supports the coordination of azo-N to Pd^{II}. The significant reduction in azo frequency may be due to charge delocalization from N-Ar fragment (ring C) to the azo function intramolecularly^{7,12}.

In chloroform solution of Pd(α -NaiR)Cl₂ the absorption bands are observed at 300–530 nm. On comparison with the absorption spectra of the free ligand we conclude that transitions < 400 nm are intraligand charge transfer transitions⁹ and transition at ~525 nm is assigned to

MLCT $d\pi$ (Pd) $\rightarrow \pi^*$ (ligand) transition. The spectral pattern have changed abruptly in Pd(α -NaiR-N-Ar)Cl (**3-5**) and exhibit multiple transitions in the visible to NIR region (500–850 nm). The spectral data are collected in Table 1 and a representative figure is shown in Fig. 1. The spectral transitions are assigned to HOMO \rightarrow LUMO transition and is supported in similar cases by EHMO calculation⁷. The HOMOs have major share from the arylamine fragment and the LOMOs are dominated by azoheterocyclic motif of the tridentate ligand. These transitions are influenced by the substituent R (at C-ring of naphthylazoimidazole) and R (at A-ring of imidazole). The electron donating substituents destabilize the MOs

and thus energy of HOMO is increased. The substituent R (at C-ring) influences more prominently to the LUMOs. This is expected in view of the electronic property of *p*-Me and *p*-Cl groups.

The photoluminescence properties of the complexes (**3-5**) were studied at room temperature (298 K) in MeCN solution (Fig. 1). The ligands (α -NaiR) are photo-inactive. The precursor, Pd(α -NaiR)Cl₂ and amine coupled products Pd(α -NaiR-N-Ar)Cl exhibit emission upon excitation at shorter wavelength 300–450 nm (Table 1). The absorption 300–450 nm are assigned to $n\text{-}\pi^*/\pi\text{-}\pi^*$ transitions. Thus, the emission observed in the complexes is tentatively assigned to the intraligand fluorescence. Interestingly the

Table 1. UV-Vis and emission spectral data of Pd(α -NaiR)Cl₂ and Pd(α -NaiR-N-Ar)Cl in MeCN

Complexes	$\lambda_{\text{max}}/\text{nm}$ ($10^{-3} \epsilon$ [$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$])	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$
Pd(α -NaiMe)Cl ₂ (2a)	352 (9.76), 405 (10.68), 529 (4.11)	352 405	433 496
Pd(α -NaiEt)Cl ₂ (2b)	346 (9.79), 406 (12.06), 525 (4.27)	346 406	441 451
Pd(α -NaiBz)Cl ₂ (2c)	271 (10.37), 346 (8.05), 407 (9.43), 523 (3.69)	346 407	440 460
Pd(α -NaiMe-N-C ₆ H ₅)Cl (3a)	334 (3.88), 397 (5.33), 415 (5.07), 450 (2.89), 650 (0.37), 705 (0.31), 769 (0.25), 850 (0.16)	397 415 450	444 495 515
Pd(α -NaiEt-N-C ₆ H ₅)Cl (3b)	272 (14.53), 296 (12.51), 351 (11.82), 418 (8.39), 451 (5.51), 651 (1.63), 711 (2.16), 777 (1.86), 851 (1.21)	351 418 451	438 476 516
Pd(α -NaiBz-N-C ₆ H ₅)Cl (3c)	295 (12.22), 342 (8.74), 417 (5.18), 663 (1.52), 774 (1.30), 850 (0.88)	342	417
Pd(α -NaiMe-N-C ₆ H ₄ -Me- <i>p</i>)Cl (4a)	302 (12.26), 347 (10.13), 401 (8.49), 654 (1.34), 785 (0.88), 853 (0.48)	347 401	434 483
Pd(α -NaiEt-N-C ₆ H ₄ -Me- <i>p</i>)Cl (4b)	299 (5.91), 345 (4.35), 410 (3.18), 613 (1.37), 651 (1.31), 778 (1.14), 850 (0.79)	345	438 435
Pd(α -NaiBz-N-C ₆ H ₄ -Me- <i>p</i>)Cl (4c)	275 (11.11), 302 (10.03), 404 (8.42), 417 (8.00), 551 (1.32), 651 (0.99), 778 (0.59), 854 (0.40)	302	443
Pd(α -NaiMe-N-C ₆ H ₄ -Cl- <i>p</i>)Cl (5a)	303 (9.01), 403 (7.94), 535 (1.22), 646 (0.83), 765 (0.36), 845 (0.26)	403	453 489
Pd(α -NaiEt-N-C ₆ H ₄ -Cl- <i>p</i>)Cl (5b)	271 (11.69), 303 (9.56), 346 (7.15), 402 (8.82), 627 (1.26), 774 (0.46), 853 (0.32)	346 402	440 482
Pd(α -NaiBz-N-C ₆ H ₄ -Cl- <i>p</i>)Cl (5c)	268 (17.73), 304 (13.65), 347 (8.68), 405 (7.77), 554 (1.29), 647 (1.51), 779 (0.93), 851 (0.65)	347 405	438 470

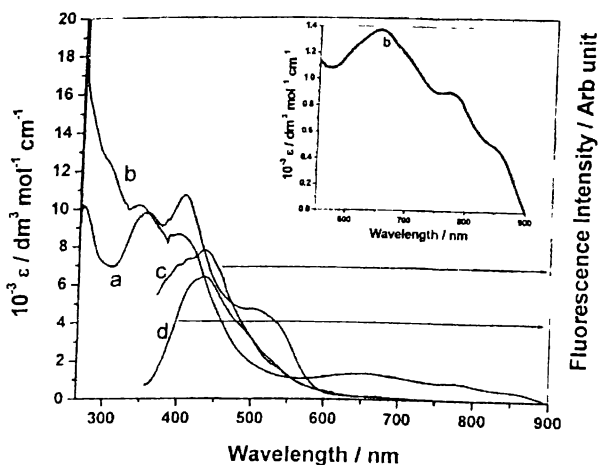


Fig. 1. Absorption spectra of (a) Pd(α -NaiMe)Cl₂, (b) Pd(α -NaiMe-N-C₆H₄-Me-*p*)Cl and fluorescence spectra of (c) Pd(α -NaiMe)Cl₂, (d) Pd(α -NaiMe-N-C₆H₄-Me-*p*)Cl in acetonitrile solution at room temperature.

complexes show multiple emissions in the range 400–525 nm. Longer wavelength ($\lambda > 500$ nm) excitation do not show emission which indirectly supports Khasa's rule¹⁵. In absence of metal ions fluorescence of ligand is probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to presence of a lone pair of

nitrogen atoms. Such a PET process is prevented by the complexation of ligand with metal ions¹⁵; thus fluorescence intensity may be enhanced by the coordination to metal ion.

The ¹H NMR spectra of α -NaiR, Pd(α -NaiR)Cl₂ and Pd(α -NaiR-N-Ar)Cl (3-5) have been compared to determine the bonding and stereochemistry. The signals were assigned on the basis of chemical shifts, spin-spin interaction and their effect on substitution. The spectral data are given in Table 2. The compounds Pd(α -NaiR-N-Ar)Cl show complex NMR spectra. A representative spectrum is shown in Fig. 2. The imidazole-H (4 and 5-H) (A-ring) and N-aryl (C-ring) portion appear in the up-field side. Effect of substituent R (R-C₆H₄-N-) on the signal movement of C-ring, 15-H-19-H are in accordance with the electronic effect of the group¹⁶. It is observed that the electron donating substituent (Me) move the signals upfield δ while electron withdrawing group, -Cl, moves them towards the downfield with reference to Pd(α -NaiR-N-C₆H₅)Cl (3). N-Aryl ring (ring C) is σ -donor and may support intramolecular charge transfer transition. This may be reason for large up-field shifting of naphthyl-azoimidazole protons (8-H-13-H) in the fused compound.

Electrochemistry :

The electrochemical properties of Pd(α -NaiR-N-Ar)Cl

Table 2. ¹H NMR spectral data of Pd(α -NaiR-N-Ar)Cl (3-5) in CDCl₃

Compd.	δ /ppm (J/Hz)											
	4-H ^a	5-H ^b	8,9-H ^a	10-12-H ^c	13-H ^a	15,19-H ^a	16,18-H	17-H ^b	N-CH ₃ ^d	N-CH ₂	(N-CH ₂)CH ₃	17-CH ₃ ^d
(3a)	7.18 (7.0)	6.47 (7.0)	7.37 (7.0)	7.69	7.92 (7.0)	7.65 (8.0)	7.54 ^b (8.0)	7.54 (8.0)	3.74			
(3b)	7.13 (7.0)	6.68 (7.0)	7.34 (7.0)	7.60	7.84 (7.0)	7.60 ^c (8.0)	7.55 ^b (8.0)	7.55 ^b (8.0)		4.55 ^c (10.0)	1.48 ^b (8.0)	
(3c) ^f	7.17 (7.0)	6.78 (7.0)	7.34 (7.0)	7.57	7.90 (7.0)	7.57 ^c (8.0)	7.42 ^b (8.0)	7.42 ^b (8.0)		5.15 ^d		
(4a)	7.09 (7.0)	6.47 (7.0)	7.37 (7.0)	7.50	7.94 (7.0)	7.48 (8.0)	6.96 ^b (8.0)		3.72			2.32
(4b)	7.04 (7.0)	6.48 (7.0)	7.30 (7.0)	7.43	7.79 (7.0)	7.40 (8.0)	6.82 ^b (8.0)			3.97 (10.0)	1.44 (7.0)	2.34
(4c) ^f	7.04 (7.0)	6.43 (7.0)	7.35 (7.0)	7.53	7.95 (7.0)	7.46 (8.0)	6.80 ^b (8.0)			5.70 ^d		2.27
(5a)	7.11 (7.0)	6.60 (7.0)	7.30 (7.0)	7.57	7.89 (7.0)	7.48 (8.0)	7.50 ^b (8.0)		4.03			
(5b)	7.11 (7.0)	6.57 (7.0)	7.35 (7.0)	7.55	8.06 (7.0)	7.64 ^c (8.0)	7.55 ^b (8.0)			4.46 ^e (10.0)	1.54 ^b (8.0)	
(5c) ^f	7.06 (7.0)	6.60 (7.0)	7.33 (7.0)	7.54	7.92 (7.0)	7.58 ^c (8.0)	7.47 ^b (8.0)			5.08 ^d		

^aDoublet, ^bTriplet, ^cMultiplet, ^dSinglet, ^equartet; ^f δ (Ph) : 7.35–7.50 ppm.

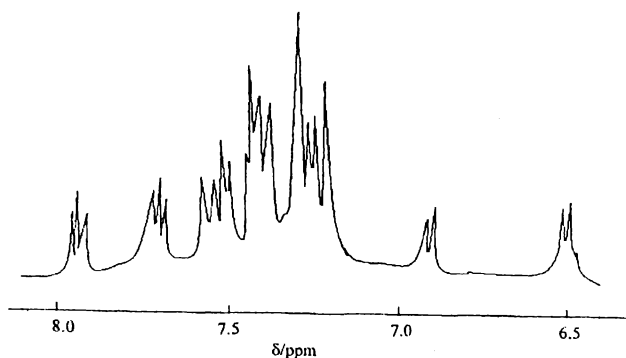


Fig. 2. ^1H NMR spectrum (aromatic region only) of $\text{Pd}(\alpha\text{-NaiMe-N-C}_6\text{H}_5)\text{Cl}$ in CDCl_3 .

(3-5) have been investigated by cyclic voltammetry. The results are given in Table 3 and a representative voltammogram is shown in Fig. 3. $\text{Pd}(\alpha\text{-NaiR}')\text{Cl}_2$ exhibit two quasireversible ($\Delta E_p > 100$ mV) reduction couples at negative to SCE and have assigned to reduction of azo group^{7,12}. $\text{Pd}(\alpha\text{-NaiR-N-Ar})\text{Cl}$ (3-5) show three successive redox couples. One redox couple appears at positive side to SCE in the potential range 0.8–1 V and oxidative in nature. This redox response is quasireversible in nature which is supported from $\Delta E_p \geq 80$ mV ($\Delta E_p = [E_{pa} - E_{pc}]$, peak-to-peak separation). One electron nature of the redox couple is supported from i_{pa}/i_{pc} (≈ 1.0) and differential pulse voltammetry (DPV). Palladium(II) is hardly oxidisable so this oxidative response is referred to the ligand oxidation at the easily oxidisable azonaphthylarylamine chelated center (chelating ring 2), eq. (2).

Three redox responses those appear at negative to SCE

Table 3. Cyclic voltammetric data^a of $\text{Pd}(\alpha\text{-NaiR-N-Ar})\text{Cl}$ (3-5)

Compd.	Oxidation E/V ($\Delta E_p/\text{mV}$)	Reduction $-E/V$ ($\Delta E_p/\text{mV}$)
(3a)	0.95 (180)	-0.44 (140), -1.00 (190), -1.40 ^b
(3b)	0.95 (170)	-0.40 (100), -0.94 (120), -1.34 ^b
(3c)	0.98 (170)	-0.42 (115), -0.80 (130), -1.30 ^b
(4a)	0.85 (180)	-0.47 (140), -0.82 (180), -1.38 ^b
(4b)	0.89 (170)	-0.33 (150), -0.86 (190), -1.40 ^b
(4c)	0.95 (180)	-0.35 (140), -0.75 (180), -1.45 ^b
(5a)	1.00 (140)	-0.22 (120), -0.70 (170), -1.40 ^b
(5b)	0.98 (160)	-0.26 (150), -0.74 (180), -1.39 ^b
(5c)	1.08 (170)	-0.25 (140), -0.65 (180), -1.25 ^b

^aSolvent MeCN, supporting electrolyte $[\text{Bu}_4\text{N}](\text{ClO}_4)$, Pt-disk milli working electrode, Pt-wire auxiliary electrode, reference electrode SCE, at 298 K, $E = 0.5 (E_{pa} + E_{pc})$ where E_{pa} is anodic peak potential and E_{pc} is cathodic peak potential, $\Delta E_p = |E_{pa} - E_{pc}|$; ^b E_{pc} .

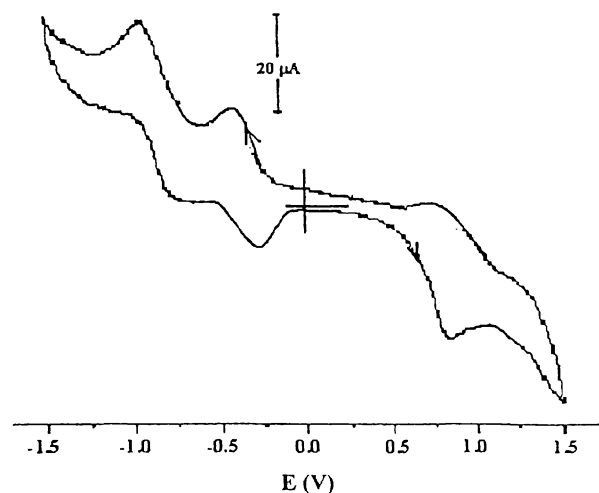
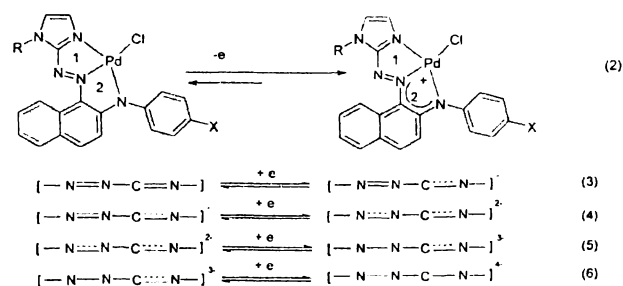


Fig. 3. Cyclic voltammogram of $\text{Pd}(\alpha\text{-NaiEt-N-C}_6\text{H}_4\text{-Me-}p)\text{Cl}$ (4b) in MeCN.

are reductive in nature. The reduction is regarded as the electron accommodation in the LUMO characterized by azoimine function. There are four successive redox accessible levels in $-\text{N}=\text{N}-\text{C}=\text{N}-$ group (eqs. (2-5)). In this series of complexes we observe three negative couples and they may correspond to three reductions eqs. (3-5).



Conclusion : $\text{Pd}(\text{naphthylazoimidazole})\text{Cl}_2$ have been reacted with arylamine (ArNH_2). The coupled products have been characterized by spectroscopic and electrochemical studies. The complexes are weakly fluorescent in solution.

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References

- G. Wilkinson, R. D. Gillard and J. McCleverty (eds.), "Comprehensive Coordination Chemistry", Pergamon Press, Oxford, 1987, Vol. 1-7; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5th ed., John Wiley & Sons, New York, 1988; M. Cais, "Progress in Coordination

- Chemistry", American Elsevier, New York, 1968; J. Reedijk, in "Comprehensive Coordination Chemistry", eds. G. Wilkinson and J. A. McCleverty, Pergamon, Oxford, UK, 1987, Vol. 2, p. 430; W. T. Wong, *Coord. Chem. Rev.*, 1994, **131**, 45.
2. S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 2246; 1982, **21**, 2173; 1983, **22**, 602; S. Goswami, R. N. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 2825; P. Ghosh and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1985, 361; B. K. Ghosh and A. Chakravorty, *Coord. Chem. Rev.*, 1989, **95**, 239; G. K. Lahiri, S. Bhattacharya, S. Goswami and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 561; N. Bag, A. Pramanik, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 40 and references therein.
 3. R. A. Krause and K. Krause, *Inorg. Chem.*, 1980, **19**, 2600; 1982, **21**, 1714; 1984, **23**, 2195.
 4. E. C. Constable, *Coord. Chem. Rev.*, 1989, **93**, 205; T. Yamamoto, Z. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, T. Takamura, T. Fukuda, B. Lee, N. Ooba, S. Tomaru, T. Kurihera, T. Kaino, K. Kubota and S. Sasaki, *J. Am. Chem. Soc.*, 1996, **118**, 1038.
 5. C. K. Pal, S. Chattopadhyay, C. Sinha, D. Bandhyopadhyay and A. Chakravorty, *Polyhedron*, 1994, **13**, 999; P. K. Santra, R. Roy and C. Sinha, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 2000, **112**, 523.
 6. B. K. Santra, P. Munshi, G. Das, P. Bharadwaj and G. K. Lahiri, *Polyhedron*, 1999, **18**, 617.
 7. P. K. Santra, P. Byabratra, S. Chattopadhyay, C. Sinha and L. R. Falvello, *Eur. J. Inorg. Chem.*, 2002, 1124; M. Panda, S. Das, G. Mostafa, A. Castineiras and S. Goswami, *Dalton Trans.*, 2005, 1249.
 8. P. Bhuina, U. S. Ray, G. Mostafa, J. Ribas and C. Sinha, *Inorg. Chim. Acta*, 2006, **359**, 4660.
 9. P. Datta, P. Gayen and C. Sinha *Polyhedron*, 2006, **25**, 3435.
 10. T. Mathur, U. S. Ray, J.-C. Liou, T.-H. Lu and C. Sinha, *Polyhedron*, 2005, **24**, 739.
 11. G. K. Routh, S. Pal, D. Das, C. Sinha, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 2001, **20**, 363.
 12. S. Senapati, P. K. Santra and C. Sinha, *Transition Met. Chem.*, 2002, **27**, 888.
 13. S. Senapati, Sk. Jasimuddin and C. Sinha, *Indian J. Chem., Sect. A*, 2006, **45**, 1153.
 14. J. Dinda, P. K. Santra, C. Sinha and L. R. Falvello, *J. Organomet. Chem.*, 2001, **629**, 28.
 15. B. Valuer, "Molecular Fluorescence : Principles and Applications", Willey-VCH, Weinheim, 2001.
 16. (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969; (b) C. Sinha, *Polyhedron*, 1993, **12**, 2363.