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Cyclopalladation versus hydroxylation. A case of pH dependence

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Abstract

1-Alkyl-2-(naphthyl-α-azo)imidazoles (NaiR, **2**) ($C_{10}H_7$–N=N–$C_3H_2N_2$1–R; R = Me (**a**), Et (**b**), $PhCH_2$ (**c**)) have been reacted with Na_2PdCl_4 in MeOH or MeCN solutions of $Pd(MeCN)_2Cl_2$ to synthesise $Pd(NaiR)Cl_2$ (**3**). The reaction of $Pd(OAc)_2$ in boiling benzene with NaiR followed by the addition of LiCl has resulted in the synthesis of the cyclopalladated complex Pd(NaiR–H)Cl (**4**). The ligand, NaiR, acts as a *N*,*N*′-bidentate chelator while NaiR–H acts as a tridentate *N*,*N*′,*C*-cyclometallating ligand. The infrared spectra of **3** exhibit two Pd–Cl stretches correspond to a *cis*-$PdCl_2$ geometry, and a single *ν*(Pd–Cl) band in **4** suggests one Pd–Cl bond. Cyclopalladation is supported by a single crystal X-ray crystal structural study of Pd(NaiEt–H)Cl (**4b**) and the metallation takes place at C(8′)-position. The solution of $Pd(NaiR)Cl_2$ (**3**) is also irreversibly transformed into Pd(NaiR–H)Cl (**4**) when the pH is adjusted to 4.5–6.0 by NaOAc or other bases (NaOMe, NaOH, LiOH, Li_2CO_3 etc.). At higher pH values (8–10) the reaction shows the chelative hydroxylation at the C(2′)-site to synthesise Pd(NaiRO)Cl (**5**). The structure of the hydroxylated blue product is also supported by a single crystal X-ray crystal structure of Pd(NaiEtO)Cl (**5b**). The reaction of $Pd(NaiR)Cl_2$ in MeCN with dilute sodium hydroxide in air, or aqueous silver nitrate under boiling conditions, or its treatment with Tollen's reagent in MeCN solution under ambient conditions has also yielded the hydroxylated product. All the compounds have been characterised by elemental analyses, IR, UV–vis and ^{1}H-NMR data. The solution spectral behaviour has been interpreted by EHMO calculations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: α-Naphthylazoimidazoles; Palladium(II) complex; Cyclopalladated compound; Hydroxylation; X-ray structure; EHMO calculations

1. Introduction

Metal mediated C–H bond activation is a conspicuous challenge in organic synthesis [1–3]. The activation may occur either by forming the M–C bond (intermolecular or intramolecular) [1,2] or via the functionalisation of the C–H group nearest to the metal centre [4–6] of the complex. Over the last three decades, cyclopalladated compounds have found numerous applications in organic synthesis [7], in material sciences [8] as compounds exhibiting liquid crystal properties [9] and as biologically active compounds [10].

Orthometallating reagents containing mono or polypyridine binding sites have attracted immense interest because of the higher ligand field strength due to the strong σ-donation capacity [11] of C^- compared to N, the ability to act as a multinucleating bridging ligand [12] in supramolecular chemistry and their photochemical and photophysical properties [13]. The potential activity of these systems may be due to the π-acidity (low lying LUMO) of the heterocyclic system. This property is largely dependent on the number of hetero atoms, the ring size and the substituents in the heterocyclic ring [14]. In the search for a new cyclometallating reagent with a heterocyclic system, imidazole is chosen in the first place because of its biological activity [15] and appearance as such in proteins, enzymes etc. For the last few years, we have been engaged in the exploration of the chemistry [16–18] and analytical applications [19] of arylazoimidazoles. At present, we have designed naphthylazoimidazoles (**1**) and 1-alkyl-2-(naphthyl-α-azo)imidazoles (**2**) [23]. The purpose behind this choice is to synthesise cyclometallated compounds of the ligands having an imidazole back-

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bone. The cyclometallation process involves the elimination of H^+ from the ligand molecule and requires addition of a base to maintain the pH of the medium [2a]. The increase in pH of the medium has another problem, as evident from the hydroxylation [4] of the C–H function of the pendant aryl ring in $Pd(aap)Cl_2$ (aap = 2-(arylazo)pyridine). Although the regiospecific cyclopalladation of 1-(arylazo)naphthalene is well established [2b], there is no report on the reaction of the heterocyclic-azonaphthalenes. Here we will take into account the effect of pH on cyclopalladation vis-a-vis hydroxylation at two different sites of the naphthyl ring in dichloro-[1-alkyl-2-(naphthyl-α-azo)imidazole]-palladium(II), and this is supported by X-ray crystal structure determinations of the products.

2. Experimental

2-(Naphthyl-α-azo)imidazole (NaiH, **1**), 1-methyl- and 1-ethyl-2-(naphthyl-α-azo)imidazole (NaiMe (**2a**) and NaiEt (**2b**)) were prepared by the stated procedure [20]. $PdCl_2$ was obtained from Arrora Matthey, Calcutta. MeI, EtBr and $PhCH_2Br$ were obtained from Aldrich. Commercially available SRL silica gel (160–120, 230–400 mesh) was used for column and preparative chromatography. All other reagents and solvents were used as received.

The ^{1}H-NMR spectra were obtained on a Bruker AC 300F and Varian Gemini 300 MHz FTNMR and referenced to internal $SiMe_4$. Infrared spectra were recorded as KBr discs on a JASCO-420 FTIR machine. UV–vis spectra were obtained from a JASCO UV–VIS–NIR model V-570 spectrophotometer. Elemental analyses data were collected on a Perkin–Elmer 2400 CHNO/S instrument. The pH of the solution was measured by using a Systronics μ-361 pH-meter.

2.1. Synthesis

*2.1.1. Pd(NaiMe)Cl$_2$ (**3a**)*

To the boiling solution of $PdCl_2$ (0.278 g, 1.52 mM) in MeCN (15 ml), NaiMe (**2a**) (0.3 g, 1.27 mM) was added and stirred for 0.5 h. The pink–red precipitate slowly appeared on slow evaporation in air. It was filtered and washed with cold MeCN and finally with Et_2O. Then it was dried in vacuo, and the purity tested by TLC. Yield was 70%.

$Pd(NaiEt)Cl_2$ (**3b**) and $Pd(NaiCH_2Ph)Cl_2$ (**3c**) were prepared by identical procedures with 75% yield. The reaction of a methanolic solution of $Na_2[PdCl_4]$ and NaiR also yielded the same product but in a lower percentage.

*2.1.2. Pd(NaiMe–H)Cl (**4a**)*

The complex was prepared by two different routes as given below.

2.1.2.1. Method 1. $Pd(OAc)_2$ (0.27 g, 1.20 mM) was boiled in benzene (25 ml) and filtered hot. To this solution NaiMe (0.24 g, 1.02 mM) was added and further refluxed for 1.5 h. The brown-red solution slowly turned green with a dark precipitate. The solution was filtered in the hot condition, digested with LiCl (5 mM) for 0.5 h and reduced by slow evaporation to half of its original volume. The precipitate so formed was filtered and dried over P_4O_{10}. The dry dark mass was dissolved in CH_2Cl_2 and chromatographed over silica gel column (30 × 1 ml). A light pink–red band was eluted first by C_6H_6 and rejected. The desired green band was eluted by a $MeCN–C_6H_6$ mixture (1:4, v/v) and a pink mass adhered to the top of the column. The solution was then evaporated, and the yield was 80%.

Pd(NaiEt–H)Cl (**4b**) and $Pd(NaiCH_2Ph–H)Cl$ (**4c**) were prepared by following identical procedures and the yield was 85%.

2.1.2.2. Method 2. To CH_2Cl_2–MeOH (1:2, v/v, 20 ml) a solution of $Pd(NaiMe)Cl_2$ (0.2 g, 0.48 mM) CH_3COONa (0.5 M) in MeOH was slowly added, and the pH of the solution was adjusted to 5 (tested by pH-meter, the working range of pH is 4.5–6). The solution was stirred and the pH was measured at 10 min intervals and adjusted by adding more AcONa solution. The pink–red colour of the solution turned greenish brown slowly and finally green. The stirring was continued for 5 h. The solution was then evaporated, washed with plentiful water, and then dried over P_4O_{10}. A CH_2Cl_2 solution of the compound was chromatographed over silica gel, and a small pink–red band was eluted first by CH_2Cl_2. The green band was eluted by $MeCN–C_6H_6$ (1:4, v/v) and after evaporation, the yield was 70%.

The use of NaOH, LiOH, CH_3ONa, Li_2CO_3, K_2CO_3 or Cs_2CO_3 as base was tested by following method 2. The yield of cyclopalladated complexes was not satisfactory and varied in the 20–40% range.

*2.1.3. Pd(NaiMeO)Cl (**5a**)*

2.1.3.1. By sodium hydroxide. A dilute solution of NaOH (0.02 M) in 2:3 H_2O–MeCN mixture (5 ml) was added drop by drop for a period of 4 h to a magnetically stirred suspension of **3a** (0.2 g, 0.48 mM) in MeCN (20 ml) in air. Stirring was continued for another 24 h and the pH was checked by the pH-meter (working range of pH 8–10). The colour of the solution changed gradually from pink–red to blue. The solution was then evaporated to dryness in vacuo and the residue was washed thoroughly with water and was then dried over P_4O_{10}. The solid residue was dissolved in CH_2Cl_2 and the solution was chromatographed over a silica gel column prepared in benzene. A MeCN–C_6H_6 (1:2) mixture was eluted into the desired blue compound. The solution was evaporated in vacuo and gave the pure complex with 70% yield. A pink mass remained at the top of the column.

The identical procedure was applied for the chelatative hydroxylation of Pd(NaiEt)Cl_2 and Pd(NaiCH$_2$-Ph)Cl_2 to synthesise Pd(NaiEtO)Cl (**5b**) Pd(NaiCH$_2$-PhO)Cl (**5c**) with yields of 75 and 82%, respectively.

When excess (say fivefold) NaOH solution was added all at once, the suspended Pd(NaiR)Cl_2 underwent dissolution, forming a red–violet solution with subsequent precipitation of a dark violet product. The hydroxylated product was not formed under these conditions.

A similar reaction was carried out by using NaOMe, LiOH, Li_2CO_3, K_2CO_3 or Cs_2CO_3, with pH adjusted at 8–10. The product was isolated as above with 50–70% yield.

2.1.3.2. By silver nitrate solution. Pd(NaiMe)Cl_2 (0.2 g, 0.48 mM) was suspended in H_2O–MeCN (1:1, v/v; 20 ml), and aqueous silver nitrate (0.1 g, 0.59 mM) solution was added to it. The mixture was refluxed for 30 h. The pink–red solution slowly turned green and finally bluish–green. AgCl was filtered out and the solution was evaporated. The dark precipitate so formed was filtered and washed with water and dried over P_4O_{10}. When the product was dissolved in a small volume of CH_2Cl_2 and chromatographed over a silica gel column, a pink–red band was eluted first by C_6H_6–MeCN (9:1, v/v), followed by the desired blue band by using a 2:1 C_6H_6–MeCN mixture. The solution was then evaporated, and the pure compound was isolated with 10% yield.

Table 1
Summarised crystallographic data for **4b** and **5b**

Crystal parameters	**4b**	**5b**
Empirical formula	$C_{15}H_{13}ClN_4Pd$	$C_{15}H_{13}ClN_4OPd$
Formula weight	391.14	421.30
Temperature (K)	297	294
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\overline{1}$
Unit cell dimensions		
a (Å)	7.2237(5)	7.6324(4)
b (Å)	16.3178(13)	22.139(2)
c (Å)	12.1354(10)	27.660(3)
α (°)	90	84.325(10)
β (°)	90.490(6)	86.554(6)
γ (°)	90	81.450(7)
V (Å^3)	1430.41(19)	4594.2(7)
Z	4	12
D_{calc} (g cm^{-3})	1.816	1.827
Transmission coefficient[a]	0.7348	0.977
Parameters refined	234	1222
Crystal size (mm^3)	$0.35 \times 0.30 \times 0.26$	$0.51 \times 0.11 \times 0.08$
R[b] (%)	2.85	5.07
wR_2[c] (%)	7.10	10.92
Goodness-of-fit on F^2[d]	1.085	0.961

[a] Maximum value normalised to 1.

[b] $R = \Sigma F_o - F_c / \Sigma F_o$.

[c] $wR_2 = \Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]^{-1}$, $P = [\max(F_o^2;\ 0) + 2F_c^2]/3$; $g_1 = 0.0038$; $g_2 = 1.28$.

[d] The goodness-of-fit is defined as $[\Sigma w(F_o^2 - F_c^2)^2/(N_0 - N_P)]^{1/2}$, where N_0 and N_P denote the numbers of data and variables, respectively.

2.1.3.3. By Tollen's reagent. To a H_2O–MeCN (1:1, 20 ml) suspension of Pd(NaiMe)Cl_2 (0.2 g, 0.4 mM), Tollen's reagent (0.1 g $AgNO_3$ in 5 ml water + 1 ml NaOH (0.2 M) and excess NH_3) was added and stirred for 20 min (on further stirring the solution turned brownish-blue gradually and finally into a brown insoluble precipitate). The colour of the solution quickly turned from pink–red to blue. The reaction was monitored by TLC test at 2 min intervals. The mixture was quickly filtered (G-4) and evaporated in vacuo. The dark mass was washed with water, filtered and dried over P_4O_{10}. The dried mass was chromatographed as before, a light orange band was rejected and a blue band was formed by C_6H_6–MeCN (2:1, v/v). The yield was 84%.

A similar reaction was carried out by using Tl_2CO_3 and $TlNO_3$ + NaOH under suspension, and the hydroxylated product was isolated with a yield $> 75\%$.

2.2. X-ray diffraction studies

Crystals suitable for X-ray work were grown by slow diffusion of hexane into CH_2Cl_2 solution at 298 K. The crystal data, data collection and refinement parameters for the two structures are listed in Table 1. The data were gathered by using an automated cad4 four-circle diffractometer [21] with graphite-monochromatised Mo–K$_\alpha$ ($\lambda = 0.71073$) radiation. After the initial reflection search and indexing, two-dimensional (ω–θ) plots were used to determine the optimum scan parameters for the collection of intensity data. Through data collections, the intensities of three standard reflections were monitored at regular intervals, which in no case showed variations of $> 5\%$. The intensities were corrected for Lorentz and polarisation effects and monitor absorption by using a technique based on azimuthal ψ scans. ψ-Scans were made for 14 and 8 reflections with bisecting-mode χ values in the range 6–70° and 11–86°, respectively, for Pd(NaiEt–H)Cl (**4b**) and Pd(NaiEtO)Cl (**5b**) for use in absorption corrections [22]. The structures were solved by direct methods [23a] and refined by full-matrix least-squares [23b]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions with

Table 2
Microanalytical, UV–vis[a] and ^{1}H-NMR[b] spectral data

Compound	Elemental analyses			UV–vis spectral data	δ (ppm)			
	Found (calc.)%			λ_{max} (nm) [10^{-3} ε (M^{-1} cm^{-1})]	1-R	4-H^{c}	5-H^{c}	Naphthyl-H
	C	H	N					
1^{d}	70.19(70.27)	4.46(4.51)	25.31(25.23)	395(17.84), 439(10.58)^{e}	10.42^{f}	7.50	7.50	7.60–8.11
2a	Gummy			396(15.66), 418(13.87)^{e}	3.72^{g}	6.91	6.80	7.75–7.92
2b	Gummy			399(13.41), 425(12.22)^{e}	4.25^{h}, 1.50^{i}	7.11	6.92	7.80–7.95
2c	Gummy			400(14.39), 430(12.49)^{e}	5.45^{g}	7.20	7.02	7.77–7.93
3a	40.55(40.64)	2.79(2.90)	13.62(13.55)	405(6.78), 510(5.77), 652(0.48)^{e}	4.08^{g}	7.58	7.05	7.94–8.20
3b	42.04(42.12)	3.21(3.28)	13.17(13.10)	400(6.16), 511(4.77), 650(0.67)^{e}	4.43^{h}, 1.56^{i}	7.64	7.14	7.98–8.25
3c	49.00(49.04)	3.21(3.27)	11.37(11.44)	395(6.16), 500(4.03), 652(0.89)^{e}	5.52	7.35	7.16	7.20–8.00
4a	44.64(44.57)	2.99(2.92)	14.77(14.86)	400(11.52), 453(4.66)^{e}, 640(3.90), 690(2.14)^{e}	3.96^{g}	7.21	6.95	7.60–8.10
4b	40.00(40.05)	3.40(3.33)	14.40(14.33)	400(13.80), 456(5.31)^{e}, 645(4.59), 688(2.80)^{e}	4.40^{h},1.55^{i}	7.29	7.00	7.70–8.15
4c	53.08(52.99)	3.26(3.31)	12.43(12.36)	402(10.80), 450(4.840), 630(3.79), 690(2.42)^{e}	5.40^{g}	7.24	6.91	7.20–7.90
5a	42.70(42.76)	2.84(2.80)	14.14(14.25)	411(6.59), 614(3.08)^{e}, 661(4.46), 711(4.36)	3.85^{g}	7.11	6.85	7.40–8.50
5b	44.16 (44.24)	3.12 (3.14)	13.70 (13.76)	423(6.95), 618(4.66)^{e}, 650(6.28), 706(6.65)	4.30^{h},1.59^{i}	7.15	6.94	7.35–8.60
5c	51.24(51.18)	3.26(3.20)	11.87(11.94)	382(11.82), 446(8.88)^{e}, 610(5.00), 644(7.40), 705(6.86)	5.55^{g}	7.20	6.94	7.60–8.00

[a] In $CHCl_3$.
[b] In $CDCl_3$.
[c] Doublet ($J = 7.0$–8.0).
[d] M.p: **1**, 200 ± 1°C.
[e] Shoulder.
[f] Broad.
[g] Singlet.
[h] Quartet ($J = 7.0$ 8.0).
[i] Triplet ($J = 7.0$–8.0).

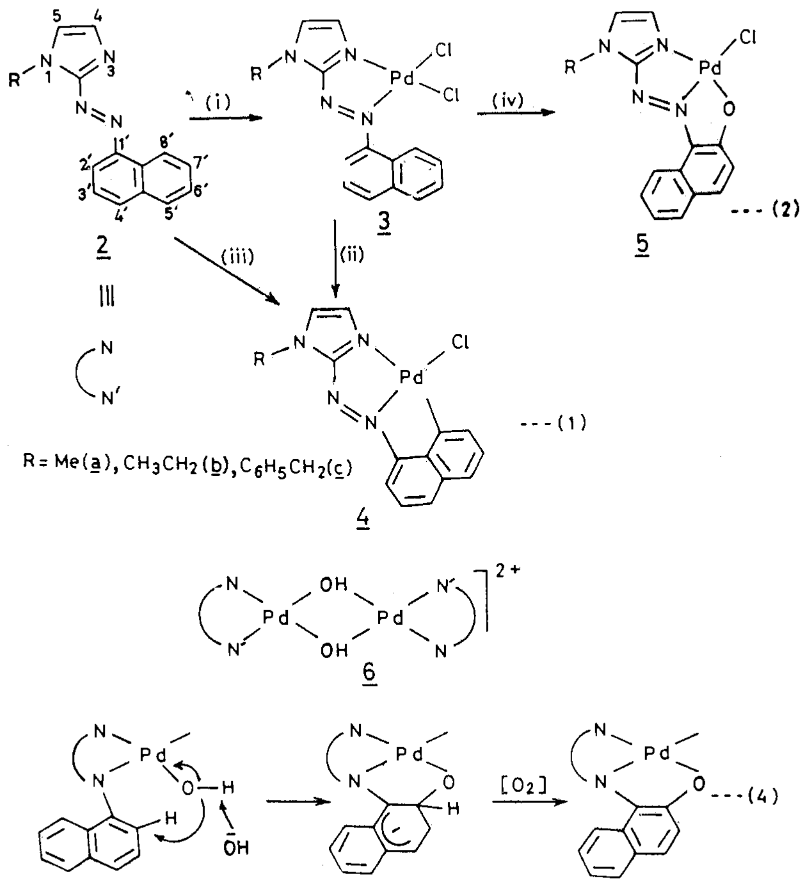
isotropic displacement parameters 1.2 times the isotropic equivalent for their respective parent atoms. Atomic coordinates, H-atom coordinates, thermal parameters with a complete list of bond distances and angles and a list of structure factors were obtained from the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK on request, the deposition numbers being 154016 (for **4b**) and 154017 (for **5b**).

3. Results and discussion

2-(Naphthyl-α-azo)imidazole ($C_{10}H_7$–N=N–$C_3H_3N_2$, NaiH, **1**) is obtained by coupling α-naphthyldiazonium ion with imidazole at pH 7 and 1-alkyl-2-(naphthyl-α-azo)imidazole ($C_{10}H_7$–N=N–$C_3H_2NN(1)$–R, NaiR (**2**), where R = Me (**a**), Et (**b**), $PhCH_2$ (**c**)) is synthesised from there by adding alkyl halide in THF in the presence of NaH [20]. All the complexes presented here have been characterised by IR, UV–vis and ^{1}H-NMR spectra (Table 2) and elemental (C, H, N) analyses.

*3.1. Coordination [(Pd(NaiR)Cl$_2$, **3**)] and cyclopalladated complexes [(Pd(NaiR–H)Cl, **4**)]*

The treatment of $Na_2[PdCl_4]$ in methanol [4a] or $Pd(MeCN)_2Cl_2$ in acetonitrile [16] with NaiR affords a pink–red solid **3**, which shows the common pattern for a *cis*-$PdCl_2$ configuration [4a] with two ν(Pd–Cl) at 340 and 318 cm^{-1}. On addition of NaOAc in MeOH to the reaction mixture or separately to a CH_2Cl_2–MeOH solution of $Pd(NaiR)Cl_2$ (**3**) (the pH of the solution is checked by the pH-meter and is adjusted at 4.5–6) under stirring conditions (5 h), the pink–red solution changes to green with a crystalline precipitate (**4**) (Eq. (1) in Scheme 1). The IR spectra of the green solid (**4**) show one ν(Pd–Cl) (345 cm^{-1}) and the structural study by X-ray diffraction of **4b** (Fig. 1) suggests a cyclopalladated complex. The ligand is then regarded as N,N′,C^{-} donor type analogue of 2-acetylpyridine phenylhydrazone or 6-phenyl-2,2′-bipyridine, and related ligands are used to prepare cyclometallated complexes [11–13]. The use of NaOMe, NaOH, LiOH, Li_2CO_3, K_2CO_3 or Cs_2CO_3 as the base in the MeOH to CH_2Cl_2 solution of



Scheme 1. (i) $PdCl_2$ in $MeCN/Na_2[PdCl]$ in MeOH, stirr; (ii) CH_2Cl_2=MeOH, NaOAc, pH 4.5–6.0, stirr; (iii) $Pd(OAC)_2$ in C_6H_6, reflux; and (iv) NaOH in MeCN/AgOH, stirr or $AgNO_3$ reflux.

complex **3** also yields the cyclopalladated complex (with low yield, 10–20%) when the pH of the medium is adjusted to 4.5–6.0.

Alternatively, complex **4** can also be prepared in high yield (> 80%) by treatment of NaiR with $Pd(OAc)_2$ in boiling benzene followed by the addition of LiCl [24]. $Pd(OAc)_2$ has been regarded as an ideal electrophile for C–H activation and cyclopalladation reaction [25]; hence it is used for a similar purpose. The treatment of AgOAc with **3** in CH_2Cl_2–MeOH also yields **4** with a comparatively lower yield along with another product, which is identified as hydroxylated complex **5**. A slurry of the complex and silica gel (230–400 mesh) in a CH_2Cl_2–MeOH mixture is kept airtight under thermostatic conditions (295 K) overnight and the green product is separated chromatographically with 20% yield and is also identified as the cyclopalladated compound **4**. A pink mass adheres to the top of the column. The solid surface activation of the C–H bond is well known in literature [26]. In this case the C–H activation leading to cyclopalladation is achieved by the SiO_2 surface.

*3.2. Hydroxylated complexes (Pd(NaiRO)Cl, **5**)*

Slow addition of dilute solution of sodium hydroxide in aqueous MeCN to a stirred suspension of $Pd(NaiR)Cl_2$ (**3**) in MeCN, under ambient conditions whilst maintaining the pH at 8–10, leads to a colour change from pink–red to greenish–blue, and the naph-

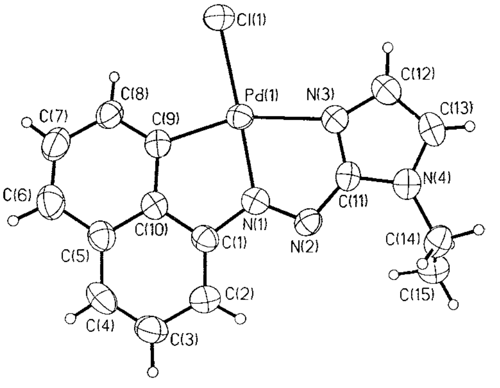


Fig. 1. Thermal ellipsoid plot of Pd(NaiEt–H)Cl (**4b**), showing the atom labelling scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

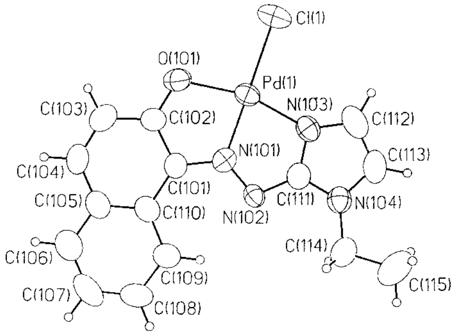


Fig. 2. Thermal ellipsoid plot of molecule 1, of Pd(NaiEtO)Cl (**5b**), showing the atom labelling scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

tholato complex **5** can be isolated from the reaction mixture with 70% yield (Eq. (2) in Scheme 1). The IR spectra of the complexes show one ν(Pd–Cl) and the X-ray structure determination (Fig. 2) suggests hydroxylation of the C(2′)–H bond leading to naphtholato-palladium(II) (C(2′)–OPd) complex formation.

Activation of the C–H bond of the pendant phenyl ring in a metal complex of 2-(arylazo)-pyridines (aap), such as Pd(aap)Cl_2 [4a], $[Co(aap)_3](ClO_4)_2$ [4b], Ru-$(aap)_2Cl_2$ [5], leading to an insertion of oxygen (hydroxylation [4], C–H → C–OH) or sulphur (thiolation [5], C–H → C–SH) is known in the literature. Some common observations in this reaction are: (i) the yield is heavily suppressed when it is carried out in the presence of Cl^- (LiCl) (1–5 M equivalent); (ii) the pH of the medium during hydroxylation must lie at 8–10; (iii) the presence of air and alkali is mandatory for the reaction to occur; and (iv) the addition of a Cl^- scavenger (Ag^+, Tl^+) followed by a base completes the reaction quickly yielding > 80% product.

3.3. X-ray crystallography

The X-ray crystal structures of cyclopalladated Pd(NaiEt–H)Cl (**4b**) and hydroxylated Pd(NaiEtO)Cl (**5b**) have been determined. Views of the molecules are shown in Figs. 1 and 2, respectively, and selected bond parameters are listed in Table 3. The crystal lattice of Pd(NaiEt–H)Cl consists of discrete molecules in which the bonding fashion of ligand is of the N,N′,C^- type (Fig. 1). The entire molecule is essentially planar with the exception of the ethyl group. The square planar configuration around the palladium atom involves Pd–N(3) (N(imi)), Pd–N(1) (N(azo)), Pd–C and Pd–Cl bonds. N(3)–Pd–C(9) deviates from linearity (~ 20°) more than N(1)–Pd–Cl(1) (deviation ~ 5°). This deviation may be due to the acute chelate angle in N(1)–Pd–N(3) (76.57°), while that of the other chelate ring N(1)–Pd–C(9) is just a slight one from the ideal square planar angle. The bond distances are almost comparable to the reported results [4a,27,28]. The N(1)–N(2) and Pd–N(3) distances are 1.286(4) and 2.177(3) Å, respectively, and they are slightly longer

Table 3
Selected bond distances and angles for (i) **4b** and (ii) **5b**

*(i) Cyclopalladated complex ($C_{15}H_{13}ClN_4Pd$ (**4b**))*

Distances (Å)		Angles (°)	
Pd–C(9)	1.985(4)	N(1)–Pd–C (9)	82.78(15)
Pd–N(1)	1.969(3)	N(1)–Pd–N(3)	76.57(12)
Pd–N(3)	2.177(3)	C(9)–Pd–Cl(1)	95.72(12)
Pd–Cl(1)	2.3149(10)	N(1)–Pd–Cl(1)	175.88(9)
N(1)–N(2)	1.286(4)	N(3)–Pd–Cl(1)	104.83(9)
		N(3)–Pd–C(9)	159.34(14)

*(ii) Hydroxylated product ($C_{15}H_{13}ClN_4OPd$, $1/6CH_2Cl_2$ (**5b**))*
Distances (Å)

Molecule *n*	1	2	3	4	5	6
Pd(*n*)–N(*n*01)	1.929(6)	1.944(6)	1.949(5)	1.936(6)	1.918(6)	1.937(6)
Pd(*n*)–N(*n*03)	1.996(6)	1.989(6)	2.004(6)	1.990(7)	1.976(7)	1.993(6)
Pd(*n*)–O(*n*)	2.023(5)	2.030(5)	2.025(5)	2.031(5)	2.028(6)	2.013(5)
Pd(*n*)–Cl(*n*)	2.292(2)	2.292(2)	2.295(2)	2.291(2)	2.296(2)	2.289(2)
N(*n*01)–N(*n*02)	1.317(7)	1.303(7)	1.299(7)	1.300(7)	1.327(7)	1.316(7)
Angles (°)						
N(*n*01)–Pd(*n*)–N(*n*03)	80.2(2)	80.3(3)	80.2(2)	79.4(3)	80.4(3)	80.5(3)
N(*n*01)–Pd(*n*)–O(*n*)	82.8(2)	82.4(2)	82.5(2)	82.6(2)	82.0(2)	82.2(2)
N(*n*03)–Pd(*n*)–Cl(*n*)	99.36(19)	99.5(2)	100.25(18)	99.7(2)	99.7(2)	99.71(19)
O(*n*)–Pd(*n*)–Cl(*n*)	97.67(16)	97.73(18)	97.09(15)	98.46(16)	97.89(18)	97.65(17)
N(*n*03)–Pd(*n*)–O(*n*)	163.0(2)	162.7(2)	162.7(2)	161.8(2)	162.4(3)	162.6(2)
N(*n*01)–Pd(*n*)–Cl(*n*)	179.30(18)	179.82(17)	179.32(18)	176.54(19)	178.68(19)	179.4(2)

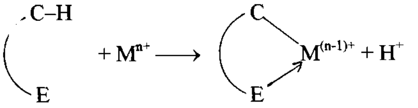
than the chloro-[2-(azophenolato)pyridine]Pd(II) (elongated by 0.03 Å) [27]. This may be due to a more reduced π-acidity of imidazole than that of pyridine [14b].

The crystal structure of Pd(NaiEtO)Cl is unusual, having six molecules of the palladium complex along with one molecule of CH_2Cl_2 in the crystallographic asymmetric unit. These six molecules are organised into three dimeric units. That is, molecule 1 (around Pd(1)) and molecule 2 (around Pd(2)) are located together, parallel to each other, with an interplanar distance of 4.04(2) Å and a dihedral angle of 1.69(7)°. Other pairs are located at an interplanar spacing (Å) and a dihedral angle (°), respectively, as follows: molecule 3 and 4, 3.251(9) Å, 0.97(7)°; molecule 5 and 6, 3.28(2) Å and 1.34(7)°. As an indication of the relative orientations of the three dimers, we note that the dihedral angle between molecules 1 and 3 is 53.14(4)° and between molecules 1 and 5 is 4.21(7)°, and the angle between the planes of molecules 3 and 5 is 49.65(4)°. The three dimers are not equivalent to each other. The Pd···Pd intra-dimer distances are different: Pd(1)···Pd(2) = 4.7721(9) Å; Pd(3)···Pd(4) = 4.3683(9) Å and Pd(5)···Pd(6) = 5.1419(10) Å. The bond distances (Table 3) in the coordination sphere of six molecules differ slightly and the values are in the range: Pd–N(1), 1.918–1.949; Pd–N(3), 1.976–2.004; Pd–O(1), 2.013–2.030; Pd–Cl, 2.289–2.296 and N(1)–N(2), 1.299–1.32 Å. The chelate angles [N(1)–Pd–N(3), N(1)–Pd–O] and the angles around the square plane are also comparable (differ by 0–3°). The torsion angles vary in a characteristic manner. All of them represent an unusual and subtle form of conformational isomerism in a metal chelate sustained by the crystal lattices. The Pd–Cl and Pd–N(1) (N(azo)) distances contract slightly in going from **4b** to **5b**. In contrast, the Pd–N(3) (N(imidazole)) distance is contracted by > 0.2 Å and may be due to the *trans* influence [28] given by the Pd–C bond in **4b**, which is absent in **5b**. The N(1)–N(2) distance varies in the range 1.299–1.317 Å. The electron releasing effect of phenolic oxygen in the tightly bound planar tridentate structure may play a role for the contraction of bond distances in the square plane [4a]. This induces better π-backbonding in **5b** and the azo distance is slightly elongated. The N(imidazole)-Pd–N(azo) chelate bite angle is expanded ($\sim 4°$) in going from **4b** to **5b**. In both the cases all the angles around the metal except N(1)–Pd–Cl (176–179°) deviate severely from the square planar value. The structure of **5b** agrees well with those of analogous pyridine derivatives [4a].

In the parent complex **3**, two C–H bonds remain closer to the metal centre; the chelatative hydroxylation at the C(2′)–H will lead to a five-membered chelate ring, while the C(8′)–H will constitute a six-membered ring. In a square planar arrangement, the six-membered chelate ring may need a larger angular strain than that of the five-membered chelate ring. As there are positions to form the five-membered chelate ring in this molecular frame, so the C(2′)–H activation takes place, followed by the chelation to achieve the product **5**.

3.4. Effect of pH on the reaction type

C–H bond activation followed by cyclopalladation is observed in acidic pH, 4.5–6.0, while in basic pH, 8.0–10.0, the C–H bond is hydroxylated (C–H → C–OH) with subsequent metallation. The nature of the base is immaterial and has the property to maintain the pH of the medium. The cyclometallation process is associated with a decrease in pH (Eq. (3)), and therefore base addition is not only necessary to increase the yield of the product, but also mandatory sometimes for the C–M bond formation [2,29].



(3)

In the hydroxylation process, the initial step is the Cl^- substitution and the formation of the Pd–OH bond. It is noted that external Cl^- suppresses the yield of the hydroxylated product, while Cl^- scavenger Ag^+ or Tl^+ quickly completes the reaction with a very high yield of the product, **5**. The addition of excess OH^- to an acetonitrile solution of **3** changes the colour instantaneously to violet and subsequently precipitates out an unidentified sticky dark mass, which is on suspension in a polar solvent and slowly changes to blue, and the complex **5** is obtained on addition of dilute HCl. The sticky mass, on acidification with dilute HCl returns to the parent complex **3**. Addition of dilute $HClO_4$ (followed by $NaClO_4$) to the violet suspension precipitates out a pink product, which is also obtained from the reaction with $AgClO_4$ followed by the addition of $NaClO_4$. Initial observation (C, H, N; IR and conductance data) suggests a 1:2 electrolyte of type **6**. All these data support a metal-coordinated hydroxide ion at higher pH values (8–10) that attacks the C–H bond at the *ortho* position of the pendant aromatic ring [4a]. This suggests a nucleophilic attack by the metal coordinated hydroxide ion at the *ortho* position of the pendant aromatic ring, which is subjected to electron withdrawal by the combined effects of the metal centre, the azoimine function and the heterocyclic backbone. This is equivalent to hydroxylation of 1,3,5-trinitrobenzene by OH^- in air [29]. Although there are two C–H bonds (C(2′)–H, C(8′)–H) closest to the metal centre, hydroxylation occurs only to C(2′)–H, probably on account of the formation of a five-membered chelate ring that is more stable than the six-membered chelate ring. A plausible mechanism of the reaction is given in Eq. (4) of Scheme 1.

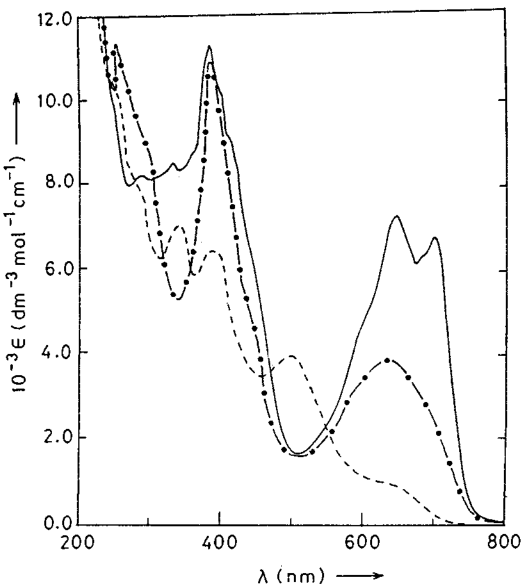


Fig. 3. UV–vis spectra of Pd(NaiCH$_2$Ph)Cl$_2$ (**3c**) (----), Pd(NaiCH$_2$Ph-H)Cl (**4c**) (- ●-● -) and Pd(NaiCH$_2$PhO)Cl (**5c**) (—) in MeCN at 298 K.

At low pH values (4.5–6), the base acts as a H$^+$ scavenger that is released during the C–H activation by palladium(II) as given in Eq. (3) and is not sufficiently strong to augment the nucleophilic substitution at the metal centre.

3.5. Solution spectra

Dichloromethane solutions of the coordination complexes, Pd(NaiR)Cl$_2$ (**3**), cyclopalladated compounds Pd(NaiR–H)Cl (**4**) and hydroxylated products Pd(NaiRO)Cl (**5**) exhibit distinctly different UV–vis spectra. The ligands, NaiR, exhibit intra-ligand charge transfer transitions near 400 nm along with a shoulder at 420 nm. The pink–red solution of **3** shows transitions near 410 and 500 nm. Green solutions of the cyclopalladated complexes exhibit three consecutive transitions near 400, 450, 640 and 690 nm, along with high-energy transitions corresponding to intra-ligand charge transfer bands. The spectral differences of **4** from **3** are characteristic of the orthopalladation reaction and the low energy structured absorption in Pd(NaiR–H)Cl (**4**) may probably represent a dπ(Pd)–π*(L) (L = ligand) charge transfer transition [30,31]. This is also supported by EHMO calculation (vide infra). On the other hand, naphtholatopalladium(II) complexes Pd(NaiRO)Cl (**5**) display a characteristic absorption pattern in the low energy region of higher intensities (nearly at 400–650 and 710 nm) than that of the respective *ortho* palladated complexes. The diagnostic spectral features are listed in Table 2 and representative spectra are shown in Fig. 3.

The ^{1}H-NMR spectra of the ligands and the complexes were recorded in CDCl$_3$. 2-(Naphthyl-α-azo)imidazole shows a characteristically broad, concentration dependent N(1)–H resonance at 10.45 ppm, which disappears upon the addition of D$_2$O. The alkylation of azoimidazole was supported by the disappearances of δ (N–H). NaiMe gives a singlet at 3.72 ppm for δ Me; NaiEt gives a quartet at 4.25 ppm (J = 8.0 Hz) and a triplet at 1.5 ppm, respectively, for the –CH$_2$– group and the –CH$_3$ group. A singlet at 5.45 ppm is referred to the signal of the –CH$_2$– group of NaiCH$_2$Ph [20]. Imidazole protons 4- and 5-H in NaiH appear as an unsplit band at 7.50 ppm, possibly owing to an intermolecular proton exchange between them. In alkylated derivatives NaiR, 4- and 5-H appear as doublets, and the upperfield signal corresponds to 5-H (Table 2). The naphthyl ring protons are affected due to the electron withdrawing effect of the azo group [20]. In the coordination complexes, Pd(NaiR)Cl$_2$ (**3**), all the protons suffer significant downfield shifting compared to the ligand values, which may be due to the electron-withdrawing effect of the coordinated palladium(II). In the cyclopalladated complexes, Pd(NaiR–H)Cl (**4**), and the hydroxylated products, Pd(NaiRO)Cl (**5**), the protons shift to an upperfield portion compared with the coordinated complexes (**3**). This reflects the involvement of metal d-orbitals in the construction of a molecular orbital in these complexes more efficiently compared with Pd(NaiR)Cl$_2$. The EHMO calculation also supports the metal orbital contribution to HOMOs (vide infra).

3.6. EHMO calculation and spectral properties

The approximate composition of the frontier orbitals in the cyclopalladated complexes and the hydroxylated products has been estimated by extended Hückel calculations performed by using the crystallographic parameters of the respective single crystal data. The HOMO and LUMO of the complexes are depicted in Fig. 4. In Pd(NaiEt–H)Cl (**4b**) the HOMO is composed of 74% metal (64% d-orbital of Pd) orbitals and 24% ligand orbitals and the LUMO is a ligand dominated (89%) function. Hence, the intense absorption at 635 nm may be assigned to MLCT transition [32]. In Pd(NaiEtO)Cl (**5b**) the HOMO is constituted by a 61% ligand share and a 36% contribution from metal orbitals. The LUMO is made up mainly from a ligand (91%) function. The imidazolylazonaphthol in **5b** has two interdependent parts bridged by azo group: imidazole and naphthol. In HOMO the imidazolyl group shares 33% and naphthol shares 13% of the function while the LUMO is constituted by a 70% azonaphthol group. Thus, the high intense absorption at ca. 650–700 nm has been characterised as HOMO → LUMO and may not be considered as a pure MLCT type;

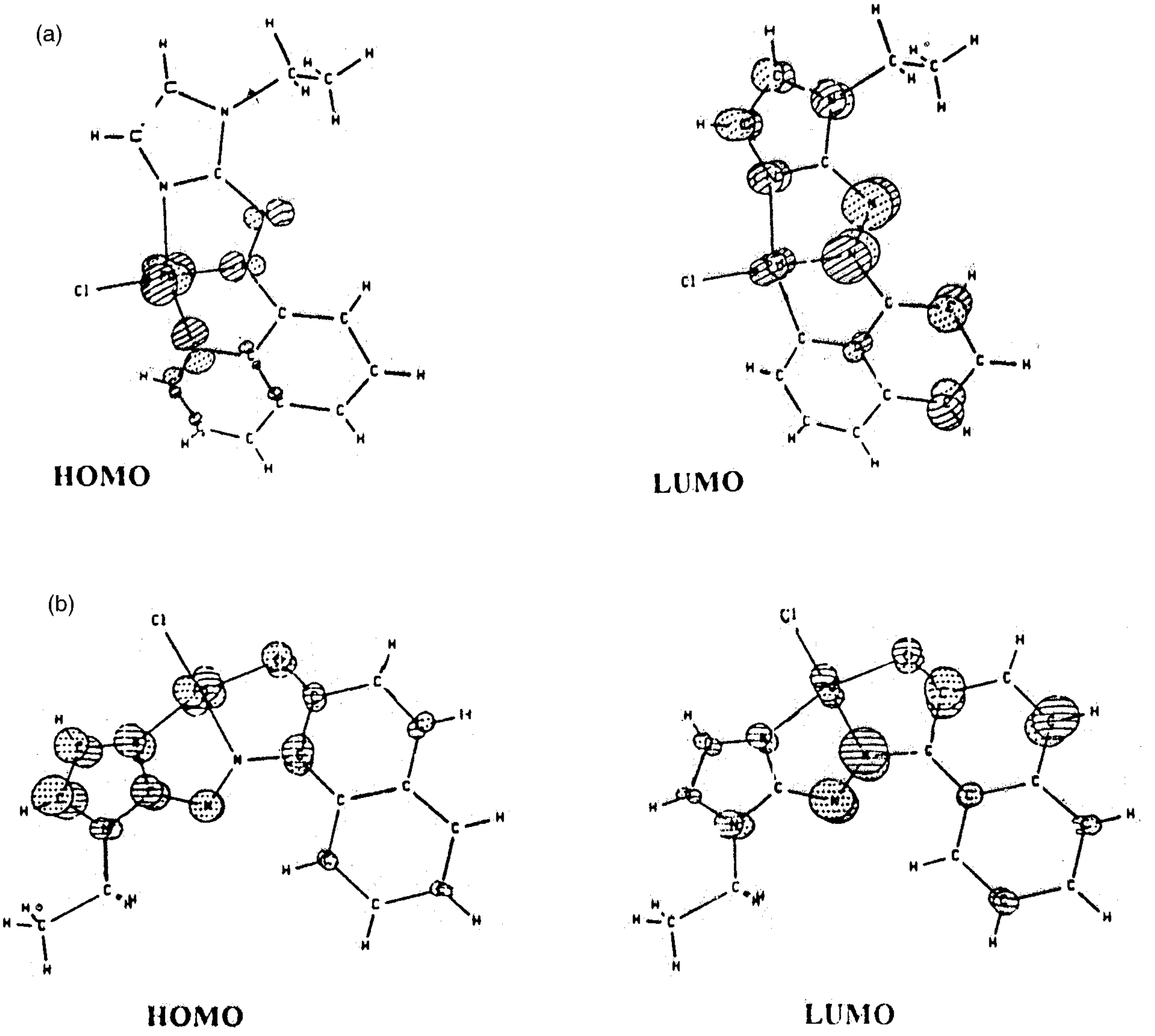


Fig. 4. EHMO derived HOMO and LUMO of: (a) Pd(NaiEt–H)Cl; and (b) Pd(NaiEtO)Cl.

rather, it may be a transition of intra-valence charge transfer (IVCT) type.

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