

# Cyclopalladated complexes with *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine: syntheses, characterization and structural studies

Sunirban Das, Samudranil Pal \*

*School of Chemistry, University of Hyderabad, Hyderabad 500 046, India*

Received 27 August 2003; accepted 20 October 2003

## Abstract

Cyclopalladated complexes with the Schiff base *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine ( $H_2L$ , **1**) have been described. The reaction of **1** with  $Li_2[PdCl_4]$  in methanol yields the complex  $[Pd(HL)Cl]$  (**2**).  $[Pd(HL)(CH_3CN)Cl]$  (**3**) has been prepared by dissolving **2** in acetonitrile. In methanol–acetonitrile mixture, treatment of **2** with two mole equivalents of  $PPh_3$  produces  $[PdL(PPh_3)]$  (**4**) and that with one mole equivalent of  $PPh_3$  produces  $[Pd(HL)(PPh_3)Cl]$  (**5**). Crystallization of **2** from  $dms\text{-}d_6$  results into isolation of  $[Pd(HL)((CD_3)_2SO)Cl]$  (**6**). In **2**, the monoanionic ligand ( $HL^-$ ) is C,N,O-donor and the Cl-atom is *trans* to the azomethine N-atom. In **3**, **5** and **6**,  $HL^-$  is C,N-donor and the Cl-atom is *trans* to the metallated C-atom. The remaining fourth coordination site is occupied by the N-atom of  $CH_3CN$ , the P-atom of  $PPh_3$  and the S-atom of  $(CD_3)_2SO$  in **3**, **5** and **6**, respectively. Thus on dissolution in acetonitrile and dms $\text{-}o$  and in reaction with stoichiometric  $PPh_3$  the incoming ligand imposes a rearrangement of the coordinating atoms on the palladium centre. On the other hand, in presence of excess  $PPh_3$  deprotonation of the amide functionality in **2** occurs and the Cl-atom is replaced by the P-atom of  $PPh_3$  to form **4**. Here the dianionic ligand ( $L^{2-}$ ) remains C,N,O-donor as in **2**. The compounds have been characterized with the help of elemental analysis (C, H, N), infrared,  $^1H$  NMR and electronic absorption spectroscopy. Molecular structures of **3**, **4**, and **6** have been determined by X-ray crystallography. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Palladium; Benzoylhydrazone; *Ortho*-cyclometallation; Crystal structures

## 1. Introduction

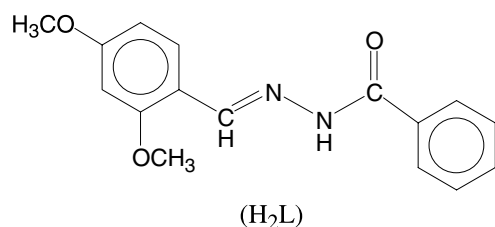
Cyclometallated complexes form an important class of organometallic species [1–7]. Formation of such complexes involves ligand C–H activation. Interest on this activation process and the corresponding metallated complexes stems from their utilization in insertion reactions, regio- and stereo-selective reactions and as catalysts in organic synthesis [8–12]. Thus there is a continuing quest for new cyclometallated species with different types of ligands. Compounds containing two non-carbon donor atoms are well known to act as tridentate ligands for palladium(II) or platinum(II) via

*ortho*-metallation and can produce cyclometallated complexes having two fused rings at the metal centre [12–23]. Thiosemicarbazones and semicarbazones of aromatic aldehydes belong to this type of ligands [18–21]. Thiosemicarbazones can coordinate the metal ion as monoanionic or biantionic tridentate C,N,S-donor ligand [18,19]. On the other hand, semicarbazones act only as monoanionic C,N,O-donor ligand [20,21]. It has been also found that in these complexes the metal–oxygen bond cleaves more easily than the metal–sulfur bond [18]. There is no report on species containing biantionic C,N,O-donor semicarbazone ligand. Like semicarbazones, aryl- or acyl-hydrazones of aromatic aldehydes are also potential tridentate C,N,O-donor ligands. In principle, such a ligand can be either monoanionic or dianionic. However structurally characterized cyclometallated species of this class of ligands are scarce. To the best of our knowledge the lone example reported

\* Corresponding author. Tel.: +91-40-2301-0500; fax: +91-40-2301-2460.

E-mail address: [spsc@uohyd.ernet.in](mailto:spsc@uohyd.ernet.in) (S. Pal).

is a cationic palladium(II) complex with a monoanionic C,N,O-donor acetylhydrazone having triphenylphosphine as the ancillary ligand [22]. A couple of cyclopalladated complexes are reported with benzoylhydrazones of phenyl 2-pyridyl ketone [23] and 2,6-diacetyl pyridine [24]. In both cases, the metal centre is bound to the pyridine-N and the deprotonated amide-N. The *ortho*-metallation occurs at the phenyl ring of the benzoyl group. In this work, we report new palladium(II) complexes with *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine ( $H_2L$  (**1**), two H represent the amide proton and the 6-H of the 2,4-dimethoxy phenyl ring). Unlike the previously reported complexes with benzoylhydrazones [23,24], in the present complexes the cyclometallation occurs at the benzylidene ring. In the cationic cyclopalladated compounds of semicarbazone [20,21] and acetylhydrazone [22] containing monodentate  $PPh_3$ , the ligands act as monoanionic C,N,O-donor. In contrast the analogous compound with  $H_2L$  contains dianionic C,N,O-donor ligand ( $L^{2-}$ ). In the following account, we describe the syntheses, characterization and structures of these cyclopalladated compounds of  $H_2L$ .



## 2. Experimental

### 2.1. Materials

The chemicals and solvents used in this work were of analytical grade available commercially and were used as received.

### 2.2. Physical measurements

Elemental (C, H, N) analysis data were obtained with a Perkin–Elmer Model 240C elemental analyzer. Room temperature solid state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu 3101-PC UV/vis/NIR spectrophotometer was used to record the electronic spectra. Proton NMR spectra of the complexes in  $(CD_3)_2SO$  solutions were recorded on a Bruker 200 MHz spectrometer using  $Si(CH_3)_4$  as an internal standard.

### 2.3. Synthesis of *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine ( $H_2L$ , **1**)

To a methanol solution (20  $cm^3$ ) of benzoylhydrazine (0.545 g, 4.0 mmol) 2,4-dimethoxybenzaldehyde (0.665 g, 4.0 mmol) and a few drops of acetic acid were added. The mixture was refluxed for 6 h and then cooled to room temperature. The white crystalline solid separated was collected by filtration, washed with cold methanol and finally dried in air. Yield, 0.966 g (85%). M.p. 196–198 °C. Anal. Calc. for  $C_{16}H_{16}N_2O_3$ : C, 67.59; H, 5.67; N, 9.85. Found: C, 67.4; H, 5.5; N, 9.7%. Selected IR bands ( $cm^{-1}$ ): 3175m, 3009m, 2843m, 1642s ( $\nu_{C=O}$ ), 1603s ( $\nu_{C=N}$ ), 1503m, 1466s, 1416m, 1360s, 1281s, 1208s, 1159m, 1105m, 1026s, 968m, 939m, 909m, 822s, 700s, 505m.  $^1H$  NMR (200 MHz) data in  $(CD_3)_2SO$  ( $\delta$  (J (Hz))): 3.81 (s, 3H,  $-OCH_3$ ); 3.83 (s, 3H,  $-OCH_3$ ); 6.42 (s, 1H,  $H^3$ ); 6.51 (d, 1H,  $H^6$ ); 7.48 (m, 3H,  $H^{11}$ ,  $H^{12}$ ,  $H^{13}$ ); 7.89 (d, 2H,  $H^{10}$ ,  $H^{14}$ ); 8.05 (d, 1H,  $H^5$ ); 8.56 (s, 1H,  $-HC=N-$ ); 9.40 (s, 1H,  $-NH-$ ). Electronic spectral data in  $CH_3OH$  ( $\lambda$  (nm) ( $\epsilon$  ( $M^{-1} cm^{-1}$ ))): 331 (30 200), 298 (16 500), 287 (15 000), 231 (18 800).

### 2.4. Synthesis of $[Pd(HL)Cl]$ (**2**)

A mixture of  $PdCl_2$  (89 mg, 0.5 mmol) and LiCl (43 mg, 1.0 mmol) was taken in 15  $cm^3$  methanol and refluxed with stirring for 1 h. It was then cooled to room temperature and filtered. The filtrate was added dropwise with stirring to a methanol solution (20  $cm^3$ ) of  $H_2L$  (141 mg, 0.5 mmol). The mixture was then stirred at room temperature for 3 days followed by another 3 days of refluxing. The red solid separated was collected by filtration, washed with methanol and finally dried in air. Yield, 100 mg (47%). Anal. Calc. for  $C_{16}H_{15}N_2O_3ClPd$ : C, 45.20; H, 3.55; N, 6.59. Found: C, 44.9; H, 3.5; N, 6.4%. Selected IR bands ( $cm^{-1}$ ): 3206w, 2926w, 1641s ( $\nu_{C=O}$ ), 1566s ( $\nu_{C=N}$ ), 1506m, 1449m, 1373w, 1319w, 1252s, 1217s, 1142s, 1026s, 802m, 723w, 689m, 528w. Electronic spectral data in  $CH_3OH$  ( $\lambda$  (nm) ( $\epsilon$  ( $M^{-1} cm^{-1}$ ))): 476sh (7100), 448 (10 970), 428sh (9900), 360sh (6700), 347 (7400), 271 (42 100).

### 2.5. Synthesis of $[Pd(HL)(CH_3CN)Cl]$ (**3**)

$[Pd(HL)Cl]$  (**2**) (50 mg, 0.12 mmol) was taken in 50  $cm^3$  of acetonitrile and then refluxed for 10 h. The mixture was then filtered to remove the undissolved  $[Pd(HL)Cl]$ . The filtrate was concentrated to 15  $cm^3$  on a rotary evaporator and left for slow evaporation in air at room temperature. The orange crystalline solid separated was collected by filtration and dried in air. Yield, 40 mg (73%). Anal. Calc. for  $C_{18}H_{18}N_3O_3ClPd$ : C, 46.37; H, 3.89; N, 9.01. Found: C, 46.1; H, 3.6; N, 8.8%. Selected IR bands ( $cm^{-1}$ ): 3219w, 2942w, 2168w ( $\nu_{C\equiv N}$ ),

1672m ( $\nu_{\text{C=O}}$ ), 1570s ( $\nu_{\text{C=N}}$ ), 1508m, 1487w, 1466m, 1412m, 1348m, 1262s, 1202m, 1153s, 1028s, 831m, 789w, 702s, 592w.  $^1\text{H}$  NMR (200 MHz) data in  $(\text{CD}_3)_2\text{SO}$  ( $\delta$  (J (Hz))): 2.08 (s, 3H,  $\text{CH}_3\text{CN}$ ); 3.80 (s, 3H,  $-\text{OCH}_3$ ); 3.83 (s, 3H,  $-\text{OCH}_3$ ); 6.28 (s, 1H,  $\text{H}^3$ ); 7.22 (s, 1H,  $\text{H}^5$ ); 7.54 (m, 3H,  $\text{H}^{11}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ); 7.90 (7) (d, 2H,  $\text{H}^{10}$ ,  $\text{H}^{14}$ ); 8.37 (s, 1H,  $-\text{HC=N}$ ); 8.74 (s, 1H,  $-\text{NH}$ ). Electronic spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ))): 487sh (1500), 458sh (2500), 391 (11 300), 358sh (10 900), 267sh (18 000), 242sh (27 200), 217 (46 000).

#### 2.6. Synthesis of $[\text{PdL}(\text{PPh}_3)]$ (**4**)

$[\text{Pd}(\text{HL})\text{Cl}]$  (**2**) (43 mg, 0.1 mmol) was taken in a 1:1 mixture of methanol and acetonitrile (50  $\text{cm}^3$ ) and stirred at room temperature for 3 h followed by the addition of triphenyl phosphine (58 mg, 0.22 mmol). The mixture was stirred at room temperature for 2 days. The orange microcrystalline solid formed was collected by filtration, washed with methanol and then dried in air. Yield, 52 mg (80%). Anal. Calc. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{O}_3\text{PPd}$ : C, 62.73; H, 4.49; N, 4.30. Found: C, 62.4; H, 4.4; N, 4.0%. Selected IR bands ( $\text{cm}^{-1}$ ): 1574s ( $\nu_{\text{C=N}}$ ), 1478s, 1431s, 1414m, 1360m, 1339s, 1296m, 1260m, 1242s, 1221w, 1200m, 1148s, 1098m, 1051m, 1028s, 910w, 843m, 793m, 745s, 706s, 692s, 590w, 530s, 513s, 498m.  $^1\text{H}$  NMR (200 MHz) data in  $(\text{CD}_3)_2\text{SO}$  ( $\delta$  (J (Hz))): 3.14 (s, 3H,  $-\text{OCH}_3$ ); 3.74 (s, 3H,  $-\text{OCH}_3$ ); 5.31 (s, 1H,  $\text{H}^5$ ); 6.09 (s, 1H,  $\text{H}^3$ ); 7.40 (m, 3H,  $\text{H}^{11}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ); 7.58 (m,  $\text{PPh}_3$  protons); 7.80 (10) (d, 2H,  $\text{H}^{10}$ ,  $\text{H}^{14}$ ); 7.86 (8) (d, 1H,  $-\text{HC=N}$ ). Electronic spectral data in  $\text{CH}_3\text{OH}$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ))): 487sh (5800), 457 (9400), 438sh (8500), 360sh (5700), 348 (5900), 275 (34 400).

#### 2.7. Synthesis of $[\text{Pd}(\text{HL})(\text{PPh}_3)\text{Cl}]$ (**5**)

To a suspension of  $[\text{Pd}(\text{HL})\text{Cl}]$  (**2**) (64 mg, 0.15 mmol) in 1:1 methanol–acetonitrile (25  $\text{cm}^3$ ) solid  $\text{PPh}_3$  (39 mg, 0.15 mmol) was added and the mixture was stirred at room temperature. In about 10 min a clear deep yellow solution was obtained. The stirring was continued for 10 h and a orange microcrystalline solid separated. The compound was collected by filtration, washed with methanol and finally dried in air. Yield, 50 mg (48%). Anal. Calc. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{O}_3\text{PPd}$ : C, 59.40; H, 4.40; N, 4.07. Found: C, 59.2; H, 4.2; N, 3.9%. Selected IR bands ( $\text{cm}^{-1}$ ): 3233m, 1658s ( $\nu_{\text{C=O}}$ ), 1576s ( $\nu_{\text{C=N}}$ ), 1510m, 1487m, 1435s, 1346s, 1267s, 1209s, 1155s, 1096m, 1030s, 829s, 752s, 690s, 638m, 532s, 513s, 496m, 436w.  $^1\text{H}$  NMR (200 MHz) data in  $(\text{CD}_3)_2\text{SO}$  ( $\delta$  (J (Hz))): 3.01 (s, 3H,  $-\text{OCH}_3$ ); 3.79 (s, 3H,  $-\text{OCH}_3$ ); 5.50 (s, 1H,  $\text{H}^5$ ); 6.12 (s, 1H,  $\text{H}^3$ ); 7.50 (m,  $\text{PPh}_3$  protons); 7.68 (m, 3H,  $\text{H}^{11}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ); 7.87 (7) (d, 2H,  $\text{H}^{10}$ ,  $\text{H}^{14}$ ); 8.20 (s, 1H,  $-\text{HC=N}$ ); 9.46 (s, 1H,  $-\text{NH}$ ). Electronic

spectral data in  $\text{CH}_3\text{OH}$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ))): 485sh (6800), 457 (10 700), 438sh (9700), 352 (6900), 274 (39 600).

#### 2.8. Isolation of $[\text{Pd}(\text{HL})(\text{CD}_3)_2\text{SO}]\text{Cl}$ (**6**)

A  $(\text{CD}_3)_2\text{SO}$  solution of **2** was used to collect the NMR (200 MHz) data. However, the solution gave crystals of  $[\text{Pd}(\text{HL})(\text{CD}_3)_2\text{SO}]\text{Cl}$  (**6**). Selected IR bands ( $\text{cm}^{-1}$ ): 3289m, 3094w, 2823w, 1661s ( $\nu_{\text{C=O}}$ ), 1578s ( $\nu_{\text{C=N}}$ ), 1514s, 1487s, 1452m, 1416m, 1354s, 1265s, 1206s, 1159s, 1119s, 1030s, 939m, 853w, 826s, 783w, 698s, 588m, 552w, 501m.  $^1\text{H}$  NMR data ( $\delta$  (J (Hz))): 3.80 (s, 3H,  $-\text{OCH}_3$ ); 3.84 (s, 3H,  $-\text{OCH}_3$ ); 6.43 (s, 1H,  $\text{H}^3$ ); 7.13 (s, 1H,  $\text{H}^5$ ); 7.65 (m, 3H,  $\text{H}^{11}$ ,  $\text{H}^{12}$ ,  $\text{H}^{13}$ ); 7.90 (8) (d, 1H,  $\text{H}^{14}$ ); 8.03 (7) (d, 1H,  $\text{H}^{10}$ ); 8.36 (s, 1H,  $-\text{HC=N}$ ); 8.74 (s, 1H,  $-\text{NH}$ ). Electronic spectral data in  $(\text{CH}_3)_2\text{SO}$  ( $\lambda$  (nm) ( $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ))): 487sh (5800), 458 (8800), 434sh (7700), 390sh (10 200), 358 (12 900), 273 (30 100).

#### 2.9. X-ray crystallography

Single crystals of **3** were obtained by slow evaporation of an acetonitrile solution of the complex and that of **4** were grown by slow evaporation of a dimethylsulfoxide–acetonitrile (1:2) solution of the complex. Single crystals of  $[\text{Pd}(\text{HL})(\text{CD}_3)_2\text{SO}]\text{Cl}$  (**6**) were obtained by slow evaporation of the  $\text{dms}\text{-d}_6$  solution of **2**. X-ray data were collected on an Enraf–Nonius Mach-3 single crystal diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by  $\omega$ -scan method at 298 K. In each case, unit cell parameters were determined by least-squares fit of 25 reflections having  $\theta$  values in the range 9–12°. Intensities of three check reflections were measured after every 1.5 h during the data collection to monitor the crystal stability. In all the three cases, there is no significant change in the intensities of the check reflections. Empirical absorption correction was applied to each of the three datasets based on the  $\psi$ -scans [25] of four reflections ( $\chi$  68.82–70.97° and  $\theta$  5.66–17.89°) for **3**, eight reflections ( $\chi$  83.22–89.13° and  $\theta$  4.25–19.31°) for **4** and six reflections ( $\chi$  82.13–87.53° and  $\theta$  3.90–15.64°) for **6**. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures. In each case, all non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen and deuterium atoms were included in the structure factor calculation at idealized positions by using riding model, but not refined. The programs of WinGX [26] were used for data reduction and absorption correction. Structure solution and refinement were performed with the SHELX-97 programs [27]. The ORTEP6a package was used for molecular graphics [28]. Selected crystal and refinement data for **3**, **4** and **6** are listed in Table 1.

Table 1

Crystal data for [Pd(HL)(CH<sub>3</sub>CN)Cl] (**3**), [PdL(PPh<sub>3</sub>)] (**4**) and [Pd(HL)((CD<sub>3</sub>)<sub>2</sub>SO)Cl] (**6**)

| Complex   | <b>3</b>   | <b>4</b>  | <b>6</b>   |
|---|--|---|--|
| Chemical formula                                      | PdC <sub>18</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> Cl | PdC <sub>34</sub> H <sub>29</sub> N <sub>2</sub> O <sub>3</sub> P | PdC <sub>18</sub> H <sub>15</sub> D <sub>6</sub> N <sub>2</sub> O <sub>4</sub> ClS |
| Formula weight  | 466.20   | 650.96  | 509.31   |
| Crystal system  | Monoclinic   | Triclinic   | Monoclinic   |
| Space group   | P2 <sub>1</sub> /n   | P1  | P2 <sub>1</sub> /c   |
| <i>a</i> (Å)  | 7.3111(11)   | 9.755(4)  | 16.968(3)  |
| <i>b</i> (Å)  | 23.570(3)  | 12.198(2)   | 6.1762(11)   |
| <i>c</i> (Å)  | 11.0760(14)  | 13.995(4)   | 20.455(4)  |
| $\alpha$ (°)  | 90   | 113.75(2)   | 90   |
| $\beta$ (°)   | 97.750(13)   | 101.29(4)   | 111.203(13)  |
| $\gamma$ (°)  | 90   | 93.00(3)  | 90   |
| <i>V</i> (Å <sup>3</sup> )                            | 1891.2(4)  | 1478.8(8)   | 1998.5(6)  |
| <i>Z</i>  | 4  | 2   | 4  |
| $\rho$ (g cm <sup>-3</sup> )                          | 1.637  | 1.462   | 1.693  |
| $\mu$ (mm <sup>-1</sup> )                             | 1.145  | 0.719   | 1.193  |
| Reflections measured                                  | 4424   | 8533  | 4986   |
| Reflections unique                                    | 3952   | 8533  | 4555   |
| Reflections <i>I</i> > 2 $\sigma$ <sub><i>I</i></sub> | 2385   | 6766  | 3172   |
| Parameters  | 238  | 372   | 248  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>              | 1.009  | 1.035   | 1.033  |
| R1, wR2 ( <i>I</i> > 2 $\sigma$ <sub><i>I</i></sub> ) | 0.0431, 0.0788   | 0.0357, 0.0804  | 0.0374, 0.0797   |
| R1, wR2 (all data)                                    | 0.1009, 0.0948   | 0.0542, 0.0884  | 0.0682, 0.0932   |
| Largest peak (e Å <sup>-3</sup> )                     | 1.033  | 0.344   | 0.567  |

### 3. Results and discussion

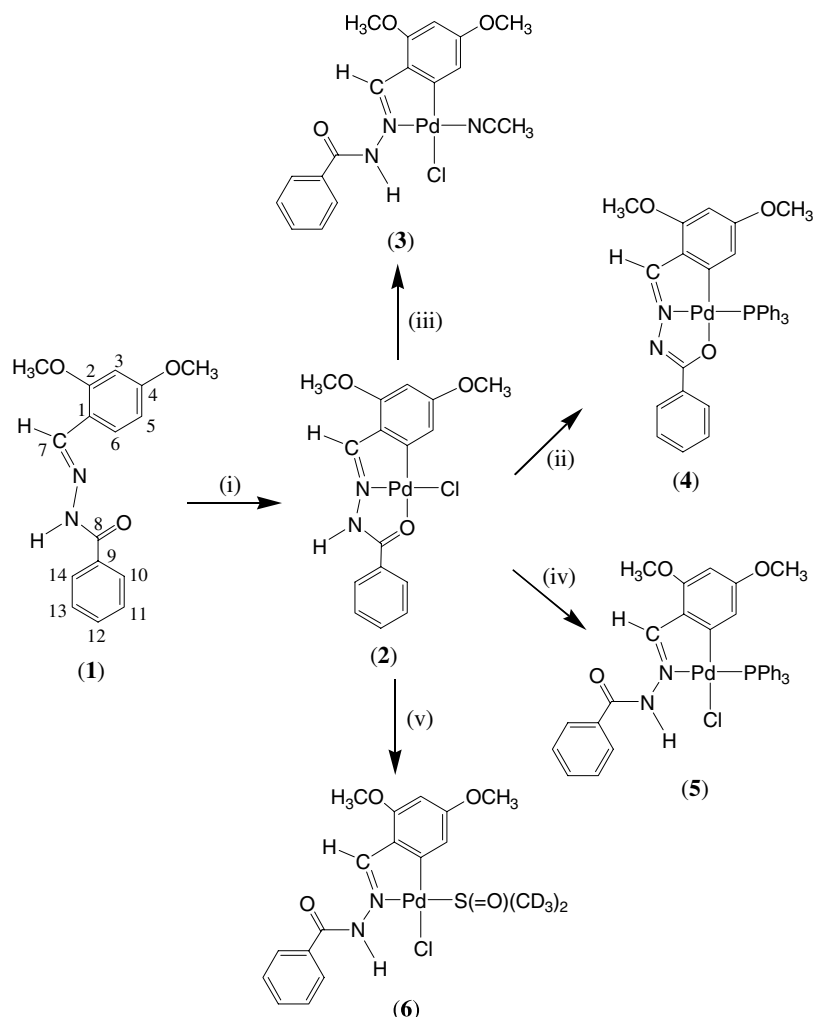
#### 3.1. Synthesis and characterization

The Schiff base *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine (H<sub>2</sub>L, **1**), was obtained in high yield by condensation reaction of one mole equivalent each of 2,4-dimethoxy benzaldehyde and benzoylhydrazine in methanol in presence of acid. All the *ortho*-metallated species synthesized using **1** are shown in Scheme 1. In methanol, the reaction of **1** with Li<sub>2</sub>[PdCl<sub>4</sub>] (generated in situ by treatment of one mole equivalent of PdCl<sub>2</sub> with two mole equivalents of LiCl) produces the *ortho*-metallated species [Pd(HL)Cl] (**2**). When dissolved in acetonitrile, **2** produces [Pd(HL)(CH<sub>3</sub>CN)Cl] (**3**). Reaction of **2** with excess triphenyl phosphine results into the formation of [PdL(PPh<sub>3</sub>)] (**4**). On the other hand, reaction of **2** with PPh<sub>3</sub> in 1:1 mole ratio produces [Pd(HL)(PPh<sub>3</sub>)Cl] (**5**). The elemental analysis data of all the compounds are consistent with the molecular formulae given above. The complexes are orange to red in the solid state and sparingly soluble in the common organic solvents. All the four complexes are diamagnetic and electrically non-conducting in solutions. The molecular structures of **3** and **4** have been determined by X-ray crystallography (*vide infra*). Both complexes are square-planar. In **3**, the monoanionic ligand (HL<sup>-</sup>) acts as bidentate C,N-donor and the Cl-atom is at the *trans* position with respect to the metallated C-atom. In **4**, the dianionic ligand (L<sup>2-</sup>) acts as C,N,O-donor. We were unable to grow X-ray quality single crystals of **2**. However, (CD<sub>3</sub>)<sub>2</sub>SO solution of **2** used to collect the proton NMR spectrum gave crystals of [Pd(HL)((CD<sub>3</sub>)<sub>2</sub>

SO)Cl] (**6**). The structure of **6** determined by X-ray crystallography reveals the same coordination mode of HL<sup>-</sup> as in **3**. The Cl-atom occupies the *trans* position with respect to the metallated C-atom. The (CD<sub>3</sub>)<sub>2</sub>SO coordinates the metal ion through the S-atom. The molecular structures of **3** and **6**, and the comparison of the infrared and electronic spectral properties (*vide infra*) of **2**, **3**, **5** and **6** suggests that HL<sup>-</sup> is possibly C,N,O-donor in **2** and C,N-donor in **5**. In acetonitrile or dmsO and in reaction with one equivalent of PPh<sub>3</sub>, the solvent or the PPh<sub>3</sub> molecule comes in between the C- and Cl-atom and binds the metal ion in **2** followed by the Pd–O bond cleavage to form the product (Scheme 1). Thus in each of **3**, **5** and **6** the incoming ligand is situated *trans* to the azomethine N-atom. The N-atom of acetonitrile, P-atom of PPh<sub>3</sub> and the S-atom of dmsO are softer than the amide keto-O. Thus the protonated amide keto-O of HL<sup>-</sup> is replaced by the N-donor acetonitrile, P-donor PPh<sub>3</sub> and the S-donor dmsO but not in a stereo-retentive way. During the formation of **4** by treating **2** with excess PPh<sub>3</sub>, most likely **5** is formed first followed by deprotonation of the amide functionality by the remaining unreacted PPh<sub>3</sub> and then the Cl-atom is replaced by the amide O-atom. Here the O-atom of the deprotonated amide functionality can replace the Cl-atom and bind the metal ion possibly due to the better  $\sigma$ -bonding ability of the enolate-O than that of the chloride and chelate effect (Scheme 1).

#### 3.2. Spectral properties

Infrared spectra of all the compounds have been collected using KBr pellets. The free Schiff base (**1**)



Scheme 1. (i) Li<sub>2</sub>[PdCl<sub>4</sub>] (1:1 in methanol), (ii) PPh<sub>3</sub> (1:2 in methanol–acetonitrile), (iii) in acetonitrile, (iv) PPh<sub>3</sub> (1:1 in methanol–acetonitrile), (v) in dmsO-d<sub>6</sub>.

shows three medium intensity bands at 3175, 3009 and 2843 cm<sup>-1</sup>. These are assigned to the N–H, aromatic C–H and methyl C–H stretches, respectively. Two strong bands observed at 1642 and 1603 cm<sup>-1</sup> are likely to be due to the C=O and C=N stretches [20–22]. The spectra of **2**, **3**, **5** and **6** display a weak peak in the range 3289–3206 cm<sup>-1</sup>. The origin of this peak is most likely the N–H group of the protonated amide functionality in the ligand HL<sup>-</sup>. The appearance of this stretch at higher wavenumbers for the complexes as compared to that observed for **1** is most likely due to the involvement of the N–H proton of **1** in intermolecular hydrogen bonding. Crystal structures of **3** and **6** reveal no intermolecular hydrogen bonding involving the amide functionality of HL<sup>-</sup>. All the complexes display weak multiple bands in the range 3100–2800 cm<sup>-1</sup> due to the aromatic and methyl C–H stretches. Complex **3** displays a weak band at 2168 cm<sup>-1</sup> ascribable to the C≡N of the coordinated acetonitrile. In the spectra of **2**, **3**, **5** and **6**, the highest wavenumber strong band appears at 1641,

1672, 1658 and 1661 cm<sup>-1</sup>, respectively. This band is assigned to the C=O stretch of the ligand in each complex. For **2** the position of this band is essentially identical with that of **1**. On the other hand, C=O stretch appears at higher wavenumber for **3**, **5** and **6**. In **3** and **6**, the ligand HL<sup>-</sup> is bidentate C,N-donor (*vide infra*). The higher wavenumber shift of the C=O stretch for **5** indicates a similar coordination behavior of HL<sup>-</sup> in **5**. It is known that the attachment of electron withdrawing group to the amide-N causes higher energy shift of the C=O stretch [29]. The C,N coordination of HL<sup>-</sup> to the metal ion is very likely to cause a similar electronic effect on the amide functionality. Possibly for this reason the C=O stretch appears at higher wavenumbers for **3**, **5** and **6** compared to that for **1**. There is an interesting trend in the C=O stretching frequencies in **3**, **5** and **6**. The observed values are decreasing in the order **3** > **6** > **5**. The *trans* directing ability is expected to be in the order PPh<sub>3</sub> > dmsO > CH<sub>3</sub>CN and hence the *trans* Pd–N(azomethine) bond strength is expected to decrease

in the order  $3 > 6 > 5$ . Indeed this bond length is significantly shorter in **3** than that in **6** (*vide infra*). As a result the electron withdrawing effect on the amide-N due to metal coordination to the adjacent azomethine N-atom will be decreasing in the order  $3 > 6 > 5$ . Therefore the values of the amide C=O stretching frequencies should be also decreasing in the same order. It is not very clear whether  $HL^-$  is C,N- or C,N,O-donor in **2** due to the appearance of the C=O stretch at the same position ( $1641\text{ cm}^{-1}$ ) for both **1** and **2**. If the ligand is C,N-donor, **2** has to be a dichloro bridged species. In such a situation, as observed for **3**, **5**, and **6** the C=O stretch for **2** should appear at a higher frequency than that in **1**. In an unlikely situation of the bridging chlorine atom being a stronger *trans* directing group than  $PPh_3$ , the C=O stretch will appear at a lower frequency compared to that in **5**. On the other hand, if  $HL^-$  is C,N,O-donor in **2**, the amide C=O stretch should shift to the lower wavenumber [20–22] compared to that for the free Schiff base (**1**) due to the O-coordination to the metal. The formation of **3**, **5**, and **6** from **2** does not differentiate the dichloro bridged or a mononuclear structure as both structures can give the same products either by cleavage of Pd–Cl (bridging) bond or by cleavage of Pd–O bond. Considering the appearance of the C=O stretch at the same position for both **1** and **2** as a consequence of possible intermolecular hydrogen bonding involving the O-atom of the C=O in **1** and metal coordination of the same in **2** we have tentatively assigned the C,N,O-coordinating mode of  $HL^-$  in **2** (Scheme 1). It also may be noted that analogous complexes of Pd with semi-carbozanes and acetylhydrazone are mononuclear and the ligand is monoanionic C,N,O-donor [20–22]. The spectrum of **4** does not display any band assignable to either the C=O or the N–H group. This observation is consistent with the deprotonation of the amide functionality and the C,N,O binding mode of the dianionic ligand ( $L^{2-}$ ) in **4**. All the five *ortho*-metallated species display a strong band in the range  $1566\text{--}1578\text{ cm}^{-1}$ . This band is assigned to the azomethine ( $-HC=N-$ ) fragment of the ligand. The shift of the C=N stretch to lower wavenumbers as compared to that ( $1603\text{ cm}^{-1}$ ) of the free Schiff base is expected due to the N-coordination of the azomethine in all the complexes [17,30].

The  $^1H$  NMR spectra of **1**, **3**, **4**, **5** and **6** in  $dms\text{-}d_6$  have been recorded. Compound **6** is generated by dissolving **2** in  $dms\text{-}d_6$  (*vide supra*). The  $H^6$  resonance is observed as a doublet at  $\delta$  6.51 for **1**. The absence of this proton in the spectra of **3**, **4**, **5** and **6** is in agreement with the *ortho*-metallation of the 2,4-dimethoxybenzylidene ring in these complexes. The signal corresponding to the  $H^5$  is observed at  $\delta$  8.05, 7.22 and 7.13 for **1**, **3** and **6**, respectively. This upfield shift of the  $H^5$  resonance for **3** and **6** further supports the metallation of the C6 atom in these two complexes. For **1**, **3** and **6**, the methyl protons of the two methoxy groups appear as two closely spaced

singlets. There is no significant variation in the chemical shifts ( $\delta$  3.80–3.84) of these two signals due to *ortho*-metallation. The  $H^5$  proton of **5** resonates at  $\delta$  5.50. This indicates that the  $PPh_3$  is *cis* to the metallated C-atom (C6) and the significant upfield shift of the  $H^5$  resonance compared to that of **1**, **3** and **6** is due to the shielding by the phosphine phenyl rings [17,19,22]. For the same reason the 4-methoxy group is expected to be observed at lower  $\delta$  value. Indeed the two singlets due to the two methoxy group protons are relatively well separated for **5** as compared to **1**, **3** and **6** and one of them shows a significant upfield shift ( $\delta$  3.79 and 3.01). The signal at the lower  $\delta$  value is assigned to the 4-methoxy group. The  $-HC=N-$  and  $-NH-$  protons of **1** appear as singlets at  $\delta$  8.56 and 9.40, respectively. For **3**, **5** and **6** the  $-HC=N-$  proton appears as singlet. But these are shifted upfield as compared to **1**. These shifts are by  $\delta$  0.2–0.3. The upfield shift of the azomethine proton is consistent with the weakening of the C=N bond due to the N-coordination and the *trans* disposition of the Pd and the proton around the C=N [12,16,31,32]. The  $-NH-$  proton of **3** and also of **6** is observed at  $\delta$  8.47. However, the  $-NH-$  proton for **5** appears as a broad singlet at  $\delta$  9.47 which is very close to that of **1**. The methyl protons of the acetonitrile in **3** are observed as a singlet at  $\delta$  2.08. In the spectrum of **4**, there is no signal attributable to the  $-NH-$  proton. Thus the amide functionality is deprotonated and the dianionic ligand is C,N,O-donor in **4**. As observed for **3**, **5** and **6** the  $-HC=N-$  proton in **4** is upfield shifted ( $\delta$  7.86) as compared to **1** due to the N-coordination and the *trans* disposition of the Pd and the proton around the C=N. However, for this complex it appears as a doublet due to coupling with the  $^{31}P$  nucleus that is *trans* (*vide infra*) to the N-atom [16,18,31]. Due to the *cis* arrangement of the metallated C-atom and the  $PPh_3$  in **4**, the  $H^5$  proton is considerably upfield shifted ( $\delta$  5.31) and the signals due to the 2-methoxy ( $\delta$  3.74) and 4-methoxy ( $\delta$  3.14) groups are well separated as observed for **5**.

The electronic spectral data of all the compounds are listed in Section 2. The free Schiff base displays four intense absorptions in the range 331–231 nm. On the other hand, the complexes show six to seven absorptions within 491–217 nm. The lower energy absorptions are likely to be due to ligand-to-metal charge transfer transitions and the absorptions below 360 nm involve intraligand transitions. The electronic spectral profiles of **2**, **3** and **6** in methanol solutions are identical. On the other hand, the spectral profiles of **2** and **3** in acetonitrile solutions are same. Similarly the spectra of **2** and **6** in dimethylsulfoxide solutions are alike. These observations suggest that in acetonitrile **2** is transformed to **3** and in dimethylsulfoxide **2** is transformed to **6**. Similarly both **3** and **6** in methanol are converted to **2**. The spectral profiles of **1**, **4** and **5** in methanol are very similar. Unlike **2**, **3** and **6**, the spectral profile of **4** is

unaffected by the change of solvent. Thus the C,N,O,P square-plane around the metal ion in **4** remains intact in the above mentioned solvents.

### 3.3. Description of structures

The molecular structures of **3**, **4** and **6** are depicted in Figs. 1–3, respectively. The selected bond parameters associated with the metal ion are listed in Table 2. In **3** and **6**, the ligand  $\text{HL}^-$  binds the palladium(II) centre through the aryl C-atom and the azomethine N-atom forming a five-membered metallacycle. The Cl-atom occupies the *trans* site with respect to the metallated C-atom in both complexes. An acetonitrile N-atom and the S-atom of  $\text{dmsO-d}_6$  satisfies the fourth coordination site in **3** and **6**, respectively. In **4**, the planar tridentate ligand  $\text{L}^{2-}$  coordinates the metal ion through the aryl C-atom, azomethine N-atom and the O-atom of the deprotonated amide functionality forming two five-membered rings. The fourth coordination site is satisfied by the P-atom of  $\text{PPh}_3$ . The N2–C8 and C8–O1 bond distances in **3** and **6** are significantly larger than the distances observed for the same bonds in **4** (Table 2). These values clearly suggest the deprotonation of the amide functionality in **4** [33,34]. In each complex, the palladium(II) centre is in a slightly distorted square-planar environment. The average deviations of the *trans* atoms from the mean plane are 0.07 and  $-0.07$ , 0.02 and  $-0.04$  and 0.06 and  $-0.07$  Å for **3**, **4** and **6**, respectively. In **4**, the O(1)–Pd–N(1) angle in the five-membered ring formed by the O-atom of the deprotonated amide functionality and the azomethine N-atom is  $76.92(8)^\circ$ . In the five-membered metallacycle, the C(1)–Pd–N(1) angles in **3** ( $80.90(19)^\circ$ ) and **6** ( $80.32(14)^\circ$ ) are very similar but slightly smaller than that ( $82.14(9)^\circ$ ) in **4**. The Pd–C(1) bond lengths are in the range  $1.987(5)$ – $2.011(3)$  Å in these complexes. These C–Pd–N angles and Pd–C bond lengths are comparable with the values reported for similar *ortho*-metallated complexes with Schiff bases [12,13,17–22,32]. The Pd–N1 bond lengths are  $2.011(4)$  and  $2.059(3)$  Å in **3** and **6**, respectively. The better *trans* directing ability of dmsO compared to acetonitrile is likely to be the reason for the lengthening of the Pd–N1 bond in **6**. This bond length ( $1.9945(19)$  Å) in **4** is expected to be the largest as the *trans* directing ability of  $\text{PPh}_3$  is higher than that of dmsO. Most likely the rigidity [34] of the tridentate  $\text{L}^{2-}$  causes the observed shortening of the Pd–N1 bond length in **4**. As expected the Pd–O1 bond length ( $2.102(2)$  Å) in **4** is shorter than the bond lengths ( $2.153(2)$ – $2.168(4)$  Å) observed for palladium(II) complexes of C,N,O-donor ligands in which the O-coordinating amide functionality is protonated [20–22]. However, this bond length is longer than the Pd–O distance ( $2.016(3)$ – $2.033(4)$  Å) observed in palladium(II) complexes with N,N,O-donor ligand containing deprotonated amide functionality [23]. The reason for this is most likely the

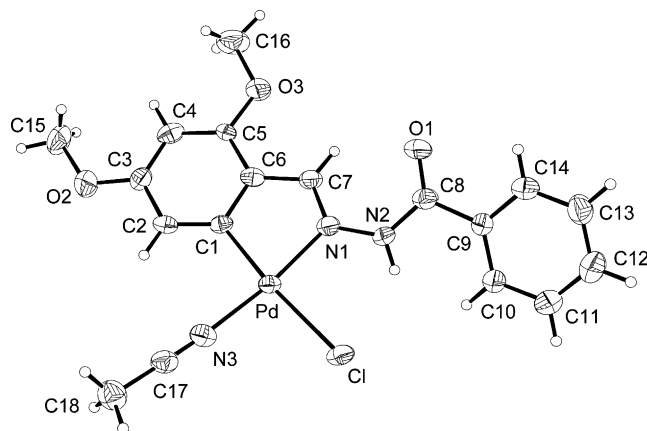


Fig. 1. Molecular structure of  $[\text{Pd}(\text{HL})(\text{CH}_3\text{CN})\text{Cl}]$  (**3**) with the atom-labeling scheme. All non-hydrogen atoms are represented by their 40% probability thermal ellipsoids.

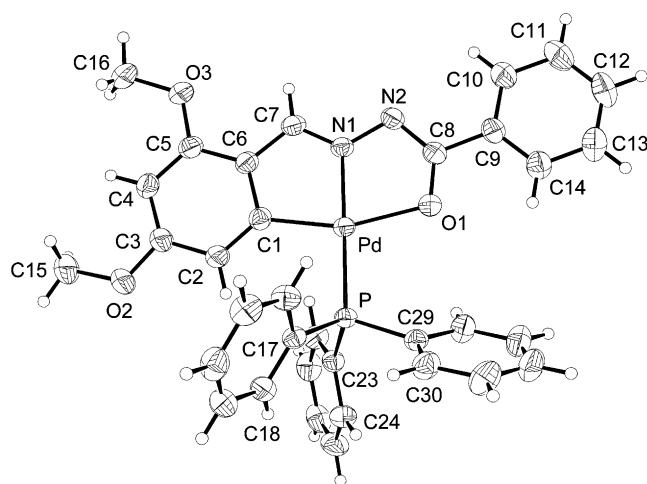


Fig. 2. Molecular structure of  $[\text{PdL}(\text{PPh}_3)]$  (**4**). Selected C-atoms of the  $\text{PPh}_3$  phenyl rings are labeled for clarity. All non-hydrogen atoms are represented by their 40% probability thermal ellipsoids.

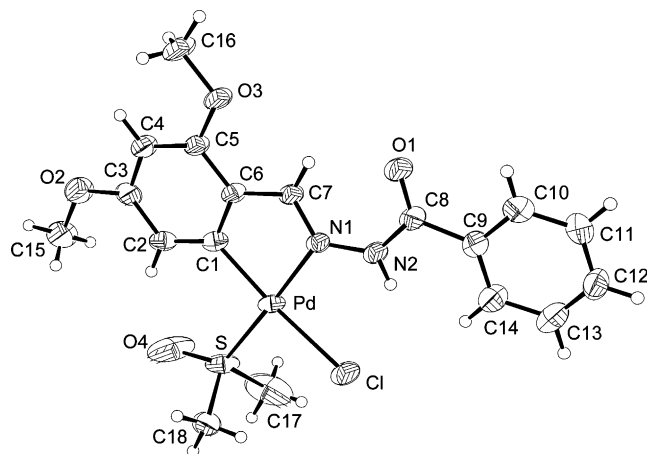


Fig. 3. Molecular structure of  $[\text{Pd}(\text{HL})((\text{CD}_3)_2\text{SO})\text{Cl}]$  (**6**) with the atom-labeling scheme. All non-hydrogen atoms are represented by their 40% probability thermal ellipsoids.

Table 2  
Selected bond lengths (Å) and angles (°) for **3**, **4**, and **6**

|   |            |              |            |
|---|------------|--------------|------------|
| [Pd(HL)(CH <sub>3</sub> CN)Cl] ( <b>3</b> )                 |            |              |            |
| Pd–C(1)   | 1.987(5)   | Pd–N(1)      | 2.011(4)   |
| Pd–N(3)   | 2.010(5)   | Pd–Cl        | 2.4418(14) |
| N(2)–C(8)   | 1.361(6)   | C(8)–O(1)    | 1.211(4)   |
| C(1)–Pd–N(1)  | 80.90(19)  | N(1)–Pd–N(3) | 172.45(17) |
| C(1)–Pd–N(3)  | 93.3(2)    | N(1)–Pd–Cl   | 92.76(12)  |
| C(1)–Pd–Cl  | 172.62(14) | N(3)–Pd–Cl   | 93.33(13)  |
| [PdL(PPh <sub>3</sub> )] ( <b>4</b> )                       |            |              |            |
| Pd–C(1)   | 2.011(3)   | Pd–N(1)      | 1.9945(19) |
| Pd–O(1)   | 2.102(2)   | Pd–P         | 2.2659(8)  |
| N(2)–C(8)   | 1.332(3)   | C(8)–O(1)    | 1.292(3)   |
| C(1)–Pd–N(1)  | 82.14(9)   | N(1)–Pd–O(1) | 76.92(8)   |
| C(1)–Pd–O(1)  | 159.05(9)  | N(1)–Pd–P    | 175.75(6)  |
| C(1)–Pd–P   | 97.71(8)   | O(1)–Pd–P    | 103.20(6)  |
| [Pd(HL)((CD <sub>3</sub> ) <sub>2</sub> SO)Cl] ( <b>6</b> ) |            |              |            |
| Pd–C(1)   | 2.003(4)   | Pd–N(1)      | 2.059(3)   |
| Pd–S  | 2.2582(11) | Pd–Cl        | 2.4089(12) |
| N(2)–C(8)   | 1.351(5)   | C(8)–O(1)    | 1.207(4)   |
| C(1)–Pd–N(1)  | 80.32(14)  | N(1)–Pd–S    | 176.68(9)  |
| C(1)–Pd–S   | 97.49(11)  | N(1)–Pd–Cl   | 91.62(9)   |
| C(1)–Pd–Cl  | 170.64(11) | S–Pd–Cl      | 90.77(4)   |

better *trans* directing ability of the aryl C-atom in **4** than that of the pyridine N-atom in the reported complexes. The Pd–Cl bond lengths observed in **3** and **6** are within the range reported for *ortho*-palladated species [12,16,35–38] having the Cl-atom at the *trans* position with respect to the metallated C-atom. The Pd–N(3) [23,39], Pd–P [16–18,31] and Pd–S [40] bond lengths in **3**, **4** and **6**, respectively are unexceptional.

#### 4. Conclusion

In conclusion, we have synthesized and characterized *ortho*-palladated complexes with *N*-(benzoyl)-*N'*-(2,4-dimethoxybenzylidene)hydrazine (H<sub>2</sub>L, **1**). In one of the complexes (**2**), HL<sup>−</sup> acts as a tridentate C,N,O-donor ligand. In presence of coordinating solvents such as acetonitrile or dimethylsulfoxide or one mole equivalent of PPh<sub>3</sub> the Pd–O bond in **2** cleaves and HL<sup>−</sup> behaves as a bidentate C,N-donor ligand (**3**, **5** and **6**). However, in presence of excess PPh<sub>3</sub> the deprotonation of the amide functionality in **2** occurs and L<sup>2−</sup> remains as a tridentate C,N,O-donor ligand in the new complex (**4**), which is stable in coordinating solvents. Thus the dianionic ligand can tightly uphold three coordination sites making the remaining position available for other ligands. We are currently involved in synthesizing such new complexes with this and similar Schiff bases.

#### 5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition

numbers are CCDC-218178, CCDC-218179 and CCDC-218180 for **3**, **4** and **6**, respectively). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK.

#### Acknowledgements

X-ray crystallographic studies were performed at the National Single Crystal Diffractometer Facility, School of Chemistry, University of Hyderabad (funded by the Department of Science and Technology, New Delhi). We thank the University Grants Commission, New Delhi for the facilities provided under the UPE program. Mr. S. Das thanks the Council of Scientific and Industrial Research, New Delhi for a research fellowship.

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