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# Cyclopalladated complexes with 9-anthraldehyde aroylhydrazones: Synthesis, properties and structures

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#### ABSTRACT

Reactions of equimolar amounts of Li<sub>2</sub>PdCl<sub>4</sub>, 9-anthraldehyde 4-*R*-benzoylhydrazones (H<sub>2</sub>L<sup>*n*</sup>; *n* = 1 and 2 for R = H and NMe<sub>2</sub>, respectively) and CH<sub>3</sub>COONa·3H<sub>2</sub>O in methanol produce the cyclopalladated complexes with the formula [Pd(HL<sup>*n*</sup>)Cl] (**1** (R = H) and **2** (R = NMe<sub>2</sub>)). Reactions of [Pd(HL<sup>*n*</sup>)Cl] (**1** and **2**) with 2 mol equivalents of PPh<sub>3</sub> in acetone provide the complexes of formula [Pd(L<sup>*n*</sup>)(PPh<sub>3</sub>)] (**3** (R = H) and **4** (R = NMe<sub>2</sub>)). Complexes **1**–**4** have been characterized by elemental analysis and spectroscopic (IR, UV–vis, fluorescence and NMR) measurements. Molecular structures of **1**–**4** have been confirmed by X-ray crystallography. In [Pd(HL<sup>*n*</sup>)Cl] (**1** and **2**), the C,N,O-donor (HL<sup>*n*</sup>)<sup>–</sup> and the chloride form a CNOCl square-plane around the metal centre, while (L<sup>*n*</sup>)<sup>2–</sup> and the PPh<sub>3</sub> assemble a CNOP square-plane around the metal centre in [Pd(L<sup>*n*</sup>)(PPh<sub>3</sub>)] (**3** and **4**).

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#### 1. Introduction

The long-standing and continuing interest in cyclometallated complexes is due to their applications in a wide variety of research areas ranging from organic synthesis to catalysis, photochemistry, biological and pharmaceutical chemistry and materials science [1–18]. A common strategy to generate metallacycles is the metallation of a pendant aromatic ring of the coordinated ligand. In literature ortho-metallation of pendant phenyl ring is more prevalent than the metallation of hetero cyclic rings and fused aromatic rings. We have been working for quite some time now on orthometallated species with C.N.O-donor Schiff bases derived from acid hydrazides and benzaldehyde or its substituted derivatives [19-22]. Recently we have reported a series of cylcometallated palladium(II) complexes with indole-3-carboxaldehyde aroylhydrazones [23]. These complexes provide examples of regioslective peri-palladation of the indole fragment of the ligand. In all these complexes, endocyclic cyclometallation [24] of the Schiff bases and the coordination of the amide- or amidate-O lead to the formation of fused chelate rings. Ortho-metallation of the benzaldimine moiety provides 5,5-membered [19-22], while peri-metallation of the indole fragment produces 6,5-membered fused chelate rings [23]. In view of the very few reports on cyclopalladated complexes involving anthracene [25-29], in the present work we have

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explored the palladium(II) chemistry with Schiff bases  $(H_2L^n)$  prepared from 4-*R*-benzoylhydrazines (R = H and NMe<sub>2</sub>) and 9-anthraldehyde. In this effort, we have isolated two types of complexes [Pd(HL<sup>n</sup>)Cl] and [Pd(L<sup>n</sup>)(PPh<sub>3</sub>)] (Scheme 1). In the following account, we have described the synthesis, properties and X-ray structures of these complexes.

## 2. Experimental

#### 2.1. Materials

All the chemicals used in this work were of analytical grade available commercially and were used as received. The solvents used were purified by standard methods [30].

#### 2.2. Physical measurements

Microanalytical (C, H, N) data were obtained with a Thermo Finnigan Flash EA1112 series elemental analyser. IR spectra in KBr pellets were recorded on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu LCMS 2010 liquid chromatograph mass spectrometer was used for the purity verification of  $H_2L^1$  and  $H_2L^2$ . Solution electrical conductivities were measured with a Digisun DI-909 conductivity metre. A Perkin–Elmer Lambda 35 UV/vis spectrophotometer was used to collect the electronic spectra. The fluorescence spectra were recorded using a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. The NMR spectra were recorded with the help of Bruker 400 and 500 MHz NMR spectrometers.



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Scheme 1. (i) Li<sub>2</sub>PdCl<sub>4</sub> and CH<sub>3</sub>COONa · 3H<sub>2</sub>O (equimolar amounts in methanol) and (ii) PPh<sub>3</sub> (2 mol equivalents in acetone).

#### 2.3. Synthesis of $H_2L^1$

9-Anthraldehyde (206 mg, 1 mmol) and a few drops of acetic acid were added to an ethanol solution of benzoylhydrazine (136 mg, 1 mmol). The mixture was boiled under reflux for 3 h. The pale yellow solid separated was collected by filtration, washed with ethanol and then dried in air. Yield: 265 mg (82%). Anal. calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O: C, 81.45; H, 4.97; N, 8.65. Found: C, 81.23; H, 4.78; N, 8.47. Mass in Me<sub>2</sub>NCHO: m/z = 325. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) ( $10^{-3} \times \varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) = 438sh (10.3), 390 (52.4), 374 (47.5), 350sh (27.4), 334sh (15.5), 300sh (33.9). Emission in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$  (nm)) = 480 (390). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (J (Hz)) = 12.12 (s, 1H, NH), 9.69 (s, 1H, H<sup>15</sup>), 8.79 (s, 1H, H<sup>10</sup>), 8.77 (5) (d, 2H, H<sup>1</sup>, H<sup>8</sup>), 8.19 (8) (d, 2H, H<sup>4</sup>, H<sup>5</sup>), 8.05 (7) (d, 2H, H<sup>18</sup>, H<sup>22</sup>), 7.66 (m, 3H, H19, H20, H21), 7.61 (m, 4H, H<sup>2</sup>, H<sup>3</sup>, H<sup>6</sup>, H<sup>7</sup>).

H<sub>2</sub>L<sup>2</sup> was prepared in 83% yield from equimolar amounts of 9anthraldehyde and 4-dimethylaminobenzoylhydrazine in presence of acetic acid using the same procedure as described for H<sub>2</sub>L<sup>1</sup>. Anal. calcd for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O: C, 78.44; H, 5.76; N, 11.44. Found: C, 78.26; H, 5.69; N, 11.32. Mass in Me<sub>2</sub>NCHO: m/z = 368. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) ( $10^{-3} \times \epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) = 440sh (22.3), 417sh (49.2), 398 (54.9), 370sh (39.3), 314 (71.1). Emission in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$  (nm)) = 700 and 490 (415). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (*J* (Hz)) = 11.81 (s, 1H, NH), 9.61 (s, 1H, H<sup>15</sup>), 8.78 (s, 1H, H<sup>10</sup>), 8.73 (14) (d, 2H, H<sup>1</sup>, H<sup>8</sup>), 8.16 (8) (d, 2H, H<sup>4</sup>, H<sup>5</sup>), 7.91 (8) (d, 2H, H<sup>18</sup>, H<sup>22</sup>), 7.61 (m, 4H, H<sup>2</sup>, H<sup>3</sup>, H<sup>6</sup>, H<sup>7</sup>), 6.81 (9) (d, 2H, H<sup>19</sup>, H<sup>21</sup>), 3.02 (s, 6H, NMe<sub>2</sub>).

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

A mixture of PdCl<sub>2</sub> (178 mg, 1.0 mmol) and LiCl (86 mg, 2.0 mmol) was taken in methanol (20 ml) and boiled with stirring under reflux for 1 h. It was then cooled to room temperature and filtered. The filtrate was added drop-wise with stirring to a methanol solution (20 ml) of H<sub>2</sub>L<sup>1</sup> (324 mg, 1.0 mmol) and CH<sub>3</sub>COO-Na·3H<sub>2</sub>O (136 mg, 1.0 mmol). The mixture was stirred at room temperature for 48 h. The complex precipitated as orange solid was collected by filtration, washed with methanol and finally dried in air. Yield: 290 mg (62%). Anal. calcd for PdC<sub>22</sub>H<sub>15</sub>N<sub>2</sub>OCl: C, 56.80; H, 3.25; N, 6.02. Found: C, 56.95; H, 3.33; N, 6.12. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$ (nm) (10<sup>-3</sup>× $\varepsilon$ (M<sup>-1</sup> cm<sup>-1</sup>)) = 512 (13.9), 482 (15.9), 453 (11.2), 424sh (9.1), 390 (9.8), 368sh (8.5), 323sh (12.8), 288 (26.6). Emission in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$ (nm)) = 570 (510). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (J (Hz)) = 12.11

(s, 1H, NH), 10.11 (s, 1H,  $H^{15}$ ), 8.98 (s, 1H,  $H^{10}$ ), 8.76 (8) (d, 1H,  $H^8$ ), 8.63 (br, s, 1H,  $H^4$ ), 8.27 (8) (d, 1H,  $H^5$ ), 8.14 (7) (d, 2H,  $H^{18}$ ,  $H^{22}$ ), 8.02 (8) (d, 1H,  $H^2$ ), 7.86 (8) (t, 1H,  $H^{20}$ ), 7.70 (m, 4H,  $H^6$ ,  $H^7$ ,  $H^{19}$ ,  $H^{21}$ ), 7.41 (8) (t, 1H,  $H^3$ ).

The red [Pd(HL<sup>2</sup>)Cl] (**2**) was synthesized in 65% yield by following a procedure very similar to that described for **1** using  $H_2L^2$  instead of  $H_2L^1$ . Anal. calcd for  $PdC_{24}H_{20}N_3OCl$ : C, 56.71; H, 3.97; N, 8.27. Found: C, 56.58; H, 3.91; N, 8.36. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) ( $10^{-3} \times \epsilon$  ( $M^{-1}$  cm<sup>-1</sup>)) = 524 (15.2), 490 (16.0), 461 (9.8), 381sh (11.2), 314sh (23.4), 287 (29.2). Emission in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$  (nm)) = 645 (460). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (J (Hz)) = 13.70 (s, 1H, NH), 10.10 (s, 1H, H<sup>15</sup>), 8.96 (s, 1H, H<sup>10</sup>), 8.78 (9) (d, 1H, H<sup>8</sup>), 8.61 (br, s, 1H, H<sup>4</sup>), 8.26 (8) (d, 1H, H<sup>5</sup>), 8.02 (8) (d, 1H, H<sup>2</sup>), 7.98 (9) (d, 2H, H<sup>18</sup>, H<sup>22</sup>), 7.85 (8) (t, 1H, H<sup>7</sup>), 7.68 (8) (t, 1H, H<sup>6</sup>), 7.40 (8) (t, 1H, H<sup>3</sup>), 6.90 (6) (d, 2H, H<sup>19</sup>, H<sup>20</sup>), 3.09 (s, 6H, NMe<sub>2</sub>).

#### 2.5. Synthesis of $[Pd(L^1)(PPh_3)]$ (3)

Solid PPh<sub>3</sub> (131 mg, 0.5 mmol) was added to a suspension of [Pd(HL<sup>1</sup>)CI] (**1**) (116 mg, 0.25 mmol) in acetone (10 ml) and the mixture was stirred at room temperature for 24 h. The complex [Pd(L<sup>1</sup>)(PPh<sub>3</sub>)] (**3**) separated as an orange solid was collected by filtration, washed with acetone and finally dried in air. Yield: 104 mg (60%). Anal. calcd for PdC<sub>40</sub>H<sub>29</sub>N<sub>2</sub>OP: C, 69.52; H, 4.23; N, 4.05. Found: C, 69.31; H, 4.32; N, 3.91. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) ( $10^{-3} \times \varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) = 515 (17.7), 485 (21.2), 460 (15.1), 425sh (6.8), 388 (5.2), 368sh (4.5), 292 (25.2). Emission in Me<sub>2</sub>N-CHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$  (nm)) = 585 (510). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (*J*(Hz)) = 10.06 (s, 1H, H<sup>15</sup>), 8.92 (s, 1H, H<sup>10</sup>), 8.87 (br, s, 1H, H<sup>8</sup>), 8.24 (8) (d, 1H, H<sup>5</sup>), 7.65 (m, 24H, H<sup>2</sup>, H<sup>4</sup>, H<sup>6</sup>, H<sup>7</sup>, H<sup>18–22</sup>, Hs of PPh<sub>3</sub>), 6.78 (br, s, 1H, H<sup>3</sup>). <sup>31</sup>P NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) = 25.51.

[Pd(L<sup>2</sup>)(PPh<sub>3</sub>)] (**4**) was synthesized as an orange-red solid in 65% yield from 1 mol equivalent of [Pd(HL<sup>2</sup>)CI] (**2**) and 2 mol equivalents of PPh<sub>3</sub> using a very similar procedure described above. Anal. calcd for PdC<sub>42</sub>H<sub>34</sub>N<sub>3</sub>OP: C, 68.71; H, 4.67; N, 5.72. Found: C, 68.49; H, 4.74; N, 5.57. UV–vis in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) ( $10^{-3} \times \varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) = 523 (20.0), 491 (21.4), 460sh (12.6), 431sh (6.3), 370sh (13.2), 284(44.9). Emission in Me<sub>2</sub>NCHO:  $\lambda_{max}$  (nm) (excitation at  $\lambda$  (nm)) = 660 (460). <sup>1</sup>H NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) (*J*(Hz)) = 10.28 (s, 1H, H<sup>15</sup>), 8.98 (s, 1H, H<sup>10</sup>), 8.75 (br, s, 1H, H<sup>8</sup>), 8.27 (8) (d, 1H, H<sup>5</sup>), 7.95 (7) (d, 1H, H<sup>4</sup>), 7.87 (8) (t, 1H, H<sup>7</sup>), 7.65 (m, 19H, H<sup>2</sup>, H<sup>6</sup>, H<sup>18</sup>, H<sup>22</sup>, and Hs of PPh<sub>3</sub>), 6.81 (br, s, 1H, H<sup>3</sup>), 6.76 (br, s, 2H, H<sup>19</sup>, H<sup>21</sup>), 3.04 (s, 6H, NMe<sub>2</sub>), <sup>31</sup>P NMR in (CD<sub>3</sub>)<sub>2</sub>SO:  $\delta$  (ppm) = 25.53.

#### 2.6. X-ray crystallography

Single crystals of  $[Pd(HL^n)Cl]$  (**1** and **2**) were grown by diethyl ether vapour diffusion into their corresponding dimethylformamide solutions, while those of  $[Pd(L^n)(PPh_3)]$  (3 and 4) were obtained by slow evaporation of their corresponding acetonitrile solutions. Both **1** and **2** crystallize as  $[Pd(HL^n)Cl] \cdot Me_2NCHO$  $(1 \cdot Me_2NCHO and 2 \cdot Me_2NCHO)$ . Complex 3 crystallizes as  $3 \cdot CH_3CN$ . while complex 4 crystallizes as it is. 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 to determine the unit cell parameters and intensity data collection at 298 K for 1. Me<sub>2</sub>NCHO and 4. The SMART and the SAINT-Plus packages [31] were used for data acquisition and data extraction, respectively. The SADABS program [32] was used for absorption corrections. Determination of the unit cell parameters and the intensity data collection at 298 K for each of 2 · Me<sub>2</sub>NCHO and 3-CH<sub>3</sub>CN were performed on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The CrysAlisPro software [33] was used for data collection, reduction and absorption correction. The structures of all four complexes were solved by direct method and refined on  $F^2$  by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atom of the amide functionality of the tridentate ligand in each of 1. Me<sub>2</sub>NCHO and 3. CH<sub>3</sub>CN was located in a difference map and refined with  $U_{iso}(H) = 1.2U_{iso}(N)$ . The remaining hydrogen atoms of 1 · Me<sub>2</sub>NCHO and 3 · CH<sub>3</sub>CN and all the hvdrogen atoms of **2**·Me<sub>2</sub>NCHO and **4** were included in the structure factor calculation at idealized positions by using a riding model. The SHELX-97 programs [34] available in the WinGX package [35] were used for structure solution and refinement. The ORTEX6a [36] and Platon [37] packages were used for molecular graphics. Selected crystallographic data are summarized in Table 1.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The Schiff bases  $H_2L^n$  (n = 1 and 2) [38] were synthesized in slightly more than 80% yields by condensation of 9-anthraldehyde

**Table 1**Selected crystallographic data.

and 4-*R*-benzoylhyrazines (R = H and NMe<sub>2</sub>) in presence of a few drops of acetic acid in ethanol. Elemental analysis and spectroscopic (IR, <sup>1</sup>H NMR and mass) measurements were used to characterize these Schiff bases. Reactions of equimolar amounts  $H_2L^n$ , CH<sub>3</sub>COONa·3H<sub>2</sub>O and Li<sub>2</sub>PdCl<sub>4</sub> (generated in situ using PdCl<sub>2</sub> and LiCl in 1:2 mol ratio) in methanol produce  $[Pd(HL^n)Cl]$  (1 (R = H) and  $2 (R = NMe_2)$  in 62 and 65% yields. Reactions of  $[Pd(HL^n)Cl]$  (1) and **2**) with PPh<sub>3</sub> in 1:2 mol ratio in acetone provide the complexes  $[Pd(L^{n})(PPh_{3})]$  (**3** (R = H) and **4** (R = NMe<sub>2</sub>)) in 60 and 65% yields. Presumably the excess PPh<sub>3</sub> provides a mild basic environment for the deprotonation of the amide functionality of  $(HL^n)^-$  in **1** and **2**. It is very likely that this deprotonation increases the Pd-O bond strength (vide infra) and facilitates the dissociation of Pd-Cl bond resulting in the formation of **3** and **4** (Scheme 1). All the four complexes are orange to red in colour and they are diamagnetic. The elemental analysis data of **1–4** are in good agreement with their corresponding molecular formula. Complexes 1 and 2 are highly soluble in dimethylformamide and dimethylsulfoxide and sparingly soluble in acetone and acetontrile. The solubility behaviours of 3 and 4 are very similar to that of 1 and 2, except for their high solubility in halogenated solvents such as chloroform and dichloromethane. In solution, they behave as nonelectrolyte.

#### 3.2. Spectroscopic properties

IR spectra of all the compounds display a large number of bands in the frequency range 400–1650  $\text{cm}^{-1}$  and a few bands within 3000-3220 cm<sup>-1</sup> of various intensities. We have only attempted to assign a few characteristic bands by comparing with the spectra of similar compounds reported earlier [19-23,38-40]. The free Schiff bases  $(H_2L^n)$  show the medium intensity N–H stretching band at  $\sim$  3210 cm<sup>-1</sup>. The strong band at  $\sim$  1645 cm<sup>-1</sup> and the following overlapping medium intensity band at  $\sim 1615 \text{ cm}^{-1}$  are assigned to the C=O and C=N stretches, respectively. In the spectra of 1 and 2, a weak band observed at  $\sim$  3200 cm<sup>-1</sup> is possibly due to the N–H stretch of the ligand  $(HL^n)^-$ . Two strong bands observed at ~ 1610 and  $\sim 1570 \text{ cm}^{-1}$  are attributed to the coordinated C=O and C=N groups of  $(HL^n)^-$ , respectively. The spectra of **3** and **4** do not display any band assignable to the N-H and C=O stretches. Thus the amide functionality of the tridentate  $(L^n)^{2-}$  in **3** and **4** is in deprotonated form (Scheme 1). The strong and sharp band observed at

Complex	$1 \cdot Me_2NCHO$	$2 \cdot Me_2 NCHO$	<b>3</b> · MeCN	4
Empirical formula	PdC <sub>25</sub> H <sub>22</sub> N <sub>3</sub> O <sub>2</sub> Cl	PdC <sub>27</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> Cl	PdC <sub>42</sub> H <sub>32</sub> N <sub>3</sub> OP	PdC <sub>42</sub> H <sub>34</sub> N <sub>3</sub> OP
Formula weight	538.34	581.41	732.13	734.15
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P1	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	9.1279(7)	10.7700(4)	12.300(4)	10.3624(6)
b (Å)	11.3041(8)	30.1455(11)	13.354(3)	14.4229(8)
<i>c</i> (Å)	11.9347(9)	8.0191(4)	21.260(8)	22.6557(13)
α (°)	65.176(1)	90	90	90
β (°)	77.392(1)	105.383(4)	104.35(4)	96.096(1)
γ (°)	75.122(1)	90	90	90
$V(Å^3)$	1071.60(14)	2510.26(18)	3383.1(2)	3366.9(3)
Ζ	2	4	4	4
$\rho$ (g cm <sup>-3</sup> )	1.668	1.538	1.437	1.448
$\mu ({ m mm^{-1}})$	1.020	0.878	0.634	0.637
Reflections collected	10,272	10,588	12,407	31,774
Reflections unique	3762	4412	5947	5926
Reflections $(I \ge 2\sigma(I))$	3622	3413	3489	5491
Parameters	294	323	434	435
R1, wR2 ( $I \ge 2\sigma(I)$ )	0.0239, 0.0619	0.0529, 0.1094	0.0405, 0.0820	0.0297, 0.0742
R1, wR2 (all data)	0.0249, 0.0626	0.0745, 0.1144	0.0796, 0.0892	0.0323, 0.0759
$GOF(F^2)$	1.080	1.151	0.871	1.068
Largest peak and hole (e $Å^{-3}$ )	0.647 and -0.336	0.736 and -0.675	0.552 and -0.867	0.353 and -0.333

~1600 cm<sup>-1</sup> for these two complexes is very likely to be due to the conjugated C=N-C=N fragment of  $(L^n)^{2-}$ .

Dimethylformamide solutions of the Schiff bases ( $H_2L^1$  and  $H_2L^2$ ) and the corresponding complexes **1–4** with them were used to record the electronic spectra. Representative spectra are shown in Fig. 1. The spectral profiles of all the four complexes and the free Schiff bases ( $H_2L^n$ ) are very similar. Interestingly except for the highest energy band all the spectra resemble that of pure anthracene [38,41,42]. Thus the absorptions in **1–4** are by and large due to ligand centred transitions only. However, there is a gradual red-shift of the band positions from anthracene to the Schiff bases to the complexes. This type of red-shift of  $\pi-\pi^*$  absorption bands due to alteration of the  $\pi$ -energy levels and thus the decrease of the  $\pi-\pi^*$ gap caused by substituent on the arene and also by metal coordination to aromatic heterocycle is documented before [42–44].

Fluorescence spectra of both Schiff bases  $(H_2L^1 \text{ and } H_2L^2)$  and complexes 1-4 were collected using their corresponding dimethylformamide solutions. All the compounds are emissive in nature. On excitation at 390 nm  $H_2L^1$  shows a broad emission band centred at 480 nm. On excitation at 510 nm complexes  $\mathbf{1}$  and  $\mathbf{3}$  with  $H_2L^1$ also display a similar broad emission band centred at 570 and 585 nm, respectively. In contrast to H<sub>2</sub>L<sup>1</sup>, H<sub>2</sub>L<sup>2</sup> displays dual fluorescence property. On excitation at 410 nm, it shows two emission bands at 490 and 700 nm (Fig. 2). Presumably after excitation the strong donor group NMe<sub>2</sub> on the aroyl moiety of H<sub>2</sub>L<sup>2</sup> induces a conformational change and hence it exhibits two emission bands from two conformational isomers of the excited state [45,46]. However, dual fluorescence has not been observed for the complexes with  $H_2L^2$ . On excitation at 460 nm 2 and 4 display a broad emission band at 645 and 660 nm, respectively (Fig. 2). Perhaps in these cases metal ion coordination causes stabilization of only one conformation of the excited state.



Fig. 1. Electronic spectra of  $H_2 L^1$  (0.62  $\times$   $10^{-5}$  M) (--) and  $[Pd(L^1)(PPh_3)]$  (3) (0.58  $\times$   $10^{-4}$  M) (-) in dimethylformamide.



Fig. 2. Fluorescence spectra of  $H_2L^2$  (0.54  $\times$  10 $^{-3}$  M) (—) and [Pd(HL^2)Cl] (2) (0.59  $\times$  10 $^{-3}$  M) (—) in dimethylformamide.

<sup>1</sup>H NMR spectra of  $H_2L^1$ ,  $H_2L^2$  and complexes **1–4** with them were recorded in dimethylsulfoxide-d6. The spectra of **1** and **2** show all the protons of  $(HL^n)^-$ , whereas for **3** and **4** except for a few the remaining aromatic protons of  $(L^n)^{2-}$  could not be clearly assigned due to the PPh<sub>3</sub> phenyl ring protons. The Schiff bases and the complexes **1** and **2** display the resonance corresponding to the N–H proton as a singlet in the range  $\delta$  11.81–13.70. As expected, **3** and **4** do not display any such signal due to the deprotonated form of the amide functionality in  $(L^n)^{2-}$  (Scheme 1). The methyl protons of NMe<sub>2</sub> in H<sub>2</sub>L<sup>2</sup>, **2** and **4** appear as singlet within  $\delta$  3.02–3.09. The  $H^1$  and  $H^8$  protons resonate together as a doublet at  $\delta$  8.77 and 8.73 in  $H_2L^1$  and  $H_2L^2$ , respectively. In contrast, **1–4** display a doublet or a broad singlet in the same range ( $\delta$  8.75–8.87) corresponding to a single proton  $(H^8)$  due to the metallation at C<sub>1</sub> position. By and large, there is a downfield shift of the  $H^2$  and  $H^4$  protons and an upfield shift of the H<sup>3</sup> proton in the complexes compared to the free Schiff bases. These shifts further substantiate the metallation at C<sub>1</sub> position in **1–4**. Generally the resonances corresponding to  $H^{2-4}$ and  $H^{18-22}$  are upfield shifted in **3** and **4** compared to that in free Schiff bases and the chloro complexes (1 and 2) due to the shielding effects of the PPh<sub>3</sub> phenyl rings. The <sup>31</sup>P NMR spectra of **3** and **4** have been also examined. A signal around  $\delta$  25.5 confirms the phosphine coordination in 3 and 4.

#### 3.3. X-ray structures

The molecular structures of  $[Pd(HL^n)Cl]$  (**1** and **2**) and  $[Pd(L^n)(PPh_3)]$  (**3** and **4**) determined by X-ray crystallography are illustrated in Figs. 3 and 4, respectively. Selected bond parameters associated with the metal ion for **1–4** are listed in Table 2. The metal centres are in distorted square-planar environment in all the complexes. The anthracenyl *peri*-C, the azomethine-N and the amide-O atom donor planar (HL<sup>n</sup>)<sup>–</sup> and the chloride form a CNOCI





**Fig. 3.** Molecular structures of (a) [Pd(HL<sup>1</sup>)Cl] (1) and (b) [Pd(HL<sup>2</sup>)Cl] (2) with the atom labelling schemes. All non-hydrogen atoms are represented by their 50% probability thermal ellipsoids.

square-plane around the metal centres in **1** and **2**. On the other hand, the anthracenyl peri-C, the azomethine-N and the amidate-O atom donor  $(L^n)^{2-}$  and the PPh<sub>3</sub> assemble a CNOP square-plane around the metal centres in **3** and **4**. In both type of complexes the tridentate ligands form 6,5-membered fused chelate rings. Each chelate ring is satisfactorily planar (rms deviations 0.01-0.13 Å). The values of the dihedral angle between the two fused chelate rings in 1 and **2** are 1.0(1) and  $3.1(2)^\circ$ , respectively, while that in **3** and **4** are 12.3(2) and 6.00(3)°, respectively. This relatively more noncoplanarity of the two chelate rings in 3 and 4 is most likely due to the bulky PPh<sub>3</sub>. In **1** and **2**, the C(16)-O(1) bond length is shorter and the C(16)-N(2) bond length is longer compared to the corresponding bond lengths in **3** and **4** (Table 2). This difference is in agreement with the protonated form of the amide functionality in 1 and 2 and the deprotonated form of the amide functionality in 3 and **4** [19–23,39]. The amidate-O is expected to have better  $\sigma$ -bonding ability and hence better trans directing ability than the amide-O atom. As a consequence the Pd-O(1) bond length is shorter and the Pd-C(1) bond length is longer in **3** and **4** compared to the corresponding bond lengths in 1 and 2 (Table 2). Significantly longer Pd-N(1) bond length in **3** and **4** than that in **1** and **2** is due to the superior trans effect of PPh<sub>3</sub> compared to that of chloride. Within  $[Pd(HL^{n})Cl]$  (**1** and **2**), the Pd-O(1) bond length in **1** is longer than that in **2**. Similarly in  $[Pd(L^n)(PPh_3)]$  (**3** and **4**), the Pd-O(1) bond length in **3** is longer than that in **4**. The strong electron donating ability of the substituent NMe<sub>2</sub> at para to the aroyl group makes the amide-O of  $(HL^2)^-$  and the amidate-O atom of  $(L^2)^{2-}$  a better donor compared to the corresponding O-atoms in  $(HL^1)^-$  and  $(L^1)^{2-},$ respectively and hence the Pd-O(1) bond lengths turn out to be



**Fig. 4.** Molecular structures of (a)  $[Pd(L^1)(PPh_3)]$  (**3**) and (b)  $[Pd(L^2)(PPh_3)]$  (**4**) with the atom labelling schemes. All non-hydrogen atoms are represented by their 50% probability thermal ellipsoids.

#### Table 2

Selected bond lengths (Å) and angles (°) for  $1\cdot \text{Me}_2\text{NCHO},\,2\cdot \text{Me}_2\text{NCHO},\,3\cdot \text{MeCN}$  and 4.

Complex	$1 \cdot Me_2 NCHO$	$2 \cdot Me_2 NCHO$	3 · MeCN	4
Pd-C(1)	1.980(2)	1.994(5)	2.005(4)	2.001(2)
Pd-N(1)	1.959(2)	1.961(4)	1.990(3)	1.989(2)
Pd-O(1)	2.141(2)	2.123(3)	2.108(2)	2.070(2)
Pd-Cl/P	2.3256(6)	2.3146(16)	2.2876(11)	2.2927(6)
C(16)-O(1)	1.243(3)	1.252(5)	1.292(4)	1.280(3)
C(16)-N(2)	1.354(3)	1.348(6)	1.329(5)	1.321(3)
C(1)-Pd-N(1)	91.57(8)	91.76(18)	91.10(14)	92.28(9)
C(1)-Pd-O(1)	171.26(8)	171.60(17)	167.63(12)	169.86(8)
C(1)-Pd-Cl/P	99.00(7)	98.26(15)	97.36(11)	98.93(7)
N(1) - Pd - O(1)	79.69(6)	79.90(14)	78.76(11)	78.43(7)
N(1)-Pd-Cl/P	169.38(5)	169.91(12)	167.67(10)	165.94(5)
O(1)-Pd-Cl/P	89.74(4)	90.10(10)	93.81(8)	90.87(4)

different in **1** and **2** and in **3** and **4**. Overall the Pd–C, Pd–N, Pd–O, Pd–Cl and Pd–P bond lengths and the bond angles observed in **1–4** are comparable with the values reported for cyclopalladated complexes with similar ligands [19,20,23–25,27,39,47,48].

Among **1–4** only  $[Pd(L^2)(PPh_3)]$  (**4**) crystallizes without any solvent molecule.  $[Pd(HL^n)Cl]$  (**1** and **2**) crystallize as  $[Pd(HL^n)Cl]$ · Me<sub>2</sub>NCHO (**1**·Me<sub>2</sub>NCHO and **2**·Me<sub>2</sub>NCHO) from dimethyl-formamide–diethylether. In each case, the solvent molecule is hydrogen bonded to the complex molecule. The O-atom of the Me<sub>2</sub>NCHO is connected to the adjacent amide N–H and metal coordinated polarized azomethine C–H groups of the ligand (HL<sup>n</sup>)<sup>-</sup>. The N(2)···O(2) distances and the N(2)–H···O(2) angles are 2.762(2) Å and 168(3)° and 2.765(5) Å and 162(5)° for **1**·Me<sub>2</sub>NCHO and **2**·Me<sub>2</sub>NCHO, respectively. The C(15)···O(2) distances and the C(15)–H···O(2) angles are 3.120(3) Å and 145° and 3.115(6) Å and 144° for **1**·Me<sub>2</sub>NCHO and **2**·Me<sub>2</sub>NCHO, respectively. [Pd(L<sup>1</sup>)(PPh<sub>3</sub>)] (**3**) crystallizes from acetonitrile as **3**·CH<sub>3</sub>CN. However, no significant interaction between the acetonitrile and the complex molecule could be detected here.

#### 4. Conclusions

Cyclopalladated complexes  $[Pd(HL^n)Cl]$  (1 and 2) and  $[Pd(L^{n})(PPh_{3})]$  (**3** and **4**) with the Schiff bases 9-anthraldehyde 4-*R*benzoylhydrazones (H<sub>2</sub>L<sup>n</sup>, R = H (n = 1) and NMe<sub>2</sub> (n = 2)) have been reported. The deprotonation of the amide functionality in  $[Pd(HL^n)Cl]$  occurs in presence of excess PPh<sub>3</sub> with the eventual replacement of the metal bound chloride with PPh<sub>3</sub> leading to the formation of  $[Pd(L^n)(PPh_3)]$ . Possibly a stronger Pd–O(amidate) bond than Pd-O(amide) bond plays an important role in the dissociation of Pd-Cl bond. Elemental analysis and various spectroscopic measurements have been used for the characterization of **1–4.** X-ray crystal structures show that  $(HL^n)^-$  acts as the anthracenyl peri-C, the azomethine-N and the amide-O donor in 1 and 2, while  $(L^n)^{2-}$  acts as the anthracenyl *peri*-C, the azomethine-N and the amidate-O donor in **3** and **4**. Both  $(HL^n)^-$  and  $(L^n)^{2-}$  form 6.5membered fused chelate rings. Except for the red-shift the electronic spectra of 1-4 are very similar with the spectra of the Schiff bases  $(H_2L^1 \text{ and } H_2L^2)$  and anthracene. Both  $H_2L^1$ ,  $H_2L^2$  and the complexes **1–4** are emissive. The Schiff base  $H_2L^2$  having strong electron donor substituent  $R = NMe_2$  displays dual fluoresecence but not the complexes (2 and 4) with it. Presently we are engaged in synthesis and reactivity studies of cyclometallated complexes of the present Schiff bases and analogous species derived from various polycylic aromatic aldehydes.

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#### Appendix A. Supplementary material

CCDC 847010–847013 contain 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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