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Dichlorido(3,5-dimethyl-1*H*-pyrazole)-[(3,5-dimethyl-1*H*-pyrazol-1-yl)(*o*-tolyl)methanone]palladium(II)

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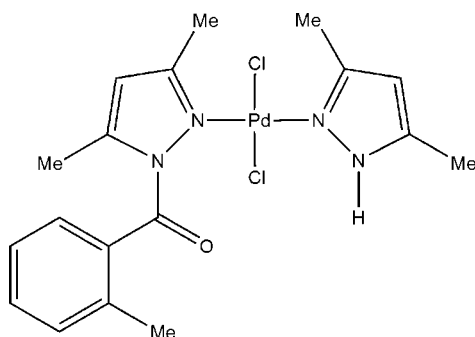
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.040; wR factor = 0.113; data-to-parameter ratio = 16.8.

In the title compound, $[\text{PdCl}_2(\text{C}_5\text{H}_8\text{N}_2)(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})]$, the Pd atom adopts a slightly distorted *trans*- PdCl_2N_2 square-planar arrangement. The different Pd–N bond lengths can be related to the the electron-withdrawing effect of the *o*-toluoyl group on the substituted pyrazole ligand. The complex crystallizes as centrosymmetric hydrogen-bonded dimers through N–H···Cl linkages.

Related literature

For related literature, see: Mukherjee (2000); Komeda *et al.* (2000); Li *et al.* (2002); Guzei *et al.* (2003); Guzei *et al.* (2005); Ojwach *et al.* (2005); Spencer *et al.* (2006); Allen (2002).



Experimental

Crystal data

 $[\text{PdCl}_2(\text{C}_5\text{H}_8\text{N}_2)(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})]$ $M_r = 487.70$ Orthorhombic, *Pbca* $a = 15.908$ (3) Å $b = 15.479$ (3) Å $c = 16.602$ (3) Å $V = 4088.0$ (12) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 1.18$ mm⁻¹ $T = 293$ (2) K $0.32 \times 0.28 \times 0.15$ mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
 $T_{\min} = 0.703$, $T_{\max} = 0.843$

43509 measured reflections
4023 independent reflections
2686 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.114$
 $S = 1.08$
4023 reflections

240 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.09$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|-------------|-------------|
| Pd1–N11 | 1.989 (4) | Pd1–Cl1 | 2.2981 (15) |
| Pd1–N21 | 2.042 (4) | Pd1–Cl2 | 2.3001 (15) |
| N11–Pd1–N21 | 174.88 (15) | N11–Pd1–Cl2 | 89.98 (13) |
| N11–Pd1–Cl1 | 88.39 (13) | N21–Pd1–Cl2 | 91.84 (12) |
| N21–Pd1–Cl1 | 90.02 (12) | Cl1–Pd1–Cl2 | 176.71 (5) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| N12–H12A···Cl2 ⁱ | 0.86 | 2.35 | 3.194 (4) | 169 |

Symmetry code: (i) $-x, -y, -z + 1$.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2003) and *pubCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2672).

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supplementary materials

Acta Cryst. (2008). E64, m206-m207 [doi:10.1107/S1600536807066627]

Dichlorido(3,5-dimethyl-1*H*-pyrazole)[(3,5-dimethyl-1*H*-pyrazol-1-yl)-*o*-toluylmethanone]palladium(II)

S. M. Nelana, G. J. Kruger and J. Darkwa

Comment

Pyrazole and pyrazolyl ligands have been used to form N-donor metal complexes with interesting catalytic applications (Mukherjee, 2000) and as mimics for imidazole coordination in metalloenzymes (Komeda *et al.*, 2000). Catalytic behaviour of such N-donor metal complexes, in particular, depends on the nature of substituents on the pyrazolyl ligands. The introduction of dicarbonylbenzene linkers (Guzei *et al.*, 2003) to bis(pyrazole)palladium complexes (Li *et al.*, 2002), for instance, improves the activity of these complexes as ethylene polymerization catalysts. The presence of carbonyl functional groups in palladium complexes, however, reduces their stability as catalysts. We initially attributed the reduced stability to the effect of two carbonyl groups on the N-donor ability of the pyrazolyl ligands. In an attempt to improve the stability of the palladium catalysts, monocarbonylbenzene units were attached to pyrazolyl units to prepare the bis(pyrazolylcarbonylbenzene)palladium dichloride. Surprisingly, with (3,5-dimethyl-pyrazol-1-yl)-*o*-toluoyl-methanone as a ligand during complexation with PdCl₂, we isolated the title compound, (I), a mixed ligand palladium complex, containing (3,5-dimethyl-pyrazol-1-yl)-*o*-toluoyl-methanone and 3,5-dimethylpyrazole as ligands. The formation of compound I appears to occur *via* partial hydrolysis of one of the (3,5-dimethyl-pyrazol-1-yl)-*o*-toluoyl-methanone ligands, presumably by traces of water in the reaction mixture.

Compound (I) displays square planar geometry around the palladium atom, with the two different pyrazolyl ligands ((3,5-dimethyl-pyrazol-1-yl)-*o*-toluoyl-methanone and 3,5-dimethylpyrazole) bonding *trans* to the metal centre *via* N atoms (Fig. 1). The slight distortion of the square planar configuration around the palladium atom can be seen in the differences in bond angles involving palladium (Table 1) and the deviations from the least-squares plane through the central five atoms [Pd1 = -0.0116 (12) Å, Cl1 = -0.0684 (12) Å, Cl2 = -0.0665 (12) Å, N11 = 0.0754 (17) Å, N21 = 0.0711 (16) Å], with the biggest deviations being observed for the nitrogen atoms. The pyrazolyl rings of the coordinating ligands are roughly perpendicular to this central plane, with interplanar angles of 86.66 (12)° and 68.13 (14)° respectively. The Pd—Cl bond distances in (I) are similar to Pd—Cl distances in related complexes (*e.g.* Spencer *et al.*, 2006) and consistent with the average of 2.33 (4) Å calculated for 2151 Pd—Cl distances in 1306 complexes reported to the Cambridge Structural Database (CSD, Version 5.26, updated May 2005; Allen 2002). One interesting feature of (I) is the significant difference of 0.053 Å in the Pd—N bond distances for the two ligands, illustrating the electron-withdrawing effect of the *o*-toluoyl-methanone substituent on the pyrazolyl ligand.

Intermolecular hydrogen bonding is responsible for the formation of centrosymmetric dimers through N—H...Cl linkages [Figure 2, Table 2]. In contrast to previous observations (Li *et al.*, 2002), the hydrogen bonding in (I) has no effect on the bond order: we observed two virtually identical Pd—Cl bond lengths, although only Cl1 was involved in a N—H...Cl hydrogen bond.

Experimental

To a solution of $[\text{PdCl}_2(\text{NCMe})_2]$ (0.10 g, 0.47 mmol) in dichloromethane (30 ml), was added (3,5-dimethyl-pyrazol-1-yl)-*o*-toluoyl-methanone (0.06 g, 0.23 mmol). The formation of an orange-yellow solution was observed and the reaction mixture was stirred at room temperature for 24 h. The solution was then concentrated to 15 ml and an equal amount of hexane was added and kept at -4°C for 3 days to yield yellow crystals suitable for X-ray analysis. Yield = 0.08 g, 59%. IR (Nujol): $\nu(\text{C}=\text{O}) = 1699$. ^1H NMR (CDCl_3): δ 9.50 (s, 1H, N—H), 7.54 (m, 4H, *o*-toluoyl), 6.13 (s, 1H, 4-pz, *o*-toluoyl), 5.74 (s, 1H, 4-pz), 2.94 (s, 3H, *o*-toluoyl), 2.56 (s, 3H, 5-CH₃, *o*-toluoyl), 2.35 (s, 3H, 3-CH₃, *o*-toluoyl), 2.31 (s, 3H, 5-CH₃), 2.21 (s, 3H, 3-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.4, 157.4, 137.6, 133.3, 131.5, 128.4, 118.6, 106.5, 33.1, 32.4, 30.1.

Refinement

The H atoms were geometrically positioned and refined in the riding-model approximation, with C—H = 0.93–0.96 Å, N—H = 0.86 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. The highest peak in the final difference map is 0.87 Å from Cl1 and the deepest hole is 0.88 Å from N11.

Figures

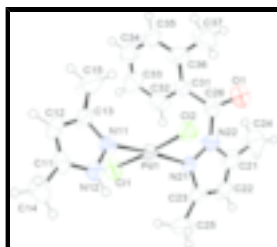


Fig. 1. : The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms).

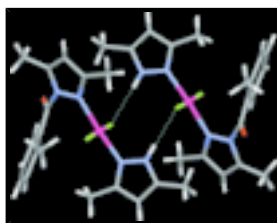


Fig. 2. : A hydrogen-bonded dimer in (I) with the H bonds indicated by thin blue lines.

Dichlorido(3,5-dimethyl-1*H*-pyrazole)[(3,5-dimethyl-1*H*-pyrazol-1-yl)(*o*-tolyl)methanone]palladium(II)

Crystal data

$[\text{PdCl}_2(\text{C}_5\text{H}_8\text{N}_2)(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})]$

$M_r = 487.70$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 15.908(3) \text{ \AA}$

$b = 15.479(3) \text{ \AA}$

$F_{000} = 1968$

$D_x = 1.585 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2686 reflections

$\theta = 2.2\text{--}26.0^\circ$

$\mu = 1.18 \text{ mm}^{-1}$

$c = 16.602 (3) \text{ \AA}$
 $V = 4088.0 (12) \text{ \AA}^3$
 $Z = 8$

$T = 293 (2) \text{ K}$
 Block, yellow
 $0.32 \times 0.28 \times 0.15 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer
 Radiation source: fine-focus sealed tube
 Monochromator: graphite
 $T = 293(2) \text{ K}$
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.703, T_{\max} = 0.843$
 43509 measured reflections

4023 independent reflections
 2686 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\text{max}} = 26.0^\circ$
 $\theta_{\text{min}} = 2.2^\circ$
 $h = -19 \rightarrow 19$
 $k = -18 \rightarrow 19$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.114$
 $S = 1.08$
 4023 reflections
 240 parameters
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 9.9045P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.09 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
 Extinction correction: none

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.

Atoms 'Deviations (\AA)' Pd1 - 0.0116 (12) C 11 - 0.0684 (12) C 12 - 0.0665 (12) N11 0.0754 (17) N21 0.0711 (16)

Atoms 'Deviations (\AA)' N11 - 0.0012 (32) N12 0.0016 (33) C11 - 0.0010 (51) C12 - 0.0021 (49) C13 - 0.0038 (56) C14 0.0023 (42) C15 0.0042 (45)

Atoms 'Deviations (\AA)' N21 0.0327 (35) N22 - 0.0225 (38) C21 - 0.0159 (65) C22 0.0319 (54) C23 0.0057 (55) C24 - 0.0040 (49) C25 - 0.0279 (46)

Atoms 'Deviations (\AA)' C32 0.0353 (49) C31 0.0478 (44) C33 - 0.0055 (54) C34 - 0.0356 (52) C35 - 0.0064 (49) C36 0.0160 (51) C37 0.0075 (42) C26 - 0.0592 (38)

supplementary materials

'Plane 1' 'Plane 2' 'Interplanar Angle (°)' Square 'Ring 1' 86.66 (12) Square 'Ring 2' 68.13 (14) 'Ring 2' 'Ring 3' 55.98 (25)

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|-------------|------------|----------------------------------|
| C11 | 0.1260 (3) | -0.2107 (3) | 0.4805 (3) | 0.0544 (13) |
| C12 | 0.1495 (4) | -0.2290 (3) | 0.4037 (4) | 0.0588 (14) |
| H12 | 0.1646 | -0.2829 | 0.3836 | 0.071* |
| C13 | 0.1468 (4) | -0.1521 (3) | 0.3608 (3) | 0.0551 (13) |
| C14 | 0.1168 (4) | -0.2659 (4) | 0.5543 (4) | 0.087 (2) |
| H14A | 0.1677 | -0.2977 | 0.5631 | 0.130* |
| H14B | 0.0709 | -0.3054 | 0.5470 | 0.130* |
| H14C | 0.1057 | -0.2297 | 0.6001 | 0.130* |
| C15 | 0.1668 (5) | -0.1341 (4) | 0.2743 (4) | 0.095 (2) |
| H15A | 0.1195 | -0.1067 | 0.2491 | 0.142* |
| H15B | 0.1791 | -0.1874 | 0.2472 | 0.142* |
| H15C | 0.2148 | -0.0966 | 0.2712 | 0.142* |
| C21 | 0.1020 (4) | 0.3084 (3) | 0.3533 (4) | 0.0726 (18) |
| C22 | 0.1203 (4) | 0.3102 (4) | 0.4313 (4) | 0.0668 (16) |
| H22 | 0.1299 | 0.3593 | 0.4623 | 0.080* |
| C23 | 0.1226 (4) | 0.2247 (3) | 0.4582 (3) | 0.0580 (14) |
| C24 | 0.0921 (6) | 0.3799 (4) | 0.2929 (5) | 0.115 (3) |
| H24A | 0.0338 | 0.3952 | 0.2886 | 0.173* |
| H24B | 0.1122 | 0.3608 | 0.2414 | 0.173* |
| H24C | 0.1238 | 0.4293 | 0.3100 | 0.173* |
| C25 | 0.1364 (5) | 0.1919 (4) | 0.5424 (4) | 0.095 (2) |
| H25A | 0.0850 | 0.1676 | 0.5626 | 0.142* |
| H25B | 0.1536 | 0.2388 | 0.5764 | 0.142* |
| H25C | 0.1793 | 0.1483 | 0.5419 | 0.142* |
| C26 | 0.0658 (4) | 0.1895 (4) | 0.2552 (3) | 0.0679 (16) |
| C32 | 0.2068 (4) | 0.1314 (4) | 0.2339 (4) | 0.0711 (17) |
| H32 | 0.2248 | 0.1655 | 0.2767 | 0.085* |
| C31 | 0.1223 (3) | 0.1290 (3) | 0.2129 (3) | 0.0495 (12) |
| C33 | 0.2646 (4) | 0.0820 (5) | 0.1902 (4) | 0.086 (2) |
| H33 | 0.3213 | 0.0829 | 0.2038 | 0.103* |
| C34 | 0.2379 (5) | 0.0334 (5) | 0.1288 (4) | 0.085 (2) |
| H34 | 0.2763 | 0.0012 | 0.0992 | 0.102* |
| C35 | 0.1495 (5) | 0.0305 (4) | 0.1079 (3) | 0.0738 (18) |
| H35 | 0.1312 | -0.0047 | 0.0659 | 0.089* |
| C36 | 0.0945 (4) | 0.0783 (4) | 0.1488 (3) | 0.0687 (17) |
| C37 | 0.0019 (5) | 0.0762 (5) | 0.1242 (4) | 0.093 (2) |
| H37B | -0.0105 | 0.1254 | 0.0910 | 0.140* |
| H37C | -0.0328 | 0.0776 | 0.1715 | 0.140* |

| | | | | |
|------|--------------|-------------|--------------|--------------|
| H37A | -0.0092 | 0.0242 | 0.0945 | 0.140* |
| N11 | 0.1224 (3) | -0.0881 (3) | 0.4099 (2) | 0.0491 (10) |
| N12 | 0.1103 (3) | -0.1256 (3) | 0.4824 (2) | 0.0521 (10) |
| H12A | 0.0943 | -0.0982 | 0.5248 | 0.062* |
| N21 | 0.1115 (2) | 0.1715 (2) | 0.3970 (2) | 0.0425 (9) |
| N22 | 0.0961 (3) | 0.2227 (3) | 0.3322 (3) | 0.0650 (13) |
| O1 | 0.0029 (4) | 0.2206 (3) | 0.2275 (3) | 0.1102 (19) |
| Cl1 | 0.25848 (9) | 0.04521 (9) | 0.42155 (10) | 0.0660 (4) |
| Cl2 | -0.02466 (9) | 0.02924 (9) | 0.36848 (9) | 0.0614 (4) |
| Pd1 | 0.11619 (2) | 0.03965 (2) | 0.39821 (2) | 0.04292 (14) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|-------------|--------------|---------------|---------------|
| C11 | 0.058 (3) | 0.038 (3) | 0.068 (3) | 0.002 (2) | -0.001 (3) | 0.012 (2) |
| C12 | 0.064 (3) | 0.033 (3) | 0.080 (4) | -0.004 (2) | 0.005 (3) | -0.006 (3) |
| C13 | 0.070 (4) | 0.041 (3) | 0.054 (3) | 0.002 (3) | 0.014 (3) | -0.009 (2) |
| C14 | 0.110 (6) | 0.063 (4) | 0.088 (5) | 0.006 (4) | 0.000 (4) | 0.026 (4) |
| C15 | 0.156 (7) | 0.071 (4) | 0.058 (4) | -0.007 (5) | 0.025 (4) | -0.009 (3) |
| C21 | 0.106 (5) | 0.037 (3) | 0.074 (4) | 0.011 (3) | 0.004 (4) | 0.001 (3) |
| C22 | 0.082 (4) | 0.046 (3) | 0.072 (4) | 0.003 (3) | -0.001 (3) | -0.022 (3) |
| C23 | 0.077 (4) | 0.043 (3) | 0.053 (3) | 0.008 (3) | -0.002 (3) | -0.011 (2) |
| C24 | 0.182 (9) | 0.053 (4) | 0.111 (6) | 0.023 (5) | 0.007 (6) | 0.022 (4) |
| C25 | 0.162 (8) | 0.072 (4) | 0.051 (4) | 0.014 (5) | -0.011 (4) | -0.012 (3) |
| C26 | 0.090 (5) | 0.057 (4) | 0.056 (3) | 0.022 (3) | -0.004 (3) | 0.006 (3) |
| C32 | 0.078 (4) | 0.082 (4) | 0.054 (3) | -0.003 (4) | 0.002 (3) | 0.011 (3) |
| C31 | 0.066 (3) | 0.043 (3) | 0.040 (2) | 0.006 (3) | 0.004 (2) | 0.008 (2) |
| C33 | 0.070 (5) | 0.109 (6) | 0.078 (5) | 0.017 (4) | 0.018 (4) | 0.005 (4) |
| C34 | 0.099 (6) | 0.089 (5) | 0.069 (4) | 0.030 (4) | 0.028 (4) | 0.008 (4) |
| C35 | 0.117 (6) | 0.056 (4) | 0.049 (3) | 0.016 (4) | 0.013 (3) | 0.001 (3) |
| C36 | 0.108 (5) | 0.053 (3) | 0.045 (3) | 0.000 (3) | 0.010 (3) | 0.008 (3) |
| C37 | 0.093 (5) | 0.096 (5) | 0.090 (5) | -0.014 (4) | -0.029 (4) | 0.000 (4) |
| N11 | 0.065 (3) | 0.041 (2) | 0.041 (2) | -0.002 (2) | -0.004 (2) | 0.0020 (17) |
| N12 | 0.065 (3) | 0.044 (2) | 0.047 (2) | 0.006 (2) | 0.003 (2) | 0.0008 (19) |
| N21 | 0.055 (2) | 0.034 (2) | 0.039 (2) | 0.0076 (17) | -0.0045 (19) | -0.0001 (17) |
| N22 | 0.107 (4) | 0.039 (2) | 0.049 (3) | 0.010 (2) | -0.006 (2) | -0.003 (2) |
| O1 | 0.126 (4) | 0.119 (4) | 0.085 (3) | 0.064 (4) | -0.030 (3) | -0.013 (3) |
| Cl1 | 0.0588 (8) | 0.0530 (8) | 0.0862 (10) | -0.0017 (7) | -0.0193 (7) | 0.0089 (7) |
| Cl2 | 0.0509 (7) | 0.0671 (9) | 0.0661 (8) | 0.0038 (7) | -0.0010 (6) | -0.0147 (7) |
| Pd1 | 0.0545 (2) | 0.0340 (2) | 0.0403 (2) | 0.00246 (17) | -0.00455 (17) | -0.00125 (16) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------|-----------|----------|-----------|
| C11—N12 | 1.342 (6) | C25—H25C | 0.9600 |
| C11—C12 | 1.358 (8) | C26—O1 | 1.202 (7) |
| C11—C14 | 1.501 (8) | C26—N22 | 1.459 (7) |
| C12—C13 | 1.388 (7) | C26—C31 | 1.475 (7) |
| C12—H12 | 0.9300 | C32—C31 | 1.389 (8) |
| C13—N11 | 1.340 (6) | C32—C33 | 1.398 (8) |

supplementary materials

| | | | |
|---------------|-----------|---------------|-------------|
| C13—C15 | 1.498 (8) | C32—H32 | 0.9300 |
| C14—H14A | 0.9600 | C31—C36 | 1.394 (8) |
| C14—H14B | 0.9600 | C33—C34 | 1.336 (10) |
| C14—H14C | 0.9600 | C33—H33 | 0.9300 |
| C15—H15A | 0.9600 | C34—C35 | 1.449 (10) |
| C15—H15B | 0.9600 | C34—H34 | 0.9300 |
| C15—H15C | 0.9600 | C35—C36 | 1.333 (8) |
| C21—C22 | 1.328 (9) | C35—H35 | 0.9300 |
| C21—N22 | 1.377 (7) | C36—C37 | 1.529 (9) |
| C21—C24 | 1.501 (8) | C37—H37B | 0.9600 |
| C22—C23 | 1.398 (8) | C37—H37C | 0.9600 |
| C22—H22 | 0.9300 | C37—H37A | 0.9600 |
| C23—N21 | 1.319 (6) | N11—N12 | 1.350 (5) |
| C23—C25 | 1.503 (8) | Pd1—N11 | 1.989 (4) |
| C24—H24A | 0.9600 | Pd1—N21 | 2.042 (4) |
| C24—H24B | 0.9600 | Pd1—Cl1 | 2.2981 (15) |
| C24—H24C | 0.9600 | Pd1—Cl2 | 2.3001 (15) |
| C25—H25A | 0.9600 | N12—H12A | 0.8600 |
| C25—H25B | 0.9600 | N21—N22 | 1.359 (5) |
| N12—C11—C12 | 106.2 (5) | N22—C26—C31 | 116.0 (5) |
| N12—C11—C14 | 121.3 (5) | C31—C32—C33 | 119.4 (6) |
| C12—C11—C14 | 132.5 (5) | C31—C32—H32 | 120.3 |
| C11—C12—C13 | 107.1 (5) | C33—C32—H32 | 120.3 |
| C11—C12—H12 | 126.5 | C32—C31—C36 | 120.9 (5) |
| C13—C12—H12 | 126.5 | C32—C31—C26 | 117.0 (5) |
| N11—C13—C12 | 109.3 (5) | C36—C31—C26 | 121.7 (5) |
| N11—C13—C15 | 120.5 (5) | C34—C33—C32 | 119.6 (7) |
| C12—C13—C15 | 130.1 (5) | C34—C33—H33 | 120.2 |
| C11—C14—H14A | 109.5 | C32—C33—H33 | 120.2 |
| C11—C14—H14B | 109.5 | C33—C34—C35 | 120.6 (6) |
| H14A—C14—H14B | 109.5 | C33—C34—H34 | 119.7 |
| C11—C14—H14C | 109.5 | C35—C34—H34 | 119.7 |
| H14A—C14—H14C | 109.5 | C36—C35—C34 | 119.8 (6) |
| H14B—C14—H14C | 109.5 | C36—C35—H35 | 120.1 |
| C13—C15—H15A | 109.5 | C34—C35—H35 | 120.1 |
| C13—C15—H15B | 109.5 | C35—C36—C31 | 119.6 (7) |
| H15A—C15—H15B | 109.5 | C35—C36—C37 | 118.9 (6) |
| C13—C15—H15C | 109.5 | C31—C36—C37 | 121.5 (6) |
| H15A—C15—H15C | 109.5 | C36—C37—H37B | 109.5 |
| H15B—C15—H15C | 109.5 | C36—C37—H37C | 109.5 |
| C22—C21—N22 | 106.5 (5) | H37B—C37—H37C | 109.5 |
| C22—C21—C24 | 131.2 (6) | C36—C37—H37A | 109.5 |
| N22—C21—C24 | 122.2 (6) | H37B—C37—H37A | 109.5 |
| C21—C22—C23 | 107.3 (5) | H37C—C37—H37A | 109.5 |
| C21—C22—H22 | 126.3 | C13—N11—N12 | 105.4 (4) |
| C23—C22—H22 | 126.3 | C13—N11—Pd1 | 133.6 (3) |
| N21—C23—C22 | 110.0 (5) | N12—N11—Pd1 | 120.5 (3) |
| N21—C23—C25 | 121.6 (5) | C11—N12—N11 | 112.0 (4) |
| C22—C23—C25 | 128.4 (5) | C11—N12—H12A | 124.0 |

| | | | |
|-----------------|------------|-----------------|-------------|
| C21—C24—H24A | 109.5 | N11—N12—H12A | 124.0 |
| C21—C24—H24B | 109.5 | C23—N21—N22 | 105.7 (4) |
| H24A—C24—H24B | 109.5 | C23—N21—Pd1 | 127.7 (3) |
| C21—C24—H24C | 109.5 | N22—N21—Pd1 | 126.6 (3) |
| H24A—C24—H24C | 109.5 | N21—N22—C21 | 110.4 (4) |
| H24B—C24—H24C | 109.5 | N21—N22—C26 | 123.3 (4) |
| C23—C25—H25A | 109.5 | C21—N22—C26 | 125.8 (5) |
| C23—C25—H25B | 109.5 | N11—Pd1—N21 | 174.88 (15) |
| H25A—C25—H25B | 109.5 | N11—Pd1—Cl1 | 88.39 (13) |
| C23—C25—H25C | 109.5 | N21—Pd1—Cl1 | 90.02 (12) |
| H25A—C25—H25C | 109.5 | N11—Pd1—Cl2 | 89.98 (13) |
| H25B—C25—H25C | 109.5 | N21—Pd1—Cl2 | 91.84 (12) |
| O1—C26—N22 | 117.9 (5) | Cl1—Pd1—Cl2 | 176.71 (5) |
| O1—C26—C31 | 125.4 (6) | | |
| N12—C11—C12—C13 | -0.2 (6) | C14—C11—N12—N11 | 180.0 (5) |
| C14—C11—C12—C13 | -179.9 (6) | C13—N11—N12—C11 | -0.1 (6) |
| C11—C12—C13—N11 | 0.1 (7) | Pd1—N11—N12—C11 | -173.1 (3) |
| C11—C12—C13—C15 | 179.5 (7) | C22—C23—N21—N22 | -4.3 (6) |
| N22—C21—C22—C23 | -2.1 (7) | C25—C23—N21—N22 | 176.5 (6) |
| C24—C21—C22—C23 | -179.4 (7) | C22—C23—N21—Pd1 | 175.7 (4) |
| C21—C22—C23—N21 | 4.1 (7) | C25—C23—N21—Pd1 | -3.5 (8) |
| C21—C22—C23—C25 | -176.7 (7) | C23—N21—N22—C21 | 3.0 (6) |
| C33—C32—C31—C36 | -0.2 (8) | Pd1—N21—N22—C21 | -177.0 (4) |
| C33—C32—C31—C26 | -173.4 (6) | C23—N21—N22—C26 | -168.9 (5) |
| O1—C26—C31—C32 | 149.9 (7) | Pd1—N21—N22—C26 | 11.1 (7) |
| N22—C26—C31—C32 | -21.1 (7) | C22—C21—N22—N21 | -0.5 (7) |
| O1—C26—C31—C36 | -23.3 (10) | C24—C21—N22—N21 | 177.0 (6) |
| N22—C26—C31—C36 | 165.7 (5) | C22—C21—N22—C26 | 171.1 (6) |
| C31—C32—C33—C34 | 0.2 (10) | C24—C21—N22—C26 | -11.3 (11) |
| C32—C33—C34—C35 | -0.9 (11) | O1—C26—N22—N21 | 125.6 (7) |
| C33—C34—C35—C36 | 1.7 (10) | C31—C26—N22—N21 | -62.7 (7) |
| C34—C35—C36—C31 | -1.7 (9) | O1—C26—N22—C21 | -45.1 (10) |
| C34—C35—C36—C37 | 178.3 (6) | C31—C26—N22—C21 | 126.6 (6) |
| C32—C31—C36—C35 | 1.0 (8) | C13—N11—Pd1—Cl1 | -79.2 (5) |
| C26—C31—C36—C35 | 173.9 (5) | N12—N11—Pd1—Cl1 | 91.4 (3) |
| C32—C31—C36—C37 | -179.0 (5) | C13—N11—Pd1—Cl2 | 97.9 (5) |
| C26—C31—C36—C37 | -6.1 (8) | N12—N11—Pd1—Cl2 | -91.5 (3) |
| C12—C13—N11—N12 | 0.0 (6) | C23—N21—Pd1—Cl1 | -68.9 (4) |
| C15—C13—N11—N12 | -179.5 (6) | N22—N21—Pd1—Cl1 | 111.1 (4) |
| C12—C13—N11—Pd1 | 171.6 (4) | C23—N21—Pd1—Cl2 | 113.8 (4) |
| C15—C13—N11—Pd1 | -7.9 (9) | N22—N21—Pd1—Cl2 | -66.2 (4) |
| C12—C11—N12—N11 | 0.2 (6) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N12—H12A \cdots Cl2 ⁱ | 0.86 | 2.35 | 3.194 (4) | 169 |

Symmetry codes: (i) $-x, -y, -z+1$.

Fig. 1

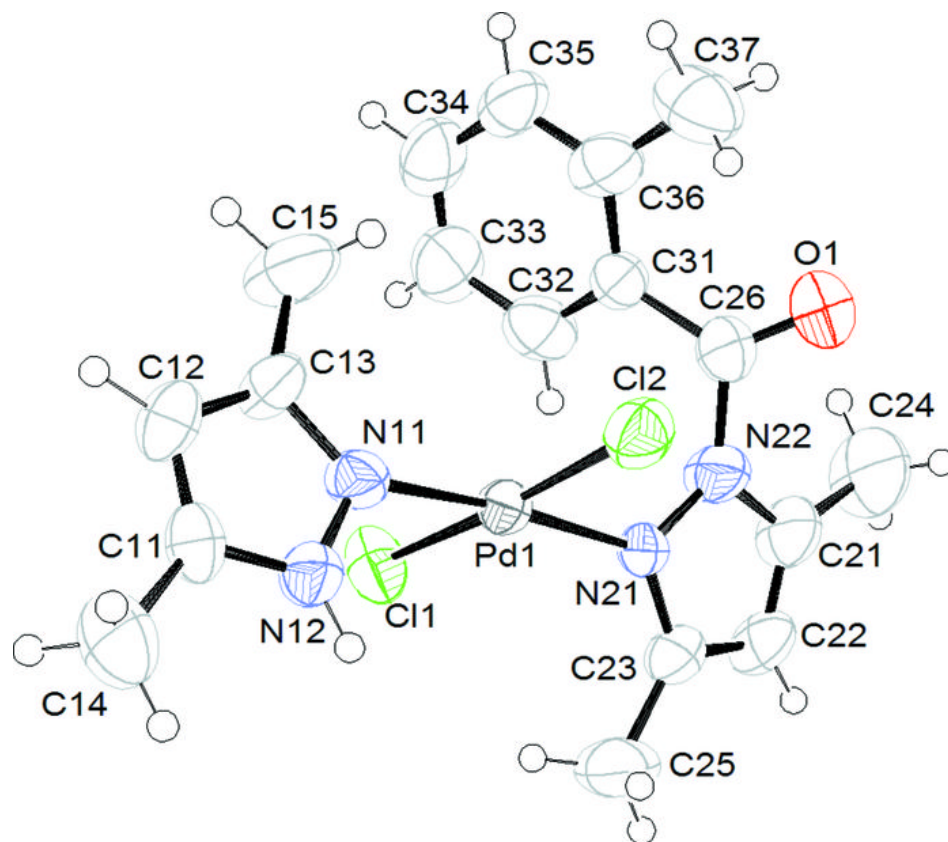


Fig. 2

