

# Dichlorido{2-[(2,6-diethylphenyl)iminomethyl]quinoline- $\kappa^2N,N'$ }palladium(II) acetonitrile monosolvate

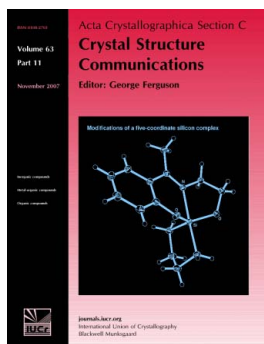
**William M. Motswainyana, Martin O. Onani, Jeroen Jacobs and Luc Van Meervelt**

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Dichlorido{2-[(2,6-diethylphenyl)- $\kappa^2N,N'$ ]-iminomethyl}quinoline- $\kappa^2N,N'$ -palladium(II) acetonitrile monosolvate

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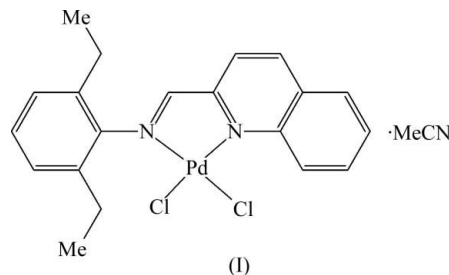
Online 14 November 2012

The title complex, [PdCl<sub>2</sub>(C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>)]·CH<sub>3</sub>CN, was synthesized by the reaction of 2-[(2,6-diethylphenyl)iminomethyl]quinoline with dichlorido(cycloocta-1,5-diene)palladium(II) in dry CH<sub>2</sub>Cl<sub>2</sub>. The Pd<sup>II</sup> ion is coordinated by two N atoms of the bidentate quinoline ligand and by two chloride anions, generating a distorted square-planar coordination geometry around the metal centre. There is a detectable *trans* influence for the chloride ligands. The crystal packing is characterized by  $\pi$ - $\pi$  stacking between the quinoline rings. The use of acetonitrile as the crystallization solvent was essential for obtaining good-quality crystals.

Comment

Imino-quinoline ligands coordinate as neutral bidentate species when they react with labile transition metal precursors to form air-stable complexes, which show hemilability due to the weakly coordinating N atoms (Segapelo *et al.*, 2009). These complexes could be investigated in various applications, such as olefin oligomerization, polymerization and cyclopropanation, and Heck–Suzuki coupling reactions (Segapelo *et al.*, 2009; Ojwach *et al.*, 2007; Bianchini *et al.*, 2010; Ittel *et al.*, 2000; Motswainyana *et al.*, 2011). Besides their preferred use in various catalytic applications, palladium(II) complexes with N-donor ligands have been explored in biological investigations with a view to developing less toxic and more selective anticancer drugs. For example, chelating *N,N'*-bidentate ligands have been viewed as important in preventing *trans*-labilization and the undesired displacement of ligands by biomolecules (Wong & Giandomenico, 1999). In our study of sterically hindered imino-quinoline palladium(II) complexes which could exert cytotoxicity on tumour cells, we have now synthesized and crystallized the title compound, namely dichlorido{2-[(2,6-diethylphenyl)iminomethyl]quinoline- $\kappa^2N,N'$ }palladium(II) acetonitrile monosolvate, (I).

Compound (I) exhibits growth-inhibitory activities against human breast (MCF-7) and human colon (HT-29) cancer cell lines which are superior to the reference compound, cisplatin, therefore underlining the importance of steric congestion in preventing an axial approach to the coordinated metal atom and permitting high selectivity to DNA binding (Hotze *et al.*, 2002). It is reasonable to suggest that the cytotoxicity of this compound is derived from DNA binding when considering the proposed mechanism of action of cisplatin, because the compound is square-planar with metal–chloride bonds in the *cis* positions (Fuentes *et al.*, 2003; Jung & Lippard, 2007).



A view of the molecular structure of (I) is shown in Fig. 1. The Pd<sup>II</sup> atom is coordinated by the two N atoms of the 2-[(2,6-diethylphenyl)iminomethyl]quinoline ligand and by two chloride anions, generating a distorted square-planar coordination geometry around the Pd<sup>II</sup> metal centre. The bond angles around Pd1 (Table 1) show significant deviations from 90°, which confirms the distortion of the square-planar geometry. These angles are close to those of a similar compound (Motswainyana *et al.*, 2012). The Pd1–Cl bond lengths (Table 1) are in good agreement with the average Pd–Cl bond length of 2.298 (15) Å for known palladium complexes (Chen *et al.*, 2007; Allen, 2002). There is a detectable *trans* influence for the chloride ligands since the Pd1–Cl1 bond is slightly longer than Pd1–Cl2, thus reflecting the stronger *trans* influence of the quinoline group compared with the secondary amine group (Doherty *et al.*, 2002). Atom Cl1 has a short intramolecular contact with atom H4 (Cl1···H4 = 2.50 Å) and as a result Cl1 deviates more [1.284 (1) Å] from the best least-squares plane through the quinoline ring than Cl2 [0.003 (1) Å]. The angle between the quinoline least-squares plane and the plane through atoms C9, C10 and N2 is

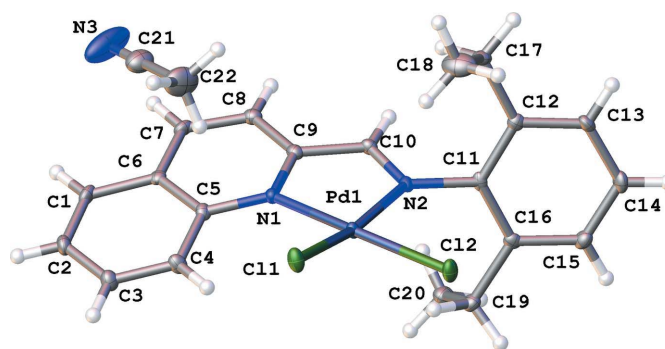
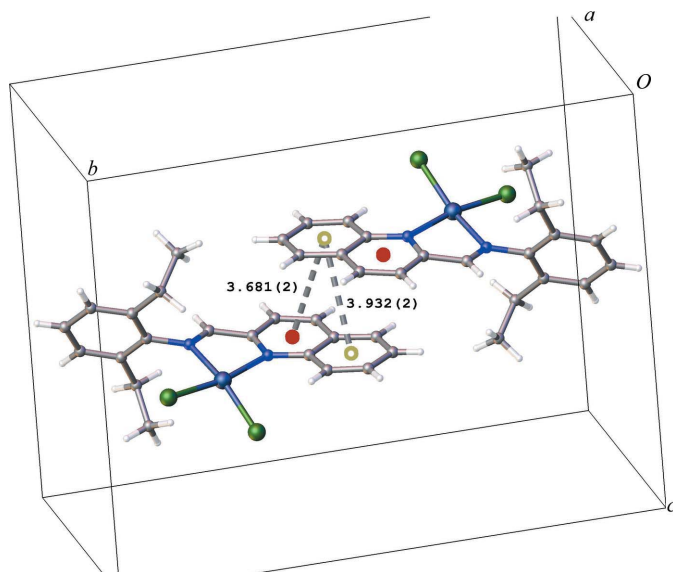


Figure 1 The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.



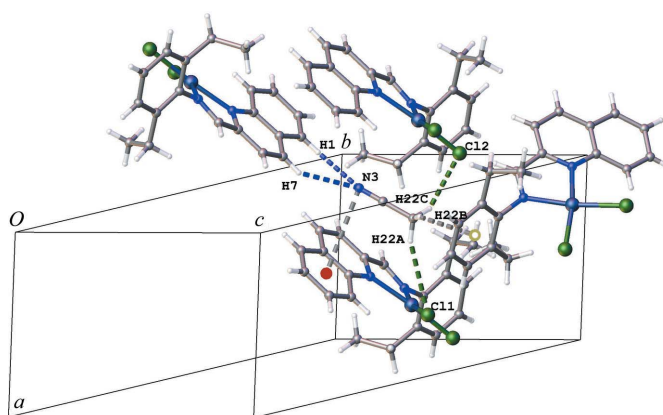
**Figure 2**

$\pi$ - $\pi$  interactions (dashed lines) between quinoline rings in (I). The centroid of the C1–C6 ring is indicated by a hollow dot (yellow in the electronic version of the paper) and the centroid of the N1/C5–C9 ring is indicated by a solid dot (red). Distances are in Å.

$9.37(10)^\circ$ . This is at the higher end of the range observed in the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002) for 2-iminopyridyl groups involved in dichloridopalladium complexes ( $0.31$ – $9.65^\circ$ , 24 hits). The overall r.m.s. deviations are  $0.005$  and  $0.044$  Å, respectively, for the benzene and quinoline rings; the angle between the least-squares planes is  $65.54(10)^\circ$ . The two ethyl groups are situated on different sides of the benzene plane but show similar conformations, as indicated by the C11–C12–C17–C18 [ $74.5(3)^\circ$ ] and C11–C16–C19–C20 [ $80.4(3)^\circ$ ] torsion angles.

In the crystal packing of (I),  $\pi$ - $\pi$  interactions between quinoline rings link pairs of molecules into centrosymmetric dimers (Fig. 2), with a  $Cg1 \cdots Cg2^i$  distance of  $3.681(2)$  Å and a  $Cg2 \cdots Cg2^i$  distance of  $3.932(2)$  Å [ $Cg1$  and  $Cg2$  are the centroids of the N1/C5–C9 and C1–C6 rings, respectively; symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ]. Furthermore, the packing shows a number of weaker contacts of the C–H  $\cdots \pi$  type (C3–H3  $\cdots Cg3^{ii} = 2.80$  Å and C22–H22B  $\cdots Cg3^{iii} = 2.86$  Å;  $Cg3$  is the centroid of the C11–C16 ring; symmetry codes: (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ].

During the crystallization experiments, it became clear that the presence of acetonitrile in the crystallization solution was essential. For example, when using dichloromethane as solvent the quality of the crystals was not good enough to obtain an accurate structure determination. On further analysis of the crystal packing, the importance of the presence of acetonitrile becomes clear. Without acetonitrile the unit cell would show four voids of  $97$  Å<sup>3</sup> each, which are here filled by one acetonitrile molecule having a molar volume of about  $42$  Å<sup>3</sup>. In the packing, the position of this acetonitrile molecule is fixed by two  $\pi$ -interactions, *viz.* a C22–H22B  $\cdots \pi$  interaction (see above) and a C21 $\equiv$ N3  $\cdots Cg2$  interaction [ $N3 \cdots Cg2 = 3.793(3)$  Å] (Fig. 3). Furthermore, atom N3 interacts with



**Figure 3**

The interaction of acetonitrile solvent molecules with neighbouring complex molecules. Dashed lines indicate the various interactions. The centroid of the C1–C6 ring is indicated by a solid dot (red in the electronic version of the paper) and the centroid of the C11–C16 ring is indicated by a hollow dot (yellow).

atoms H1 and H3 of a neighbouring molecule [ $N3 \cdots H1^{iv} = 2.66$  Å and  $N3 \cdots H3^{iv} = 2.69$  Å; symmetry code: (iv)  $-x, -y + 1, -z + 1$ ]. This bifurcated interaction of the acetonitrile N atom has been observed before in crystal structures (13 hits in the CSD, with  $N \cdots H$  contact distances ranging between  $2.436$  and  $2.744$  Å). The acetonitrile methyl group interacts with both Cl atoms [ $H22C \cdots Cl2^v = 2.89$  Å and  $H22A \cdots Cl1 = 3.24$  Å; symmetry code: (v)  $x - 1, y, z$ ].

## Experimental

All reactions were carried out under an  $N_2$  atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Solvents were dried and purified by heating under reflux under an  $N_2$  atmosphere in the presence of a suitable drying agent.

For the preparation of 2-[(2,6-diethylphenyl)iminomethyl]quinoline, 2,6-diethylaniline ( $0.2972$  g,  $1.99$  mmol) was added dropwise to a solution of quinoline-2-carbaldehyde ( $0.3130$  g,  $1.99$  mmol) in  $CH_2Cl_2$  ( $10$  ml). The reaction was stirred at room temperature for  $10$  h and a crude product was obtained after evaporation of the solvent. The product was washed with water ( $10$  ml), and the organic material extracted with  $CH_2Cl_2$  ( $2 \times 10$  ml) and dried over anhydrous magnesium sulfate. A red-brown oil was obtained upon evaporation of the solvent (yield  $0.5509$  g,  $96\%$ ). IR (Nujol,  $\nu$ ,  $cm^{-1}$ ):  $1641$  (C=N imine),  $1596$  (C=N quinolyl),  $1563$  (C=C quinolyl),  $1504$  (C=C phenyl). Analysis calculated for  $C_{20}H_{20}N_2$ : C  $83.30$ , H  $6.99$ , N  $9.71\%$ ; found: C  $83.54$ , H  $6.78$ , N  $9.99\%$ .

For the preparation of complex (I), a solution of dichlorido(cyclo-octa-1,5-diene)palladium(II),  $[PdCl_2(cod)]$  ( $0.0650$  g,  $0.228$  mmol), in  $CH_2Cl_2$  ( $5$  ml) was added dropwise to a solution of 2-[(2,6-diethylphenyl)iminomethyl]quinoline ( $0.0640$  g,  $0.222$  mmol) in dry  $CH_2Cl_2$  ( $10$  ml). The yellow solution was refluxed for  $4$  h, resulting in the formation of a yellow precipitate. The precipitate was filtered off and washed with  $Et_2O$  ( $2 \times 10$  ml) to obtain a pure yellow solid, (I). Crystals of (I) suitable for X-ray crystallography were grown by slow evaporation from an acetonitrile solution of the complex (yield  $0.0848$  g,  $82\%$ ). IR (Nujol,  $\nu$ ,  $cm^{-1}$ ):  $1602$  (C=N imine),  $1584$  (C=N quinolyl),  $1563$  (C=C quinolyl),  $1506$  (C=C phenyl). Analysis calculated for  $C_{20}H_{20}Cl_2N_2Pd$ : C  $51.58$ , H  $4.33$ , N  $6.02\%$ ; found: C  $51.89$ , H  $4.18$ , N  $5.83\%$ .

**Table 1**  
Selected geometric parameters (Å, °).

Cl1—Pd1	2.3093 (7)	N1—Pd1	2.086 (2)
Cl2—Pd1	2.2773 (7)	N2—Pd1	2.035 (2)
Cl2—Pd1—Cl1	87.56 (2)	N2—Pd1—Cl1	167.35 (6)
N1—Pd1—Cl1	101.20 (6)	N2—Pd1—Cl2	92.11 (6)
N1—Pd1—Cl2	170.49 (6)	N2—Pd1—N1	80.15 (8)

### Crystal data

[PdCl <sub>2</sub> (C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> )]·C <sub>2</sub> H <sub>3</sub> N	$V = 2127.99 (16) \text{ \AA}^3$
$M_r = 506.73$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.8874 (3) \text{ \AA}$	$\mu = 1.14 \text{ mm}^{-1}$
$b = 19.3046 (8) \text{ \AA}$	$T = 100 \text{ K}$
$c = 14.2966 (7) \text{ \AA}$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$\beta = 102.164 (4)^\circ$	

### Data collection

Agilent SuperNova diffractometer (single source at offset, Eos detector)	8662 measured reflections 4314 independent reflections 3798 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.971$ , $T_{\text{max}} = 1.000$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	256 parameters
$wR(F^2) = 0.071$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
4314 reflections	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$

All H atoms were placed in idealized positions and refined in riding mode, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

*OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3458). Services for accessing these data are described at the back of the journal.

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## supplementary materials

*Acta Cryst.* (2012). C68, m356–m358 [doi:10.1107/S0108270112045970]

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#### Crystal data

[PdCl<sub>2</sub>(C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>)]·C<sub>2</sub>H<sub>3</sub>N

$M_r = 506.73$

Monoclinic,  $P2_1/n$

$a = 7.8874$  (3) Å

$b = 19.3046$  (8) Å

$c = 14.2966$  (7) Å

$\beta = 102.164$  (4)°

$V = 2127.99$  (16) Å<sup>3</sup>

$Z = 4$

$F(000) = 1024$

$D_x = 1.582$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5179 reflections

$\theta = 2.7$ – $26.3$ °

$\mu = 1.14$  mm<sup>-1</sup>

$T = 100$  K

Block, yellow

$0.3 \times 0.2 \times 0.2$  mm

#### Data collection

Agilent SuperNova (single source at offset, Eos) diffractometer

Radiation source: SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 15.9631 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)

$T_{\min} = 0.971$ ,  $T_{\max} = 1.000$

8662 measured reflections

4314 independent reflections

3798 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 26.3$ °,  $\theta_{\min} = 2.7$ °

$h = -9 \rightarrow 9$

$k = -24 \rightarrow 23$

$l = -17 \rightarrow 9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.071$

$S = 1.03$

4314 reflections

256 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.925P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.39$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.52$  e Å<sup>-3</sup>

Special details

**Experimental.** Absorption correction: CrysAlisPro, Agilent Technologies, Version 1.171.36.20, Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2913 (3)	0.46279 (14)	0.5574 (2)	0.0152 (6)
H1	0.2000	0.4432	0.5136	0.018*
C2	0.3898 (3)	0.42270 (14)	0.6262 (2)	0.0151 (6)
H2	0.3646	0.3758	0.6297	0.018*
C3	0.5299 (3)	0.45173 (14)	0.69256 (19)	0.0156 (6)
H3	0.5980	0.4234	0.7381	0.019*
C4	0.5672 (3)	0.52114 (14)	0.69081 (19)	0.0141 (6)
H4	0.6591	0.5396	0.7355	0.017*
C5	0.4663 (3)	0.56455 (14)	0.62124 (18)	0.0112 (5)
C6	0.3278 (3)	0.53484 (14)	0.55220 (19)	0.0111 (5)
C7	0.2331 (3)	0.57652 (14)	0.47949 (19)	0.0134 (6)
H7	0.1383	0.5585	0.4364	0.016*
C8	0.2815 (3)	0.64441 (14)	0.47242 (19)	0.0131 (6)
H8	0.2240	0.6723	0.4227	0.016*
C9	0.4189 (3)	0.67081 (14)	0.54134 (18)	0.0112 (5)
C10	0.4863 (3)	0.74008 (14)	0.53032 (18)	0.0109 (5)
H10	0.4327	0.7688	0.4806	0.013*
C11	0.6937 (3)	0.82770 (14)	0.57919 (18)	0.0106 (5)
C12	0.6015 (3)	0.88821 (14)	0.59076 (18)	0.0118 (5)
C13	0.6807 (3)	0.95138 (14)	0.58095 (19)	0.0134 (6)
H13	0.6222	0.9922	0.5881	0.016*
C14	0.8450 (3)	0.95484 (15)	0.56067 (19)	0.0155 (6)
H14	0.8966	0.9976	0.5555	0.019*
C15	0.9322 (3)	0.89411 (14)	0.54811 (19)	0.0152 (6)
H15	1.0411	0.8967	0.5330	0.018*
C16	0.8592 (3)	0.82957 (14)	0.55772 (18)	0.0114 (5)
C17	0.4237 (3)	0.88743 (15)	0.61655 (19)	0.0145 (6)
H17A	0.3707	0.9327	0.6035	0.017*
H17B	0.3504	0.8541	0.5762	0.017*
C18	0.4320 (4)	0.86908 (19)	0.7209 (2)	0.0331 (8)
H18A	0.5045	0.9019	0.7613	0.050*
H18B	0.4795	0.8234	0.7336	0.050*
H18C	0.3174	0.8704	0.7337	0.050*
C19	0.9507 (3)	0.76333 (14)	0.54014 (19)	0.0145 (6)
H19A	0.9318	0.7284	0.5857	0.017*

H19B	1.0744	0.7719	0.5506	0.017*
C20	0.8863 (3)	0.73574 (15)	0.4385 (2)	0.0179 (6)
H20A	0.9283	0.6894	0.4344	0.027*
H20B	0.9284	0.7649	0.3940	0.027*
H20C	0.7618	0.7356	0.4235	0.027*
C21	0.0756 (4)	0.58019 (18)	0.7278 (2)	0.0274 (7)
C22	0.1805 (4)	0.6129 (2)	0.8104 (3)	0.0402 (9)
H22A	0.3006	0.6095	0.8072	0.060*
H22B	0.1624	0.5903	0.8673	0.060*
H22C	0.1487	0.6609	0.8119	0.060*
C11	0.71391 (9)	0.63912 (3)	0.85021 (5)	0.01621 (15)
C12	0.89474 (8)	0.77099 (3)	0.78145 (5)	0.01569 (15)
N1	0.5052 (3)	0.63426 (11)	0.61660 (15)	0.0102 (5)
N2	0.6208 (3)	0.76040 (11)	0.59064 (15)	0.0098 (5)
N3	-0.0073 (4)	0.5546 (2)	0.6630 (2)	0.0591 (11)
Pd1	0.68518 (2)	0.696873 (10)	0.706264 (13)	0.00930 (7)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0123 (13)	0.0169 (15)	0.0167 (14)	-0.0063 (12)	0.0036 (11)	-0.0054 (12)
C2	0.0179 (14)	0.0097 (14)	0.0183 (14)	-0.0021 (12)	0.0055 (11)	-0.0004 (12)
C3	0.0195 (14)	0.0124 (14)	0.0141 (14)	-0.0006 (12)	0.0020 (11)	-0.0005 (12)
C4	0.0177 (13)	0.0132 (14)	0.0098 (13)	0.0013 (12)	-0.0005 (11)	-0.0005 (11)
C5	0.0136 (13)	0.0099 (13)	0.0108 (13)	-0.0006 (11)	0.0044 (10)	-0.0023 (11)
C6	0.0090 (12)	0.0129 (14)	0.0128 (13)	0.0001 (11)	0.0052 (10)	-0.0006 (11)
C7	0.0085 (12)	0.0172 (15)	0.0137 (13)	-0.0017 (12)	0.0008 (10)	-0.0039 (12)
C8	0.0122 (13)	0.0152 (15)	0.0122 (13)	0.0024 (12)	0.0033 (10)	0.0013 (11)
C9	0.0118 (12)	0.0111 (14)	0.0111 (13)	0.0021 (12)	0.0036 (10)	0.0007 (11)
C10	0.0125 (13)	0.0107 (13)	0.0091 (13)	0.0017 (11)	0.0011 (10)	0.0010 (11)
C11	0.0154 (13)	0.0097 (13)	0.0055 (12)	-0.0015 (12)	-0.0007 (10)	0.0021 (11)
C12	0.0123 (12)	0.0135 (14)	0.0090 (12)	-0.0005 (11)	0.0009 (10)	0.0000 (11)
C13	0.0157 (13)	0.0091 (13)	0.0142 (14)	0.0030 (12)	0.0005 (11)	0.0007 (11)
C14	0.0199 (14)	0.0117 (14)	0.0144 (14)	-0.0031 (12)	0.0022 (11)	0.0035 (12)
C15	0.0131 (13)	0.0176 (15)	0.0154 (14)	-0.0016 (12)	0.0037 (11)	0.0032 (12)
C16	0.0109 (12)	0.0133 (14)	0.0086 (12)	0.0012 (11)	-0.0011 (10)	0.0004 (11)
C17	0.0113 (12)	0.0142 (14)	0.0174 (14)	0.0031 (12)	0.0020 (11)	-0.0015 (12)
C18	0.0312 (17)	0.046 (2)	0.0255 (18)	0.0111 (17)	0.0142 (14)	0.0063 (17)
C19	0.0126 (13)	0.0154 (15)	0.0161 (14)	-0.0004 (12)	0.0044 (11)	0.0015 (12)
C20	0.0167 (14)	0.0165 (15)	0.0210 (15)	0.0016 (12)	0.0049 (12)	-0.0027 (13)
C21	0.0234 (16)	0.0327 (19)	0.0268 (17)	0.0017 (15)	0.0069 (14)	-0.0080 (16)
C22	0.0339 (19)	0.048 (2)	0.033 (2)	0.0005 (18)	-0.0047 (16)	-0.0149 (18)
C11	0.0254 (3)	0.0124 (3)	0.0098 (3)	-0.0033 (3)	0.0013 (3)	0.0013 (3)
C12	0.0197 (3)	0.0127 (3)	0.0124 (3)	-0.0052 (3)	-0.0018 (3)	0.0001 (3)
N1	0.0104 (10)	0.0094 (11)	0.0107 (11)	-0.0002 (9)	0.0017 (9)	-0.0003 (9)
N2	0.0125 (10)	0.0087 (11)	0.0094 (11)	0.0005 (10)	0.0048 (9)	-0.0003 (9)
N3	0.0310 (16)	0.102 (3)	0.045 (2)	-0.0153 (19)	0.0088 (15)	-0.042 (2)
Pd1	0.01144 (12)	0.00772 (12)	0.00791 (11)	-0.00080 (8)	0.00020 (8)	0.00001 (8)

Geometric parameters (Å, °)

C1—H1	0.9300	C14—H14	0.9300
C1—C2	1.359 (4)	C14—C15	1.390 (4)
C1—C6	1.425 (4)	C15—H15	0.9300
C2—H2	0.9300	C15—C16	1.391 (4)
C2—C3	1.412 (4)	C16—C19	1.515 (4)
C3—H3	0.9300	C17—H17A	0.9700
C3—C4	1.373 (4)	C17—H17B	0.9700
C4—H4	0.9300	C17—C18	1.521 (4)
C4—C5	1.411 (4)	C18—H18A	0.9600
C5—C6	1.429 (3)	C18—H18B	0.9600
C5—N1	1.385 (3)	C18—H18C	0.9600
C6—C7	1.400 (4)	C19—H19A	0.9700
C7—H7	0.9300	C19—H19B	0.9700
C7—C8	1.375 (4)	C19—C20	1.530 (4)
C8—H8	0.9300	C20—H20A	0.9600
C8—C9	1.398 (4)	C20—H20B	0.9600
C9—C10	1.460 (4)	C20—H20C	0.9600
C9—N1	1.345 (3)	C21—C22	1.438 (4)
C10—H10	0.9300	C21—N3	1.129 (4)
C10—N2	1.279 (3)	C22—H22A	0.9600
C11—C12	1.404 (4)	C22—H22B	0.9600
C11—C16	1.403 (4)	C22—H22C	0.9600
C11—N2	1.444 (3)	C11—Pd1	2.3093 (7)
C12—C13	1.391 (4)	C12—Pd1	2.2773 (7)
C12—C17	1.523 (4)	N1—Pd1	2.086 (2)
C13—H13	0.9300	N2—Pd1	2.035 (2)
C13—C14	1.388 (4)		
C2—C1—H1	119.9	C15—C16—C11	117.9 (2)
C2—C1—C6	120.2 (2)	C15—C16—C19	121.2 (2)
C6—C1—H1	119.9	C12—C17—H17A	109.0
C1—C2—H2	119.8	C12—C17—H17B	109.0
C1—C2—C3	120.5 (3)	H17A—C17—H17B	107.8
C3—C2—H2	119.8	C18—C17—C12	112.8 (2)
C2—C3—H3	119.5	C18—C17—H17A	109.0
C4—C3—C2	121.0 (3)	C18—C17—H17B	109.0
C4—C3—H3	119.5	C17—C18—H18A	109.5
C3—C4—H4	120.0	C17—C18—H18B	109.5
C3—C4—C5	120.1 (2)	C17—C18—H18C	109.5
C5—C4—H4	120.0	H18A—C18—H18B	109.5
C4—C5—C6	119.0 (2)	H18A—C18—H18C	109.5
N1—C5—C4	120.9 (2)	H18B—C18—H18C	109.5
N1—C5—C6	120.1 (2)	C16—C19—H19A	109.2
C1—C6—C5	119.2 (2)	C16—C19—H19B	109.2
C7—C6—C1	121.2 (2)	C16—C19—C20	112.1 (2)
C7—C6—C5	119.5 (2)	H19A—C19—H19B	107.9
C6—C7—H7	120.3	C20—C19—H19A	109.2
C8—C7—C6	119.3 (2)	C20—C19—H19B	109.2



C8—C7—H7	120.3	C19—C20—H20A	109.5
C7—C8—H8	120.6	C19—C20—H20B	109.5
C7—C8—C9	118.8 (2)	C19—C20—H20C	109.5
C9—C8—H8	120.6	H20A—C20—H20B	109.5
C8—C9—C10	120.2 (2)	H20A—C20—H20C	109.5
N1—C9—C8	124.0 (2)	H20B—C20—H20C	109.5
N1—C9—C10	115.6 (2)	N3—C21—C22	179.8 (4)
C9—C10—H10	120.8	C21—C22—H22A	109.5
N2—C10—C9	118.5 (2)	C21—C22—H22B	109.5
N2—C10—H10	120.8	C21—C22—H22C	109.5
C12—C11—N2	120.4 (2)	H22A—C22—H22B	109.5
C16—C11—C12	122.2 (2)	H22A—C22—H22C	109.5
C16—C11—N2	117.3 (2)	H22B—C22—H22C	109.5
C11—C12—C17	123.1 (2)	C5—N1—Pd1	131.48 (17)
C13—C12—C11	117.6 (2)	C9—N1—C5	117.9 (2)
C13—C12—C17	119.3 (2)	C9—N1—Pd1	110.57 (17)
C12—C13—H13	119.3	C10—N2—C11	119.5 (2)
C14—C13—C12	121.5 (2)	C10—N2—Pd1	113.10 (18)
C14—C13—H13	119.3	C11—N2—Pd1	126.66 (16)
C13—C14—H14	120.1	Cl2—Pd1—Cl1	87.56 (2)
C13—C14—C15	119.7 (3)	N1—Pd1—Cl1	101.20 (6)
C15—C14—H14	120.1	N1—Pd1—Cl2	170.49 (6)
C14—C15—H15	119.5	N2—Pd1—Cl1	167.35 (6)
C14—C15—C16	121.1 (2)	N2—Pd1—Cl2	92.11 (6)
C16—C15—H15	119.5	N2—Pd1—N1	80.15 (8)
C11—C16—C19	120.8 (2)		
C1—C2—C3—C4	1.7 (4)	C10—N2—Pd1—Cl2	-173.06 (18)
C1—C6—C7—C8	-174.7 (2)	C10—N2—Pd1—N1	12.50 (18)
C2—C1—C6—C5	-1.3 (4)	C11—C12—C13—C14	-0.1 (4)
C2—C1—C6—C7	177.2 (2)	C11—C12—C17—C18	74.5 (3)
C2—C3—C4—C5	-0.8 (4)	C11—C16—C19—C20	80.4 (3)
C3—C4—C5—C6	-1.1 (4)	C11—N2—Pd1—Cl1	85.5 (3)
C3—C4—C5—N1	-178.1 (2)	C11—N2—Pd1—Cl2	-2.8 (2)
C4—C5—C6—C1	2.2 (4)	C11—N2—Pd1—N1	-177.3 (2)
C4—C5—C6—C7	-176.3 (2)	C12—C11—C16—C15	0.2 (4)
C4—C5—N1—C9	171.4 (2)	C12—C11—C16—C19	-176.5 (2)
C4—C5—N1—Pd1	-6.7 (4)	C12—C11—N2—C10	67.1 (3)
C5—C6—C7—C8	3.8 (4)	C12—C11—N2—Pd1	-102.5 (2)
C5—N1—Pd1—Cl1	-26.2 (2)	C12—C13—C14—C15	1.1 (4)
C5—N1—Pd1—N2	166.6 (2)	C13—C12—C17—C18	-103.4 (3)
C6—C1—C2—C3	-0.6 (4)	C13—C14—C15—C16	-1.5 (4)
C6—C5—N1—C9	-5.5 (3)	C14—C15—C16—C11	0.9 (4)
C6—C5—N1—Pd1	176.37 (17)	C14—C15—C16—C19	177.5 (2)
C6—C7—C8—C9	-3.3 (4)	C15—C16—C19—C20	-96.1 (3)
C7—C8—C9—C10	173.2 (2)	C16—C11—C12—C13	-0.5 (4)
C7—C8—C9—N1	-1.8 (4)	C16—C11—C12—C17	-178.4 (2)
C8—C9—C10—N2	-174.5 (2)	C16—C11—N2—C10	-113.8 (3)
C8—C9—N1—C5	6.2 (4)	C16—C11—N2—Pd1	76.6 (3)

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C8—C9—N1—Pd1	-175.2 (2)	C17—C12—C13—C14	177.8 (2)
C9—C10—N2—C11	177.7 (2)	N1—C5—C6—C1	179.1 (2)
C9—C10—N2—Pd1	-11.3 (3)	N1—C5—C6—C7	0.6 (4)
C9—N1—Pd1—C11	155.52 (16)	N1—C9—C10—N2	1.0 (4)
C9—N1—Pd1—N2	-11.68 (17)	N2—C11—C12—C13	178.5 (2)
C10—C9—N1—C5	-169.0 (2)	N2—C11—C12—C17	0.7 (4)
C10—C9—N1—Pd1	9.5 (3)	N2—C11—C16—C15	-178.9 (2)
C10—N2—Pd1—C11	-84.8 (3)	N2—C11—C16—C19	4.4 (4)

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