

# Cyclometallation reactions of 2-phenylpyridine; crystal and molecular structure of (2-{2-pyridyl}phenyl)palladium(II) tetramer and (2-{2-pyridyl}phenyl)mercury(II) tetramer

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## Abstract

The reaction of 2-phenylpyridine (HL) with palladium(II) compounds has been investigated. Cyclometallated and non-cyclometallated complexes may be obtained, dependent upon the reaction conditions. Cyclometallated derivatives are obtained directly by the reaction of HL with  $\{\text{Pd}(\text{OAc})_2\}_3$ , by thermal reactions of monodentate N-bonded HL complexes, or by a transmetallation reaction with  $\{[\text{HgCl}]_4\}$ . The crystal and molecular structure of (2-{2-pyridyl}phenyl)palladium chloride tetramer (monoclinic,  $a = 9.342(2)$ ,  $b = 19.582(6)$ ,  $c = 10.897(2)$  Å,  $\beta = 104.56(2)^\circ$ ,  $P2_1/c$ ) has been determined, and is reported, together with that of (2-{2-pyridyl}phenyl)mercury chloride tetramer (monoclinic,  $a = 10.334(2)$ ,  $b = 7.484(1)$ ,  $c = 27.052(6)$  Å,  $\beta = 97.60(2)^\circ$ ,  $P2_1/n$ ).

## Introduction

Cyclometallated complexes contain polydentate ligands bonded to metals through carbon and other (usually nitrogen, phosphorus, oxygen or sulfur) donor atoms [1]. Those complexes in which the non-carbon atom is located in a heterocyclic ring form a class which has attracted particular attention [2]. 2-Phenylpyridine (HL) was one of the earliest heterocyclic ligands reported to exhibit this bonding mode [3], and has been shown to form cyclometallated complexes with a wide range of transition and main-group elements. Although cyclopalladated complexes of 2-phenylpyridine were among the first to be described, the preparations of such compounds have tended to be serendipitous. We have recently developed methodologies for the preparation of transition metal cyclometallates based upon transmetallation [4, 5] or controlled metallation reactions [6–8]. In this paper we wish to report an investigation of the reactions of 2-phenylpyridine with palladium(II) compounds, and the structural characterisation of the cyclometallated complexes  $\{[\text{PdLCl}]_4\}$  and  $\{[\text{HgLCl}]_4\}$ . A preliminary report describing the

crystal and molecular structure of  $\{[\text{HgLCl}]_4\}$  has appeared [5].

## Experimental

Infrared spectra were recorded in Nujol mull on Perkin-Elmer 983 or 1710 FT spectrophotometers;  $^1\text{H}$  NMR spectra were recorded on Brüker WM250 or AM400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on Kratos MS50 and Kratos MS30 mass spectrometers, respectively, using 3-nitrobenzyl alcohol as the matrix for FAB spectra. 2-Phenylpyridine was used as supplied by Aldrich and palladium salts as supplied by Johnson Matthey;  $\{[\text{HgLCl}]_4\}$  was prepared by the published method [4, 5, 9].

### Preparation of $\{[\text{PdL}(\mu\text{-OAc})_2]\}$

#### Method 1

A solution of  $\text{Pd}(\text{OAc})_2$  (0.400 g, 1.78 mmol) in  $\text{CH}_2\text{Cl}_2$  (28  $\text{cm}^3$ ) was added to a suspension of  $[\text{HgLCl}]$  (0.682 g, 1.75 mmol) in EtOH (70  $\text{cm}^3$ ) and the mixture heated to reflux for 4 h, after which period a brown cloudy suspension was obtained. This was filtered through Celite to remove elemental mercury,

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and the filtrate concentrated to 20 cm<sup>3</sup> volume when yellow crystals of [ $\text{PdL}(\mu\text{-OAc})_2$ ] separated (0.47 g, 83%). <sup>1</sup>H NMR, CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  7.8, 1H, d, H<sub>6</sub>; 7.4, 1H, td, H<sub>4</sub>; 7.1, 1H, d, H<sub>3</sub>; 6.8–6.9, 4H, m, H<sub>3'</sub>, 4', 5', 6'; 6.5, 1H, ddd, H<sub>5</sub>; 2.2, 3H, CH<sub>3</sub>. IR: 1606, 1585, 1570, 1485, 1440, 1417, 770, 739, 728, 686 cm<sup>-1</sup>, *m/z* 640 (Pd<sub>2</sub>L<sub>2</sub>(OAc)<sub>2</sub>), 320 (PdL(OAc)), 261 (PdL).

#### Method 2

2-Phenylpyridine (0.78 cm<sup>3</sup>, 5.5 mmol) was added to a solution of Pd(OAc)<sub>2</sub> (0.133 g, 0.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) and the mixture heated to reflux for 2 h. The solvent was removed *in vacuo* to yield pure [ $\text{PdL}(\mu\text{-OAc})_2$ ] (0.18 g, 96%). Similar yields were obtained after stirring at room temperature for 2 h in either CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN solution.

#### Preparation of *cis*-[Pd(HL)<sub>2</sub>Cl<sub>2</sub>]

2-Phenylpyridine (0.78 cm<sup>3</sup>, 5.5 mmol) was added to a solution of Na<sub>2</sub>[PdCl<sub>4</sub>] (0.194 g, 0.65 mmol) in MeOH (10 cm<sup>3</sup>) and the mixture stirred at room temperature for 10 min. Yellow crystals of pure *cis*-[Pd(HL)<sub>2</sub>Cl<sub>2</sub>] separated (0.21 g, 66%).  $\nu_{\text{Pd-Cl}}$  319, 332 cm<sup>-1</sup>. *Anal.* Found: C, 53.8; H, 3.6; N, 5.8. *Calc.* for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>PdCl<sub>2</sub>: C, 54.0; H, 3.7; N, 5.7%.

#### Preparation of *trans*-[Pd(HL)<sub>2</sub>Cl<sub>2</sub>]

2-Phenylpyridine (0.23 cm<sup>3</sup>, 5.5 mmol) was added to a solution of Na<sub>2</sub>[PdCl<sub>4</sub>] (0.336 g, 0.65 mmol) in MeOH (25 cm<sup>3</sup>) and the mixture stirred at room temperature for 18 h. The yellow solid was collected by filtration and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The insoluble material is pure [ $\text{PdL}(\mu\text{-Cl})_2$ ], whilst the solution contains *trans*-[Pd(HL)<sub>2</sub>Cl<sub>2</sub>] which may be obtained as an orange solid by concentration *in vacuo* ( $\nu_{\text{Pd-Cl}}$  339 cm<sup>-1</sup>).

#### X-ray structural determination of (2-{2-pyridyl}-phenyl)palladium chloride

Yellow blocks were obtained by the slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution.

##### Crystal data

C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub>Pd<sub>2</sub>, yellow blocks, *M* = 592.10, monoclinic, *a* = 9.342(2), *b* = 19.582(6), *c* = 10.897(2) Å,  $\beta$  = 104.56(2)°, *U* = 1930 Å<sup>3</sup>, *F*(000) = 1152, space group *P*2<sub>1</sub>/*c*, *Z* = 4, *D*<sub>calc</sub> = 2.04 g cm<sup>-3</sup>, *D*<sub>m</sub> = not measured, Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo K $\alpha$ ) = 21.3 cm<sup>-1</sup>.

##### Data collection and processing

A crystal having overall dimensions 0.35 × 0.20 × 0.70 mm was mounted in a glass capillary and used for the structure determination. All geometric and intensity data were taken from this crystal using

an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. The  $\omega$ -2 $\theta$  technique was used to measure 3733 reflections (3394 unique) in the range 5 ≤ 2 $\theta$  ≤ 50°. Three standard reflections remeasured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects and empirically for absorption. There are 2728 unique reflections with *I* ≥ 3 $\sigma$ (*I*). The structure was solved and refined in the space group *P*2<sub>1</sub>/*c*.

##### Structural analysis and refinement

The asymmetric unit contains one complete dimer, and the two palladium atoms were located from the Patterson map. Alternating cycles of least-squares refinement and difference Fourier synthesis led to the identification of all non-hydrogen atoms. The metallated carbon and nitrogen atoms were assigned on three bases:

- (i) the thermal parameters are most reasonable with the given assignment;
- (ii) Pd–L bond lengths (Pd–N 2.00, 2.01; Pd–C, 1.97, 1.98 Å) show the expected alternation;
- (iii) Pd–Cl bond lengths show a dramatic variation consistent with the expected *trans* influences of Pd–N and Pd–C bonds.

Non-hydrogen atoms were refined anisotropically, while H atoms were placed in idealised positions with a fixed isotropic temperature factor (*U*<sub>iso</sub> = 0.08 Å<sup>2</sup>). The final least-squares cycle included 253 parameters for 2728 variables, and gave *R* = 0.0297, *R*<sub>w</sub> = 0.0350 and did not shift any parameter by more than 0.02 times its estimated standard deviation. The final difference Fourier synthesis is featureless with the largest peak 0.48 e Å<sup>-3</sup>. Calculations were performed using SHELXTL+ on a Microvax II computer [10]. Positional coordinates are given in Table 1 and selected molecular dimensions in Table 2.

#### X-ray structural determination of (2-{2-pyridyl}-phenyl)mercury chloride

Pale yellow needles of the complex were obtained by recrystallisation from methanol.

##### Crystal data

C<sub>11</sub>H<sub>8</sub>NClHg, pale yellow needles, *M* = 390.24, monoclinic, *a* = 10.334(2), *b* = 7.484(1), *c* = 27.052(6) Å,  $\beta$  = 97.60(2)°, *U* = 2073.9 Å<sup>3</sup>, *F*(000) = 1424, space group *P*2<sub>1</sub>/*n*, *Z* = 8, *D*<sub>calc</sub> = 2.50 g cm<sup>-3</sup>, *D*<sub>m</sub> = not measured, Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo K $\alpha$ ) = 150.6 cm<sup>-1</sup>.

TABLE 1. Atomic coordinates ( $\times 10^4$ ) for  $\{[\text{PdLCl}_4]_4\}$ 

	x	y	z
Pd(1)	999(1)	1111(1)	320(1)
Pd(2)	138(1)	17(1)	2548(1)
Cl(1)	2253(1)	567(1)	2206(1)
Cl(2)	-1245(1)	659(1)	731(1)
N(1)	29(4)	1665(2)	-1212(3)
N(2)	-1596(5)	-458(2)	2957(4)
C(1)	-1433(5)	1663(2)	-1776(5)
C(2)	-2015(5)	2067(3)	-2834(5)
C(3)	-1091(6)	2460(3)	-3317(5)
C(4)	417(6)	2460(2)	-2748(5)
C(5)	951(5)	2061(2)	-1694(4)
C(6)	2514(5)	1994(2)	-1004(4)
C(7)	3658(6)	2345(3)	-1320(5)
C(8)	5101(6)	2205(3)	-662(5)
C(9)	5369(5)	1739(3)	288(5)
C(10)	4226(5)	1395(3)	624(5)
C(11)	2783(5)	1532(2)	-13(4)
C(12)	-3023(6)	-380(3)	2302(6)
C(13)	-4145(7)	-715(3)	2671(7)
C(14)	-3809(8)	-1131(3)	3705(7)
C(15)	-2383(7)	-1212(3)	4374(6)
C(16)	-1249(6)	-871(2)	4005(5)
C(17)	319(6)	-899(2)	4614(4)
C(18)	941(7)	-1277(3)	5685(5)
C(19)	2448(8)	-1279(3)	6188(5)
C(20)	3325(7)	-887(3)	5632(5)
C(21)	2725(6)	-507(2)	4575(5)
C(22)	1204(5)	-506(2)	4053(4)

TABLE 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $\{[\text{PdLCl}_4]_4\}$ . Where appropriate, atoms in the two discrete binuclear units are indicated a and b as depicted in Fig. 3

Pd(1)–Cl(1)	2.349(2)	Pd(1)–N(1)	2.005(4)
Pd(1)–C(11)	1.972(5)	Pd(2)–Cl(2)	2.426(1)
Pd(2)–N(2)	2.013(5)	Pd(2)–C(22)	1.978(4)
Pd(1)–Cl(2)	2.419(2)	Pd(2)–Cl(1)	2.361(2)
Pd(1)–Pd(2)	3.481(2)	Pd(1a)–Pd(2b)	3.757(3)
Pd(1a)–Cl(2b)	3.677(4)	Pd(2a)–N(1b)	3.588(9)
Cl(1)–Pd(1)–N(1)	174.2(1)	Cl(1)–Pd(1)–C(11)	95.3(1)
N(1)–Pd(1)–C(11)	81.2(2)	Cl(2)–Pd(2)–N(2)	97.3(1)
Cl(2)–Pd(2)–C(22)	178.0(1)	N(2)–Pd(2)–C(22)	80.9(2)
Cl(1)–Pd(1)–Cl(2)	86.4(1)	Cl(1)–Pd(2)–Cl(2)	86.0(1)
C(11)–Pd(1)–Cl(2)	176.8(1)	N(1)–Pd(1)–Cl(2)	96.9(1)
C(22)–Pd(2)–Cl(1)	95.8(1)	N(2)–Pd(2)–Cl(1)	176.3(1)
Pd(1)–Cl(1)–Pd(2)	95.3(1)	Pd(1)–Cl(2)–Pd(2)	91.8(1)

#### Data collection and processing

A crystal having overall dimensions  $0.25 \times 0.10 \times 0.05$  mm was mounted on a glass fibre and used for the structure determination. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo

$K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 29 reflections taken from a rotation photograph and centred by the diffractometer. The  $\omega$ - $2\theta$  technique was used to measure 7608 reflections (3637 unique) in the range  $5 \leq 2\theta \leq 50^\circ$ . Three standard reflections remeasured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied. There are 3072 unique reflections with  $I \geq 1.5\sigma(I)$ . The structure was solved in the space group  $P2_1/n$ .

#### Structural analysis and refinement

The asymmetric unit contains two independent mononuclear units, and the positions of the two mercury atoms were obtained by direct methods. The remaining non-hydrogen atoms were found by iterative application of least-squares refinement and difference Fourier analysis. Hydrogen atoms were not included in the refinement. All non-hydrogen atoms were refined anisotropically. The final least-squares cycle included 253 parameters for 3072 variables, and gave  $R = 0.0596$ ,  $R_w = 0.0560$  and did not shift any parameter by more than 0.004 times its estimated standard deviation. Calculations were performed using SHELXTL+ on a Microvax II computer [10]. Positional coordinates are given in Table 3 and selected molecular dimensions in Table 4.

See also 'Supplementary material'.

#### Results and discussion

The reaction of 2-phenylpyridine with  $\text{Na}_2[\text{PdCl}_4]$  in ethanol was first described in 1968 when the product was reported to be  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  [3]. This material was obtained in 70% yield, and was formulated upon the basis of IR and mass spectra, and degradative reactions with  $\text{Li}[\text{AlH}_4]$ . The complex was assigned the *transoid* geometry indicated in Fig. 1, although no rationale for this structure was presented. This same complex has been reported by a number of other workers, although the yields and precise method of preparation vary considerably [11–13]. The complex has also been prepared in high yield by the reaction of  $[\text{LPd}(\mu\text{-OAc})_2\text{PdL}]$  with  $\text{LiCl}$  [12, 14] or by a transmetalation reaction of  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  with  $\text{Pd}(\text{OAc})_2$  or  $[\text{PdCl}_4]^{2-}$  [4]. The corresponding acetato-bridged dimer,  $[\text{LPd}(\mu\text{-OAc})_2\text{PdL}]$  is reported to be the sole product from the reaction of HL with  $\text{Pd}(\text{OAc})_2$  [14, 15]. The reaction of HL with  $[\text{PdCl}_4]^{2-}$  has proved to be extremely variable in our hands, and we have intensively in-

TABLE 3. Atomic coordinates ( $\times 10^4$ ) for  $[\{\text{HgLCl}\}_4]$ 

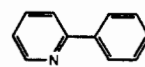
	x	y	z
Hg(1)	9221(1)	4311(1)	1158(1)
Hg(2)	8447(1)	7361(1)	-57(1)
Cl(1)	8492(4)	3373(5)	355(1)
Cl(2)	7680(4)	6231(6)	-846(1)
N(1)	7135(11)	5069(15)	1578(4)
N(2)	6371(10)	7796(14)	424(4)
C(1)	9869(14)	5236(18)	1868(5)
C(2)	11220(15)	5209(22)	2036(6)
C(3)	11684(16)	5923(21)	2495(6)
C(4)	10855(16)	6655(23)	2788(6)
C(5)	9497(16)	6657(18)	2628(5)
C(6)	9013(13)	5923(14)	2167(5)
C(7)	7562(13)	5973(16)	2004(5)
C(8)	6713(14)	6920(20)	2260(6)
C(9)	5395(15)	6952(22)	2085(7)
C(10)	4964(15)	6018(19)	1640(6)
C(11)	5832(15)	5100(19)	1419(5)
C(12)	9107(13)	8503(18)	627(5)
C(13)	10487(15)	8577(20)	785(6)
C(14)	10921(17)	9311(23)	1265(7)
C(15)	10052(14)	9897(20)	1564(5)
C(16)	8694(16)	9739(19)	1416(6)
C(17)	8216(13)	9054(16)	938(5)
C(18)	6823(13)	8968(16)	772(5)
C(19)	5941(16)	10108(21)	989(6)
C(20)	4561(18)	9987(26)	831(6)
C(21)	4170(15)	8665(27)	479(6)
C(22)	5092(16)	7657(22)	282(7)

TABLE 4. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $[\{\text{HgLCl}\}_4]$ . Where appropriate, atoms in the two discrete binuclear units are indicated a and b as depicted in Fig. 4

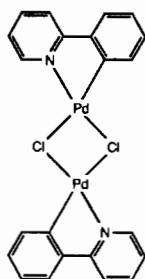
Hg(1)–Cl(1)	2.314(4)	Hg(1)–N(1)	2.627(12)
Hg(1)–C(1)	2.069(13)	Hg(2)–Cl(2)	2.335(4)
Hg(2)–N(2)	2.673(12)	Hg(2)–C(12)	2.070(13)
Hg(1)–Cl(2a)	3.442(6)	Hg(1)–C(12)	3.447(21)
Hg(1)–Hg(2)	3.496(4)	Hg(2)–Cl(1)	3.184(5)
Hg(2)–Cl(1a)	3.410(6)	Hg(1)–Hg(2a)	4.259(6)
Cl(1)–Hg(1)–N(1)	106.7(2)	Cl(1)–Hg(1)–C(1)	178.1(4)
N(1)–Hg(1)–C(1)	73.1(5)	Cl(2)–Hg(2)–N(2)	107.0(3)
Cl(2)–Hg(2)–C(12)	176.9(4)	N(2)–Hg(2)–C(12)	72.8(4)
Cl(1)–Hg(1)–Cl(2a)	86.1(2)	Cl(2)–Hg(2)–Cl(1a)	86.5(2)
C(1)–Hg(1)–Cl(2a)	94.0(4)	N(1)–Hg(1)–Cl(2a)	167.0(4)
C(12)–Hg(2)–Cl(1a)	94.1(4)	N(2)–Hg(2)–Cl(1a)	164.6(4)
Hg(1)–Cl(1)–Hg(2)	91.8(6)	Hg(1)–C(12)–Hg(2)	89.2(9)
Hg(1)–Cl(1)–Hg(2a)	94.2(4)	Hg(1)–Cl(2a)–Hg(2a)	93.0(4)

investigated the preparation of metallated and non-metallated complexes of 2-phenylpyridine.

The most unambiguous method for the preparation of cyclopalladated complexes of 2-phenylpyridine is by the transmetalation reaction of palladium(II) compounds with  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  [4]. This reason



HL

Fig. 1. Previously proposed configuration of  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$ .

is essentially quantitative and may be modified to the synthesis of a wide range of cyclometallated complexes, the limitation being the availability of the organomercury compound. The reaction of 2-phenylpyridine with mercury(II) acetate is clean, and allows the isolation of relatively good yields of  $[\text{LHg}(\mu\text{-OAc})_2\text{HgL}]$ , which may be readily converted to  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  by metathesis with LiCl [4, 9]. The crystal and molecular structure of  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  is discussed later in this paper.

The reaction of  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  with palladium(II) acetate in EtOH/ $\text{CH}_2\text{Cl}_2$  solution results in the deposition of elemental mercury and the formation of  $[\text{LPd}(\mu\text{-OAc})_2\text{PdL}]$  in 86% yield. The same deep yellow compound is obtained in 96% yield from the direct reaction of palladium(II) acetate with 2-phenylpyridine in  $\text{CH}_2\text{Cl}_2$  or MeCN solution at room temperature or at reflux. This extremely high yield is in contrast to the lower yields which are reported for the direct reaction with palladium acetate in boiling acetic acid solution [14]. In none of these reactions are there any traces of non-metallated products. The complex is very soluble in  $\text{CH}_2\text{Cl}_2$ , but only sparingly so in methanol. The  $^1\text{H}$  NMR spectrum of the acetato-bridged cyclometallated complex obtained by either synthetic method corresponds exactly to that reported previously for this compound [14]. The IR spectrum of the complex exhibits absorptions at 1570 and 1417  $\text{cm}^{-1}$  which may be assigned to the asymmetric and symmetric stretching modes of the acetate, respectively, and are consistent with the presence of a bridging acetate ligand [16]. The FAB mass spectrum of the complex exhibits peaks at  $m/z$  640 ( $\{\text{Pd}_2\text{L}_2(\text{OAc})_2\}$ ), 320 ( $\{\text{PdL}(\text{OAc})\}$ ) and 261 ( $\{\text{PdL}\}$ ), all exhibiting the expected isotopomer distribution.

The reactions of solutions containing  $[\text{PdCl}_4]^{2-}$  with HL may produce a number of products, depending upon the reaction time and temperature. The reaction of  $\text{Na}_2[\text{PdCl}_4]$  with an eight-fold excess of HL in methanol for short periods (10 min) at room temperature results in the deposition of a yellow solid. The  $^1\text{H}$  NMR spectrum of a  $\text{CD}_2\text{Cl}_2$  solution of this complex is shown in Fig. 2(a). Analysis of this spectrum reveals the presence of nine aromatic protons, which is only compatible with the presence of the non-metallated HL ligand. The FAB mass spectrum exhibits peaks assigned to  $\text{Pd}(\text{HL})_2\text{Cl}_2$ ,  $\text{Pd}(\text{HL})_2\text{Cl}$ ,  $\text{Pd}(\text{HL})_2$  and  $\text{Pd}(\text{HL})$ , in addition to lower intensity peaks to higher mass; isotopomer distributions were correct for the formulations proposed. Analysis indicated a formulation  $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  to be appropriate. The infrared spectrum of the compound exhibit Pd-Cl modes at 319 and  $332\text{ cm}^{-1}$ . This suggests that a *cis* complex has been formed. The IR spectrum may be compared with that of *cis*- $[\text{Pd}(\text{py})_2\text{Cl}_2]$  which exhibits Pd-Cl modes at 333 and  $342\text{ cm}^{-1}$  [17]. It is particularly convincing that the difference between the *asym* and *sym* stretching modes is so similar. The *cis*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  complex is the kinetic product expected on the basis of the *trans* effect (Cl > pyridine).

If the reaction of  $\text{Na}_2[\text{PdCl}_4]$  with an excess of HL at room temperature is allowed to proceed for

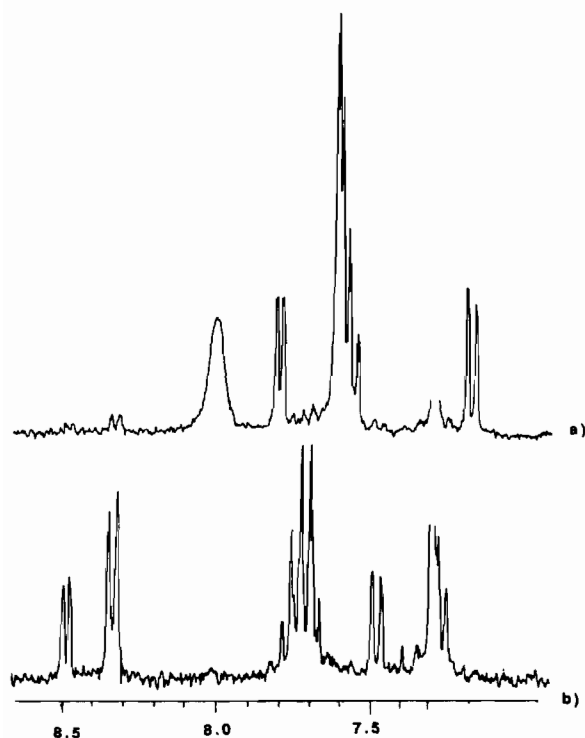


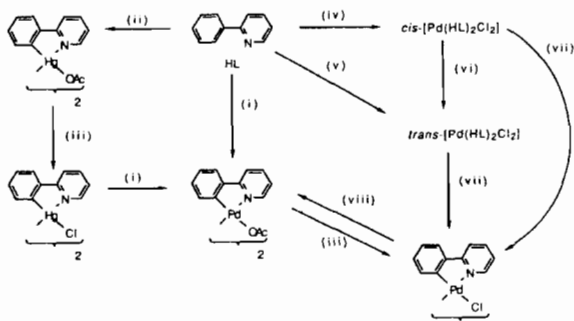
Fig. 2.  $^1\text{H}$  NMR spectra (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) of *cis*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  (a) and *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  (b).

longer periods, or the reaction mixture is slightly warmed, orange-yellow crystals are precipitated. After reaction times longer than 2 h, this orange-yellow product consists of a single compound, but shorter reaction times result in the formation of mixtures of *cis*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  and the new compound. The  $^1\text{H}$  NMR spectrum of the new product is shown in Fig. 2(b), and also exhibits nine aromatic resonances. The IR spectrum of the pure compound exhibits a single strong Pd-Cl stretching mode at  $339\text{ cm}^{-1}$ . This is comparable to the value of  $358\text{ cm}^{-1}$  reported for *trans*- $[\text{Pd}(\text{py})_2\text{Cl}_2]$  [17]. The major peak in the EI mass spectrum is assigned to  $\text{Pd}(\text{HL})_2$ , but peaks due to  $\text{Pd}(\text{HL})_2\text{Cl}_2$ ,  $\text{Pd}(\text{HL})_2\text{Cl}$ ,  $\text{Pd}(\text{HL})_2$  and  $\text{Pd}(\text{HL})$  are observed in the FAB mass spectrum. The second product is *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$ , which is the expected thermodynamic product. The *cis* complex is quantitatively converted to the *trans* compound upon warming to  $40^\circ\text{C}$  in chloroform. This conversion may be followed by observation of the  $^1\text{H}$  NMR spectrum of a  $\text{CDCl}_3$  solution of *cis*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  maintained at  $40^\circ\text{C}$ ; at  $40^\circ\text{C}$  the reaction proceeds cleanly, and the sole product is the *trans* compound, although at higher temperatures small amounts of a third solution species become apparent.

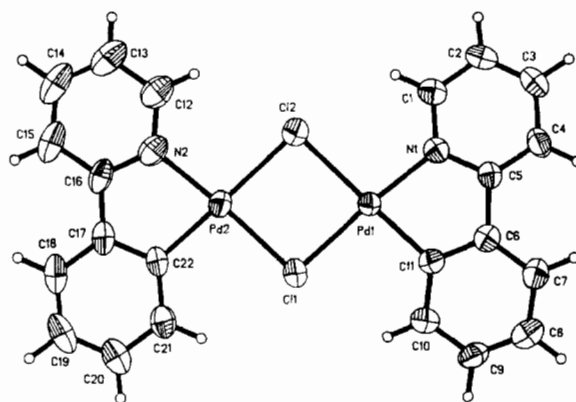
The reaction of methanolic solutions  $\text{Na}_2[\text{PdCl}_4]$  with approximately equimolar amounts of HL (1.0–1.5 equiv.) or the prolonged reaction with an excess of HL in boiling methanol results in the precipitation of orange-yellow solids. The IR spectra of these solids suggest the presence of varying amounts of *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  and a new compound. Extraction of these mixtures with  $\text{CH}_2\text{Cl}_2$  results in the formation of a yellow solution containing *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  and a pale yellow solid with an IR spectrum identical to that previously reported for  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  [3, 4, 11–14]. The FAB mass spectrum of the pale yellow cyclometallated product exhibits peaks assigned to  $\text{Pd}_2\text{L}_2\text{Cl}_2$ ,  $\text{PdL}_2\text{Cl}$ ,  $\text{PdL}_2$ ,  $\text{Pd}_2\text{LCl}$  and  $\text{PdL}$ . The compound is insoluble in most solvents and an NMR spectrum could not be obtained, although we believe that the minor species observed on heating solutions of *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  may be the cyclometallated complex. Compatible with this is the observation that  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  is obtained in quantitative yield upon heating *cis*- or *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  in boiling toluene. This provides a reproducible and easy method for the preparation of the cyclometallated complex from any of the mixtures of products which are obtained from the reaction of  $[\text{PdCl}_4]^{2-}$  with HL. This is a far more convenient (and reproducible) method than the extraction with dmf proposed by Craig and Watts [13]. Dichloromethane solutions of *trans*- $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  deposit X-ray quality crystals of  $[\text{LPd}(\mu\text{-Cl})_2\text{PdCl}]$  upon slow evaporation in air. The

addition of LiCl to  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{LPd}(\mu\text{-OAc})_2\text{PdL}]$  results in the precipitation of  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  identical in all respects to that prepared by the above methods. The addition of  $\text{Na}[\text{OAc}]$  to a suspension of  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  in  $\text{CD}_3\text{COCD}_3$  resulted in the formation of a yellow solution, the  $^1\text{H}$  NMR spectrum of which is identical to that of a solution of  $[\text{LPd}(\mu\text{-OAc})_2\text{PdL}]$ . These transformations are summarised in Scheme 1.

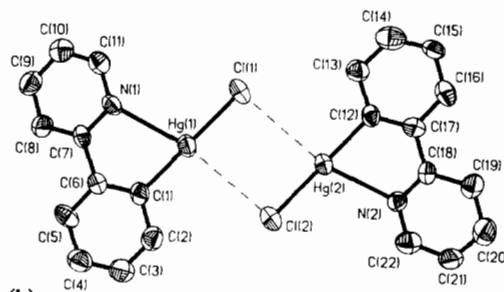
The crystal and molecular structure of (2-(2-pyridyl)phenyl)palladium(II) chloride is shown in Fig. 3. The structure is reminiscent of that of  $[\{\text{HgLCl}\}_4]$  and consists of two chloro-bridged  $\{\text{PdLCl}\}_2$  units associated to form a tetramer. The molecular structure of the dimeric  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  unit is shown in Fig. 3(a), whilst the tetranuclear assembly of two dimers is depicted in Fig. 4(a). Within each  $\{\text{PdLCl}\}_2$  unit the palladium centres are connected by two asymmetric chloride bridges. The asymmetry within the bridges arises from the differing *trans* groups; the Pd–Cl bond *trans* to the carbon atom of the cyclometallated ligand is slightly longer (2.426(1) Å) than that *trans* to the Pd–N bond (2.349(2) Å). The distances are typical for bridging Pd–Cl–Pd, and consistent with the known strong *trans* influence associated with C-donor ligands. The Pd–N distances (2.005(4), 2.013(5) Å) are significantly longer than the Pd–C distances (1.972(5), 1.978(4) Å). These distances correspond closely to those observed in bis( $\mu$ -acetato)di[2-pyridyl-4-nitrophenyl]palladium(II) [Pd–C, 1.94(1); Pd–N, 2.02(2) Å [15] and bis( $\mu$ -acetato)di[2-{6-(4-methylphenyl)-2-pyridyl}(5-methylphenyl)palladium(II)] [Pd–C, 1.944(7); Pd–N, 2.047(5) Å [15] compounds in which there is no ambiguity about the assignment of the C and N atoms of the metallated ligand. There is a potential crystallographic ambiguity in the assignment of the C and N atoms of the cyclometallated ligand; however the thermal parameters, the *trans* effect upon the bridging chloride ligands, and the bond lengths are



Scheme 1. (i)  $\text{Pd}(\text{OAc})_2$ ; (ii)  $\text{Hg}(\text{OAc})_2$ ; (iii) LiCl; (iv)  $[\text{PdCl}_4]^{2-}$ , 10 min; (v)  $[\text{PdCl}_4]^{2-}$ , 2h; (vi) 40 °C,  $\text{CDCl}_3$ ; (vii)  $\text{C}_6\text{H}_5\text{CH}_3$ , 100 °C.



(a)



(b)

Fig. 3. (a) The crystal and molecular structure of the dimeric  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  unit and (b) the crystal and molecular structure of the dimeric  $[\text{LHg}(\mu\text{-Cl})_2\text{HgL}]$  unit showing the numbering schemes adopted in each case for the tetrameric assembly of two  $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$  dimers. The hydrogen atoms have been omitted from (b) for clarity.

all consistent with the assignment that we have made, and we are confident that the *cisoid* arrangement of the cyclometallated ligands about the  $\text{Pd}_2\text{Cl}_2$  unit is correct. This is contrary to all previous representations of this molecule, for which a *transoid* arrangement has been tacitly assumed. The two palladium atoms are in an approximately square planar geometry, with Pd(1) lying 0.071 Å out of the plane Cl(1)Cl(2)N(1)C(11) and Pd(2) lying 0.024 Å out of the Cl(1)Cl(2)N(2)C(22) plane; the angle between the two planes is 4.3°. There is no direct metal–metal interaction within the dimer (Pd(1)–Pd(2), 3.48 Å). The two independent cyclometallated ligands are twisted about the interannular C–C bonds (5.3 and 0.2°), and a normal bite angle is observed at the cyclometalated ligand of 81° (cf. 79.7° in  $[\text{Rh}(\text{bipy})_2\text{L}][\text{PF}_6]_2$  [7], 81.4° in bis( $\mu$ -acetato)di[2-pyridyl-4-nitrophenyl]palladium(II) [15], 81.8° in bis( $\mu$ -acetato)di[2-{6-(4-methylphenyl)-2-pyridyl}(5-methylphenyl)palladium(II)] [15] and 80.3° in chloro(2-{6-(2,2'-bipyridyl)}phenyl)palladium(II) [8]).

The tetranuclear  $[\{\text{PdLCl}\}_4]$  molecule is formed by the association of two dimers, as shown in Fig. 4(a). There are two types of interaction responsible

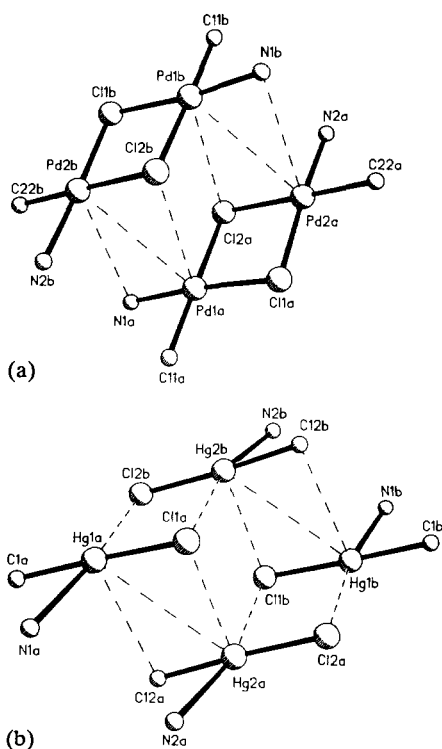


Fig. 4. Depiction of the tetranuclear assembly of the two dimeric subunits in  $[\{LPd(\mu\text{-Cl})_2PdL\}_2]$  (a) and  $[\{LHg(\mu\text{-Cl})_2HgL\}_2]$  (b). In each case, atoms not directly involved in the formation of the tetramer have been omitted for clarity.

for the association of the dimers. The first interaction is between Pd(1a) and Cl(2b) which exhibit a contact of 3.68 Å, and generally resembles that observed in  $[\{HgLCl\}_4]$ , whilst the second is a contact of 3.59 Å between Pd(2a) and N(1b). This latter interaction between the metal and the nitrogen atom of the other dimer is in contrast to the interaction with carbon which is observed with the mercury compound. This may reflect an adventitious positioning of the pyridyl ring resulting from the considerably shorter M–N distances observed in the palladium compound. As noted above, the cyclometallated ligand is closer to planarity in the palladium complex, and this may be traced to the lack of the interaction with the ring carbon atom. In the palladium tetramer, the two dimeric fragments are coplanar by crystal symmetry and the aromatic rings are stacked at a distance of 3.40 Å, reminiscent of interactions we have observed in other complexes with planar aromatic ligands [18].

The crystal and molecular structure of (2-{2-pyridyl}phenyl)mercury chloride is presented in Fig. 3(b). The structure consists of two  $\{HgLCl\}_2$  dimeric units combined to form a tetramer, as shown in Fig. 4(b). Within each  $\{HgLCl\}_2$  dimer, there are two inde-

pendent  $\{HgLCl\}$  units. The two independent 2-pyridylphenyl ligands show short Hg–C contacts (2.069(13), 2.070(13) Å) and long Hg–N interactions (2.627(12), 2.673(12) Å). In contrast to the palladium compound discussed above the chloride bridging ligands within the dimeric unit are highly asymmetrically placed with respect to the two metal ions (Hg–Cl 2.314, 2.334 Å versus Hg⋯Cl 3.442, 3.410 Å). The two independent  $\{HgLCl\}$  units show significant differences in the amount of twisting about the interannular C–C bonds of the 2-phenylpyridine ligands (twist angles 9 and 24°). The interdimer interaction is most apparent through the triply bridging chloride ligand Cl(1), which exhibits a short contact (3.184 Å) with Hg(2). This closest approach is substantially less than was found for the Pd analogue. Given these observations, it is perhaps remarkable that the two species exhibit such closely similar structures.

### Supplementary material

Tables of anisotropic displacement parameters, hydrogen atom coordinates, bond lengths and bond angles are available from the authors.

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