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# FACILE REGIOSPECIFIC AROMATIC HYDROXYLATION IN PALLADIUM AZOPYRIDINES AND STRUCTURAL CHARACTERIZATION OF PHENOLATO PRODUCT

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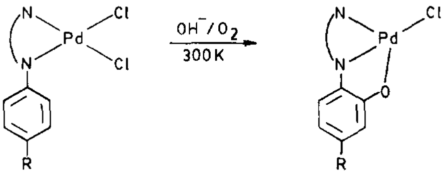
**Abstract**—The reaction of $Na_2PdCl_4$ with 2-(arylazo)pyridines (A) in ethanol affords yellow complexes of composition [$PdACl_2$] in which the $PdCl_2$ fragment has a *cis* configuration [$\nu$(Pd—Cl): 350, 365 $cm^{-1}$]. Upon treating [$PdACl_2$] with dilute sodium hydroxide in air the pendent aryl group is selectively hydroxylated at the *ortho* position, affording the phenolato complex [PdBCl] in high yields [$B^-$ is deprotonated 2-(2′-hydroxyarylazo)pyridine]. A possible reaction pathway is proposed by analogy with the hydroxylation of certain organic compounds by $OH^-/O_2$. The crystal and molecular structure of one [PdBCl] complex is reported. In the highly planar complex, the Pd—N(azo) length is significantly shorter than the Pd—N(pyridine) length. A single Pd—Cl stretch at 365 $cm^{-1}$ characterizes [PdBCl] which, unlike [$PdACl_2$], has a structured intense absorption in the visible region near 670 nm.

Hydroxylation of aromatic compounds assisted by transition metal ions is an important chemical reaction.[1–7] Herein, we report a case where a simple reagent brings about high-yield regiospecific hydroxylation of an N,N-chelated palladium(II) system affording a phenolato derivative, as shown schematically in eq. (1):



(1)

The synthesis and characterization of a pair of reactive complexes are described. The phenolato products derived therefrom have been characterized including X-ray structure determination of one complex. A probable pathway of the reaction is noted.

## EXPERIMENTAL

### Materials

Disodium tetrachloropalladate(II) was prepared by reacting palladium(II) chloride with sodium chloride in water and evaporating the aqueous solution.[4b] The 2-(arylazo)pyridines (A) were synthesized by condensing 2-aminopyridine with the appropriate nitrosobenzene according to the reported procedure.[8] Commercial grade BDH silica gel (60–120 mesh) was used for column chromatography. Argon gas was purified by successively bubbling it through alkaline dithionite and concentrated sulphuric acid. Sodium hydroxide and all other chemicals and solvents used for the preparative works were of reagent grade and were used as received.

### Physical measurements

Electronic spectra were recorded by a Hitachi model 330 spectrophotometer fitted with a ther-

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mostatted cell compartment. IR (4000–250 $cm^{-1}$) spectra were taken on a Perkin–Elmer 783 spectrophotometer. Microanalyses (C, H, N) were done using a Perkin–Elmer 240C elemental analyser.

### *Synthesis of complexes*

The synthesis of complexes of type [$PdACl_2$] were achieved by using a general method. Specific details are given for [$PdA^1Cl_2$], dichloro (phenylazo)pyridine palladium(II). A solution of 2-(phenylazo)pyridine (200 mg, 1.09 mmol) in ethanol (5 $cm^3$) was slowly added to a magnetically stirred solution of $Na_2PdCl_4$ (300 mg, 1.02 mmol) in ethanol (10 $cm^3$). The yellow precipitate thus obtained was filtered after 5 min. The precipitate was washed successively with ethanol (3 × 2 $cm^3$) and water (3 × 2 $cm^3$), and dried over $P_4O_{10}$. Yield: 90%.

The [$PdACl_2$] complexes are insoluble in water and benzene but are sparingly soluble in dichloromethane and acetonitrile.

### *Hydroxylation of* [$PdACl_2$] *by dilute sodium hydroxide: synthesis of* [PdBCl]

A dilute solution of sodium hydroxide (0.04 M) in a 2:3 water–acetonitrile mixture (5 $cm^3$) was added dropwise for 2 h to a magnetically stirred suspension of [$PdA^1Cl_2$] (50 mg, 0.14 mmol) in acetonitrile (30 $cm^3$) in air. Stirring was continued for another 24 h. The colour of the solution changed gradually from yellow to green. The solution was evaporated to dryness *in vacuo* and the residue was washed thoroughly with water (5 × 3 $cm^3$) and was then dried over $P_4O_{10}$. The solid residue was dissolved in dichloromethane (50 $cm^3$) and the solution was chromatographed over a silica gel column (60 × 1 cm) prepared in benzene. A very small amount of yellow compound was eluted first and rejected. An acetonitrile–benzene (1:3) mixture was then used to elute the desired compound as a deep green band. The eluted solution on evaporation *in vacuo* gave the pure [$PdB^1Cl$] complex. Yield: 70%. Found: C, 38.6; H, 2.5; N, 11.9. Calc. for $PdC_{11}H_8N_3OCl$: C, 38.8; H, 2.3; N, 12.4%.

The same procedure was also applied for the hydroxylation of [$PdA^2Cl$] to [$PdB^2Cl$]. Yield: 67%. Found: C, 40.6; H, 2.9; N, 12.0. Calc. for $PdC_{12}H_{10}N_3OCl$: C, 40.7; H, 2.8; N, 11.9%.

When excess (say five-fold) sodium hydroxide solution is added all at once, the suspended [$PdACl_2$] undergoes dissolution, forming a red–violet solution with subsequent precipitation of a dark violet product. The [PdBCl] complex is not formed under these conditions. The nature of the violet product is under scrutiny.

### *X-ray structure determination*

Single crystals of [$PdB^1Cl$] were grown by slow evaporation of a dilute solution of complex in dichloromethane–hexane (1:1). Cell dimensions were obtained by the least-squares refinement of diffractometer angles of 30 reflections chosen from rotation photographs. Data were collected at 296 K on a Nicolet R3m/V diffractometer with graphite monochromated Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) radiation in the $\omega$–$2\theta$ scan mode. Two check reflections measured after every 98 reflections showed no significant variations. Lorentz and polarization corrections were followed by semi-empirical absorption correction on the basis of azimuthal scans.[9] The structure was solved by the Patterson heavy atom method and was refined by full-matrix

Table 1. Crystal data, intensity data collection and structural refinement for [$PdB^1Cl$]

| | |
|---|---|
| Formula | $PdClON_3C_{11}H_8$ |
| Crystal size (mm) | 0.12 × 0.26 × 0.30 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 8.333(2) |
| $b$ (Å) | 10.286(2) |
| $c$ (Å) | 7.069(2) |
| $\alpha$ (°) | 97.44(2) |
| $\beta$ (°) | 110.67(2) |
| $\gamma$ (°) | 87.74(2) |
| $U$ (Å$^3$) | 562.1(2) |
| $Z$ | 2 |
| $M$ | 340.07 |
| $D_c$ (g $cm^{-3}$) | 2.01 |
| $\mu$ (Mo-$K_\alpha$)($cm^{-1}$) | 18.53 |
| $F$(000) | 332 |
| $2\theta$ range (°) | 2–55 |
| Total no. of reflections | 2757 |
| No. of unique reflections | 2573 |
| No. of observed reflections [$I > 3\sigma(I)$] | 2227 |
| Transmission factors | 0.8349 |
| Weighing scheme $g$ in $w = 1/[\sigma^2(F)+gF^2]$ | 0.0006 |
| No. of parameters refined | 154 |
| Final $R$ | 0.0222 |
| Final $R_w$ | 0.0298 |
| Goodness-of-fit | 0.9274 |
| Largest and mean $\Delta/\sigma$ | 0.001, 0.000 |
| Data-to-parameter ratio | 14.4:1 |
| Largest difference peak (e Å$^{-3}$) | 0.43 |
| Largest difference hole (e Å$^{-3}$) | −0.42 |

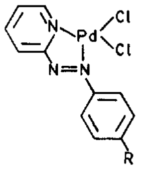
least-squares procedures. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at the calculated positions in the final refinement cycle with isotropic thermal parameters (0.08 Å$^2$). Crystal data and other details are collected in Table 1. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program system.[10]

Tables of atomic coordinates, anisotropic thermal parameters, full listings of bond lengths and angles, and observed and calculated structure factors are available as supplementary material from the Editor.

## RESULTS AND DISCUSSION

### *Parent complexes*

The reaction of 2-(arylazo)pyridines[11–13] (A) with sodium tetrachloropalladate(II) in ethanol affords yellow coloured [PdACl$_2$] (**1**) in high yields. Two ligands of type A have been used, A$^1$ and A$^2$ (see structure **1**). Characterization data for the complexes are given in a later section.



| | R |
|---|---|
| [PdACl$_2$] | R |
| [PdA$^1$Cl$_2$] | H |
| [PdA$^2$Cl$_2$] | Me |

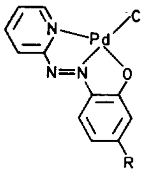
(1)

### *Hydroxylation*

Slow addition of a dilute solution of sodium hydroxide in aqueous acetonitrile to a stirred suspension of [PdACl$_2$] in acetonitrile under ambient condition leads to a colour change from yellow to green, and from the reaction mixture the green phenolato complex [PdBCl] (**2**) can be isolated in 70% yield [B$^-$ is deprotonated 2-(2′-hydroxyarylazo)pyridine].

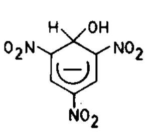
The above conversion of **1** to **2** requires the presence of oxygen (air) as well as alkali. Hydroxylation does not occur when air is replaced by pure argon. The conversion **1** → **2** can also be achieved, but only in low yields (10–20%), by simply boiling **1** in water with or without the addition of Ag$^+$.[14] The present work reveals that the active reagent is OH$^-$/O$_2$.

Aromatics bearing strongly electron-withdrawing groups, such as 1,3,5-trinitrobenzene, are hydroxylated by hydroxide ions in air via oxidation of the intermediate **3**.[15] An analogous route can be conceived for the conversion **1** → **2** via an intermediate such as **4**. The latter can arise from nucleophilic attack by metal-coordinated hydroxide ion at the *ortho* position of the pendent aromatic ring, which is subject to electron withdrawal by the metal centre and the azo function.



| | R |
|---|---|
| [PdBCl] | R |
| [PdB$^1$Cl] | H |
| [PdB$^2$Cl] | Me |

(2)



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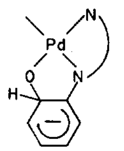

(4)

### *Characterization of the complexes and X-ray structure of* [PdB$^1$Cl]

Characterization data of the [PdACl$_2$] and [PdBCl] complexes are set out in Table 2. The presence of two distinct Pd—Cl stretches in [PdACl$_2$] is in agreement with the *cis*-PdCl$_2$ configuration (Fig. 1). In contrast, [PdBCl] has a single Pd—Cl stretch. Solutions of [PdACl$_2$] absorb strongly near 400 nm, while [PdBCl] has a characteristic structured absorption profile in the visible region near 670 nm (Fig. 1).

The crystal lattice of [PdB$^1$Cl] consists of discrete molecules in which the ligands are bonded as in **2**. A perspective view is shown in Fig. 2 and selected bond parameters are listed in Table 3. The entire molecule is excellently planar, the largest deviation from the mean plane being 0.03 Å. Interestingly, the Pd—N(azo) length is ~0.1 Å shorter than the Pd—N(pyridine) length, suggesting the presence of metal–azo back-bonding.[11,16]

## CONCLUSIONS

It is demonstrated that the pendent aryl groups of 2-(arylazo)-pyridine ligands bonded to palladium(II) as in *cis*-[PdACl$_2$] undergo facile and high-yield *ortho* hydroxylation by the unusual reagent OH$^-$/O$_2$ under ambient conditions, affording phenolato complexes of type [PdBCl], one of which has been structurally characterized. A poss-

Table 2. Electronic spectra[a] and IR spectra[b] of palladium azopyridines

| Compound | $\lambda$ (nm) ($\varepsilon$, dm$^3$mol$^{-1}$ cm$^{-1}$) | $\nu$(Pd—Cl) (cm$^{-1}$) | $\nu$(Pd—O) (cm$^{-1}$) |
|---|---|---|---|
| $[\mathrm{PdA^1Cl_2}]$ | 390 (14,218), 380[c] (13,762), 290 (4700), 235 (24,100) | 345, 365 | — |
| $[\mathrm{PdA^2Cl_2}]$ | 410 (15,240), 385 (12,221), 295 (4456), 245 (15,062) | 350, 365 | — |
| $[\mathrm{PdB^1Cl}]$ | 710[c] (5580), 665 (6660), 620[c] (4614), 425[c] (5256), 375 (20,830), 360[c] (17,457), 320 (13,140) | 365 | 500 |
| $[\mathrm{PdB^2Cl}]$ | 700[c] (5692), 655 (6675), 610[c] (4586), 460[c] (3604), 430[c] (9000), 400 (14,900), 375 (13,841), 360[c] (10,975), 320 (10,810), 240 (2950) | 365 | 485 |

[a] In dichloromethane.

[b] In KBr discs.

[c] Shoulder.

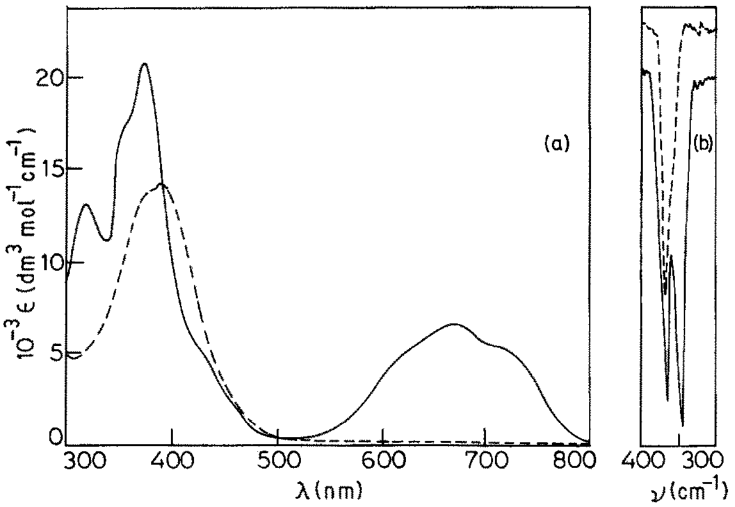

Fig. 1. (a) Absorption spectra of $[\mathrm{PdA^1Cl_2}]$ (- - -) and $[\mathrm{PdB^1Cl}]$ (——) in dichloromethane at 298 K. (b) IR spectra of $[\mathrm{PdA^1Cl_2}]$ (——) and $[\mathrm{PdB^1Cl}]$ (- - -) in KBr discs showing only Pd—Cl stretches.

Table 3. Selected bond distances (Å) and bond angles (°)[a] for $[\mathrm{PdB^1Cl}]$

| | | | |
|---|---|---|---|
| Pd—N(1) | 2.013(2) | Pd—N(3) | 1.924(2) |
| Pd—Cl | 2.299(1) | N(2)—N(3) | 1.279(3) |
| Pd—O | 2.022(2) | C(11)—O | 1.308(3) |
| N(1)—Pd—N(3) | 78.8(1) | N(3)—Pd—O | 83.6(1) |
| N(1)—Pd—Cl | 100.3(1) | N(3)—Pd—Cl | 179.0(1) |
| O—Pd—Cl | 97.3(1) | N(1)—Pd—O | 162.4(1) |

[a] Estimated standard deviations are given in parentheses.

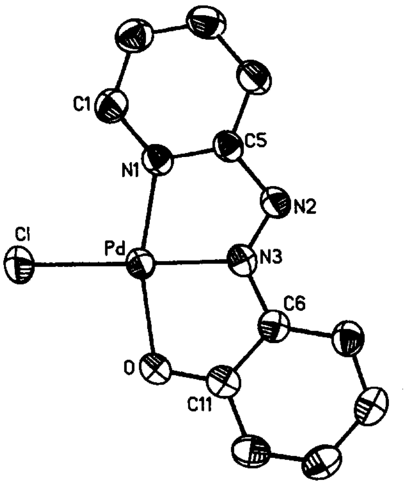

Fig. 2. Perspective view and atom labelling scheme of $[PdB^1Cl]$. Atoms are shown as 50% thermal probability ellipsoids.

ible pathway of the reaction is indicated on the basis of analogy.

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