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Chemistry of azopyrimidines. Part IV[†]. Aromatic hydroxylation in palladium(II)-arylazopyrimidines

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Abstract. 2-(Arylazo)pyrimidines (aapm) are N,N′-chelating ligands and synthesise orange-red complexes of composition [Pd(aapm)Cl_2], **1**, with Pd(MeCN)$_2Cl_2$ in MeCN. The complex has *cis*-$PdCl_2$ configuration [*n*(Pd–Cl): 340, 360 cm^{-1}]. The treatment of Tollen's reagent ('AgOH') leads to chelatative hydroxylation in the pendant aryl ring, affording a green phenolato complex, Pd(aapmO)Cl, **5** (aapmO is deprotonated 2-((8-hydroxo)arylazo)pyrimidine). The reaction is also carried out by controlled addition of dilute sodium hydroxide in air or by the addition of PhIO/*m*-chloroperbenzoic acid to a MeCN suspension of the complex. A single Pd–Cl stretch at 360 cm^{-1} supports the composition of phenolato complex. Unlike Pd(aapm)Cl_2 the hydroxylated product, Pd(aapmO)Cl, has a structured intense absorption in the visible region near 670 nm. The Pd–Cl bond in Pd(aapmO)Cl is highly sensitive to nucleophilic substitution and slowly hydrolyses in aqueous medium.

Keywords. Arylazopyrimidines; palladium(II); aromatic hydroxylation; oxygen insertion; spectral characterization; electrochemistry.

1. Introduction

Arylazoheterocycles are *p*-acidic ligands with an azoimine, –N=N–C=N–, functional group [1–17]. The number of heteroatoms, the ring size, and the substituent in the heterocycle ring significantly modify the *p*-acidity and regulate the physical and chemical properties of the compounds [18,19]. Arylazoheterocycles have been used successfully to stabilise low oxidation states [1–7,11,12] and induce versatile reactivity to the metal ion [1–12]. The coordination of a ligand to a positively charged metal centre might enhance the reactions of nucleophiles with the ligand and thus form a fascinating area in metal-assisted organic syntheses [8,9,20,21]. Metal complexes of arylazopyridines (aap) undergo different organic transformations at the pendant aryl ring such as hydroxylation [9,22], thiolation [8], and C–N coupling reaction with aromatic amines [20,21]. This has encouraged us to explore the reactivity of arylazopyrimidine complexes. In this first report we discuss the chelatative hydroxylation of dichloro(arylazopyrimidine)palladium(II). The products are characterised by spectroscopic and electrochemical studies.

[†]For Parts I and II, see references 16 and 17; for Part III, *Synth. React. Inorg. Met.-Org. Chem.* (in press)
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2. Experimental

2-Aminopyrimidine was obtained from Aldrich. $PdCl_2$ was obtained from Arora Matthey, Calcutta. Na_2PdCl_4 was prepared by reacting palladium(II) chloride with NaCl in water and evaporating the aqueous solution [14]. 2-(Arylazo)pyrimidines were synthesised by condensing 2-aminopyrimidine and nitrosoaromatics as reported earlier [16]. Commercial grade BDH silica gel (60–120 mesh) was used for column chromatography. Nitrogen gas was purified by successively bubbling it through alkaline pyrogallol solution and concentrated sulphuric acid. Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared, and recrystallised by a previously reported method [12]. Acetonitrile for electrochemical work was prepared by known procedure [16]. All other chemicals and solvents used for the preparative works were of reagent grade and were used as received.

Microanalytical (C, H, N) data were obtained from a Perkin–Elmer 2400 CHN elemental analyser. Spectroscopic data were obtained by the use of the following instruments: UV–Vis spectra, Shimadzu UV–160 A; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420 spectrometer; ^1H NMR spectra, Brucker 200 and 300 MHz FT-NMR spectrometers. Electrochemical measurements were obtained with the use of EG & G PAR model 270 VERSASTAT using a glassy carbon working electrode. The solution was IR compensated internally and the results were collected at 298 K. The reported results are referenced to the saturated calomel electrode (SCE) in acetonitrile. *p*H-measurements were carried out by Systronics *m*-362 *p*H-meter and conductance data were collected from conductivity-meter Systronics 304 model.

2.1 *Preparation of complexes*

The starting complexes Pd(aapm)Cl_2 were obtained by a modified method [14]. Generalised procedure for a representative complex Pd(papm)Cl_2 is given below. 2-(Phenylazo) pyrimidine (papm) (0·25 g, 1·36 mM) in MeCN (10 cm^3) was added to a hot filtered solution of $PdCl_2$ (0·3 g, 1·69 mM) in acetonitrile (35 cm^3). The orange-red solution was stirred vigorously and micro crystals of Pd(papm)Cl_2 gradually separated out on slow evaporation. The crystals were filtered washed with cold MeCN solution (1:1) and dried *in vacuo*. Yield, 0·44 g (90%).

2.2 *Hydroxylation reaction. Preparation of chloro[2-((8-hydroxo)phenylazo) pyrimidine]palladium(II) complex, Pd(papmO)Cl (***2a***)*

2.2a *Hydroxylation by Tollen's reagent*: Tollen's reagent ((0·12 g, 0·71 mM) $AgNO_3$ + 4 drops of 0·01 (M) NaOH, precipitated Ag_2O is dissolved in minimum volume of aqueous NH_3) was added dropwise for 10 min to a magnetically stirred suspension of Pd(papm)Cl_2 (0·25 g, 0·69 mM) in MeCN (25 cm^3) under ambient condition. Orange-red solution turned to green. The course of reaction was examined by TLC experiment at 5 min interval. The reaction was completed within 40 min (on further reaction the intense green colour turned to brown-green and finally to brown-pink with formation of an insoluble precipitate). The solution was evaporated to dryness *in vacuo* (after 40 min of

reaction); the residue was washed thoroughly with water (4×15 cm^3) and was dried over P_4O_{10}. The solid residue was dissolved in CH_2Cl_2 (minimum volume) and was chromatographed over a silica gel column (60×1 cm) prepared in benzene. An MeCN–C_6H_6 (1:3 v/v) mixture was then used to elute the desired deep green band. The solution on evaporation *in vacuo* gave Pd(papmO)Cl. Yield 85%. An orange band (unreacted compound) was eluted by MeCN. A pink mass was adsorbed on the column head.

The same procedure was also applied for the hydroxylation of other complexes. Yields: 85–95%.

2.2b *Hydroxylation by dilute sodium hydroxide solution*: A dilute solution of NaOH (0·03 M) in 2:3 H_2O–MeCN mixture (1 cm^3) was added dropwise for a period of 3 h to a magnetically stirred suspension of Pd(papm)Cl_2 (0·1 g, 0·28 mM) in MeCN (20 cm^3) under ambient conditions. Stirring was continued for 24 h. The colour of the solution turned gradually from orange-red to green. The solution was purified as before. The hydroxylated product Pd(papmO)Cl was isolated in 50% yield.

When excess (say five-fold) NaOH solution was added all at once, the suspended Pd(papm)Cl_2 underwent dissolution, colour of the solution turned to brown-pink with subsequent precipitation of a violet product. Hydroxylated product was not formed under these conditions. The violet product was insoluble in organic solvents but on suspension in MeCN for a week the solution gradually turned green and Pd(papmO)Cl was isolated as before (yield 5–15%). In another experiment, addition of dil. HCl to the suspension of violet product in MeCN changed it to orange and from this Pd(papm)Cl_2 was isolated on purification.

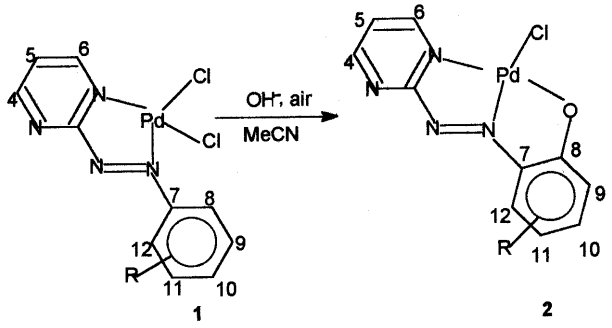
2.2c *Reaction of Pd(papm)Cl_2 with aqueous $AgNO_3$ solution*: Aqueous $AgNO_3$ solution (0·1 g, 0·65 mM) was added to an acetone suspension of Pd(papm)Cl_2 (0·2 g, 0·55 mM) and refluxed for 1 h. The precipitated AgCl was filtered (G-4 crucible). The filtrate was divided into two parts. The first part was further refluxed for 24 h, when the orange colour slowly turned to green. Hydroxylated product Pd(papmO)Cl was isolated in 15% yield. To the second part of the solution, saturated $NaClO_4$ solution was added and an orange-brown precipitate was isolated. This was thoroughly washed with water and dried over $CaCl_2$. Conductance measurement, IR spectra and elemental analyses (C, H, N) support the composition, [Pd(papm)(*m*-OH)]$_2$(ClO_4)$_2$. On standing for 72 h, an acetonitrile solution of this ionic compound orange-brown in colour, gradually changed to green and Pd(papmO)Cl was isolated as before in 8% yield.

2.2d *Hydroxylation by PhIO and m-chloroperbenzoic acid*: PhIO (0·4 g) was added to an acetonitrile suspension of Pd(papm)Cl_2 (0·2 g, 0·55 mM) and the solution stirred continuously for 72 h. The colour gradually turned from orange to green and Pd(papmO)Cl was isolated as before in 8% yield.

The experiment was carried out with *m*-chloroperbenzoic acid (*m*-CPBA) in an acetonitrile solution of Pd(papm)Cl_2. The reaction was completed within 30 min and the hydroxylated product Pd(papmO)Cl was isolated in 15% yield with an unidentified pink product.

3. Results and discussion

2-(Arylazo)pyrimidines (aapm) are N,N′-chelating molecules. The donor centres are abbreviated as N(1)(pyrimidine), N and N(azo), N′. The atom numbering scheme is shown in scheme 1. The reaction of aapm with Na_2PdCl_4 in EtOH or $Pd(MeCN)_2Cl_2$ in MeCN affords orange-red coloured $Pd(aapm)Cl_2$, **1**. The compositions of the complexes are supported by microanalytical data (table 1).



$Pd(aapm)Cl_2$ Pd(aapmO)Cl

R = H (papm/papmO, **a**), 8-Me (*o*-tapm/*o*-tapmO, **b**),
9-Me (*m*-tapm/*m*-tapmO, **c**), 10-Me (*p*-tapm/*p*-tapmO, **d**),
10-Cl (*p*-Clpapm/*p*-Clpapm O, **e**)

Scheme 1.

3.1 *Hydroxylation*

Upon addition of Tollen's reagent ('AgOH') to a stirred suspension of $Pd(aapm)Cl_2$, **1** in MeCN under ambient condition leads to a quick colour change from orange-red to green, and from the reaction mixture the green phenolato complex Pd(aapmO)Cl, **2**, can be isolated in high yield (aapmO = deprotonated 2-((8-hydroxo)arylazo)pyrimidine). The reaction time is standardised by TLC experiment and has been completed within 35–45 min. On further reaction, the solution slowly turned from green to brown-green and finally to brown-pink with an insoluble dark brown precipitate. Similar experiment is also performed with $Pd(arylazopyridine)Cl_2$ under identical condition but the second step of the conversion, green → brown-pink, does not occur even on stirring for 12 h.

The reaction has also been performed using oxo-transferring agent, PhIO and *m*-chloroperbenzoic acid [23,24]. Hydroxylation is achieved in relatively low yield (8–15%). Slow, careful addition of NaOH solution to a suspension of $Pd(aapm)Cl_2$ in MeCN leads to the formation of Pd(aapmO)Cl in 50% yield [9] but it takes about a day. Besides, the reaction is very sensitive to the presence of foreign Cl^- (LiCl), which suppresses the yield of product. No such effect is observed in the present experimental process using Tollen's reagent.

On quick addition of NaOH solution to the red-brown suspension in MeCN of $Pd(aapm)Cl_2$, the colour changes to pink and a brown mass is precipitated. The product is insoluble in common organic solvents and the precursor is recovered by adding dil. HCl solution to the precipitate. No hydroxylation is immediately observed. Upon suspension

Table 1. Microanalytical, UV-Vis spectral[b] and cyclic voltammetric data for Pd(aapm)$_2$Cl$_2$ (**4**) and Pd(aapmO)Cl (**5**).

	Elemental analyses[a]				Ligand reduction[c]
	C (%)	H (%)	N (%)	l_{max} (nm) (10^{-3} e, M^{-1} cm^{-1})	$E°_L$ (V) (ΔE_P, mV)
$_2$ (**1a**)	33·30 (33·20)	2·28 (2·21)	15·39 (15·49)	410 (5·25), 340 (9·12)[d], 300(11·20)	–0·018 (120), –1·09[e]
o-tapm)Cl$_2$ (**1b**)	35·27 (35·16)	2·60 (2·66)	14·80 (14·92)	435 (3·64), 345 (5·84)[d], 308(10·66)	–0·135 (110), –1·48[e]
m-tapm)Cl$_2$ (**1c**)	35·28 (35·16)	2·58 (2·66)	15·05 (14·92)	430 (4·89), 355 (6·95)[d], 315(11·69)	–0·082 (100), –1·37[e]
p-tapm)Cl$_2$ (**1d**)	35·24 (35·16)	2·75 (2·66)	14·84 (14·92)	425 (4·74), 355 (6·46)[d], 315(15·02)	–0·122 (130), –1·26[e]
p-Clpapm)Cl$_2$ (**1e**)	30·40 (30·31)	1·86 (1·77)	14·06 (14·15)	420 (7·96), 360 (11·36)[d], 304(19·80)	0·105 (100), –0·92[e]
2a)	35·29 (35·20)	2·10 (2·05)	16·50 (16·43)	725 (2·30), 675 (2·86), 625(2·32), 393 (5·29), 367 (6·33), 320 (10·00)	–0·16 (100), –1·05 (120)
o-tapmO)Cl (**2b**)	37·38 (37·25)	2·60 (2·54)	15·90 (15·80)	715(1·45), 680(1·98), 625(1·39), 385 (5·82), 370 (6·45), 310(9·64)	–0·37 (90), –1·24 (130)
m-tapmO)Cl (**2c**)	37·16 (37·25)	2·63 (2·54)	15·95 (15·80)	720(2·06), 672 (2·48), 610(2·06), 400(6·66), 360 (7·78), 315(10·45)	–0·24 (90), –1·17 (120)
p-tapmO)Cl (**2d**)	37·34 (37·25)	2·65 (2·54)	15·70 (15·80)	725 (2·33), 663 (2·95), 605(219), 398 (6·80), 363 (7·90), 329(10·20)	–0·31 (90), –1·18 (130)
p-ClpapmO)Cl (**2e**)	32·08 (31·96)	1·65 (1·59)	15·00 (14·92)	705 (1·40), 660 (1·96), 605(1·37), 399 (5·38), 308 (12·30)	–0·08(85), –1·00 (115)

Calculated values are in parentheses; [b]Solvent CHCl$_3$; [c]Solvent MeCN ; supporting electrolyte [Bu$_4$N][ClO$_4$], solute concentration $^{-3}$ M, Pt -working electrode, scan rate 0 ·05 Vs^{-1}, SCE reference and Pt -wire auxiliary electrode; [d]Shoulder; [e]E_{pc} (cathodic peak

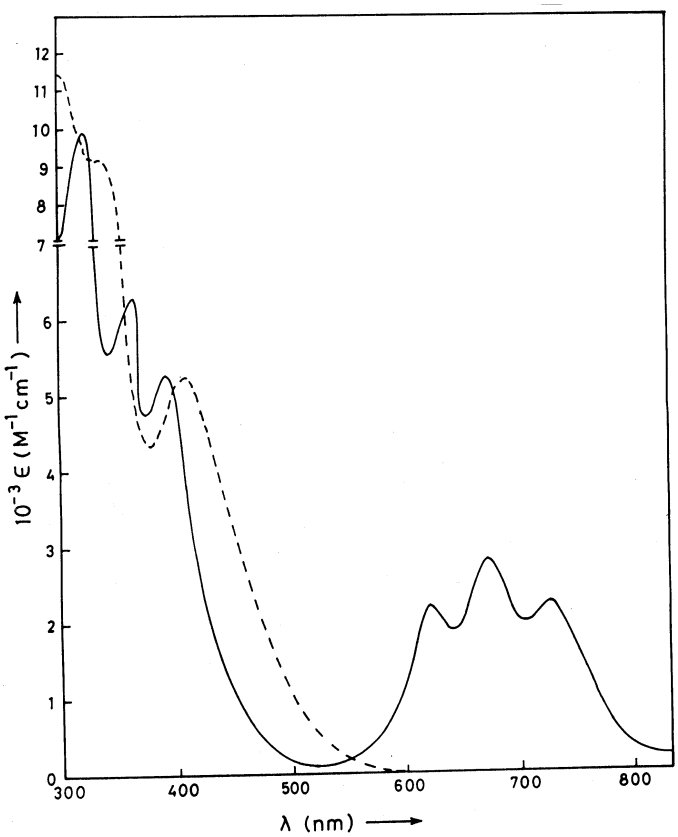


Figure 1. UV-Vis spectra of Pd(papm)Cl_2 (----) and Pd(papmO)Cl(——) in $CHCl_3$ at 298 K.

of the brown mass in MeCN solution for a long period (one week), solution colour changes to greenish pink and an addition of a small amount of dil. HCl an intense green colour is developed. Spectral studies support the formation of hydroxylated product.

Aqueous silver nitrate solution is added to an acetone suspension of Pd(aapm)Cl_2 and the mixture refluxed for 1 h. AgCl is precipitated out and filtered (G-4 crucible). On addition of saturated $NaClO_4$ solution to the filtrate an orange product precipitates out. Molar conductance (Λ_M, 170–180 Ω^{-1} cm^2 M^{-1} in MeCN), spectral (IR, UV-Vis) and microanalytical data suggest the formation of the hydroxo bridge compound, [(aapm)Pd(*m*-$OH)_2$Pd(aapm)]$(ClO_4)_2$ [6,25]. Suspension of the hydroxo bridge compound **6** in MeCN on standing for a week slowly changes colour to greenish-yellow, which on acidification with dil. HCl develops a green colour. Product isolation and spectral comparison support the hydroxylation reaction.

3.2 *Spectral characterisation*

The ligands exhibit IR band at 1420–1430 and 1600–1610 cm^{-1} corresponding to N=N and C=N respectively [16]. In Pd(aapm)Cl_2, *n*(N=N) appears at 1390–1400 cm^{-1} and the red shifting supports the coordination of azo-N to the metal centre. The presence of two distinct Pd–Cl stretches at around 340 and 360 cm^{-1} are in agreement with *cis*-$PdCl_2$

configuration. In contrast [Pd(aapmO)Cl] has a single Pd–Cl (360 cm^{-1}) stretch [9] . The electronic spectra of the complexes were recorded in $CHCl_3$ solution in the range of 900–220 nm. The spectral data are collected in table 1. Absorption below 400 nm is due to intraligand charge transfer transitions and are not considered further. Pd(aapm)Cl_2 absorb strongly near 400 nm and is attributed to the charge transition in metallated-azoimine system [9,25]. Pd(aapmO)Cl in MeCN exhibit structured absorption in the visible region (figure 1) and there are three consecutive transitions in the wavelength range 600–725 nm with absorption maxima at 660–670 nm. This spectral feature is the characteristic of heterocyclicazophenolatopalladium(II) complexes and has been compared with the absorption pattern of 1-(2-(pyridylazo)-2-naphtholatopalladium (II)chloride in MeCN [26].

All the complexes display highly resolved ^{1}H-NMR spectra in $CDCl_3$. The spectral data are collected in table 2 and representative spectra are shown in figure 2. The proton numbering pattern is shown in structures **1** and **2**. Individual protons are assigned by spin–spin interaction, comparative integration, chemical shift and changes therein on substitution. The detail of ^{1}H NMR characterisation of the ligands has been reported earlier [16]. There are distinctly two portions in the spectra; pyrimidine protons (4-H–6-H) appear relatively at higher *d* values and the lower *d* signals refer to azoaryl protons (8-H–12-H). On coordination, pyrimidine protons are shifted further downfield while azoaryl protons are perturbed randomly. There are three doublets in the spectra of Pd(*p*-Raapm)Cl_2 (for R = Me, Cl) complexes in the intensity ratio 2:1:1 (figure 2). The X-ray structural study of analogous dichloro[2-(phenylazo)pyridine]palladium(II) [23] suggests

Table 2. ^{1}H NMR spectral data for Pd(aapm)Cl_2 (**1**) and Pd(aapmO)Cl (**2**).

	Compound *d*, ppm (*J*, Hz)								
Compound	4-H[b]	5-H[d]	6-H[b]	8-H	9-H	10-H	11-H	12-H	R
Pd(papm)Cl_2 (**1a**)	8·84	8·49	9·10	7·70[b]	7·53[c]	7·60[d]	7·53[c]	7·81[b]	
	(8·0)	(9·0)	(8·0)	(8·0)	(8·0)	(8·0)	(8·0)	(8·0)	
Pd(*o*-tapm)Cl_2 (**1b**)	8·81	8·44	9·05	7·67[b]	7·49[c]	7·52[c]	7·38[b]		2·64[f]
	(8·0)	(8·5)	(8·0)	(8·0)	(8·5)	(8·5)	(8·0)		
Pd(*m*-tapm)Cl_2 (**1c**)	8·80	8·40	9·03	7·53[e]		7·42[b]	7·50[c]	7·72[b]	2·50[g]
	(8·0)	(9·0)	(8·0)			(8·0)	(8·0)	(8·0)	
Pd(*p*-tapm)Cl_2 (**1d**)	8·80	8·36	9.02	7·51[b]	7·32[b]		7·32[b]	7·59[b]	2·52[h]
	(9·0)	(9·0)	(8·0)			(8·0)	(8·0)	(8·0)	
Pd(*p*-Clpapm)Cl_2 (**1e**)	8·88	8·54	9·15	7·76[b]	7·70[b]		7·70[b]	7·85[b]	
	(9·0)	(9·0)	(8·0)	(8·0)	(8·0)		(8·0)	(8·0)	
Pd(papmO)Cl (**2a**)	8·31	8·12	8·64		6·49[b]	7·10[c]	7·14[c]	7·24[b]	
	(8·0)	(8·0)	(8·5)		(7·5)	(8·0)	(8·0)	(8·0)	
Pd(*o*-tapmO)Cl (**2b**)	8·34	8·14	8·67		6·54[b]	7·08[c]	7·22[b]		2·54[f]
	(8·5)	(8·5)	(8·0)		(8·0)	(8·0)	(8·0)		
Pd(*m*-tapmO)Cl (**2c**)	8·30	8·18	8·61			7·10[b]	7·10[c]	7·25[b]	2·33[g]
	(8·5)	(8·5)	(8·0)			(8·0)	(8·0)	(8·0)	
Pd(*p*-tapmO)Cl (**2d**)	8·28	8·08	8·60		6·31[c]		6·81[b]	7·03[b]	2·38[h]
	(8·5)	(8·0)	(8·5)				(8·0)	(8·0)	
Pd(*p*-ClpapmO)Cl (**2e**)	8·35	8·15	8·69		6·71[e]		7·24[b]	7·37[b]	
	(8·0)	(8·0)	(8·5)				(8·0)	(8·5)	

[a]In $CDCl_3$, temp. 295 K; [b]doublet; [c] triplet; [d]multiplet; [e]singlet; [f]*d* (*o*-Me); [g]*d* (*m*-Me); [h]*d*(*p*-Me).

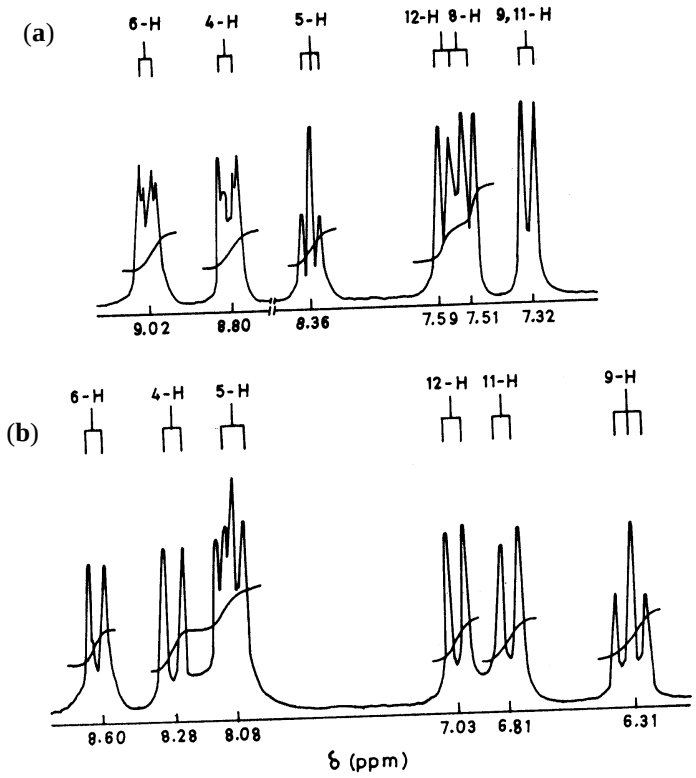


Figure 2. ^{1}H NMR spectra (**a**) Pd(*p*-tapm)Cl_2 and (**b**) Pd(*p*-tapmO)Cl in $CDCl_3$ at 300 MHz.

that the pendant phenyl ring does not lie on the plane of the chelated azoimine group and is inclined at an acute angle. Copper(I) and ruthenium(II) complexes of arylazopyrimidines [16,17] also support this stereochemical disposition of pendant aryl ring with the chelated azoimine group. Extending this information to the present work we may conclude that two ortho C–H functions are inequivalent; the nearer signal is assigned to 8-H and the second one to 12-H [13]. Hence, the doublet of two-proton intensity is assigned to 9 and 11-H. A remarkable feature in Pd(*o*-tapm)Cl_2 is the downfield shifting of the Me signal compared to others and may be due to the closest position of the electron-withdrawing azo function. Identifying signal in Pd(*m*-tapm)Cl_2 is the singlet resonance corresponding to 8-H. Other signals are assigned as above. Comparison of the NMR spectra **1** and hydroxylated product **2** reveals that one proton is short in the aromatic region of **2**. The spectra of [Pd(aapmO)Cl] (**2**) are shifted upfield in general and azoaryl protons in particular are severely affected. In [Pd(*p*-RaapmO)Cl] (R = Me, Cl) 9-H appears as a singlet and is shifted upfield by *ca.* 1·0 ppm relative to the Pd(*p*-Raapm)Cl_2 signal. The missing proton is assigned to 8-H; because of its closer proximity to the metal centre the chelative hydroxylation takes place at this centre. The upfield shifting of azoaryl protons (10-H–12-H) by 0·2–0·6 ppm may be due to the electron transmission effect of phenolato oxygen [27]. Pyrimidine protons (4-H–6-H) are also shifted upfield by 0·4–0·6 ppm. In Pd(*m*-tapm)Cl_2 there is a possibility of isomeric phenolisation at C(8)-H

or C(12-H) position. The *d*(Me) shows significant upfield shifting by 2·50 to 2·33 ppm and supports the hydroxylation at the C-8 position. Besides, the closer orientation of the C(8)-H group to the palladium centre may induce better electrophilicity at this function and accelerate nucleophilic attack.

3.3 *Electrochemistry*

The redox behaviour of the complexes was examined under N_2 in MeCN by cyclic voltammetry at a glassy carbon disk working electrode using Bu_4NClO_4 as a supporting electrolyte and the potentials were reported with reference to the SCE. The results are collected in table 1. Pd(aapm)Cl_2 undergoes quasi-reversible redox response at 0·10 to –0·14 V (ΔE_P = 100–120 mV) and an irreversible response at cathodic peak potential (E_{pc}) at –1·0 to –1·5 V versus SCE. These potentials may be due to reductions of azo function in ligand frame. The LUMO of –N=N– can accommodate two electrons [17] and the electrode reaction may be represented by,

$$[\text{–N=N–}] \underset{}{\overset{+e}{\rightleftharpoons}} \text{–N}^{\cdot\cdot}\text{–N–}]^{-} \xrightarrow{+e} [\text{–N–N–}]^{x}. \qquad (1)$$

The reduction potential in the present examples appear at the most positive position so far known for the metallated-azoimine system [1] and may be due to the high *p*-acidity in arylazopyrimidines. The potential movement is correlated with electron-donating/-withdrawing effect of the substituents and the plots of potential versus Hammett *s* of *p*-substituents are linear. The deviation of *o*- and *m*-tapm from linearity may be due to the steric effect of the –Me group.

The redox chemistry of Pd(aapmO)Cl is somewhat complicated and the nature of voltammogram and the potential is sensitive to the *p*H of the medium. Pd(papmO)Cl in MeCN solution slowly changes colour to brownish green on standing and to green on the addition of Bu_4NClO_4 (supporting electrolyte and *p*H = 4·5). This solution exhibits two consecutive quasi-reversible redox couples (figure 3) (couple 1, –0·16 (100); couple 2, –0·37 (90) V; values in parentheses refer to ΔE_P in mV) approximately in 2:1 current height ratio and two irreversible cathodic peak potentials (E_{Pc}) at –1·15 and –1·35 V. On decreasing the *p*H of the solution (upon adding dil. $HClO_4$ and measuring the *p*H with a *p*H-meter) the current height of the couple 2 at –0·37 V gradually diminishes and disappears at *p*H = 2·8. The height of couple 1 is increased slowly and becomes constant (at *p*H = 2·8) at current height 1·13 I_0 (I_0 = diffusion current height of the first voltammogram). On further acidification, the couple 1 becomes irreversible and shows an ill-defined voltammogram at *p*H < 2. Addition of sodium hydroxide solution in degassed MeCN solution shows peculiar behaviour in the voltammogram. Current height of couple 1 is reduced and of couple 2 is increased slightly. The peak separation of couples 1 and 2 decreases and shows a broad and ill-defined voltammogram at *p*H > 8·0. The solution gradually changes colour from green to brown-pink. There are two possible active centres in the complex Pd(aapmO)Cl: pyrimidine bears *m*-related peripheral-N which remains free with a labile Pd–Cl bond. Free pyrimidine-N may be protonated in acid medium and may be the reason for the reduction of current height of couple 2 [28]. Thus, couple 1 may be responsible for the azo reduction of protonated complex $[Pd(HaapmO)Cl]^{+}$ (scheme 2). At higher *p*H, the Pd–Cl bond may undergo nucleophilic substitution giving hydroxo-species, [Pd(aapmO)(OH)] (scheme 3), and the couple 2 may correspond to azo reduction of this species. Similar experiments with Pd(papm)Cl_2 show an ill-defined

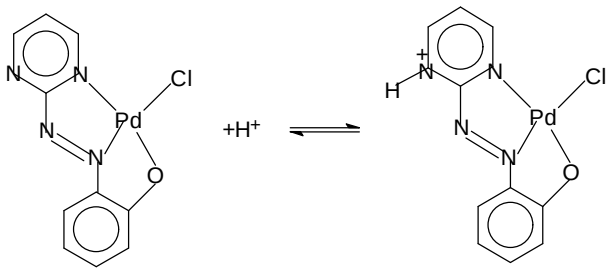
voltammogram at lower pH supporting protonation at pyrimidine-N while the reduction couple remains almost unperturbed at *p*H = 8 and becomes ill-defined at higher *p*H.

Identical experiments with Pd(papO)Cl exhibit a quasi-reversible voltammogram which is ill-defined at the initial stage on acidification (first run after $HClO_4$ addition is ill-defined) or sodium hydroxide addition. Solution behaviour of Pd(aapmO)Cl (turning from green to brownish green on base addition and restoration of green colour by acidification) supports the existence of equilibrium between protonated/deprotonated or hydroxo/chloro forms.

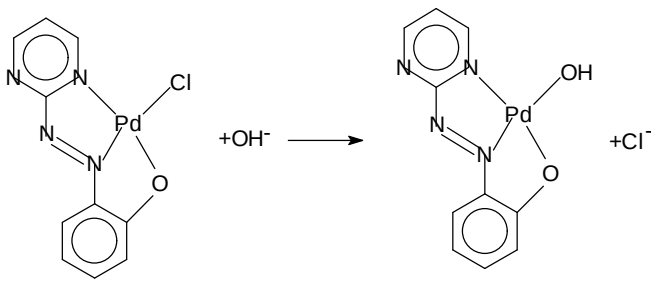
3.4 *Reaction of Pd-Cl bond in Pd(aapmO)Cl*

Hydroxylated complex Pd(aapmO)Cl (**2**) is sensitive to moisture. In MeCN, $CHCl_3$, CH_2Cl_2, or alcohols, the green colour of the solution slowly turns to yellowish green with formation of brown precipitate. Acidification with dilute $HClO_4$ restores the green colour. Slow addition of dilute NaOH to MeCN solution of Pd(papmO)Cl changes the green colour to brownish pink and restores it upon addition of dil $HClO_4$. Spectrophotometry on addition of dilute NaOH in MeCN solution of Pd(papmO)Cl (**2a**) shows the disappearance of the structured absorption bands at 625, 670 and 725 nm and appearance of a new band at 540 nm. On addition of dil $HClO_4$ the spectral structure is restored.

On isolation of the brown product, its IR spectrum does not show Pd–Cl stretching, but rather a broad band centred at 3380 cm^{-1}, is observed which may be assigned to ν(O–H) [25]. The brown product is sparingly soluble in organic solvents but addition of small amounts of acid enhances the solubility and the colour changes to green. To an



Scheme 2.



Scheme 3.

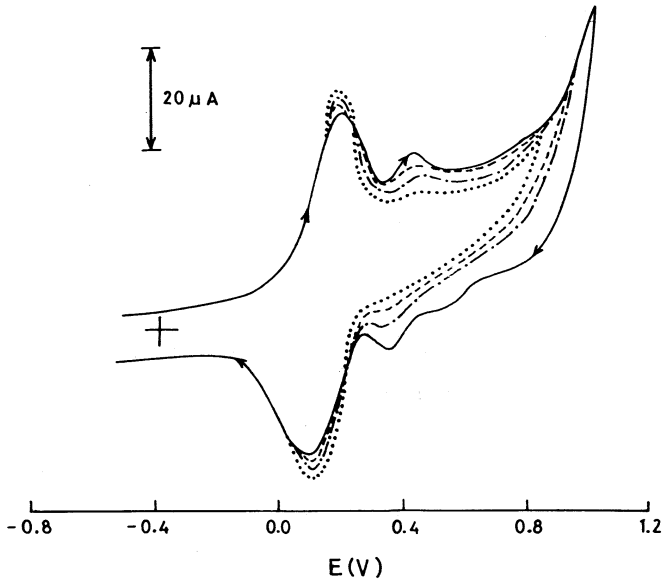


Figure 3. Effect of *p*H on cyclic voltammogram: *p*H = 4·5 (——); *p*H = 3·9 (- - -); *p*H = 3·3 (–·–); *p*H = 2·8 (·····) in MeCN solution.

acetone solution of Pd(papmO)Cl (**2a**) aqueous $AgNO_3$ is added, when the green colour changes to brown and the precipitated AgCl is filtered off. The solution is evaporated in air and dilute $HClO_4$ in saturated $NaClO_4$ solution is added. On cooling, a dark coloured precipitate is isolated. IR spectrum of dry product exhibits $n(ClO_4)$ at 1090 and 625 cm^{-1} along with a broad intense band at 3450 cm^{-1} corresponding to $n(H_2O)$. Conductance measurements ($\Lambda_M \sim 110\ \Omega^{-1}cm^{-1}mol^{-1}$) and microanalytical data support the composition $[Pd(aapmO)(OH_2)](ClO_4)$.

Considering the behaviour of the molecule as that of an acid–base indicator, the spectrophotometric determination of *pK* values are made[29] in one case only, Pd(papmO)Cl, following the decrease in absorbance at 670 nm (maximum decrease) and increase in absorbance at 540 nm. The *pK* value lies at 4·7 ± 0·05. Thus the complex may act as a non-aqueous acid–base indicator functioning in the acid range.

4. Conclusions

Dichloro-{2-(arylazo)pyrimidine}palladium(II), and $Pd(aapm)Cl_2$, react with Tollen's reagent and the chelative hydroxylation leads to isolation of chloro-{2-((8-hydroxo)arylazo)pyrimidine}palladium(II), Pd(aapmO)Cl, complexes. The complexes have been characterised by IR, UV-Vis and ^1H NMR spectral data. The hydroxylated product, Pd(aapmO)Cl, shows entirely different absorption pattern from that of the parent complex, $Pd(aapm)Cl_2$ in the visible region. The absorption spectra of Pd(aapmO)Cl are highly sensitive to *p*H of the medium and shows reversible change with the addition of acids and bases. Spectrophotometric determination of *pK* for Pd(papmO)Cl shows a value of 4·7 ± 0·05. Cyclic voltammetry shows azo reduction and is very sensitive to change in *p*H of the medium.

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