#### Polyhedron 34 (2012) 143-148

Contents lists available at SciVerse ScienceDirect

# Polyhedron



journal homepage: www.elsevier.com/locate/poly

# Novel binuclear palladium(II) complexes of 2-oxoquinoline-3-carbaldehyde Schiff bases: Synthesis, structure and catalytic applications

Sivakumar Priyarega<sup>a</sup>, Duraisamy Senthil Raja<sup>a</sup>, Sundaram Ganesh Babu<sup>b</sup>, Ramasamy Karvembu<sup>b</sup>, Takeshi Hashimoto<sup>c</sup>, Akira Endo<sup>c</sup>, Karuppannan Natarajan<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

<sup>b</sup> Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

<sup>c</sup> Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan

#### ARTICLE INFO

Article history: Received 28 September 2011 Accepted 19 December 2011 Available online 28 December 2011

Keywords: Binuclear palladium(II) complexes Schiff base Crystal structure N-arylation

#### 1. Introduction

Heterocyclic compounds containing nitrogen atom attract a great deal of attention in coordination chemistry and homogeneous catalysis [1–3]. The combination of heterocyclic ring and azomethine moiety exerts potential biological and catalytic activities [4–6]. Although extensive studies have been made on the transition metal complexes of various nitrogen heterocyclic Schiff base ligands, comparatively less is reported on transition metal complexes derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde [7–9]. The incorporation of phosphine ligands into the platinum group metal complexes brings remarkable changes in structural and electronic rearrangements, chemical reactivity and physical properties because of their large steric demands as well as  $\sigma$ -donor and  $\pi$ -acceptor properties [10].

Metal-catalyzed Ullmann-type C–N coupling reaction represents one of the most efficient methods to form various C–N bond containing compounds that have important biological, pharmaceutical, or material properties [11]. Traditional Cu-catalyzed Ullmann reactions require the use of stoichiometric amounts of copper, harsh reaction conditions, strong bases and often use of toxic polar solvents such as hexamethylphosphoramide (HMPA), and thus limited their large scale applications in industries. One of the most significant achievements in this field is the development of palladiumcatalyzed cross-coupling reactions that became a major synthetic protocol for the construction of aryl–carbon bonds [12]. The

#### ABSTRACT

A series of novel binuclear Pd(II) complexes of the type [(PPh<sub>3</sub>)<sub>2</sub>CIPd(L)PdCI] [where L = dianionic bridged ligands derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde or its derivatives with *o*-aminophenol/*o*-aminothiophenol] have been reported. The new complexes have been characterized by elemental analysis, FT-IR, UV–Vis and NMR (<sup>1</sup>H and <sup>31</sup>P) spectroscopic techniques. The coordination mode of the ligands and the geometry of the complexes were confirmed by single crystal X-ray crystallography of one of the complexes. The catalytic efficiency of one of the binuclear Pd(II) complexes was tested for N-arylation of imidazole.

© 2011 Elsevier Ltd. All rights reserved.

palladium-catalyzed cross-coupling reactions may also be applied to the formation of C-heteroatom such as C-N, C-O, C-S bonds [13]. On the other hand, Buchwald-Hartwig amination has been widely used for the preparation of aryl amines by the reactions of aryl halides with primary or secondary amines, amides, sulfonamides, imines, and heterocyclic compounds containing N-H bonds [14]. N-arylation reactions catalyzed by the palladium complexes are performed under mild conditions [15]. Though many reports are available on the palladium complexes as catalysts for C-N cross coupling reactions [16-18], palladium(II) complexes containing triphenylphosphine as well as Schiff base are rarely explored. So herein, we report the synthesis and characterization of novel binuclear Pd(II) complexes containing Schiff base ligands derived from 2-oxo-1,2-dihydroquinoline-3-carbaldehyde or its derivatives and o-aminophenol/o-aminothiophenol. The novel binuclear Pd(II) complexes have been tested as catalysts for N-arylation of imidazole. The general structure of quinoline based Schiff base ligands is given in Fig. 1.

# 2. Experimental

#### 2.1. Materials

All the reagents were purchased from Merck or Sigma–Aldrich and used as received. Solvents were freshly distilled and dried over the appropriate drying agents. 2-Oxo-1,2-dihydroquinoline-3-carbaldehyde, its derivatives or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde and the starting complex [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] were prepared according to the reported literature procedures [19–21].



<sup>\*</sup> Corresponding author. Tel.: +91 422 2428319; fax: +91 422 2422387. *E-mail address:* k\_natraj6@yahoo.com (K. Natarajan).

<sup>0277-5387/\$ -</sup> see front matter  $\circledcirc$  2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2011.12.017



Fig. 1. Structure of quinoline based Schiff base ligands.

#### 2.2. Physical measurements

IR spectra of the ligands and complexes were recorded on a Nicolet FT-IR spectrophotometer using KBr pellets. Electronic spectra of the complexes were recorded in dichloromethane using Systronics 119 spectrophotometer in the 200–800 nm range. Magnetic susceptibility measurements were made with the EG & G-Parc vibrating sample magnetometer. Nuclear Magnetic Resonance spectra were recorded on Bruker Avance 500 MHz spectrometer. <sup>1</sup>H NMR chemical shifts were reported using tetramethylsilane (TMS) as the internal standard. <sup>31</sup>P NMR spectra were measured relative to H<sub>3</sub>PO<sub>4</sub> as the external standard. Elemental analysis of the complexes was performed by Vario EL III elemental analyser. Melting points were determined with Raaga melting point apparatus.

# 2.3. General preparation of 2-oxo-1,2-dihydroquinoline-3carbaldehyde or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde Schiff bases

A methanol  $(20 \text{ cm}^3)$  solution of either *o*-aminophenol or *o*-aminothiophenol (0.44/0.50 g; 4.00 mmol) was added to 2-oxo-1, 2-dihydroquinoline-3-carbaldehyde or its derivatives or 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde (4.00 mmol) dissolved in the same solvent (20 cm<sup>3</sup>) and refluxed for 6 h. The yellow precipitate that separated out was filtered and washed with methanol and dried *in vacuo*. Yield: 73–77%.

# 2.4. Preparation of binuclear Pd(II) complexes of the type [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl] (L = binucleating 2-oxoquinoline-3-carbaldehyde Schiff base ligand)

To a solution of  $[PdCl_2(PPh_3)_2]$  (0.14 g; 0.20 mmol) in dichloromethane (20 cm<sup>3</sup>), the appropriate quinoline Schiff base ligands (0.10 mmol) in methanol (25 cm<sup>3</sup>) and two drops of triethylamine were added. The mixture was refluxed for 5 h. An orange colored precipitate that formed was separated from the solution by suction filtration. The complex was washed with ethanol and dried under *vacuum*. Yield: 66–72%.

#### 2.5. X-ray crystallography

Crystals of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN suitable for X-ray diffraction study were grown from dichloromethane/acetonitrile solution. A red block crystal having approximate dimensions of  $0.20 \times 0.10 \times 0.04$  mm was mounted on a Rigaku Mercury CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71070$  Å). The structure was solved by direct methods and expanded using Fourier techniques [22,23]. All non-hydrogen atoms

Та	ble	1

Crystal data and structure refinement parameters for  $[(PPh_3)_2CIPd(L1)PdCI] \cdot 1.5CH_3CN$ .

Empirical formula	C==H++==N===O=P=Pd=Cl=
Formula weight	1132 13
Color	red
Habit	black
Crystal dimensions (mm)	$0.20 \times 0.10 \times 0.04$
Wavelength (Å)	0.71070
Crystal system	orthorhombic
Lattice type	primitive
Space group	$Pna2_{(\#33)}$
Detector position (mm)	44.92
Pixel size (mm)	0.137
Lattice parameters	0.157
a (Å)	16 8400(10)
$h(\hat{A})$	27 7902(18)
$C(\hat{A})$	10.4866(8)
$V(Å^3)$	4907 6(6)
7	4307.0(0)
$D = (\alpha/cm^3)$	1 522
$E_{\text{calc}}(g/\text{chi})$	1.552
$u(MoK\alpha)(cm^{-1})$	0.522
$\mu(MORG)(CIII)$	Joroptz polarization
Absolption contection	full matrix loast squares on $\Gamma^2$
No. of reflections measured	totaly 27202 uniques 5025
NO. OI TEHECHOIIS IIIEASUIEU	lolal. 57292, ullique. 5955
N <sub>int</sub>	0.062
Reflection/parameter ratio	9.01
Goodness-oi-iit (GOF) on $F^-$	U.951 P 0.0426P 0.1186
K indices $[1 > 2\sigma(1)]$	$K_1 = 0.0436, WR_2 = 0.1189$
$\Delta \rho_{\rm max}$ , $\Delta \rho_{\rm min}$ (e A $\stackrel{-}{}$ )	1.93, -1.29

were refined anisotropically, using full-matrix least squares refinements on  $F^2$  with crystal structure crystallographic software package [24]. Table 1 gives further details of data collection, refinement, and the structural details of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]· 1.5CH<sub>3</sub>CN.

#### 2.6. Catalytic N-arylation of imidazole by binuclear Pd(II) complexes

In a typical N-arylation reaction,  $[(PPh_3)_2CIPd(L1)PdCI]$  (0.01 g, 0.01 mmol) was added to a mixture of 4-chlorobenzonitrile (0.137 g, 1 mmol), imidazole (0.088 g, 1.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.276 g, 2 m mol) in *N*,*N*-dimethyl acetamide (DMAc) (4 cm<sup>3</sup>) and stirred at 120 °C. After completion of the reaction (as monitored by TLC), the reaction mixture was extracted with ethyl acetate and quenched with aqueous sodium hydrogen carbonate. The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 70/30) to afford pure 4-(1H-imidazol-1-yl)benzonitrile. Melting point: 142–144 °C; MS (GC): *m/z* 169.06 (M<sup>+</sup>).

#### 3. Results and discussion

Binuclear Pd(II) complexes were obtained from the reactions of [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with 2-oxoquinoline-3-carbaldehyde Schiff base ligands (H<sub>2</sub>L1-H<sub>2</sub>L6) in presence of a base, triethylamine (Scheme 1). The complexes are pure and air stable. They are quite soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMSO and DMF, and insoluble in MeOH and EtOH. The elemental analyses data and melting points of the compounds have been tabulated (Table 2). The results of elemental analyses for the ligands and complexes are in good agreement with the proposed molecular formula. As expected, the ligands are coordinated in a tridentate fashion (ONO/ONS) to palladium ion. In addition to that, the presence of triethylamine promoted deprotonation of the NH of quinoline moiety followed by coordination to another palladium ion resulting in the formation of binuclear Pd(II) complexes.



Scheme 1. Synthesis of binuclear palladium(II) complexes.

#### Table 2

Analytical data of ligands and palladium(II) complexes.

Compound	Melting point (°C)	Elemental analysis Found (calc.)%			
		с	Н	Ν	S
H <sub>2</sub> L1	208	72.31	4.56	10.59	
		(72.72)	(4.58)	(10.60)	
$H_2L2$	211	68.71	4.30	10.05	11.39
		(68.55)	(4.31)	(9.99)	(11.44)
H <sub>2</sub> L3	221	73.36	5.09	10.07	
		(73.37)	(5.07)	(10.07)	
H <sub>2</sub> L4	226	69.35	4.79	9.55	10.95
		(69.36)	(4.79)	(9.52)	(10.89)
H <sub>2</sub> L5	206	76.47	4.45	8.94	
		(76.42)	(4.49)	(8.91)	
H <sub>2</sub> L6	213	72.76	4.26	8.48	9.71
		(72.70)	(4.27)	(8.48)	(9.70)
$[(PPh_3)_2ClPd(L1)PdCl]$ (1)	) 248	58.56	3.60	2.54	
		(58.30)	(3.76)	(2.61)	
$[(PPh_3)_2ClPd(L2)PdCl]$ (2)	) 265	57.79	3.67	2.59	3.01
		(57.45)	(3.70)	(2.57)	(2.94)
$[(PPh_3)_2ClPd(L3)PdCl]$ (3)	) >300	58.34	4.07	2.34	
		(58.66)	(3.90)	(2.58)	
$[(PPh_3)_2ClPd(L4)PdCl]$ (4)	) >300	57.96	3.91	2.41	2.96
		(57.80)	(3.80)	(2.54)	(2.91)
$[(PPh_3)_2ClPd(L5)PdCl]$ (5)	) 217	60.14	3.61	2.39	
		(59.99)	(3.77)	(2.49)	
$[(PPh_3)_2ClPd(L6)PdCl]$ (6)	) 256	59.27	3.67	2.30	2.71
		(59.14)	(3.72)	(2.46)	(2.81)

# Table 3

IR and UV-Vis spectral data of ligands and palladium(II) complexes.<sup>a</sup>

Compound	v(C=N)	v(C- O)	v(C- S)	v(C=0)	Bands due to PPh <sub>3</sub>	$\lambda_{\max} \left( \varepsilon_{\max} \right)$
$H_{2}L1$ $H_{2}L2$ $H_{2}L3$ $H_{2}L4$ $H_{2}L5$ $H_{2}L6$ <b>1</b>	1600 1592 1613 1595 1585 1598 1598	1339 1347 1331 1373	1269 1256 1258	1649 1656 1659 1647 1637 1643 1590	1419,	238 (14803), 337 (8552), 253 (4821), 414 (2738), 471
2 3	1569 1553	1371	1304	1622 1593	1097, 694 1424, 1095, 696 1405,	(2181) 262 (12462), 341 (6231), 362 (4497), 400 (2306), 423 (2172) 267 (14683), 345 (7880),
4	1550 1549	1371	1319	1589 1590	1099, 696 1428, 1094, 695 1436,	402 (4649), 425 (3343), 465 (2103) 250 (13680), 347 (8230), 405 (4212), 425 (2385), 465 (2045) 230 (14068), 340 (9100),
6	1545		1310	1582	1098, 695 1425, 1095, 694	355 (4350), 445 (2452), 480 (2185) 235 (13865), 342 (8336), 357 (4290), 434 (2562), 470 (2175)

<sup>a</sup> v in cm<sup>-1</sup>;  $\lambda$  in nm;  $\varepsilon_{max}$  in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

All the complexes are diamagnetic ( $\mu_{eff} = 0$ ) indicating +2 oxidation state of Pd ions. The electronic spectra of all the Pd(II) complexes were recorded in dichloromethane solution. Five bands were observed in the region 230–480 nm (Table 3). The bands in the region 230–347 nm have been assigned to charge transfer transitions. The electronic spectra of complexes also showed three d–d spin allowed transitions from the three low lying d levels to the empty  $d_{x^2-y^2}$  orbital. The bands are attributed to  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  and to  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  transitions in accordance with the electronic spectra of other square planar Pd(II) complexes [25,26].

#### 3.2. IR spectra

3.1. Electronic spectra

The IR spectra of Pd(II) complexes exhibited characteristic absorption bands around  $1542-1569 \text{ cm}^{-1}$  attributed to v(C=N). A shift observed in the absorption due to the imine in the free ligands ( $1585-1613 \text{ cm}^{-1}$ ) to lower wave numbers in the metal complexes, is indicative of the coordination of Pd to imine nitrogen [27]. The intense band around  $1637-1659 \text{ cm}^{-1}$  in the IR spectra (Table 3) of free ligands is associated with C=O stretching vibration

which is shifted to  $1582-1622 \text{ cm}^{-1}$  in the corresponding Pd(II) complexes, indicating the coordination of metal through carbonyl oxygen in all the complexes [28]. The infrared spectra of the free ligands (H<sub>2</sub>L1, H<sub>2</sub>L3 and H<sub>2</sub>L5) showed a band around 3375-3396 cm<sup>-1</sup> due to the stretching of phenolic OH. This band is absent in the spectra of all the complexes, indicating the deprotonation of phenolic OH followed by coordination to metal ion. This is further supported by the shift of the band around 1331-1347 cm<sup>-1</sup> due to phenolic C-O to higher wave number (1371-1373  $\mbox{cm}^{-1}\mbox{)}$  [29]. In the complexes formed from H\_2L2, H\_2L4 and H<sub>2</sub>L6, the band (2515–2590 cm<sup>-1</sup>) corresponding to v(S-H) in the free ligands disappeared and absorption due to v(C-S) of free ligands around  $1256-1269 \text{ cm}^{-1}$  is shifted to  $1304-1319 \text{ cm}^{-1}$  in the complexes, indicating that the other coordination site is thiophenolic sulfur atom. However, the characteristic absorption band around 3150-3169 cm<sup>-1</sup> due to quinoline NH has disappeared on complexation [29]. This shows the involvement of quinoline nitrogen in the coordination with the palladium ion. In addition to these, three strong bands observed around 1405-1436, 1094-1099 and 694-696 cm<sup>-1</sup> in all the complexes are attributed to coordinated PPh<sub>3</sub> ligand [27].

 Table 4

 <sup>1</sup>H NMR spectral data of ligands and palladium(II) complexes.

_	Compound	<sup>1</sup> H NMR ( $\delta$ in ppm)	<sup>31</sup> P NMR ( $\delta$ in ppm)
	$H_2L1$	12.07 (s, 1H, OH); 10.35 (s, 1H, NH(quinoline)); 8.41 (s, 1H, CH=N);	
		6.63–7.84 (m, 39H, aromatic)	
	$H_2L2$	11.93 (s, 1H, SH); 10.29 (s, 1H,	
		NH(quinoline)); 8.13 (s, 1H, CH=N);	
		6.63–7.85 (m, 39H, aromatic)	
	$H_2L3$	11.97 (s, 1H, OH); 10.39 (s, 1H,	
		NH(quinoline)); 8.37 (s, 1H, CH=N);	
		6.62–7.83 (m, 38H, aromatic); 1.72 (s,	
		3H, CH <sub>3</sub> )	
	$H_2L4$	12.04 (s, 1H, SH); 10.33 (s, 1H,	
		NH(quinoline)); 8.48 (s, 1H, CH=N);	
		6.60–7.89 (m, 38H, aromatic); 1.72 (s,	
		3H, CH <sub>3</sub> )	
	$H_2L5$	11.88 (s, 1H, OH); 10.26 (s, 1H,	
		NH(quinoline)); 8.29 (s, 1H, CH=N);	
		6.67–7.88 (m, 41H, aromatic)	
	$H_2L6$	11.93 (s, 1H, SH); 10.31 (s, 1H,	
		NH(quinoline)); 8.23 (s, 1H, CH=N);	
		6.75–7.92 (m, 41H, aromatic)	
	1	8.35 (s, 1H, CH=N), 6.62–7.83 (m, 39H,	24.5 (s)
	-	aromatic)	
	2	8.39 (s, 1H, CH=N), 6.96-7.84 (m, 39H,	25.7 (s)
	2	$\frac{d(0)(d(0))}{d(0)} = \frac{d(0)(d(0))}{d(0)} = \frac{d(0)}{d(0)} = \frac{d(0)}{d(0)$	20 5 (a)
	3	3.50(5, III, CIIII), 0.02-7.05(III, 50I),	20.3 (8)
	4	$(10111d11C), 1.01 (5, 5\pi, C\pi_3)$	29.7(c)
	4	9.17(5, 10, CO-N), 7.01-7.09(10, 500, 500)	20.7 (5)
	5	(5, 51, C13)	27.4(c)
	J	aromatic)	21.4(3)
	6	8.35 (s 1H CH=N) 6.95-7.89 (m 41H	26.7(s)
	v	aromatic)	20.7 (3)
		aromatic)	

# Table 5

Selected bond lengths (Å) and bond angles (°) of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN.

Pd(1)-Cl(1)	2.304(2)	Cl(1)-Pd(1)-O(1)	89.49(17)
Pd(1)-O(1)	1.993(5)	Cl(1)-Pd(1)-O(2)	91.20(15)
Pd(1) - O(2)	2.002(5)	Cl(1)-Pd(1)-N(1)	173.2(2)
Pd(1) - N(1)	1.974(6)	O(1)-Pd(1)-O(2)	177.7(2)
Pd(2)-Cl(2)	2.311(2)	O(1)-Pd(1)-N(1)	84.2(2)
Pd(2) - P(1)	2.3220(19)	O(2) - Pd(1) - N(1)	95.2(2)
Pd(2)-P(2)	2.3278(19)	Cl(2)-Pd(2)-P(1)	89.69(7)
Pd(2)-N(2)	2.041(6)	Cl(2)-Pd(2)-P(2)	88.69(6)
O(1) - C(1)	1.335(10)	Cl(2)-Pd(2)-N(2)	176.96(17)
O(2) - C(9)	1.293(8)	P(1)-Pd(2)-P(2)	174.48(8)
N(1)-C(2)	1.426(10)	P(1)-Pd(2)-N(2)	92.00(16)
N(1)-C(7)	1.276(11)	P(2)-Pd(2)-N(2)	89.86(16)
N(2)-C(9)	1.329(9)	Pd(1)-O(1)-C(1)	109.7(4)
N(2)-C(10)	1.383(9)	Pd(1)-O(2)-C(9)	124.4(4)
		Pd(1)-N(1)-C(2)	110.8(5)
		Pd(1)-N(1)-C(7)	124.2(5)

results in the formation of five member chelate ring. Complexes **3** and **4** showed a signal corresponding to methyl group at 1.61 and 1.66 ppm, respectively. Resonances due to aromatic protons of the ligands and triphenylphosphine are observed as multiplets around 6.62–7.89 ppm. The absence of NH signal in all the complexes suggests that the NH in the quinoline moiety underwent deprotonation and nitrogen is coordinated to another Pd ion. <sup>31</sup>P NMR spectra of the complexes exhibited only one signal at around 20.0–30.0 ppm indicating identical environment for both the phosphorus atoms and hence, *trans* positions were assigned to triphen-ylphosphine groups around one of the Pd centers.

#### 3.4. X-ray crystallography

# 3.3. NMR spectra

The <sup>1</sup>H NMR spectral data of all the ligands and their Pd(II) complexes are given in Table 4. The <sup>1</sup>H NMR spectra of all the Pd(II) complexes exhibited a singlet in the region 8.30–9.17 ppm due to imine proton. Disappearance of the signal for OH/SH proton in the complexes confirmed deprotonation followed by coordination of phenolic oxygen or thiophenolic sulfur to the Pd ion which The molecular structure of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN studied by single crystal X-ray diffraction analysis supported the spectroscopic results of Pd(II) complexes. The ORTEP diagram of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN with atom numbering scheme is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 5. The ligand is coordinated to two Pd(II) ions forming NO<sub>2</sub>Cl and NP<sub>2</sub>Cl coordination spheres. The Pd(II) ions adopt a square planar geometry as reflected from all the bond parameters



Fig. 2. ORTEP drawing of [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN showing thermal ellipsoids at the 30% probability level. The hydrogen atoms and CH<sub>3</sub>CN molecules have been omitted for clarity.

Table 6
Catalytic N-arylation of imidazole using [(PPh <sub>3</sub> ) <sub>2</sub> ClPd(L1)PdCl].

Entry	Aryl halide	Product	Reaction time (h)	Isolated yield (%)
1	CI	N N CN	28	83
2	Br		28	85
3	СІ——СООН	№_№_СООН	24	78
4	Br-COOH	№_№ СООН	24	81
5			24	89
6			24	82
7	Br		24	84

around Pd(II) centers [Cl(1)–Pd(1)–N(1) 173.2(2)°, O(1)–Pd(1)–O(2) 177.7(2)°, Cl(2)–Pd(2)–N(2) 176.96(17)°, P(1)–Pd(2)–P(2) 174.48(8)°]. The Pd–N, Pd–O, Pd–Cl and Pd–P distances are all quite normal and so are phenolic C–O, carbonyl C=O and azomethine C=N distances of the coordinated ligand [30,31]. Around Pd(2), triphenylphosphine ligands are *trans* to each other. This complex contains 1.5 acetonitrile molecules in the lattice.

The results obtained from various spectroscopic techniques and single crystal X-ray crystallography of one of the complexes revealed that the ligands act as tridentate donor to one metal center and monodentate donor to another metal center yielding binuclear Pd(II) complexes.

### 3.5. Catalytic N-arylation of imidazole by Pd(II) complexes

One of the binuclear Pd(II) complexes, [(PPh<sub>3</sub>)<sub>2</sub>CIPd(L1)PdCI] has been used as a catalyst in the N-arylation reaction of imidazole with various aryl halides and the results are summarized in Table 6. The N-arylated imidazole product was obtained in good yield (78–89%) after stirring at 120 °C in DMAc for 24–28 h in the presence of catalyst and a base, K<sub>2</sub>CO<sub>3</sub>. Since the leaving group ability of halogens are in the order of I > Br > CI > F, the aryl bromides react faster as compared to the aryl chlorides (Table 6). The highest reactivity of 4-chloronitrobenzene (Table 6, entry 5) towards N-arylation is attributed to the presence of strongest electron withdrawing group (NO<sub>2</sub>) in the phenyl ring [32].

#### 4. Conclusion

Six new binuclear palladium(II) complexes with the general formula [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L)PdCl] have been synthesized by reacting 2-oxoquinoline-3-carbaldehyde or 2-oxo-1,2-dihydrobenzo[h]quin oline-3-carbaldehyde Schiff base ligands with [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. Analytical, spectral (IR, UV–Vis, NMR) and X-ray diffraction studies revealed that the ligand is coordinated to two Pd(II) ions with the formation of NO<sub>2</sub>Cl and NP<sub>2</sub>Cl coordination spheres. Both the Pd(II) ions adopt distorted square planar geometry. The complex, [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl] showed better catalytic activity in the N-arylation reaction of imidazole.

### Acknowledgments

Financial assistance received from the Council of Scientific and Industrial Research, New Delhi, India [Grant Nos. 01(2216)/08/ EMR-II and 21(0745)/09/EMR-II], is gratefully acknowledged.

#### Appendix A. Supplementary data

CCDC 845753 contains the supplementary crystallographic data for the complex [(PPh<sub>3</sub>)<sub>2</sub>ClPd(L1)PdCl]·1.5CH<sub>3</sub>CN. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### References

- J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coord. Chem. Rev. 119 (1992) 67.
- [2] A. Togni, L.M. Venanzi, Angew. Chem., Int. Ed. Engl. 33 (1994) 497.
- [3] F. Fache, E. Schulz, M.L. Tommasino, M. Lemaire, Chem. Rev. 100 (2000) 2159.
- [4] S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar, J. Med. Chem. 49 (2006) 7242.
- [5] M. Sebastian, V. Arun, P.P. Robinson, A.A. Varghese, R. Abraham, E. Suresh, K.K.M. Yusuff, Polyhedron 29 (2010) 3014.
- [6] S.A. Filimon, C.G. Hrib, S. Randoll, I. Neda, P.G. Jones, M. Tamm, Z. Anorg. Allg. Chem. 636 (2010) 691.
- [7] D.S. Raja, N.S.P. Bhuvanesh, K. Natarajan, Eur. J. Med. Chem. 46 (2011) 4584.
- [8] D.S. Raja, N.S.P. Bhuvanesh, K. Natarajan, J. Biol. Inorg. Chem. 2011, doi:10.1007/s00775-011-0844-1.
- [9] D.S. Raja, N.S.P. Bhuvanesh, K. Natarajan, Inorg. Chem. 2011, doi:10.1021/ ic2020308.
- [10] N. Singh, B. Singh, K. Thapliyal, M.G.B. Drew, Inorg. Chim. Acta 363 (2010) 3589.
- [11] S.V. Ley, A.W. Thomas, Angew. Chem. Int. Ed. 42 (2003) 5400.
  [12] Z. Fei, D. Zhao, D. Pieraccini, W.H. Ang, T.J. Geldbach, R. Scopelliti, C. Chiappe,
- P.J. Dyson, Organometallics 26 (2007) 1588.
- [13] A.V. Vorogushin, X. Huang, S.L. Buchwald, J. Am. Chem. Soc. 127 (2005) 8146.
   [14] X. Huang, K.W. Anderson, D. Zim, L. Jiang, A. Klapars, S.L. Buchwald, J. Am.
- Chem. Soc. 125 (2003) 6653. [15] B.R. Rosen, J.C. Ruble, T.J. Beauchamp, A. Navarro, Org. Lett. 13 (2011) 2564.
- [16] S. Ueda, M. Su, S.L. Buchwald, Angew. Chem. Int. Ed. 50 (2011) 8944.
- [17] N. Yongpruksa, N.L. Calkins, M. Harmata, Chem. Commun. 47 (2011) 7665.
- [17] N. Tongpluksa, N.L. Carkins, M. Harmata, Chem. Commun. 47 (2011) 760 [18] S. Messaoudi, J.-D. Brion, M. Alami, Tetrahedron Lett. 52 (2011) 2687.
- [19] M.K. Singh, A. Chandra, B. Singh, R.M. Singh, Tetrahedron Lett. 32 (2011) 2087.
   [19] S.W.Sadudi, J.-D. Brion, W. Anani, Tetrahedron Lett. 32 (2011) 2087.
- [20] Z.C. Liu, B.D. Wang, Z.Y. Yang, Y. Li, D.D. Qin, T.R. Li, Eur. J. Med. Chem. 44 (2009) 4477.
- [21] J.L. Burmester, F. Basolo, Inorg. Chem. 3 (1964) 1587.
- [22] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
- [23] P.T. Beurskens, G. Admiral, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-99 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
- [24] J.R. Carruthers, J.S. Rollett, P.W. Betteridge, D. Kinna, L. Pearce, A. Larsen, E. Gabe, Chemical Crystallography Laboratory, Oxford, UK, 1999.
- [25] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
- [26] L.P. Romm, A.A. Malkov, S.A. Lebedev, V.V. Levashova, T.M. Buslaeva, Russ. J. Phys. Chem. A 85 (2011) 248.
- [27] M.M. Tamizh, K. Mereiter, K. Kirchner, B.R. Bhat, R. Karvembu, Polyhedron 28 (2009) 2157.

- [28] D.S. Raja, G. Paramaguru, N.S.P. Bhuvanesh, J.H. Reibenspies, R. Renganathan, K. Natarajan, Dalton Trans. 40 (2011) 4548.
  [29] N. Gunasekaran, R. Karvembu, Inorg. Chem. Commun. 13 (2010) 952.
  [30] S. Halder, M.G.B. Drew, S. Bhattacharya, J. Chem. Sci. 120 (2008) 441.

- [31] P.I.d.S. Maia, A.G.D.A. Fernandes, J.J.N. Silva, A.D. Andricopulo, S.O. Lemos, E.S. Lang, U. Abram, V.M. Deflon, J. Inorg. Biochem. 104 (2010) 1276.
  [32] Y.Z. Huang, J. Gao, H. Ma, H. Miao, J. Xu, Tetrahedron Lett. 49 (2008) 948.