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# Cyclopalladation of indole-3-carboxaldehyde aroylhydrazones

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### 1. Introduction

Cyclometallated complexes are of immense contemporary interest primarily because of their applications in a variety of research areas such as organic synthesis, biological and pharmaceutical chemistry, catalysis and materials science [1-11]. We have reported some such species with various Schiff bases prepared by condensation of benzaldehyde and its derivatives with acid hydrazides [12–15]. These amide-O coordinating Schiff bases can provide only the ortho position of the benzaldimine moiety for cyclometallation and act as tridentate C,N,O-donor ligands to form 5,5-membered fused chelate rings. On the other hand, indole-3carboxaldehyde 4-R-benzoylhydrazones (H<sub>2</sub>L<sup>n</sup>, 2 H represent the dissociable protons from the amide functionality and indole ring) offer either of the two positions namely 2 or ortho and 4 or peri of the indole moiety for cyclometallation and as C,N,O-donor it can form either 5,5- or 6,5-membered fused chelate rings (Chart 1). It may also be noted that in recent times indole containing ligands and their metal complexes are receiving considerable attention for their biological and clinical relevance [16-19]. There are two reports on X-ray structurally characterized cyclometallated complexes with such ligands. These ligands are bidentate alkaloids gramine and tryptamine and (S)-triptophan methyl ester [20] and the tridentate Schiff bases prepared by condensation of indole-3carboxaldehyde with semicarbazide, ethyl hydrazinecarboxylate

### ABSTRACT

Reactions of PdCl<sub>2</sub>, LiCl, indole-3-carboxaldehyde 4-*R*-benzoylhydrazones (H<sub>2</sub>L<sup>*n*</sup>; n = 1, 2, 3 and 4 for R = H, Cl, OMe and NMe<sub>2</sub>, respectively) and CH<sub>3</sub>COONa·3H<sub>2</sub>O in 1:2:1:1 mol ratio in methanol produce the cyclopalladated species of general formula [Pd(HL<sup>*n*</sup>)Cl] in 65–85% yields. The complexes have been characterized with the help of elemental analysis and spectroscopic (infrared, electronic and NMR) measurements. The proton NMR spectra of the complexes suggest palladation at the *peri* position of the indole moiety in (HL<sup>*n*</sup>)<sup>-</sup>. Molecular structure of a representative complex determined by X-ray crystallography confirms the *peri*-palladation and formation of a distorted CNOCl square-plane around the metal centre by the tridentate (HL<sup>*n*</sup>)<sup>-</sup> and the chloride.

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and acetylhydrazine [21]. With the bidentate system *ortho*-platination and with the tridentate system *peri*-palladation have been observed. We have tried to synthesize cylcopalladated species with  $H_2L^n$  to find out whether the aroyl moiety of  $H_2L^n$  makes any difference in the regioselectivity of the metallation site. Herein we describe the synthesis, structure and properties of a family of *peri*-metallated complexes having the general formula [Pd(HL<sup>n</sup>)Cl].

### 2. Experimental

### 2.1. Materials

Purification of solvents was performed by standard methods [22]. All the chemicals used in this work were of analytical grade available commercially and were used without further purification.

### 2.2. Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used to collect the elemental (C, H, N) analysis data. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification. Solution electrical conductivities were measured with a Digisun DI-909 conductivity metre. Infrared spectra were recorded on a Jasco-5300 FT-IR spectrophotometer by using KBr pellets. A Perkin–Elmer Lambda 35 UV/vis spectrophotometer was used to collect the electronic spectra. The proton NMR spectra were recorded with the help of a Bruker 400 MHz NMR spectrometer.



Note



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Chart 1. Indole-3-carboxaldehyde aroylhydrazone and possible cyclopalladates.

 Table 1

 Crystal data for  $[Pd(HL^1)Cl] \cdot CH_3CN (\mathbf{1} \cdot CH_3CN).$ 

Chemical formula	PdC <sub>18</sub> H <sub>15</sub> N <sub>4</sub> OCl
Formula weight	445.22
Crystal system	Triclinic
Space group	PT
a (Å)	9 3308(10)
$h(\mathbf{A})$	10 4842(11)
$c(\hat{A})$	10.6176(11)
	10.0170(11) CC 404(2)
a	66.404(2)
β(°)	84.781(2)
γ	66.675(2)
V (Å <sup>3</sup> )	871.23(16)
Ζ	2
$\rho$ (g cm <sup>-3</sup> )	1.697
$\mu ({\rm mm^{-1}})$	1.232
Reflections collected	8421
Reflections unique	3053
Reflections $[I \ge 2\sigma(I)]$	2854
Parameters	227
R1, wR2 $[I \ge 2\sigma(I)]$	0.0318, 0.0717
R1, wR2 [all data]	0.0352, 0.0730
GOF on F <sup>2</sup>	1.105
Largest diff. peak and hole (e $Å^{-3}$ )	0.500, -0.272

### 2.3. Synthesis of $[Pd(HL^1)Cl]$ (1)

A mixture of PdCl<sub>2</sub> (89 mg, 0.5 mmol) and LiCl (43 mg, 1 mmol) was taken in 15 ml of dry methanol and refluxed with stirring for 1 h. It was then cooled to room temperature and filtered.  $H_2L^1$  (132 mg, 0.5 mmol) and CH<sub>3</sub>COONa · 3H<sub>2</sub>O (68 mg, 0.5 mmol) were added to the filtrate and the mixture was stirred at room temperature for 12 h. The complex separated as a green solid was collected by filtration, washed with cold methanol and finally dried in air. Yield: 170 mg (84%).

#### Table 2

Elemental analysis	and	electronic	spectroscopic <sup>a</sup>	data.
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The other three complexes namely  $[Pd(HL^2)CI]$  (**2** (R = CI)),  $[Pd(HL^3)CI]$  (**3** (R = OMe)) and  $[Pd(HL^4)CI]$  (**4** (R = NMe<sub>2</sub>)) were synthesized from PdCl<sub>2</sub>, LiCl, the corresponding Schiff base  $(H_2L^n)$  and CH<sub>3</sub>COONa·3H<sub>2</sub>O in 65–85% yields by following procedures very similar to that described above for **1** (R = H).

### 2.4. X-ray crystallography

A Bruker-Nonius SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a Mo K $\alpha$  fine-focus sealed tube ( $\lambda = 0.71073$  Å) was used for determination of unit cell parameters and intensity data collection at 298 K. The SMART and the SAINT-Plus packages [23] were used for data acquisition and data extraction, respectively. The absorption correction was performed with the help of SADABS program [24]. The structure was solved by direct method and refined on F<sup>2</sup> by full-matrix leastsquares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model. The SHELX-97 programs [25] were used for structure solution and refinement. The ORTEX6a [26] and Platon packages [27] were used for molecular graphics. Selected crystallographic data are summarized in Table 1.

### 3. Results and discussion

The Schiff bases  $(H_2L^n)$  were prepared in 75–90% yields by condensation reactions of equimolar amounts of indole-3carboxaldehyde and the corresponding 4-*R*-benzoylhydrazine  $(R = H, Cl, OMe \text{ and } NMe_2)$  in presence of a few drops of acetic acid in ethanol [21]. Their molecular formulae and structures were confirmed with the help of elemental analysis and spectroscopic (mass and proton NMR) measurements. Reactions of  $H_2L^n$  and

Complex	Found (calc.) (%)			$\lambda_{ m max}~( m nm)~(10^{-4} imes~arepsilon~( m M^{-1}~ m cm^{-1}))$
	С	Н	Ν	
1	47.55 (47.21)	2.99 (3.05)	10.40 (10.55)	407 (5.92), 386 (7.89), 370 (5.92), 350 <sup>b</sup> (3.38), 293 <sup>b</sup> (2.53)
2	43.81 (43.54)	2.53 (2.38)	9.58 (9.35)	410 (5.78), 390 (7.84), 373 (5.87), 354 <sup>b</sup> (3.43), 297 <sup>b</sup> (2.48)
3	47.03 (47.12)	3.25 (3.36)	9.68 (9.59)	406 (6.40), 386 (8.18), 369 (5.97), 348 <sup>b</sup> (3.41), 315 <sup>b</sup> (2.36)
4	48.34 (48.03)	3.83 (3.72)	12.53 (12.37)	412 (7.06), 391 (8.77), 373 (6.32), 354 <sup>b</sup> (3.84), 311 (4.56)

<sup>a</sup> In dimethylformamide.

<sup>b</sup> Shoulder.

#### Table 3

Proton NMR data<sup>a</sup> ( $\delta$  (ppm) (J (Hz))) for complexes **1–4** in dmso-d<sub>6</sub>.

Complex	H(1)	H(2)	H(5)	H(6)	H(7)	H(8)	H(10)	H(13a,13a')	H(14a,14a')	R
<b>1</b> (R = H)	12.18 (s)	8.34 (d) (2)	7.80 (d) (8)	6.98 (br,s)	7.21 (d) (7)	8.69 (s)	13.86 (s)	8.02 (d) (7)	7.63 (t) (7)	7.72 (t) (6)
<b>2</b> (R = Cl)	12.20 (s)	8.33 (br,s)	7.80 (d) (7)	6.99 (br,s)	7.21 (br,s)	8.68 (s)	13.93 (s)	8.04 (d) (8)	7.71 (br,s)	_
<b>3</b> (R = OMe)	12.14 (s)	8.30 (d) (3)	7.79 (d) (8)	6.98 (br,s)	7.20 (d) (7)	8.66 (s)	13.63 (s)	8.00 (d) (9)	7.16 (d) (8)	3.87 (s)
$\boldsymbol{4}\left(R=NMe_{2}\right)$	12.08 (s)	8.27 (d) (2)	7.78 (d) (8)	6.96 (br,s)	7.19 (d) (6)	8.64 (s)	13.31 (s)	7.87 (d) (9)	6.82 (d) (9)	3.03 (s)

<sup>a</sup> In dmso-d<sub>6</sub>.



Fig. 1. Molecular structure of  $[Pd(HL^1)Cl]$  (1) with the atom labelling scheme. All non-hydrogen atoms are represented by their 50% probability thermal ellipsoids.

CH<sub>3</sub>COONa·3H<sub>2</sub>O with Li<sub>2</sub>PdCl<sub>4</sub> (generated in situ from 1 mol equivalent of PdCl<sub>2</sub> and 2 mol equivalents of LiCl) in dry methanol provide the cyclometallated species in moderate to good yields. The elemental analysis data (Table 2) of the complexes (**1**–**4**) are consistent with the general formula [Pd(HL<sup>n</sup>)Cl]. As expected for palladium(II) species, **1**–**4** are diamagnetic. The solubility of all four complexes in polar acetone, acetonitrile, dimethylformamide and dimethylsulfoxide is moderate to high, while they are slightly soluble in relatively much less polar halogenated solvents such as dichloromethane and chloroform. In solution, **1**–**4** behave as non-electrolyte. Thus the chloride is coordinated to the metal centre in each complex.

Infrared spectra of **1–4** display the two N–H and the C=O stretches in the frequency ranges 3195–3605 and 1597–1615 cm<sup>-1</sup>, respectively [21,28]. The C=O stretches in **1–4** are about 15–25 cm<sup>-1</sup> lower than the C=O stretches displayed by the free Schiff bases (H<sub>2</sub>L<sup>n</sup>). A strong band observed in the range 1600–1612 cm<sup>-1</sup> for H<sub>2</sub>L<sup>n</sup> is attributed to the C=N stretch. The corresponding band for **1–4** appears at a lower frequency range of 1560–1580 cm<sup>-1</sup> [12–15,21]. The lowering of both C=O and C=N stretches indicates that the ligand (HL<sup>n</sup>)<sup>–</sup> coordinates to the metal centre through the azomethine N-atom and the protonated amide functionality O-atom forming a five-membered chelate ring.

The electronic spectra of 1-4 were collected in dimethylformamide. The spectral data are listed in Table 2. The spectral profiles of 1-4are very similar except for some small shifts in the band positions. They display three strong peaks in the wavelength range 412–369 nm. These are followed by two shoulders within 354–293 nm for 1-3 and a shoulder and a peak at 354 and 311 nm, respectively for 4 (Table 2). The free Schiff bases in dimethylformamide show only two absorptions

C(1)-Pd-N(2)

O(1)-Pd-N(2)

N(2)-Pd-Cl

2.156(2) 2.299(1) 1.342(4)

94.54(12)

78.26(9)

171.25(7)

Table 4			
Selected bond lengt	hs (Å) and angles (°)	for $1 \cdot CH_3CN$ .	
Pd-C(1)	1.972(3)	Pd-O(1)	
Pd-N(2)	2.016(3)	Pd-Cl	
C(10) = O(1)	1 240(4)	C(10) - N(3)	

172.57(11)

93.18(6)

94.08(10)

C(1)-Pd-O(1)

C(1)-Pd-Cl

O(1)-Pd-Cl

in the ranges 333–323 and 289–268 nm. Thus the longer and the shorter wavelength absorptions displayed by **1–4** are due to charge transfer and ligand centred transitions, respectively [12,13,29,30].

The proton NMR spectra of the complexes and the free Schiff bases were recorded in dmso-d<sub>6</sub>. The data for the complexes are listed in Table 3. The H<sub>4</sub> proton observed as a doublet within  $\delta$  7.77–7.84 for the free Schiff bases is absent in the spectra of the complexes. The absence of this resonance indicates peri-metallation of the indole moiety in 1–4. In general, the resonances in the complexes show a downfield shift compared to the corresponding resonances observed for the free Schiff bases. However, the downfield shift by  $\delta$  0.5–0.6 of the H<sub>5</sub> is significantly larger compared to that ( $\delta$  0.1–0.2) of the other C–H protons. This large shift of H<sub>5</sub> corroborates *peri*-metallation of the indole ring in **1–4**. The singlets corresponding to indole N–H (H<sub>1</sub>  $\delta$  11.52–11.60) and the amide N–H (H<sub>10</sub>  $\delta$  11.22–11.60) protons are very closely spaced for the free Schiff bases. On the other hand, these signals are well separated in the spectra of **1–4** due to disproportionate downfield shift of both. The indole N–H (H<sub>1</sub>) appears within  $\delta$  12.08–12.20, while amide N–H (H<sub>10</sub>) appears in the range  $\delta$  13.31–13.93. The much larger downfield shift of the latter indicates coordination of the azomethine N-atom adjacent to the amide N-H and hence



Fig. 2. One-dimensional ordering of N–H…N connected  $[Pd(HL^1)CI]\cdot CH_3CN$  (1-CH<sub>3</sub>CN) via N–H…CI hydrogen bonds.

formation of a six-membered metallacycle in each of **1–4** (Chart 1). In the aroyl fragment, the *meta* protons (H<sub>13</sub>, H<sub>13a</sub>) with respect to the substituent (*R*) resonate as a doublet within  $\delta$  7.87–8.04. The *ortho* protons appear as a triplet for **1** (*R* = H), broad singlet for **2** (*R* = Cl) and doublet for **3** (*R* = OMe) and **4** (*R* = NMe<sub>2</sub>) in the range  $\delta$  6.82–7.71. The methyl protons of *R* in **3** and **4** appear as singlet at  $\delta$  3.87 and 3.03, respectively; while, the proton (H<sub>15</sub>) at the same position in **1** appears as a triplet at  $\delta$  7.72.

The comparable spectral characteristics suggest that **1–4** have similar molecular structures. The coordination of the chloride to the square-planar bivalent palladium centre is confirmed by their nonelectrolytic and diamagnetic nature. Thus it becomes apparent that the deprotonated Schiff base  $(HL^n)^-$  acts as a tridentate indole *peri*-C, azomethine-N and amide-O donor ligand to form a 6,5-membered fused chelate rings system and together with the chloride constitutes a CNOCl square-plane around the metal centre in **1–4**.

To confirm the above molecular structure we have tried to grow single crystals of all the complexes. X-ray quality crystals could be grown for only 1 by slow evaporation of its acetonitrile solution. The complex crystallizes as  $1 \cdot CH_3CN$  in the space group  $P\overline{1}$ . The asymmetric unit contains one molecule each of the complex and acetonitrile. The structure of 1 is illustrated in Fig. 1. Selected bond parameters are listed in Table 4. As expected  $(HL^n)^-$  is indole peri-C, azomethine-N and amide-O donor and the fourth coordination site of the square-planar metal centre is satisfied by the chloride. The C-O and C-N bond lengths in the -C(=O)-NH- fragment in  $(HL^{1})^{-}$  clearly indicate the protonated state of the amide functionality [12,21,28,31,32]. The Pd–C, Pd–N and Pd–O bond lengths are within the range reported for bivalent palladium having similar coordinating atoms [12,13,21,31-33]. The Pd-Cl bond length is unexceptional [12,33-35]. The PdCNOCl square-plane is not ideal with respect to the bond parameters associated with the metal centre. The C(1)-Pd-N(2) angle in the six-membered ring is 94.54(12)°, while the O(1)–Pd–N(2) angle in the five-membered ring is 78.26(9)°. However, the CNOCl square-plane including the metal centre is perfectly planar (mean deviation 0.01 Å). In fact except for the phenyl ring C(11)-C(16) rest of the molecule lie in a single plane (Fig. 1). The maximum and the minimum deviations from the mean plane constituted by Pd, Cl, O(1), N(1)-N(3) and C(1)-C(10) are 0.077 and 0.003 Å, respectively. The phenyl ring plane (mean deviation 0.006 Å) is slightly twisted along the C(10)-C(11) bond. The dihedral angle between the phenyl ring plane and the plane containing remaining atoms of 1 is  $19.6(1)^{\circ}$ .

We have scrutinized the X-ray structure of  $1 \cdot CH_3CN$  for possible intermolecular non-covalent interactions to explore its selfassembly pattern and the packing in the crystal lattice. Two types of intermolecular hydrogen bonds are found. These involve the indole N(1)–H(1) and the amide N(3)–H(3) as donors and palladium bound Cl and acetonitrile-N, respectively as acceptors. The N(1)···Cl distance is 3.220(3) Å and N(1)–H(1)···Cl angle is 150° while, the N(3)···N(4) distance is 3.033(5) Å and N(3)–H(3)···N(4) angle is 152°. The amide-NH···N(acetonitrile) interaction connects the complex with the acetonitrile and the indole-NH···Cl interaction leads to a one-dimensional linear assembly of the  $1 \cdot CH_3CN$ units in the crystal lattice (Fig. 2).

### 4. Conclusions

Syntheses and characterization of a new series of cyclopalladated complexes, [Pd(HL<sup>n</sup>)Cl], with the tridentate Schiff bases indole-3-carboxaldehyde 4-*R*-benzoylhydrazones (H<sub>2</sub>L<sup>n</sup>, R = H, Cl, OMe and NMe<sub>2</sub>) have been reported. The deprotonated Schiff bases can act as C,N,O-donor ligands due to the accessibility of either the *ortho*- or the *peri*-C of their indole fragment for cyclometallation. In [Pd(HL<sup>n</sup>)Cl], *peri*-metallation with the formation of 6,5-membered fused chelate rings is preferred over *ortho*-metallation and formation of 5,5-membered fused chelate rings (Chart 1).

Cyclometallated species with a few ligands containing polycylic aromatic moieties such as 1-naphthyl and 9-phenanthryl are known [36–42]. These polycyclic moieties like indole can provide either the *ortho*- or the *peri*-C for formation of 5- or 6-membered metallacycle, respectively. Generally the bidentate ligands form *ortho*-metallated species [36–39]. Both *ortho*- and *peri*-metallation have been reported for a bidentate and a tridentate system [40,41], while only *peri*-metallated complex has been isolated with a tridentate ligand [42] as observed for (HL<sup>n</sup>)<sup>-</sup>. We are currently engaged in exploring the regioselectivity of cyclometallation in tridentate Schiff bases derived from acid hydrazides and a variety of polycylic aromatic aldehydes.

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### Appendix A. Supplementary material

CCDC 811956 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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