Transition Met Chem (2012) 37:661–669
DOI 10.1007/s11243-012-9635-y

Synthesis, characterization and catalytic activity of three palladium(II) complexes containing Schiff base ligands

**Hai-Fu Guo · Yong Pan · De-Yun Ma ·
Kuan Lu · Liang Qin**

Received: 26 May 2012 / Accepted: 16 July 2012 / Published online: 3 August 2012

Abstract Three new Pd(II) complexes of Schiff base ligands, namely, $[Pd_4(L^1)_4]$ (**1**), $[Pd_2(L^2)_2Cl_2]$ (**2**) and $[Pd(L^3)_2Cl_2]$ (**3**) [$\mathbf{HL^1}$ = N-(benzylidene)-2-aminophenol; $\mathbf{L^2}$ = N-(2,4-dichlorobenzylidene)-2,6-diethylbenzenamine, $\mathbf{L^3}$ = 4-(2,4-dichlorobenzylide-neamino)phenol] have been synthesized using solvothermal methods and characterized by elemental analysis, spectroscopy and single crystal X-ray diffraction. The crystal structures of the free ligands were also determined. The μ-oxygen-bridged tetranuclear cyclometallated Pd(II) complex (**1**) contains four nearly planar units, in which Pd^{II} is four-coordinate. Complex **2** is a μ-chloro-bridged dinuclear cyclometallated Pd(II) complex, whereas complex **3** is mononuclear. The Heck reactions of bromobenzene with acrylic acid catalyzed by complexes **1**–**3** have also been studied.

Introduction

The palladium-catalyzed formation of biaryls from aryl halides with arylboronic acids (the Suzuki reaction) [1, 2] and the arylation and alkenylation of olefins (the Heck reaction) [3] have become mainstays of modern synthetic organic chemistry for the formation of carbon–carbon bonds. Compared to homogeneous catalysis for such coupling reactions, heterogeneous catalysis involving supported metal complexes offers several advantages, such as robustness and increased air and moisture stability [4–7]. Various supports, including silica, sepiolites, zeolites and polymers have been used to heterogenize the homogeneous catalysts [8–11]. Palladium(II) complexes derived from Schiff base ligands have been extensively studied over the past few decades in light of their applications as heterogeneous catalysts in organic reactions [12]. Most Pd(II) complexes have been prepared by the reaction of $Pd(OAc)_2$ or Na_2PdCl_4 with Schiff base ligands. Examples of Pd(II) complexes obtained by the combination of $PdCl_2$ with Schiff base ligands are much rarer. Here, we report the synthesis and structures of three new Pd(II) complexes obtained by the reaction of $PdCl_2$ and Schiff base ligands ($\mathbf{HL^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$) under solvothermal conditions. The Pd(II) atoms can be anchored by the three new Schiff base ligands to generate heterogeneous catalysts. These Pd(II) Schiff base complexes show moderate catalytic activity in the Heck coupling of bromobenzene with acrylic acid.

Experimental

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H and N were carried out using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer.

Preparation of $\mathbf{HL^1}$

$\mathbf{HL^1}$ was prepared by the condensation of benzaldehyde (3.18 g, 30 mmol) with 2-aminophenol (3.27 g, 30 mmol)

Electronic supplementary material The online version of this article (doi:10.1007/s11243-012-9635-y) contains supplementary material, which is available to authorized users.

H.-F. Guo (✉) · Y. Pan · D.-Y. Ma · K. Lu · L. Qin
School of Chemistry and Chemical Engineering, Zhaoqing University, Zhaoqing 526061, People's Republic of China
e-mail: guohaifu@zqu.edu.cn

Y. Pan
College of Chemical Engineering, Inner Mongolia University of Technology, Inner Mongolia 010051, People's Republic of China

Table 1 Crystallographic data for the free ligands

Compound	**HL^1**	**L^2**	**L^3**
Empirical formula	$C_{13}H_{11}NO$	$C_{17}H_{17}Cl_2N$	$C_{13}H_9Cl_2NO$
Formula weight	197.23	306.22	266.11
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	$Pca2_1$	$P-1$	$Pccn$
a (Å)	12.304(2)	8.0047(8)	13.6884(2)
b (Å)	6.0943(11)	10.0032(11)	14.399(2)
c (Å)	13.967(2)	10.8476(11)	12.4291(2)
α (°)	90.00	98.810(2)	90.00
β (°)	90.00	103.431(2)	90.00
γ (°)	90.00	101.424(2)	90.00
V (Å^3)	1,047.3(3)	809.83(15)	2,449.7(6)
Z	4	2	8
D (Mg m^3)	1.251	1.256	1.443
Limiting indices	$-14 \le h \le 11$, $-7 \le k \le 7$, $-16 \le l \le 16$	$-9 \le h \le 8$, $-11 \le k \le 9$, $-12 \le l \le 12$	$-16 \le h \le 9$, $-11 \le k \le 17$, $-14 \le l \le 14$
Reflections collected/unique	4985/1801	4226/2883	7590/2190
R_{int}	0.0210	0.0138	0.0314
$F(000)$	416	320	1088
θ (°)	2.92–25.17	1.97–25.20	2.63–25.20
Goodness-of-fit on F^2	1.042	1.029	1.077
$R(I > 2\sigma)$	$R_1 = 0.0342$	$R_1 = 0.0527$	$R_1 = 0.0460$
	$wR_2 = 0.0861$	$wR_2 = 0.1419$	$wR_2 = 0.1249$
R (all data)	$R_1 = 0.0403$	$R_1 = 0.0840$	$R_1 = 0.0709$
	$wR_2 = 0.0912$	$wR_2 = 0.1672$	$wR_2 = 0.1480$
Largest diff. peak and hole (Å^{-3})	0.16, −0.12	0.41, −0.37	0.34, −0.38
Flack	0.3(18)		

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$

$wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$

in ethanol (20 mL) as the reaction medium. The solution was refluxed for 3–4 h and then allowed to cool to room temperature. The yellow precipitate was recrystallized from ethanol to give **HL^1** as colorless crystals. Yield 0.4259 g (72 %). Anal. For $C_{13}H_{11}NO$ (%): Calcd. C 79.1, H 5.6, N 7.1; Found C 79.2, H 5.7, N 7.0. FTIR (KBr, cm^{-1}): 3448(s), 2366(m), 1622(s), 1577(w), 1476(s), 1380(s), 1288(w), 1246(s), 1171(w), 1147(w), 1067(w), 1026(m), 967(m), 936(w), 873(w), 850(m), 788(m), 761(s), 736(w), 684(s), 640(m), 564(w), 498(m), 426(w). MP: 91–94 °C.

Preparation of L^2

L^3 was prepared by the same procedure as for **HL^1** except that benzaldehyde and 2-aminophenol were replaced by 2,4-dichlorobenzaldehyde and 2,6-diethylaniline. Yield 0.689 g (75 %). Anal. For $C_{17}H_{17}Cl_2N$ (%): Calcd. C 66.6, H 5.6, N 4.6; Found C 66.4, H 5.8, N 7.5. FTIR (KBr, cm^{-1}): 3430(m), 3068(w), 2972(m), 2927(w), 2359(m), 1639(s), 1580(s), 1558(w), 1463(s), 1384(s), 1270(w), 1249(m), 1180(s), 1136(m), 1098(s), 1049(s), 984(w), 963(w), 867(vs), 836(m), 798(m), 767(w), 736(s), 677(w), 565(w), 454(m), 423(m). MP: 72–75 °C.

Preparation of L^3

L^3 was prepared by the same procedure as for **HL^1** except that benzaldehyde and 2-aminophenol were replaced by 2, 4-dichlorobenzaldehyde and 4-aminophenol. Yield 0.689 g (75 %). Anal. For $C_{13}H_9Cl_2NO$ (%): Calcd. C 58.6, H 3.4, N 5.3; Found C 58.5, H 3.3, N 5.4. FTIR (KBr, cm^{-1}): 3427(m), 3082(m), 2810(m), 2676(m), 2600(m), 2465(m), 2362(m), 1622(s), 1584(s), 1508(s), 1470(s), 1450(s),

Table 2 Crystallographic data for complexes **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{52}H_{36}N_4O_4Pd_4$	$C_{34}H_{32}Cl_6N_2Pd_2$	$C_{26}H_{18}Cl_6N_2O_2Pd$
Formula weight	1,206.45	894.12	709.52
Temperature (K)	296(2)	147(2)	296(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P-1$	$P2_1/c$
a (Å)	12.6285(8)	8.5323(3)	8.4560(4)
b (Å)	11.7305(8)	10.6883(4)	21.3107(11)
c (Å)	29.4443(19)	10.9243(4)	7.5767(4)
α (°)	90.00	62.8600(4)	90.00
β (°)	99.1270(10)	76.7300(10)	107.1280(10)
γ (°)	90.00	76.2680(10)	90.00
V (Å^3)	4,306.6(5)	852.69(5)	1,304.79(11)
Z	4	1	2
D (Mg.m^3)	1.861	1.553	1.806
Limiting indices	$-15 \le h \le 14$, $-14 \le k \le 14$, $-35 \le l \le 35$	$-8 \le h \le 10$, $-12 \le k \le 12$, $-13 \le l \le 11$	$-10 \le h \le 10$, $-17 \le k \le 25$, $-8 \le l \le 9$
Reflections collected/unique	23304/7689	4445/3049	6688/2344
R_{int}	0.0516	0.0095	0.0286
$F(000)$	2368	444	704
θ (°)	1.87–25.20	2.12–25.20	1.91–25.20
Goodness-of-fit on F^2	1.032	1.031	1.077
$R(I > 2\sigma)$	$R_1 = 0.0357$	$R_1 = 0.0182$	$R_1 = 0.0251$
	$wR_2 = 0.0868$	$wR_2 = 0.0460$	$wR_2 = 0.0548$
R (all data)	$R_1 = 0.0698$	$R_1 = 0.0199$	$R_1 = 0.0324$
	$wR_2 = 0.1073$	$wR_2 = 0.0470$	$wR_2 = 0.0577$
Largest diff. peak and hole (Å^{-3})	0.68, −0.79	0.34, −0.37	0.37, −0.35

$R = \sum(\|F_o| - |F_c\|)/\sum|F_o|$

$wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$

1370(s), 1274(s), 1239(s), 1174(s), 1104(s), 1047(s), 981(w), 863(m), 843(s), 743(s), 714(w), 664(w), 570(s), 536(m), 456(m), 423(m). MP: 161–164 °C.

Preparation of $[Pd_4(L^1)_4]$ (**1**)

Palladium chloride (0.0887 g, 0.5 mmol) was dissolved in methanol (5 mL). **HL^1** (0.236 g, 1 mmol) was added and the mixture stirred at room temperature for 5 h under an anhydrous atmosphere. The resulting mixture was filtered under reduced pressure. The collected solid was washed with ethyl ether and dried in air to give red crystals that were purified by recrystallization from methylene chloride (11 mL) and hexane (8 mL). Yield 0.0754 g (50 %). Anal. For $C_{52}H_{36}N_4O_4Pd_4$ (%): Calcd. C 51.7, H 3.0, N 4.6; Found C 51.5, H 3.1, N 4.7. FTIR (KBr, cm^{-1}): 3442(s), 1633(w), 1600(s), 1573(m), 1490(m), 1473(s), 1398(m), 1302(w), 1269(s), 1203(w), 1114(m), 1043(w), 954(w), 868(w), 750(s), 619(w), 576(m) 526(w), 460(w).

Preparation of $[Pd_2(L^2)_2Cl_2]$ (**2**)

Complex **2** was prepared by the same procedure as **1** except that **HL^1** was replaced with **L^2**. Yield 0.1 g (45 %). Anal. For $C_{34}H_{32}Cl_6N_2Pd_2$ (%): Calcd. C 45.6, H 3.6, N 3.1; Found C 45.5, H 3.7, N 3.2. FTIR (KBr, cm^{-1}): 3450(m), 3232(s), 2970(s), 2941(m), 1647(w), 1599(s), 1577(s), 1545(m), 1458(s), 1375(m), 1344(w), 1292(w), 1228(w), 1172(m), 1095(s), 1062(m), 916(w), 858(w), 815(w), 763(s), 721(w), 576(m), 521(w), 459(w).

Preparation of $[Pd(L^3)_2Cl_2]$ (**3**)

Complex **3** was prepared by the same procedure as **1** except that HL^1 was replaced with **L^3**. Yield 0.1 g (45 %). Anal. For $C_{26}H_{18}Cl_6N_2O_2Pd$ (%): Calcd. C 44.0, H 2.5, N 3.9; Found C 44.2, H 2.4, N 3.8. FTIR (KBr, cm^{-1}): 3461(m), 3292(s), 1623(s), 1581(s), 1545(m), 1510(s), 1458(m), 1398(w), 1355(w), 1284(s), 1220(m), 1174(m), 1101(m),

Table 3 Selected bond length and angles of complexes **1**–**3**

1			
Pd1–N1	1.968(5)	Pd1–O1	2.167(4)
Pd1–C3	1.959(6)	Pd1–O3	2.064(4)
Pd2–C16	1.969(6)	Pd2–O2	2.149(4)
Pd2–N2	1.967(5)	Pd2–O1	2.051(4)
Pd3–C29	1.967(6)	Pd3–N3	1.956(5)
Pd3–O3	2.148(4)	Pd3–O4	2.054(4)
Pd4–C42	1.969(7)	Pd4–N4	1.957(5)
Pd4–O2	2.042(4)	Pd4–O4	2.136(5)
C3–Pd1–N1	82.3(2)	N1–Pd1–O3	179.23(2)
O3–Pd1–O1	99.66(2)	N2–Pd2–C16	82.7(2)
N2–Pd2–O1	97.3(2)	O1–Pd2–O2	98.80(2)
N3–Pd3–C29	82.0(2)	N3–Pd3–O4	176.0(2)
O4–Pd3–O3	98.36(2)	N4–Pd4–C42	82.5(3)
N4–Pd4–O2	179.2(2)	O2–Pd4–O4	98.03(2)
2			
Pd1–C13	1.978(2)	Pd1–Cl5^{i}	2.3291(5)
Pd1–Cl5	2.4404(5)	Pd1–N1	2.0319(2)
C13–Pd1–N1	81.429(8)	C13–Pd1–Cl5^{i}	95.41(6)
N1–Pd1–Cl5^{i}	176.79(5)	C13–Pd1–Cl5	177.74(6)
N1–Pd1–Cl5	97.20(5)	Cl5^{i}–Pd1–Cl5	85.987(2)
3			
Pd1–N1	2.033(2)	Pd1–Cl3	2.3101(6)
N1–Pd1–N1^{i}	180.0	N1–Pd1–Cl3	88.51(6)
N1–Pd1–Cl3^{i}	91.49(6)	Cl3^{i}–Pd1–Cl3	180.0

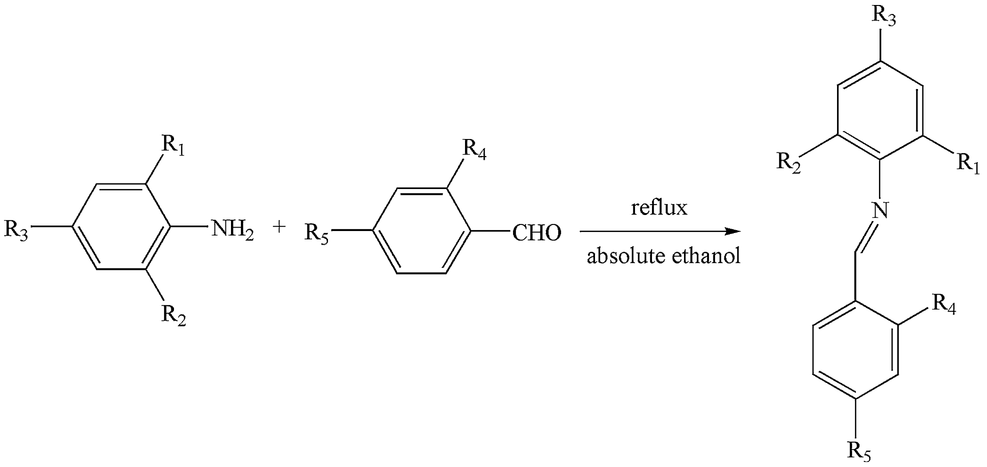
Symmetry codes: **2**, i: 1 − *x*, 2 − *y*, −*z*. **3**, i: 1 − *x*, 1 − *y*, 1 − *z*

Table 4 Hydrogen bond geometries for **HL^{1}**, **L^{3}**, **2**, **3** (Å, °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠D–H···A
HL^{1}				
O1–H1···N1	0.82	2.13	2.614(8)	118
L^{3}				
O1–H1···N1^{i}	0.82	1.98	2.801(7)	173
C2–H2···O1^{ii}	0.93	2.57	2.320(3)	138
C7–H7···Cl1	0.93	2.66	3.057(4)	106
C13–H13···O1^{ii}	0.93	2.58	3.356(7)	142
2				
C7–H7B···N1	0.99	2.53	2.882(7)	101
C9–H9A···N1	0.99	2.51	2.884(4)	102
C14–H14···Cl5^{i}	0.95	2.76	3.309(2)	118
3				
O1–H1···Cl3^{ii}	0.84	2.24	3.076(3)	174
C6–H6···Cl3	0.95	2.79	3.498(1)	132
C10–H10···O1^{iii}	0.95	2.53	3.432(7)	159
C13–H13···Cl3	0.95	2.76	3.642(5)	155

Symmetry codes: **L^{3}**, (i) 1.5 minus; *x*, *y*, −0.5 + *z*; (ii) 1.5 − *x*, *y*, 0.5 + *z*. **2**, (i) 1 − *x*, 2 − *y*, −*z*. **3**, (ii) −1 + *x*, *y*, −1 + *z*; (iii) −*x*, 0.5 + *y*, 0.5 − *z*

Scheme 1 Synthetic route for the free ligands. $R_1 = OH$, $R_2 = R_3 = R_4 = R_5 = H$, **HL^1**; $R_1 = R_2 = C_2H_5$, $R_3 = H$, $R_4 = R_5 = Cl$, **L^2**; $R_1 = R_2 = H$, $R_3 = OH$, $R_4 = R_5 = Cl$, **L^3**



1053(m), 973(w), 919(w), 883(m), 841(s), 744(m), 624(m), 580(w), 503(w), 462(w), 424(w).

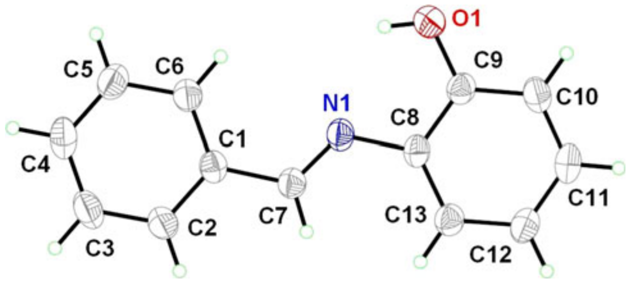


Fig. 1 The molecular structure of compound **HL^1** with numbering scheme

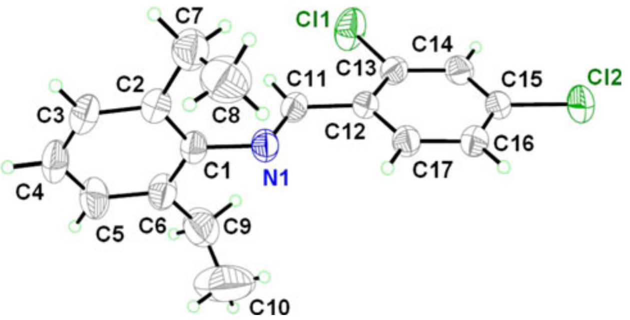


Fig. 2 The molecular structure of compound **L^2** with numbering scheme

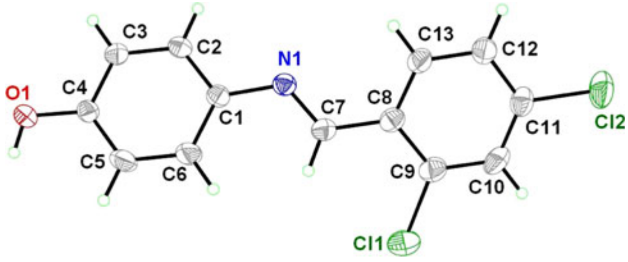


Fig. 3 The molecular structure of compound **L^3** with numbering scheme

Catalytic reactions

A mixture of bromobenzene (1.0 mmol), acrylic acid (1.3 mmol), triethylamine (2.0 mmol), DMF (6 mL) and 0.5 mol% of catalyst was stirred at 80 °C under air. Following the reaction, the catalyst was separated by filtration. The filtrate was dried over Na_2SO_4 and filtered. The products were quantified by GC–MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column). The typical GC–MS analysis program was as follows: initial column temperature 100 °C, hold 2 min, ramp temperature to 280 °C at 15 °C/min, and hold for 5 min.

X-ray crystallographic determination

Single crystal X-ray diffraction analyses of the free ligands and their complexes were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection and reduction were performed using the APEX II software [13]. Multi-scan absorption corrections were applied to all the data sets using SADABS, as included in the APEX II program [13]. All structures were solved by direct methods and refined by least squares on F^2 using the SHELXTL program package [14]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon and oxygen were placed in geometrically idealized positions and refined using a riding model. Crystallographic data are listed in Tables 1 and 2. Selected bond lengths and angles, and H-bonding parameters for the compounds are given in Tables 3 and 4, respectively.

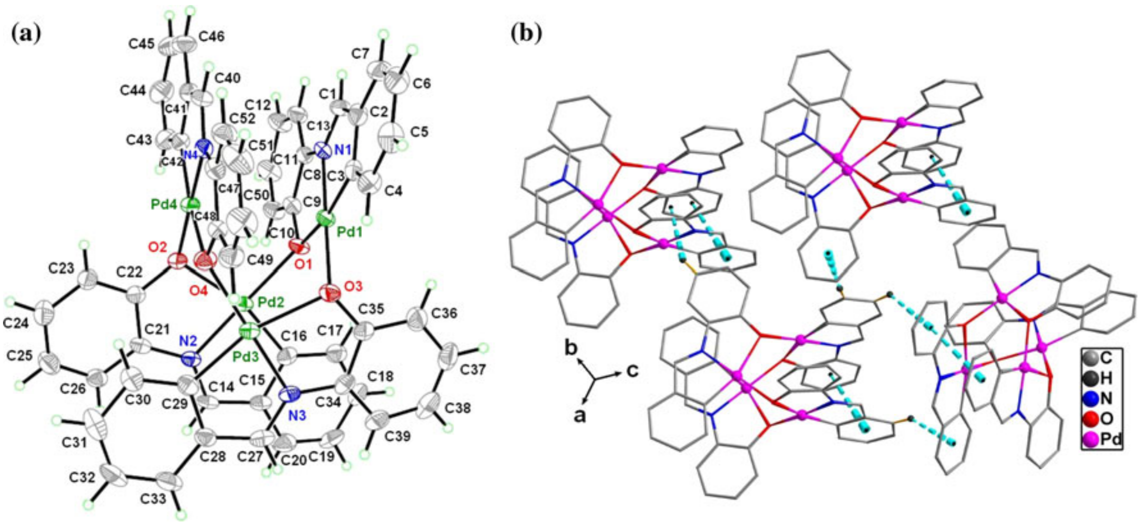


Fig. 4 **a** A perspective view of **1** with numbering scheme; **b** the packing of **1** formed by C–H···π stacking interactions with *turquoise dashes*

Results and discussion

Structures of the free ligands

The Schiff bases were prepared by condensation of benzaldehyde or 2,4-dichlorobenzaldehyde with aromatic amines in absolute ethanol (Scheme 1). The reaction progress was monitored by TLC; the reactions were terminated once the TLC showed no further reactants present.

Compound $\mathbf{HL^1}$ crystallizes in orthorhombic space group $Pca2_1$. As depicted in Fig. 1, the molecular structure is almost planar, with a dihedral angle between the benzylidene (C1–C7) and 2-(amino)phenol rings (C8–C13/N1/O1) of 1.11(2)°. In the crystal of **1**, an infinite chain is formed through C–H···π stacking interactions. The H-to-centroid distance H6···Cg1^{i} is 2.90(2) Å [Cg1 is the centroid of the C8–C13 ring. The angle C6–H6···Cg1 is 125°. Symmetry Code: (i) $0.5 + x$, $1 - y$, z]. Intramolecular O–H···N hydrogen bonds are also observed (Table 4). The melting point of $\mathbf{HL^1}$ is in good agreement with literature values [15, 16].

In $\mathbf{L^2}$ (Fig. 2), the dihedral angle between the mean planes of the benzylidene (C11–C17) and benzenamine rings is 84.37(2)°. In the crystal of $\mathbf{L^2}$, there are no directional interactions but only van der Waals interactions between neighbouring molecules.

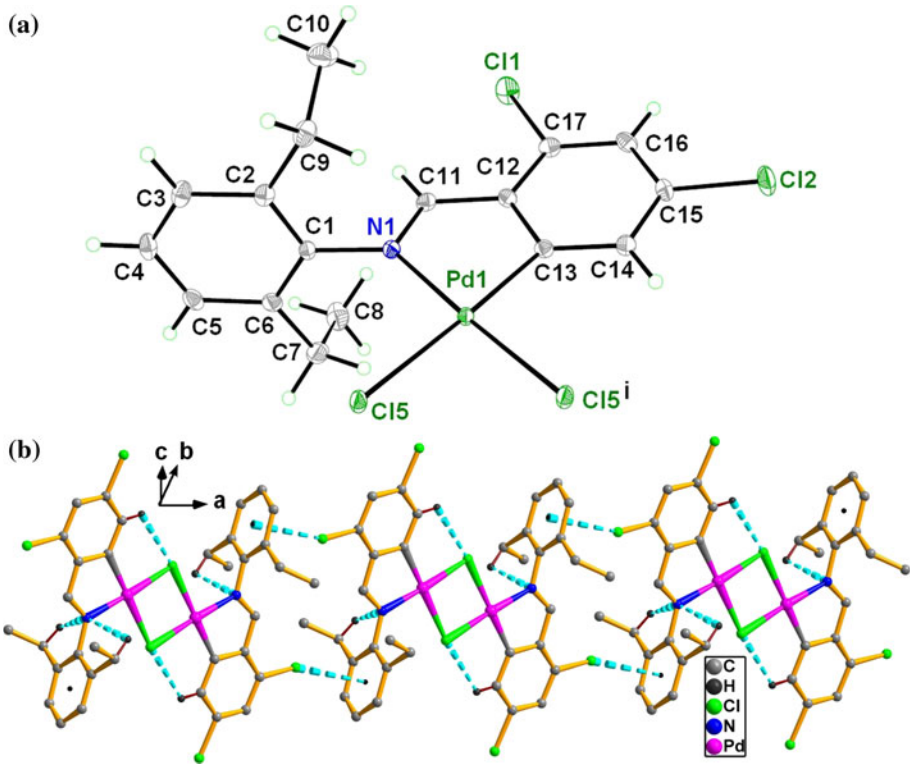
The dihedral angle between the benzene rings of compound $\mathbf{L^3}$ is 24.24(2)° (Fig. 3). In the crystal of $\mathbf{L^3}$, hydroxyl-H (H1) and phenyl-H (C2 and C13) are involved in intermolecular O–H···N and C–H···O hydrogen bonds (Table 4), linking the molecules into an infinite chain parallel to the *b* axis. This is further interconnected into a doubles-chain by C–H···π stacking interactions. The H-to-centroid distance H6···Cg2^{iii} is 2.93(2) Å [Cg2 is the centroid of the C8–C13 ring. Symmetry code: (iii) x, $0.5 - y$, $-0.5 + z$]. All the three of these Schiff bases adopt the *E* configuration with respect to the C=N bond, and all the bond lengths are within normal ranges [17].

Structures of the complexes

To prepare complexes **1**–**3**, the Schiff bases were treated with $PdCl_2$ in equimolar amounts at room temperature in methanol. The reactions proceeded without reflux under mild conditions, thus preventing oxidation of Pd(II) to Pd(IV) [18].

The asymmetric unit of complex **1** consists of one formula unit, in which all palladium atoms are crystallographically inequivalent. As shown in Fig. 4a, the core of complex **1** consists of an eight-membered ring of alternating Pd and O atoms. This structure is similar to that of $[Pd\{C_6H_4{-}CH{=}N{-}(C_6H_4{-}2{-}O)\}]_4{\cdot}2CHCl_3$, but the two complexes are not isomorphous [19]. The coordination environment about each palladium atom can be described as square planar, having two oxygen, one imine nitrogen and one aryl carbon donor atoms. Consequently, ligand $\mathbf{HL^1}$ acts as a C, N, O-chelator. The Pd–C, Pd–N and Pd–O bond distances and angles range from 1.956(5) to 2.167(4) Å and 81.25(18)° to 179.23(18)°, respectively, all of which are within normal ranges [19]. The Pd–$O_{chelating}$ distances *trans* to carbon are longer than the Pd–$O_{bridging}$ distances *trans* to nitrogen [average Pd–$O_{chelating}$ = 2.150(2) Å and average Pd–$O_{bridging}$ = 2.053(3) Å], which is attributed to the *trans* influence of the coordinated carbon of the cyclometalated ligand. The Pd1–Pd4 and Pd2–Pd3 distances are 3.349(4) and 3.376(3) Å, respectively, suggesting the absence of any Pd–Pd bonding. These are close to the corresponding distances [3.340(2) and 3.390(4) Å] found in $[Pd\{C_6H_4CH{=}N(C_6H_4{-}2{-}O)\}]_4{\cdot}2CHCl_3$

Fig. 5 **a** The molecular structure of compound **2** with numbering scheme; **b** view of an infinite chain of **2** formed by C17–Cl1···π stacking interactions with *turquoise dashes*. Symmetry codes: (i) $1 - x$, $2 - y$, $-z$



[19]. The packing shows C–H···π stacking interactions. The H-to-centroid distances of H33···Cg1^i = 2.78(2) Å, H19···Cg2^i = 2.93(4) Å, H12···Cg1^{ii} = 2.87(3) Å, H18···Cg1^{iii} = 2.84(5) Å [where Cg1, Cg2, Cg3, Cg4 and Cg5 are the centroids of the C15–C20, C21–C26, C34–C39, C47–C52 and C28–C33 rings, respectively. Symmetry codes: (i) $-x, -0.5 + y, 0.5 - z$; (ii) $x, 1 + y, z$; (iii) $-1 + x, y, z$]. A weak $\pi\cdots\pi$ stacking interaction between the parallel phenyl rings within ligand **HL^1** is also observed [the centroid–centroid distance is 3.733(3) Å] (Fig. 4b).

The molecular structure of complex **2** is shown in Fig. 5a. Selected bond distances and angles are given in Table 3. In this complex, each Schiff base ligand (**L^2**) is bonded to the di-μ-chloro-bridged unit through nitrogen atoms and an aromatic carbon atom, providing two equivalent five-membered N–C–Pd–C–chelate rings. The geometry at the Pd(II) center in **2** is square planar, with the two cyclometallated ligands in a *trans* arrangement with respect to the Pd···Pd axis. The Pd1–C13 bond [1.979(2) Å] is shorter than the expected value of 2.08 Å based on the sum of the covalent radii of carbon and palladium, but consistent with those found for related complexes where partial multiple-bond character of the Pd–C was assumed [20, 21]. The Pd1–N1 bond distance [2.032(4) Å] is in agreement with the sum of covalent radii for nitrogen and palladium [22], and similar to values reported earlier [20, 21]. The lengths of the Pd–Cl bonds *trans* to C [2.440(2) Å] and the Pd–Cl bonds *trans* to N [2.329(3) Å], reflect the different *trans* influences exerted by the phenyl carbon and nitrogen atoms. In the five-membered chelate rings, the five atoms (Pd1, N1, C11, C12 and C13) are essentially planar. The bite angle [C1–Pd1–N1 = 81.41(7)°] is in good agreement with those found in a structurally related μ-Cl dimer [21]. In the crystal of complex **2**, an infinite chain is formed through C17–Cl1···π stacking interactions (Fig. 5b). The Cl1-to-centroid distance for Cl1···Cg1^{ii} is 3.274(7) Å [where Cg1 is the centroid of the C1–C6 ring, symmetry code: (ii) $-x$, $1 - y$, $1 - z$]. Intramolecular C–H···N and C–H···Cl hydrogen bonds are also observed.

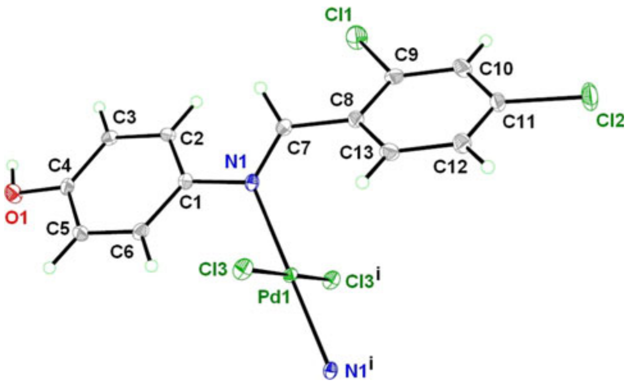


Fig. 6 The molecular structure of compound **3** with numbering scheme. Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$

The structure of complex **3** is shown in Fig. 6. The molecular structure is *trans*-[Pd(L^3)$_2$Cl$_2$], and the palladium

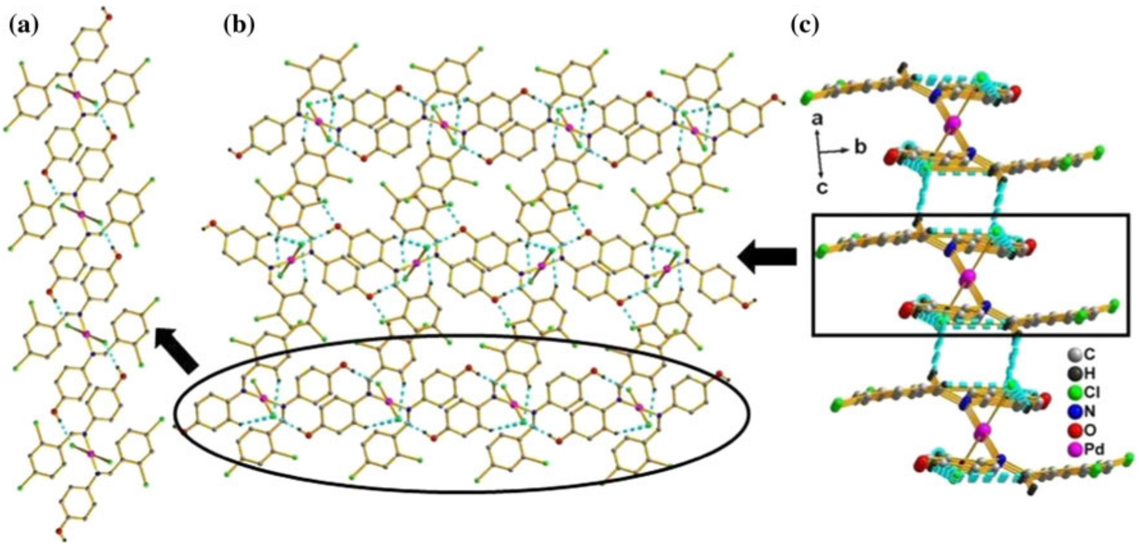


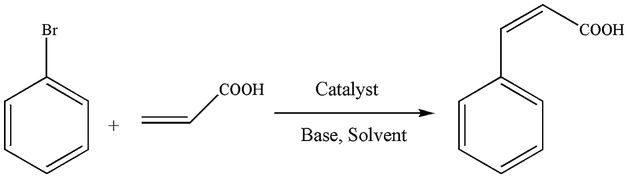
Fig. 7 **a** An infinite chain of **3** formed by O–H···Cl hydrogen bonding interactions; **b** view of a 2D sheet of **3** with cavities formed by C–H···O hydrogen bonding interactions; **c** view of the 3D supramolecular network of **3** formed through C–H···π stacking interactions

atom lies on a crystallographic inversion center such that the angles N–Pd–N and Cl–Pd–Cl are both 180°. The planes of the two phenyl rings are inclined by 71.07(3) and 79.53(2)° to the PdN_2Cl_2 coordination plane, respectively. The phenyl rings of the Schiff base ligand (**L^3**) in **3** are not coplanar, but subtend a dihedral angle of 15.24(3)°, which is similar to that in the free ligand [24.24(2)°]. The Pd–N/Cl distances are 2.032(2) and 2.3101(6) Å, and the N–Pd–Cl angles are 88.52(6) and 91.48(6) °, respectively, all of which are within the range observed for analogous Pd complexes (Table 3) [23, 24]. In the crystal structure of complex **3**, intermolecular O–H···Cl hydrogen bonding interactions (Table 4) form infinite chains involving the hydroxyl groups as donors and the chlorine atoms as acceptors (Fig. 7a), which are further self-assembled into a 2D sheet with cavities by intermolecular C–H···O hydrogen bonding interactions, as shown in Fig. 7b. The 2D sheets are connected by C–H···π stacking interactions, resulting in a 3D supramolecular network (Fig. 7c). The H-to-centroid distance of H7···Cg1^i is 2.69(2) Å [Cg1 is the centroid of the C1–C6 ring. Symmetry Code: (i) $-x$, $1 - y$, $1 - z$].

Heck reaction catalysis

The base and solvent for the Heck reaction greatly influences catalytic activity. The results for these complexes are summarized in Table 5. DMF is the best solvent for this catalytic system. In other organic solvents, e.g., methanol, acetonitrile or toluene, low yields of coupling products were obtained. Among four different bases investigated for

Table 5 The effect of base and solvent on the complexes **1**–**3** catalyzed Heck reaction of bromobenzene with acrylic acid



Entry	Base	Solvent	Temperature (°C)	Atmosphere	Time (h)	Yields (%)
1	Et_3N	DMF	80	Air	12	52/48/45
2	Et_3N	Methanol	75	Air	12	32/27/25
3	Et_3N	ACN	80	Air	12	21/19/16
4	Et_3N	Toluene	100	Air	12	15/11/8
5	K_2CO_3	DMF	80	Air	12	24/22/17
6	Na_2CO_3	DMF	80	Air	12	19/16/12
7	NaOAc	DMF	80	Air	12	9/6/5
8	KF	DMF	80	Air	12	–/–/–

these reactions, Et_3N was found to be the most effective (Table 5, entry 1); NaOAc, K_2CO_3 and Na_2CO_3 were substantially less effective. KF failed to promote the reaction (Table 5, entry 8). Compared to other Pd(II) complexes containing Schiff bases, the catalytic activities of the present complexes for the Heck reaction proved to be less effective [7].

Conclusion

In summary, the synthesis and crystal structures of three new Schiff base ligands and their Pd(II) complexes have been reported in this article. The complexes show moderate catalytic activity in the Heck coupling reaction of bromobenzene with acrylic acid, which is also very sensitive to the choice of base and solvent.

Acknowledgments We are thankful for financial support of this work provided by the Science and Technology Planning Project of Zhaoqing City (2009G013) and Zhaoqing University with doctoral start-up funds. Thanks to Dr. Sean Parkin for all his help with the suggestions for the paper.

References

1. Miyaura N, Suzuki A (1995) Chem Rev 95:2457
2. Suzuki A (1999) J Organomet Chem 576:147
3. Heck RF, Nolley JP (1972) J Org Chem 37:2320
4. Sarkar K, Nandi M, Islam M, Mubarak M, Bhaumik A (2009) Appl Catal A Gen 352:81
5. Polshettiwar V, Len C, Fihri A (2009) Coord Chem Rev 253:2599
6. Polshettiwar V, Varma RS (2008) Tetrahedron 64:4637
7. Isiam SM, Mondal P, Tuhina K, Roy AS, Mondal S, Hossain D (2010) J Inorg Organomet Polym 20:264
8. Mukherjee S, Samanta S, Roy BC, Bhaumik A (2006) Appl Catal A Gen 301:79
9. Shimizu K, Koizumi S, Hatamachi T, Yoshida H, Komai S, Kodama T, Kitayama Y (2004) J Catal 228:141
10. Bulut H, Artoka L, Yilmaz S (2003) Tetrahedron Lett 44:289
11. Kim JW, Kim JH, Lee DH, Lee YS (2006) Tetrahedron Lett 47:4745
12. Jain VK, Jain L (2005) Coord Chem Rev 249:3075
13. Bruker (2004) APEXII software, Version 6.3.1. Bruker AXS Inc., Madison
14. Sheldrick GM (2008) Acta Cryst A 64:112
15. Lane TJ, Lane CSC, Kandathil AJ (1961) J Am Chem Soc 83:3782
16. Tandon JP, Gupta SR, Prasad RN (1976) Monatsh Chem 107:1379
17. Allen FH, Kennard O, Watson DG, Brammer L, Orpen AG, Taylor R (1987) J Chem Soc Perkin Trans 2:1
18. Naeimi H, Moradian M (2010) J Coord Chem 63:156
19. López C, Caubet A, Pérez S, Solans X, Font-Bardía M (2003) J Organomet Chem 681:82
20. Fuchita Y, Yoshinaga K, Hanaki T, Kawano H (1999) Kinoshita-Nagaoka J 580:273
21. Crispini A, Munno GD, Ghedini M, Neve F (1999) J Organmet Chem 427:409
22. Pauling L (1960) The nature of chemical bond. Cornell University Press, New York
23. Qin Z, Jennings MC, Puddephatt RJ (2001) Inorg Chem 40:6220
24. Mentes A, Kemmitt RDW, Fawcett J, Russell DR (2004) J Mol Struct 693:241