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Chlorido{2-[(dimethylamino)methyl]phenyl-κ^2C^1,N}(1-methyl-1*H*-imidazole-κN^3)palladium(II)

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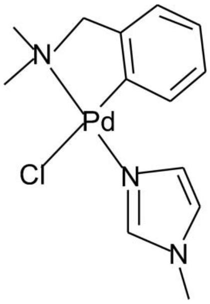
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.006 Å; R factor = 0.022; wR factor = 0.044; data-to-parameter ratio = 14.2.

In the title compound, $[Pd(C_9H_{12}N)Cl(C_4H_6N_2)]$, which was synthesized from the reaction of 1-methylimidazole with dimeric dichloridobis[2-(dimethylamino)benzyl]palladium(II), the ring-deprotonated *N*,*N*-dimethylbenzylamine ligand acts in a *C*,*N*-bidentate fashion. The dihedral angle between the ring of the 1-methylimidazole ligand and the palladacycle plane is 57.88 (16)°. The two N atoms from the *N*,*N*-dimethylbenzylamine and 1-methylimidazole ligands are *trans* coordinated to the Pd^{II} atom.

Related literature

For an overview of the application of palladacycles in organic synthesis, see: DuPont & Flores (2009); Bedford *et al.* (2003); Fors & Buchwald (2010). For detoxification of phosphorothionate pesticides, see: Lu *et al.* (2010). For studies converting the dimeric precursor (Cope & Friedrich, 1968) of the title compound into monomeric square-planar palladacycles, see: Mentes & Büyükgüngör (2004); Mentes *et al.* (2004); Deeming *et al.* (1978); Bose & Saha (1987). For crystal structures of neutral pyridine-palladacycles, see: Lu *et al.* (2005); Fun *et al.* (2006). For an approach to the study of the relative binding affinities of unidentate ligands for organopalladium(II) species, see: Hoffman *et al.* (2009).



Experimental

Crystal data

$[Pd(C_9H_{12}N)Cl(C_4H_6N_2)]$	V = 1450.27 (16) Å^3
M_r = 358.15	Z = 4
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
a = 25.5485 (15) Å	μ = 1.45 mm^{-1}
b = 10.0057 (6) Å	T = 290 K
c = 5.6733 (4) Å	0.43 × 0.15 × 0.09 mm

Data collection

Oxford Diffraction Xcalibur E diffractometer	6592 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)	2373 independent reflections
$T_{\min}$ = 0.788, $T_{\max}$ = 1.00	2057 reflections with $I > 2\sigma(I)$
	$R_{\rm int}$ = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	H-atom parameters constrained
$wR(F^2)$ = 0.044	$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
S = 0.96	$\Delta\rho_{\min}$ = −0.38 e Å^{-3}
2373 reflections	Absolute structure: Flack (1983), 852 Friedel pairs
167 parameters	Flack parameter: −0.04 (3)
1 restraint	

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); 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: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5067).

References

Bedford, R. B., Hazelwood, S. L., Limmert, M. E., Albisson, D. A., Draper, S. M., Scully, P. N., Coles, S. J. & Hursthouse, M. B. (2003). *Chem. Eur. J.* **9**, 3216–3227.
Bose, A. & Saha, C. R. (1987). *Chem. Ind. (London)*, pp. 199–201.
Cope, A. C. & Friedrich, E. C. (1968). *J. Am. Chem. Soc.* **90**, 909–913.
Deeming, A. J., Rothwell, I. P., Hursthouse, M. B. & New, L. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1490–1496.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
DuPont, J. & Flores, F. R. (2009). *Handbook of Green Chemistry*, edited by P. T. Anastas & R. H. Crabtree, Vol. 1, pp. 319–342. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fors, B. P. & Buchwald, S. L. (2010). *J. Am. Chem. Soc.* **132**, 15914–15917.
Fun, H.-K., Chantrapromma, S., Lu, Z.-L., Neverov, A. A. & Brown, R. S. (2006). *Acta Cryst.* E**62**, m3225–m3227.
Hoffman, N. W., Stenson, A. C., Sykora, R. E., Traylor, R. K., Wicker, B. F., Reilly, S., Dixon, D. A., Marshall, A. G., Kwan, M.-L. & Schroder, P. (2009). Abstracts, Central Regional Meeting, American Chemical Society, Cleveland, OH, United States, May 20–23, CRM-213.
Lu, Z.-L., Neverov, A. A. & Brown, R. S. (2005). *Org. Biomol. Chem.* **3**, 3379–3387.

Lu, Z.-L., Wang, X.-R. & Liu, B.-B. (2010). *J. Organomet. Chem.* **695**, 2191–2200.

Mentes, A. & Büyükgüngör, O. (2004). *Acta Cryst.* E**60**, m601–m602.

Mentes, A., Kemmitt, R. D. W., Fawcett, J. & Russell, D. R. (2004). *J. Mol. Struct.* **693**, 241–246.

Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

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Chlorido{2-[(dimethylamino)methyl]phenyl-κ^2C^1,*N*}(1-methyl-1*H*-imidazole-κN^3)palladium(II)

Jason W. Clements, Milorad Stojanovic, Norris W. Hoffman and Richard E. Sykora

S1. Comment

Palladacycles are an important class of catalysts for organic reactions (DuPont & Flores, 2009; Bedford *et al.*, 2003; Fors & Buchwald, 2010), including methanolysis of phosphorothionate pesticides (Lu *et al.*, 2005; Lu *et al.*, 2010). One of the most commonly used, and now commercially available, palladacyclic dimers, di-μ-chlorobis[2-(dimethylamino)benzyl-κ^2C^1,*N*]palladium(II), or [(κ^2-dmba)PdCl]$_2$ for short, was first prepared by Cope & Friedrich (1968), with its structure solved by Mentes, Kemmitt, *et al.* (2004). Many compounds of the general formula (κ^2-dmba)Pd(*L*)Cl are easily prepared by treating this dimer with two molar equivalents of neutral unidentate ligand, *L*. The great majority of these products contain pnictogen ligands, primarily phosphines; crystal structures have been published for *L* = PPh_3 (Mentes, Kemmitt, *et al.*, 2004) and $SbPh_3$ (Mentes & Büyükgüngör, 2004). Combining four molar equivalents of these triphenylpnictogens with the dimer affords dechelation of the dmba moiety and formation of the square-planar *trans*-(EPh_3)$_2$Pd(2-dmba-κC^1)Cl. Relatively few examples of (κ^2-dmba)Pd(N-ligand)Cl have been reported, and those are almost exclusively in the pyridine family (Deeming *et al.*, 1978; Bose & Saha, 1987), with crystal structures reported for the pyridine (Lu *et al.*, 2005) and 4-dimethylaminopyridine (Fun *et al.*, 2006) complexes.

Our interest in studying relative binding affinities of soft metal centers for ligands of moderate and weak donor power using ^{19}F and ^{31}P NMR spectroscopy (Hoffman *et al.*, 2009) to monitor ligand-substitution equilibria led us to prepare the title complex (**I**), whose structure is shown in Figure 1. Suitable single crystals were grown from vapor diffusion of heptane into a solution of the 1-methylimidazole complex at room temperature. All four Pd-ligand bond lengths were similar to those reported for other (κ^2-dmba)Pd(*L*)Cl structures, especially those for the two pyridine-family complexes (Lu *et al.*, 2005; Fun *et al.*, 2006). The angle between the imidazole ring and the palladacycle plane (Pd1–N2–C1–C2–C7) in **I** is 57.88 (16)°, on par with the 49.2° angle between the pyridine and palladacycle rings in (κ^2-dmba)Pd(py)Cl (Lu *et al.*, 2005). However, both these angles are quite smaller than the comparable dihedral angles in (κ^2-dmba)Pd(dmap)Cl (dmap = 4-(dimethylamino)pyridine) (Fun *et al.*, 2006) for which three crystallographically independent molecules yielded values of 76.80 (14)°, 81.85 (14)°, and 83.74 (14)°.

S2. Experimental

To a solution of 0.100 mmol [(κ^2-$C_9H_{12}N$)PdCl]$_2$ (Sigma-Aldrich) in 2.0 ml e thanol-free reagent chloroform (Fisher) in a 10-ml glass vial was added with stirring 0.200 mmol neat 1-methylimidazole (Sigma-Aldrich). The resulting pale-yellow solution was subjected to vapor diffusion with 30 ml heptane (Fisher reagent) at room temperature for 3 days. The small amount of liquid remaining was removed by disposable glass pipet from the resulting off-white needles, and the crystals were washed twice with 5.0 ml of hexanes (Fisher reagent). All reagents and solvents were used as received. The desired needles were removed from the vial and air-dried overnight in the dark (94% yield).

S3. Refinement

Hydrogen atoms were placed in calculated positions and allowed to ride during subsequent refinement, with U_{iso}(H) = 1.2U_{eq}(C) and C—H distances of 0.93 Å for the ring H atoms, U_{iso}(H) = 1.2U_{eq}(C) and C—H distances of 0.97 Å for the methylene H atoms, and U_{iso}(H) = 1.5U_{eq}(C) and C—H distances of 0.96 Å for the methyl H atoms.

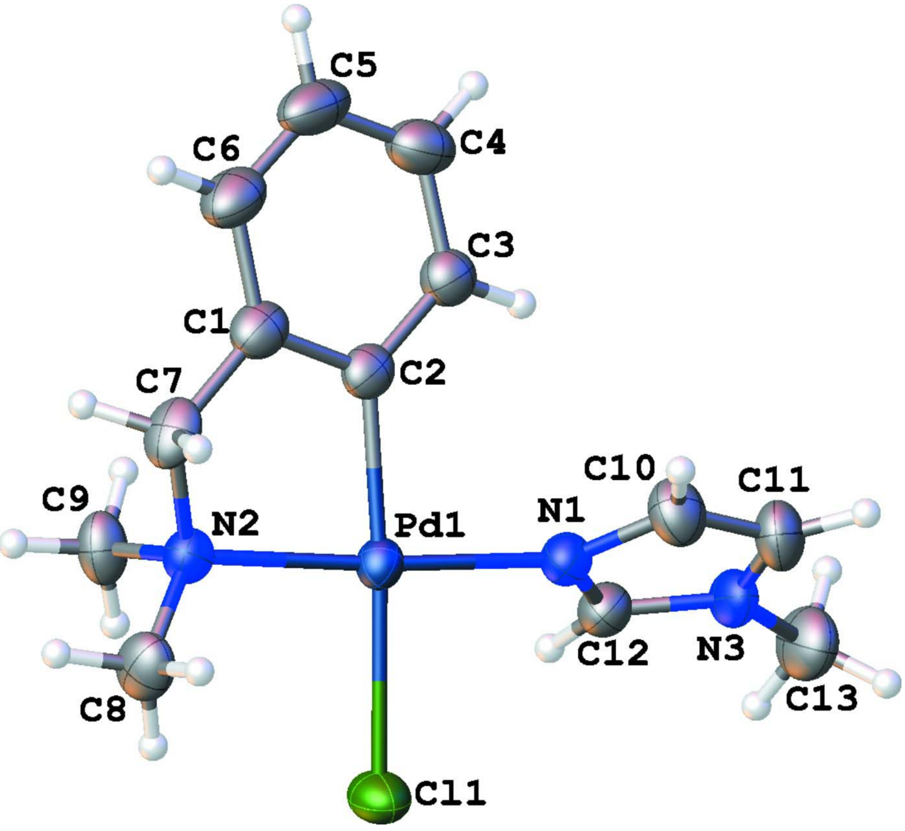

Figure 1

A thermal ellipsoid plot (50%) of **I** showing the labeling scheme.

Chlorido{2-[(dimethylamino)methyl]phenyl-κ^2*C*^{1},*N*}(1- methyl-1*H*-imidazole-κ*N*^{3}]palladium(II)

Crystal data

[Pd($C_9H_{12}N$)Cl($C_4H_6N_2$)]
M_r = 358.15
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 25.5485 (15) Å
b = 10.0057 (6) Å
c = 5.6733 (4) Å
V = 1450.27 (16) Å^3
Z = 4

F(000) = 720
D_x = 1.640 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3299 reflections
θ = 3.1–25.6°
μ = 1.45 mm^{-1}
T = 290 K
Prism, colorless
0.43 × 0.15 × 0.09 mm

Data collection

Oxford Diffraction Xcalibur E diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator

Detector resolution: 16.0514 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)

$T_{\min} = 0.788$, $T_{\max} = 1.00$
6592 measured reflections
2373 independent reflections
2057 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.028$

$\theta_{\max} = 25.7°$, $\theta_{\min} = 3.1°$
$h = -31 \rightarrow 31$
$k = -12 \rightarrow 10$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.044$
$S = 0.96$
2373 reflections
167 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0038 (2)
Absolute structure: Flack (1983), 852 Friedel pairs
Absolute structure parameter: −0.04 (3)

Special details

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
Pd1	0.644535 (8)	0.91814 (2)	0.75150 (8)	0.02903 (8)
Cl1	0.67437 (4)	0.69431 (8)	0.66642 (19)	0.0466 (3)
C1	0.65047 (13)	1.1994 (4)	0.6894 (7)	0.0385 (12)
C2	0.62563 (13)	1.1054 (3)	0.8301 (6)	0.0331 (9)
C3	0.59495 (14)	1.1503 (4)	1.0170 (7)	0.0378 (9)
H3	0.5781	1.0885	1.1131	0.045*
C4	0.58921 (15)	1.2846 (4)	1.0615 (8)	0.0494 (11)
H4	0.5694	1.3131	1.1894	0.059*
C5	0.61300 (17)	1.3768 (4)	0.9156 (9)	0.0560 (13)
H5	0.6084	1.4677	0.9432	0.067*
C6	0.64348 (13)	1.3354 (3)	0.7301 (14)	0.0507 (11)
H6	0.6594	1.3979	0.6322	0.061*
C7	0.68436 (15)	1.1482 (4)	0.4924 (7)	0.0424 (10)
H7A	0.7140	1.2075	0.4690	0.051*
H7B	0.6644	1.1446	0.3470	0.051*
C8	0.71890 (16)	0.9419 (4)	0.3383 (7)	0.0460 (10)
H8A	0.7460	0.9922	0.2615	0.069*

H8B	0.6892	0.9346	0.2354	0.069*
H8C	0.7317	0.8541	0.3754	0.069*
C9	0.74967 (12)	1.0235 (3)	0.7096 (7)	0.0422 (11)
H9A	0.7773	1.0667	0.6236	0.063*
H9B	0.7610	0.9364	0.7585	0.063*
H9C	0.7410	1.0760	0.8458	0.063*
C10	0.53338 (14)	0.8549 (4)	0.9384 (8)	0.0464 (10)
H10	0.5162	0.9102	0.8317	0.056*
C11	0.51014 (15)	0.7778 (4)	1.1018 (7)	0.0475 (11)
H11	0.4744	0.7707	1.1295	0.057*
C12	0.59415 (13)	0.7524 (3)	1.1267 (7)	0.0397 (9)
H12	0.6268	0.7233	1.1774	0.048*
C13	0.54318 (17)	0.6178 (4)	1.4131 (8)	0.0577 (12)
H13A	0.5750	0.5678	1.4306	0.087*
H13B	0.5148	0.5577	1.3805	0.087*
H13C	0.5361	0.6658	1.5561	0.087*
N1	0.58669 (10)	0.8386 (3)	0.9548 (6)	0.0344 (7)
N2	0.70326 (11)	1.0106 (3)	0.5575 (5)	0.0312 (7)
N3	0.54872 (11)	0.7121 (3)	1.2190 (7)	0.0388 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02726 (11)	0.02814 (13)	0.03167 (13)	−0.00098 (10)	0.0002 (2)	0.0043 (2)
Cl1	0.0495 (5)	0.0321 (5)	0.0582 (7)	0.0077 (4)	0.0119 (5)	0.0049 (4)
C1	0.0352 (19)	0.034 (2)	0.047 (4)	0.0014 (15)	−0.0090 (17)	0.0041 (17)
C2	0.0269 (16)	0.032 (2)	0.041 (3)	0.0007 (15)	−0.0080 (15)	0.0031 (16)
C3	0.034 (2)	0.037 (2)	0.043 (3)	0.0004 (17)	−0.0025 (18)	0.0003 (19)
C4	0.046 (2)	0.044 (3)	0.058 (3)	0.009 (2)	−0.004 (2)	−0.011 (2)
C5	0.048 (2)	0.033 (2)	0.087 (4)	0.0030 (19)	−0.018 (3)	−0.009 (2)
C6	0.0475 (19)	0.033 (2)	0.071 (3)	0.0001 (16)	−0.008 (3)	0.006 (3)
C7	0.044 (2)	0.042 (2)	0.041 (3)	−0.0068 (18)	−0.006 (2)	0.020 (2)
C8	0.051 (2)	0.053 (2)	0.034 (2)	−0.0084 (18)	0.0101 (18)	0.0017 (18)
C9	0.0295 (16)	0.060 (2)	0.037 (3)	−0.0068 (15)	−0.002 (2)	0.006 (2)
C10	0.034 (2)	0.053 (3)	0.052 (3)	0.0031 (18)	0.000 (2)	0.006 (2)
C11	0.031 (2)	0.056 (3)	0.055 (3)	−0.0065 (19)	0.006 (2)	0.002 (2)
C12	0.036 (2)	0.032 (2)	0.051 (2)	−0.0019 (17)	0.0034 (18)	0.000 (2)
C13	0.062 (3)	0.054 (3)	0.057 (3)	−0.007 (2)	0.018 (2)	0.013 (2)
N1	0.0316 (16)	0.0307 (17)	0.0410 (19)	−0.0003 (13)	0.0020 (14)	0.0018 (15)
N2	0.0309 (15)	0.0324 (17)	0.0302 (18)	−0.0020 (13)	−0.0020 (13)	0.0029 (14)
N3	0.0405 (15)	0.0363 (15)	0.039 (2)	−0.0060 (11)	0.0153 (18)	0.0031 (18)

Geometric parameters (Å, º)

Pd1—C2	1.985 (3)	C8—H8A	0.9600
Pd1—N1	2.037 (3)	C8—H8B	0.9600
Pd1—N2	2.078 (3)	C8—H8C	0.9600
Pd1—Cl1	2.4145 (9)	C9—N2	1.472 (4)

C1—C2	1.388 (5)	C9—H9A	0.9600
C1—C6	1.391 (5)	C9—H9B	0.9600
C1—C7	1.504 (5)	C9—H9C	0.9600
C2—C3	1.393 (5)	C10—C11	1.345 (5)
C3—C4	1.375 (5)	C10—N1	1.375 (4)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.381 (6)	C11—N3	1.358 (5)
C4—H4	0.9300	C11—H11	0.9300
C5—C6	1.373 (8)	C12—N1	1.316 (4)
C5—H5	0.9300	C12—N3	1.335 (4)
C6—H6	0.9300	C12—H12	0.9300
C7—N2	1.505 (4)	C13—N3	1.457 (5)
C7—H7A	0.9700	C13—H13A	0.9600
C7—H7B	0.9700	C13—H13B	0.9600
C8—N2	1.476 (4)	C13—H13C	0.9600

C2—Pd1—N1	93.72 (13)	H8B—C8—H8C	109.5
C2—Pd1—N2	82.79 (13)	N2—C9—H9A	109.5
N1—Pd1—N2	176.23 (11)	N2—C9—H9B	109.5
C2—Pd1—Cl1	175.52 (10)	H9A—C9—H9B	109.5
N1—Pd1—Cl1	88.84 (8)	N2—C9—H9C	109.5
N2—Pd1—Cl1	94.54 (8)	H9A—C9—H9C	109.5
C2—C1—C6	120.6 (4)	H9B—C9—H9C	109.5
C2—C1—C7	117.4 (3)	C11—C10—N1	108.8 (4)
C6—C1—C7	122.0 (4)	C11—C10—H10	125.6
C1—C2—C3	118.4 (3)	N1—C10—H10	125.6
C1—C2—Pd1	113.5 (3)	C10—C11—N3	107.1 (3)
C3—C2—Pd1	127.8 (3)	C10—C11—H11	126.4
C4—C3—C2	121.0 (4)	N3—C11—H11	126.4
C4—C3—H3	119.5	N1—C12—N3	111.2 (3)
C2—C3—H3	119.5	N1—C12—H12	124.4
C3—C4—C5	119.7 (4)	N3—C12—H12	124.4
C3—C4—H4	120.1	N3—C13—H13A	109.5
C5—C4—H4	120.1	N3—C13—H13B	109.5
C6—C5—C4	120.5 (4)	H13A—C13—H13B	109.5
C6—C5—H5	119.8	N3—C13—H13C	109.5
C4—C5—H5	119.8	H13A—C13—H13C	109.5
C5—C6—C1	119.7 (5)	H13B—C13—H13C	109.5
C5—C6—H6	120.1	C12—N1—C10	105.8 (3)
C1—C6—H6	120.1	C12—N1—Pd1	124.8 (2)
C1—C7—N2	108.3 (3)	C10—N1—Pd1	129.3 (3)
C1—C7—H7A	110.0	C9—N2—C8	108.5 (3)
N2—C7—H7A	110.0	C9—N2—C7	108.8 (3)
C1—C7—H7B	110.0	C8—N2—C7	107.8 (3)
N2—C7—H7B	110.0	C9—N2—Pd1	108.1 (2)
H7A—C7—H7B	108.4	C8—N2—Pd1	115.7 (2)
N2—C8—H8A	109.5	C7—N2—Pd1	107.8 (2)
N2—C8—H8B	109.5	C12—N3—C11	107.0 (3)

H8A—C8—H8B	109.5	C12—N3—C13	125.2 (3)
N2—C8—H8C	109.5	C11—N3—C13	127.8 (3)
H8A—C8—H8C	109.5		