

Hoong-Kun Fun,<sup>a\*</sup> Suchada Chantrapromma,<sup>b\*</sup> Zhong-Lin Lu,<sup>c</sup> Alexei A. Neverov<sup>c</sup> and R. Stan Brown<sup>c</sup>

<sup>a</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, <sup>b</sup>Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and <sup>c</sup>Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Correspondence e-mail: hkfun@usm.my, suchada.c@psu.ac.th

## Chloro[2-(dimethylamino)benzyl- $\kappa^2C^1,N$ ]-[4-(dimethylamino)pyridine- $\kappa N^1$ ]palladium(II)

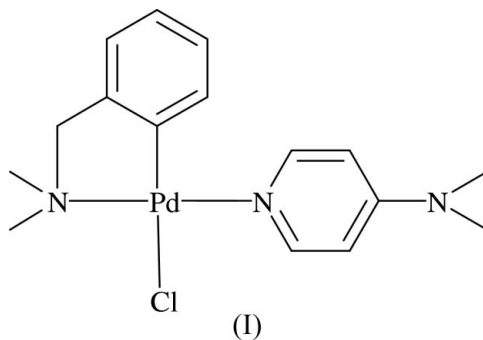
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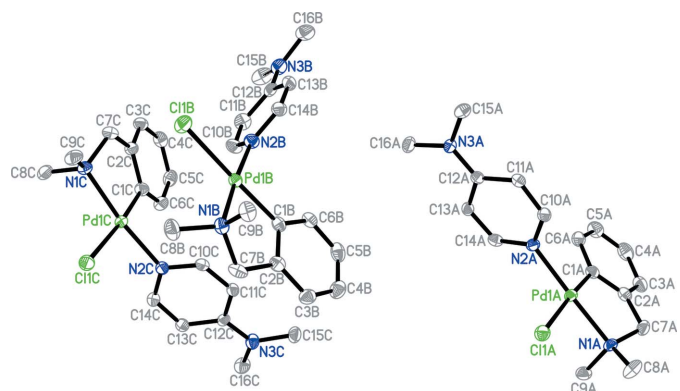
The title palladacycle, [Pd(C<sub>9</sub>H<sub>12</sub>N)Cl(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)] or [Pd(DMBA)Cl(DMP)] [DMBA is 2-(dimethylamino)benzyl, N(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, and DMP is 4-(dimethylamino)pyridine, 4-N(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N], crystallizes with three crystallographically independent but conformationally almost identical molecules (*A*, *B* and *C*) in the asymmetric unit. In all three molecules, the Pd atoms are coordinated by slightly distorted square-planar arrays of two N (pyridine and amine), benzyl C and Cl atoms. The pyridine and amine N atoms are positioned *trans* to one another. The dihedral angles between benzene and pyridine rings are 7.47 (17), 7.34 (16) and 10.83 (15)° in molecules *A*, *B* and *C*, respectively. In the crystal structure, weak intra- and intermolecular C—H···N and C—H···Cl and C—H··· $\pi$  interactions stabilize the structure.

### Comment

The synthesis, characterization and study of cyclopalladated compounds have received much attention in recent years due to their importance in organic synthesis, organometallic catalysis and molecular materials (Dupont *et al.*, 2005; Beletskaya & Cheprakov, 2004; Bedford, 2003). For example, cyclopalladated complexes containing 2-pyridylbenzene or aryl oxime ligands are effective catalysts for the degradation of thiophosphate pesticides (Kim *et al.*, 2006; Kazankov *et al.*, 2000). Palladacycles with aryl oxime ligands also efficiently catalyze carbon-carbon coupling reactions, even in aqueous solution (Alacid *et al.*, 2006). As part of our interest in the catalytic methanolysis of thiophosphate (Lu *et al.*, 2005), we report here the crystal structure of the title compound, (I) (Fig. 1).



The title complex crystallizes with three crystallographically independent molecules, *A*, *B* and *C*, in the asymmetric unit, each with slightly different bond lengths and angles (Fig. 1 and Table 1). The ligand bond distances and angles in (I) are within normal ranges (Allen *et al.*, 1987). The Pd atom displays



**Figure 1**  
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 60% probability level. H atoms have been omitted for clarity.

the expected distorted square-planar coordination, with the pyridine and amine N atoms positioned *trans* to one another. The dihedral angle between the two planes defined by C1/Pd1/N1 and N2/Pd1/Cl1 is 3.14 (14)° in molecule *A*, 2.38 (14)° in molecule *B* and 13.19 (12)° in molecule *C*. The Pd—C, Pd—Cl and Pd—N (amine and pyridine) bond lengths fall within the ranges of the values reported for other cyclopalladated derivatives of *N,N*-dimethylbenzylamine (Lu *et al.*, 2005; Mentés *et al.*, 2004) and aryl oxime ligands (Ryabov *et al.*, 1992). The five-membered palladacyclic ring is slightly strained, with C1—Pd1—N1 bond angles in the range 82.36 (11)–83.30 (11)°. The dihedral angle between the pyridine ring and the palladacycle plane (Pd1/N1/C1/C2/C7) is 83.74 (14)° in molecule *A* [81.85 (14)° in molecule *B* and 76.80 (14)° in molecule *C*], larger than those in the corresponding palladacycles with pyridine ligands (49.2° for [Pd{N(CH<sub>3</sub>)<sub>2</sub>—CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>—C<sup>1</sup>,N}(C<sub>5</sub>H<sub>5</sub>N)Cl]; Lu *et al.*, 2005). The dihedral angle between the benzene and pyridine rings is 7.47 (17)° in molecule *A*, 7.34 (16)° in molecule *B* and 10.83 (15)° in molecule *C*.

The crystal structure of (I) is stabilized by weak intra- and intermolecular C—H···N and C—H···Cl hydrogen bonds and C—H···π interactions, forming a three-dimensional network (Fig. 2 and Table 2).

## Experimental

To a solution of di- $\mu$ -chloro-bis(*N,N*-dimethylaminobenzyl-C<sup>1</sup>,N)dipalladium(II) (95.0 mg, 0.172 mmol) (Mentés *et al.*, 2004) in benzene (20 ml) was added 4-dimethylaminopyridine (1.2 equivalents). The mixture was stirred at room temperature for 3 h and then filtered through Celite. The Celite was washed with another 20 ml of dichloromethane and the solvents removed. The white solid residue was re-crystallized from a mixture of hexanes and dichloromethane (4:1 *v/v*) to give (I) in 76% yield. Single crystals of X-ray diffraction quality were recrystallized by the slow diffusion of hexane into a dichloromethane solution of (I). Analysis, calculated for C<sub>16</sub>H<sub>22</sub>ClN<sub>3</sub>Pd: C 48.26, H 5.57, N 10.55%; found: C 48.01, H 5.71, N 10.43%.

## Crystal data

[Pd(C<sub>9</sub>H<sub>12</sub>N)Cl(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)]

*M<sub>r</sub>* = 398.24

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 15.3217 (2) Å

*b* = 20.5634 (2) Å

*c* = 17.1800 (2) Å

$\beta$  = 114.907 (1)°

*V* = 4909.4 (1) Å<sup>3</sup>

*Z* = 12

*D<sub>x</sub>* = 1.616 Mg m<sup>-3</sup>

Mo *K*α radiation

$\mu$  = 1.29 mm<sup>-1</sup>

*T* = 100.0 (1) K

Block, colourless

0.25 × 0.16 × 0.07 mm

## Data collection

Bruker SMART APEXII CCD

area-detector diffractometer

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

*T<sub>min</sub>* = 0.737, *T<sub>max</sub>* = 0.918

100404 measured reflections

13045 independent reflections

10570 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.072

$\theta_{\max}$  = 29.0°

## Refinement

Refinement on *F*<sup>2</sup>

$R[F^2 > 2\sigma(F^2)]$  = 0.036

*wR*(*F*<sup>2</sup>) = 0.076

*S* = 1.05

13045 reflections

580 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 9.9822P]$

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta\sigma$ )<sub>max</sub> = 0.001

$\Delta\rho_{\max}$  = 1.28 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.90 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Pd1A—C1A	1.984 (3)	Pd1B—Cl1B	2.4237 (8)
Pd1A—N2A	2.033 (2)	N1B—C7B	1.498 (4)
Pd1A—N1A	2.078 (2)	C2B—C7B	1.514 (4)
Pd1A—Cl1A	2.4463 (8)	Pd1C—C1C	2.001 (3)
N1A—C7A	1.497 (4)	Pd1C—N2C	2.038 (2)
C2A—C7A	1.489 (4)	Pd1C—N1C	2.083 (2)
Pd1B—Cl1B	1.989 (3)	Pd1C—Cl1C	2.4130 (8)
Pd1B—N2B	2.022 (3)	N1C—C7C	1.497 (4)
Pd1B—N1B	2.080 (2)	C2C—C7C	1.500 (4)
C1A—Pd1A—N2A	92.91 (11)	C1B—Pd1B—Cl1B	176.38 (9)
C1A—Pd1A—N1A	83.30 (11)	N2B—Pd1B—Cl1B	88.72 (8)
N2A—Pd1A—N1A	176.19 (10)	N1B—Pd1B—Cl1B	95.22 (7)
C1A—Pd1A—Cl1A	174.58 (9)	C1C—Pd1C—N2C	91.73 (11)
N2A—Pd1A—Cl1A	91.26 (7)	C1C—Pd1C—N1C	82.36 (11)
N1A—Pd1A—Cl1A	92.50 (7)	N2C—Pd1C—N1C	172.76 (10)
C1B—Pd1B—N2B	92.89 (11)	C1C—Pd1C—Cl1C	173.87 (9)
C1B—Pd1B—N1B	83.13 (11)	N2C—Pd1C—Cl1C	91.92 (7)
N2B—Pd1B—N1B	175.97 (10)	N1C—Pd1C—Cl1C	94.34 (7)

**Table 2**

Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the N2A/C10A—C14A and N2C/C10C—C14C pyridine rings, respectively, and *Cg*3, *Cg*4 and *Cg*5 are the centroids of the C1A—C6A, C1B—C6B and C1C—C6C benzene rings, respectively.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C7A—H7AB···N3A <sup>i</sup>	0.97	2.57	3.519 (4)	167
C8A—H8AB···Cl1A	0.96	2.71	3.267 (3)	117
C5B—H5BA···Cl1C <sup>ii</sup>	0.93	2.83	3.738 (3)	168
C15A—H15B···Cl1A <sup>iii</sup>	0.96	2.67	3.617 (3)	171
C6B—H6BA···N2B	0.93	2.62	3.108 (4)	113
C8B—H8BA···N3B <sup>iv</sup>	0.96	2.60	3.482 (4)	153
C8B—H8BC···Cl1B	0.96	2.76	3.329 (4)	118
C3C—H3CA···Cl1C <sup>v</sup>	0.93	2.82	3.476 (3)	129
C9C—H9CC···Cl1C	0.96	2.73	3.264 (3)	116
C9A—H9AB···Cg5 <sup>ii</sup>	0.96	2.76	3.580 (3)	143

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11A—H11A $\cdots$ Cg4 <sup>iii</sup>	0.93	2.74	3.522 (4)	142
C15A—H15A $\cdots$ Cg1 <sup>iii</sup>	0.96	3.02	3.537 (3)	116
C9B—H9BB $\cdots$ Cg3 <sup>iii</sup>	0.96	2.98	3.766 (5)	140
C10B—H10B $\cdots$ Cg5	0.93	3.11	3.693 (4)	122
C11B—H11B $\cdots$ Cg5	0.93	3.00	3.625 (4)	126
C6C—H6CA $\cdots$ Cg2	0.93	2.99	3.700 (3)	134
C11C—H11C $\cdots$ Cg4	0.93	2.61	3.414 (4)	145

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (v)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

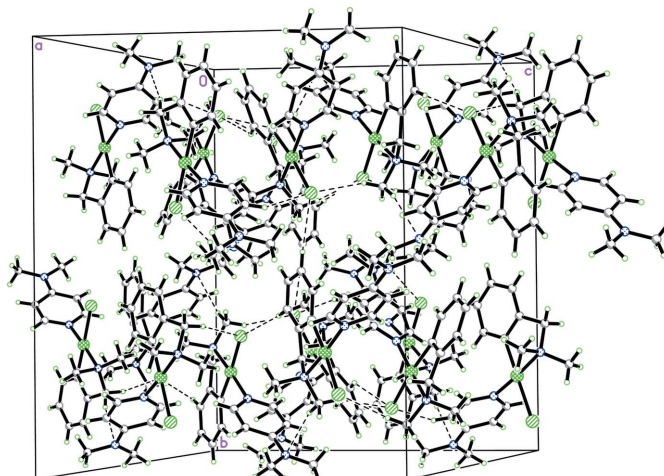
All H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms or  $1.2U_{\text{eq}}(\text{C})$  for the remaining H atoms. A rotating-group model was used for the methyl groups. The maximum residual electron-density peak is located 0.77 Å from atom Pd1B.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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**Figure 2**

The crystal packing of (I), showing the molecular network. Hydrogen bonds are drawn as dashed lines.