Dichlorido(4-methylaniline-κN)[N-(4-methylphenyl)-1-(thiophen-2-yl)methanimine-κN]palladium(II)

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The structure of a mono-amine Pd II complex, [PdCl₂(C₇H₉N)(C₁₂H₁₁NS)], which crystallizes in the triclinic space group, P1, is reported. The primary geometry around the PdII atom closely resembles square planar (τ₄ = 0.069). In the (E)-1-(thiophen-2-yl)-N-(p-tolyl)methanimine ligand, the phenyl and thiophene rings are not coplanar, subtending a dihedral angle of 38.5 (1)° because of steric effects. The PdCl₂N₂ coordination plane is almost perpendicular to the planes of the coordinated o-toluidine and the NC₂ fragment [dihedral angles of 84.7 (1) and 72.50 (4)°, respectively]. The Pd—NH₂ length of 2.040 (2) Å is slightly shorter than the observed mean value for other complexes involving a Pd atom attached to the nitrogen of an aniline derivative. The molecules display an interesting supramolecular synthon based on intermolecular N–H···Cl hydrogen-bonding interactions of the p-toluidine amine fragment, which results in centrosymmetric dimeric units. These units are further linked by C–H···Cl interactions, resulting in chains in the c-axis direction where the mean-planes of the repeating fragment are oriented in the (110) plane.

1. Chemical context

The chemistry of monodentate mono-amine Pd II compounds with amine ligands is of interest because the hydrogen bond between the amine and the catalyst plays a key role in the catalytic transformation of simple, easily accessible amines into highly substituted, biologically important amine-containing molecules and pharmaceutical agents (Calleja et al., 2015). While mono-amine Pd II complexes are generally unstable and are formed as intermediates during the reaction, the corresponding bis(amine) Pd II complex is stable and ultimately hampers the utility of these compounds in the C—H activation reaction. Probably because of this, well-characterized mono-amine Pd II complexes are relatively rare. In this article we report a well-characterized and room-temperature-stable mono-amine Pd II complex.
2. Structural commentary

In the Schiff base ligand H\textit{L} used [\textit{HL}^1 = (\textit{E})-1-(thiophen-2-yl)-\textit{N}-(p-toly)methanimine and \textit{L}^2 = \textit{p}-toluidine], we expected that the \textit{ortho} proton of the tolyl ring of \textit{HL}^1 could be acidic and thus could be employed for a metallation reaction. Ding and coworkers (Ding \textit{et al.}, 1992) have reported a series of mercuration reactions on similar Schiff base ligands through electrophilic substitution reactions. On the basis of these observations, we also envisaged that a palladation reaction should take place at the \textit{ortho} position of the tolyl ring in the Schiff base ligand. To investigate this \textit{C}—\textit{H} activation step, we attempted to prepare the complex \textit{Pd}\textsubscript{L}^1\textit{L}^2\textsubscript{Cl}. However, when we treated 2-thiophenecarboxaldehyde with \textit{H}\textsubscript{1}Cl or \textit{Pd}\textsubscript{Cl}\textsubscript{2} \textit{p}-toluidine in ethanol solvent at 343 K, none of the expected palladated molecules, \textit{Pd}\textsubscript{L}^1\textsubscript{Cl} or \textit{Pd}\textsubscript{L}^1\textsubscript{L}^2\textsubscript{Cl} were observed, and instead we directly isolated the corresponding mono-amine \textit{Pd}\textsuperscript{II} complex \textit{Pd}\textsubscript{L}^1\textsubscript{L}^2\textsubscript{Cl}\textsubscript{1}, as red needles in good yield along with a small amount of a yellow solid. The isolated solid was not soluble in common organic solvents. The filtrate of the reaction mixture was allowed to evaporate at room temperature and afforded red needles of a mono-amine \textit{Pd}\textsuperscript{II} complex. The filtrate contained 90 observations of the \textit{Pd—NH} \textsubscript{2} bond with a mean value of 2.040 (2) Å and minimum and maximum values of 2.028 Å (Baldovino-Pantaleon \textit{et al.}, 2005) and 2.171 Å (Asma \textit{et al.}, 2005), respectively. Thus, the length of 2.040 (2) Å in the title compound is slightly shorter than the observed mean value.

Not only does this result contrast with those found for other Schiff base compounds (Dubey \textit{et al.}, 2019), which readily form a stable palladated complex, but this reaction is also a relatively rare example of a mono-amine \textit{Pd}\textsuperscript{II} complex. A search of the Cambridge Structural Database (CSD, version 5.43, update of November 2021; Groom \textit{et al.}, 2016) for structures containing a \textit{Pd(NH}_2-\textit{phenyl derivative)Cl}_2 fragment gave 51 hits, of which 30 were bis(amine)\textit{PdCl}_2 moieties and among these was the complex \textit{Pd(p-toluidine)_2Cl} (YOYWOB; Tay, 2019) which is relevant for comparison with the title compound. Of the remaining 21, 11 contained the \textit{NH}_2 group as part of a chelate ring and only 10 contained a monodentate mono-amine \textit{PdCl}_2 complex (BOCTIX, Hadzovic \textit{et al.}, 2008; HIPDEP, Vicente \textit{et al.}, 1998; KASNAU, Asma \textit{et al.}, 2005; OCATEV, OCATIZ, Xia \textit{et al.}, 2021; OCEPOE, Asma & Kaminsky, 2017; XEKFEZ, Randell \textit{et al.}, 2006; XIYLOG, Liu \textit{et al.}, 2002; XORVIM, Hu \textit{et al.}, 2019; and YELMOS, Asma \textit{et al.}, 2006). One of these structures (HIPDEP; Vicente \textit{et al.}, 1998) is particularly relevant as it contains an \textit{sp}^2 \textit{C} donor attached to a \textit{PdCl}_2(\textit{o}-toluidine) fragment where the major difference with the present structure is the substitution of the \textit{sp}^2 \textit{C} for \textit{sp}^2 \textit{N}.

An ORTEP view of the molecular structure of \textit{Pd(HL}^1\textsubscript{L}^2\textsubscript{Cl}}\textsubscript{1}, \textit{I}, is shown in Fig. 1 and selected bond lengths and bond angles are given in Table 1. This mono-amine \textit{Pd}\textsuperscript{II} complex crystallizes in the triclinic space group, \textit{P}\textsubscript{T}. The primary geometry around the \textit{Pd} atom closely resembles square planar (\textit{\tau}_4 = 0.069, where 0 = square planar and 1 = tetrahedral; Okuniewski \textit{et al.}, 2015). In the (\textit{E})-1-(thiophen-2-yl)-\textit{N}-(p-toly)methanimine ligand, the phenyl and thiophene rings are not coplanar because of the steric clash of the hydrogen atoms attached to C5 and C7, exhibiting a dihedral angle of 38.5 (1)°. In addition, the coordination plane (\textit{Pd}1, C11, C12, N1, and N2) is almost perpendicular to both the planes of the coordinated \textit{o}-toluidine ring and the C5, C6, N1 fragment [dihedral angles of 84.7 (1) and 72.50 (4)°, respectively]. A search of the CSD (Groom \textit{et al.}, 2016) for structures containing a \textit{Pd(NH}_2-\textit{phenyl derivative)Cl}_2 fragment contained 90 observations of the \textit{Pd—NH} bond with a mean value of 2.065 (35) Å and minimum and maximum values of 2.028 Å (Baldovino-Pantaleon \textit{et al.}, 2007) and 2.171 Å (Asma \textit{et al.}, 2005), respectively. Thus, the length of 2.040 (2) Å in the title compound is slightly shorter than the observed mean value.

Table 1

| Bond Length (Å) | Description |
|-----------------|-------------|
| \textit{Pd1—N1} | 2.015 (2) |
| \textit{Pd1—N2} | 2.040 (2) |
| \textit{Pd1—Cl1} | 2.3067 (7) |
| N1—\textit{Pd1—N2} | 176.02 (9) |
| N1—\textit{Pd1—Cl1} | 90.55 (6) |
| N2—\textit{Pd1—Cl1} | 86.64 (7) |
| N1—\textit{Pd1—Cl2} | 92.04 (6) |

H) as a result of the presence of strong \textit{N—H}···\textit{Cl} hydrogen-bonding interactions. This observation was further supported by single-crystal X-ray studies.

Figure 1

Molecular structure of \textit{Pd(HL}^1\textsubscript{L}^2\textsubscript{Cl}}\textsubscript{1}, showing the atom-numbering scheme. Atomic displacement parameters are at the 30% probability level.
A related structure (HIPDEP; Vicente et al., 1998) contains an sp² C donor attached to a PdCl₂(o-toluidine) fragment where the major differences with the present structure are the substitution of the sp² C atom for sp² N, and the fact that there are cis Cl donors, which leads to a substantial trans effect involving the Pd—Cl distances. In this structure, the Pd—NH₂ distance is 2.050 (3) Å. The other related structure (Tay, 2019) is trans-Pd(o-toluidine)₂Cl₂ in which the Pd—NH₂ distance is 2.050 (3) Å.

### 3. Supramolecular features

The molecules display an interesting supramolecular synthon in the crystal. This synthon is based on reciprocal intermolecular N—H⋯Cl hydrogen-bonding interactions (Table 2) of the p-toluidine amine fragment and results in centrosymmetric dimeric units (Fig. 2). These units are further linked by intermolecular C—H⋯Cl interactions, resulting in chains in the c-axis direction where the mean-planes of the repeating fragment are oriented in the (110) plane.

**Figure 2**

Packing diagram for Pd(HL){Cl₂} showing the intermolecular N—H⋯Cl hydrogen-bonding interactions of the p-toluidine amine fragment resulting in centrosymmetric dimeric units that are further linked by intermolecular C—H⋯Cl interactions, resulting in chains in the c-axis direction where the mean-planes of the repeating fragment are oriented in the (110) plane.

**Table 2**

Hydrogen-bond geometry (Å, °).

|       | D—H ⋅⋅⋅A | D—H | H ⋅⋅⋅A | D—A | D—H ⋅⋅⋅A |
|-------|----------|------|--------|-----|----------|
| N2—H2N2 ⋅⋅⋅Cl²⁺ | 0.85 (2) | 2.45 (2) | 3.273 (2) | 163 (2) |
| C2—H2A ⋅⋅⋅Cl¹⁻ | 0.95 | 2.97 | 3.779 (3) | 144 |
| C5—H5A ⋅⋅⋅Cl¹⁻ | 0.95 | 2.98 | 3.759 (3) | 140 |
| C7—H7A ⋅⋅⋅Cl¹⁻ | 0.95 | 2.80 | 3.629 (3) | 147 |
| C11—H11A ⋅⋅⋅Cl²⁻ | 0.95 | 2.96 | 3.711 (3) | 137 |

Symmetry codes: (i) −x + 1, −y + 1, −z + 1; (ii) x + 1, y; (iii) −x + 1, −y + 1, −z + 2.

4. Synthesis and crystallization

A solution of 2-thiophene-carboxaldehyde (0.50 ml, 5 mmol) and 2 equivalent of p-toluidine (1.07 g, 10 mmol) in 20 ml of freshly distilled ethanol was allowed to stir at room temperature for 1 h. Then Na₂PdCl₄ (1.47 g, 10 mmol) was added. The reaction mixture was refluxed under stirring at 343 K for 2 h. A small amount of yellow solid gradually separated during the reaction. After stirring for 3 h the solid was filtered off and the filtrate underwent slow evaporation at room temperature to give red needles of (PdCl₂(C⁺η²:C₇H₉N)(C₁₂H₁₁NS))₄SbHPdCl₂; yield: 0.80 g, 33%, m.p. 533 K. FT-IR (KBr disk, cm⁻¹): 3777 (NH), 3696 (NH), 3406, 2921, 2857, 1611 (CH=NC), 1384, 1056, 754. Analysis calculated for C₁₉H₂₈N₂Cl₄PdS: C, 46.98; H, 4.15; N, 5.77. Found: C, 47.10; H, 4.30; N, 6.00%.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms were fixed geometrically with their Uiso values set to 1.2 times that of the phenyl carbons and 1.5 times that of the methyl group. The hydrogen atoms attached to nitrogen were refined isotropically.
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References
Asma, M., Badshah, A., Ali, S., Sohail, M., Fettouhi, M., Ahmad, S. & Malik, A. (2006). Transition Met. Chem. 31, 556–559.
Asma, M. & Kaminsky, W. (2017). CSD Communication (refcode OCEPOE). CCDC, Cambridge, England.
Asma, M., Kaminsky, W. & Badshah, A. (2005). Acta Cryst. E61, m1797–m1798.
Baldovino-Pantaleón, O., Morales-Morales, D., Hernández-Ortega, S., Toscano, R. A. & Valdés-Martínez, J. (2007). Cryst. Growth Des. 7, 117–123.
Bruker (2002). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
Calleja, J., Pla, D., Gorman, T. W., Domingo, V., Haffemayer, B. & Gaunt, M. J. (2015). Nat. Chem. 7, 1009–1016.
Ding, K., Wu, J., Hu, H., Shen, J. & Wang, X. (1992). Organometallics, 11, 3849–3856.
Dubey, P., Gupta, S. & Singh, A. K. (2019). Organometallics, 38, 944–961.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hadzovic, A., Janetzko, J. & Song, D. (2008). Dalton Trans. pp. 3279–3281.
Hu, H., Vasiliiu, M., Stein, T. H., Qu, F., Gerlach, D. L., Dixon, D. A. & Shaughnessy, K. H. (2019). Inorg. Chem. 58, 13299–13313.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Liu, X., Ong, T. K. W., Selvaratnam, S., Vittal, J. J., White, A. J. P., Williams, D. J. & Leung, P. H. (2002). J. Organomet. Chem. 643–644, 4–11.
Okuniewski, A., Rosiak, D., Chojnacki, J. & Becker, B. (2015). Polyhedron, 90, 47–57.
Randell, K., Stanford, M. J., Clarkson, G. J. & Rourke, J. P. (2006). J. Organomet. Chem. 691, 3411–3415.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Tay, M. G. (2019). CSD Communication (refcode YOYWOB). CCDC, Cambridge, England.
Vicente, J., Arcas, A., Blasco, M.-A., Lozano, J. & Ramírez de Arellano, M. C. (1998). Organometallics, 17, 5374–5383.
Xia, Q., Shi, S., Gao, P., Lalancette, R., Szostak, R. & Szostak, M. (2021). J. Org. Chem. 86, 15648–15657.
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Computing details

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT (Bruker, 2002); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Dichlorido(4-methylaniline-κN)[N-(4-methylphenyl)-1-(thiophen-2-yl)methanimine-κN]palladium(II)

Crystal data

$[\text{PdCl}_2(\text{C}_7\text{H}_9\text{N})(\text{C}_{12}\text{H}_{11}\text{NS})]$ Z = 2
$F(000) = 488$
$D_{x} = 1.661 \text{ Mg m}^{-3}$
Mo Kα radiation, $\lambda = 0.71073$ Å
Cell parameters from 7754 reflections
$\theta = 2.6^\circ$–31.6°
$\mu = 1.34 \text{ mm}^{-1}$
$T = 100 \text{ K}$
Prism, red-orange
$0.21 \times 0.16 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
$T_{\text{min}} = 0.622$, $T_{\text{max}} = 0.747$
22977 measured reflections
7379 independent reflections
5166 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.074$
$\theta_{\text{max}} = 33.2^\circ$, $\theta_{\text{min}} = 2.6^\circ$
h = −14→14
k = −14→14
l = −19→19

Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.090$
$S = 1.04$
7379 reflections
236 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.1526P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta\sigma)_{\text{max}} = 0.001$
$\Delta \rho_{\text{max}} = 0.75 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -1.04 \text{ e Å}^{-3}$
**Special details**

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

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|   | x     | y     | z     | U_iso*/U_eq |
|---|-------|-------|-------|-------------|
| Pd1 | 0.53572 (2) | 0.53405 (2) | 0.70240 (2) | 0.01680 (6) |
| Cl1 | 0.33922 (8) | 0.70208 (8) | 0.83363 (6) | 0.02463 (14) |
| Cl2 | 0.71210 (8) | 0.36598 (7) | 0.56567 (5) | 0.02350 (14) |
| S1  | 0.85995 (9) | 0.55990 (9) | 0.70536 (6) | 0.02886 (16) |
| N1  | 0.6002 (3)  | 0.3778 (2)  | 0.82190 (18) | 0.0176 (4) |
| N2  | 0.4704 (3)  | 0.7036 (3)  | 0.5873 (2)  | 0.0220 (5) |
| H2N1| 0.377 (3)   | 0.770 (3)   | 0.622 (2)   | 0.032 (9)* |
| H2N2| 0.444 (3)   | 0.674 (3)   | 0.540 (19)  | 0.028 (9)* |
| C1  | 1.0173 (4)  | 0.5879 (3)  | 0.7297 (3)  | 0.0305 (7) |
| H1A | 1.076419    | 0.650381    | 0.682505    | 0.037* |
| C2  | 1.0496 (3)  | 0.5118 (3)  | 0.8234 (3)  | 0.0298 (7) |
| H2A | 1.133321    | 0.516183    | 0.848589    | 0.036* |
| C3  | 0.9467 (3)  | 0.4256 (3)  | 0.8798 (2)  | 0.0198 (5) |
| H3A | 0.952608    | 0.364962    | 0.946424    | 0.024* |
| C4  | 0.8334 (3)  | 0.4419 (3)  | 0.8232 (2)  | 0.0197 (5) |
| C5  | 0.7160 (3)  | 0.3650 (3)  | 0.8615 (2)  | 0.0198 (5) |
| H5A | 0.724011    | 0.295542    | 0.924122    | 0.024* |
| C6  | 0.4938 (3)  | 0.2900 (3)  | 0.8769 (2)  | 0.0192 (5) |
| C7  | 0.4335 (3)  | 0.2799 (3)  | 0.9911 (2)  | 0.0227 (6) |
| H7A | 0.463677    | 0.329462    | 1.034377    | 0.027* |
| C8  | 0.3296 (3)  | 0.1977 (3)  | 1.0415 (2)  | 0.0238 (6) |
| H8A | 0.288941    | 0.191174    | 1.119823    | 0.029* |
| C9  | 0.2829 (3)  | 0.1243 (3)  | 0.9811 (2)  | 0.0225 (6) |
| C10 | 0.3476 (3)  | 0.1323 (3)  | 0.8664 (2)  | 0.0258 (6) |
| H10A| 0.320210    | 0.079781    | 0.823403    | 0.031* |
| C11 | 0.4510 (3)  | 0.2156 (3)  | 0.8141 (2)  | 0.0240 (6) |
| H11A| 0.492453    | 0.221808    | 0.735826    | 0.029* |
| C12 | 0.1631 (3)  | 0.0410 (3)  | 1.0382 (3)  | 0.0301 (7) |
| H12A| 0.190105    | -0.017694   | 1.103815    | 0.045* |
| H12B| 0.169958    | -0.029332   | 0.987540    | 0.045* |
| H12C| 0.051154    | 0.115955    | 1.060209    | 0.045* |
| C13 | 0.5932 (3)  | 0.7750 (3)  | 0.5331 (2)  | 0.0198 (5) |
| C14 | 0.6077 (3)  | 0.8804 (3)  | 0.5877 (2)  | 0.0223 (6) |
| H14A| 0.539342    | 0.903607    | 0.661152    | 0.027* |
| C15 | 0.7222 (3)  | 0.9519 (3)  | 0.5351 (2)  | 0.0240 (6) |
| H15A| 0.731007    | 1.025059    | 0.572709    | 0.029* |
| C16 | 0.8240 (3)  | 0.9187 (3)  | 0.4286 (2)  | 0.0257 (6) |
| C17 | 0.8092 (4)  | 0.8100 (3)  | 0.3760 (2)  | 0.0287 (6) |
| H17A| 0.878381    | 0.785164    | 0.303024    | 0.034* |
### Supporting Information

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| C18   | 0.6952 (3) | 0.7373 (3) | 0.4283 (2) | 0.0253 (6) |       |       |
| H18A  | 0.687823 | 0.661983 | 0.391948 | 0.030* |       |       |
| C19   | 0.9476 (4) | 0.9977 (4) | 0.3690 (3) | 0.0348 (7) |       |       |
| H19A  | 0.938923 | 1.073179 | 0.416289 | 0.052* |       |       |
| H19B  | 0.925215 | 1.050022 | 0.300474 | 0.052* |       |       |
| H19C  | 1.058806 | 0.921028 | 0.351413 | 0.052* |       |       |

#### Atomic displacement parameters (Å²)

|       |      |      |      |      |      |      |
|-------|------|------|------|------|------|------|
| Pd1   | 0.01898 (10) | 0.01641 (10) | 0.01739 (10) | −0.00721 (7) | −0.00816 (8) | 0.00119 (7) |
| Cl1   | 0.0253 (3) | 0.0249 (3) | 0.0226 (3) | −0.0071 (3) | −0.0069 (3) | −0.0032 (3) |
| Cl2   | 0.0275 (3) | 0.0217 (3) | 0.0215 (3) | −0.0066 (3) | −0.0086 (3) | −0.0033 (2) |
| S1    | 0.0309 (4) | 0.0297 (4) | 0.0300 (4) | −0.0159 (3) | −0.0113 (3) | 0.0054 (3) |
| N1    | 0.0217 (11) | 0.0162 (10) | 0.0173 (11) | −0.0082 (9) | −0.0082 (9) | 0.0017 (8) |
| N2    | 0.0245 (12) | 0.0213 (12) | 0.0232 (13) | −0.0078 (10) | −0.0127 (11) | 0.0022 (9) |
| C1    | 0.0253 (15) | 0.0279 (15) | 0.0389 (18) | −0.0150 (12) | −0.0021 (14) | −0.0050 (13) |
| C2    | 0.0245 (15) | 0.0322 (16) | 0.0368 (18) | −0.0118 (12) | −0.0078 (14) | −0.0103 (13) |
| C3    | 0.0145 (12) | 0.0182 (12) | 0.0269 (14) | −0.0071 (10) | −0.0031 (11) | −0.0047 (10) |
| C4    | 0.0219 (13) | 0.0195 (12) | 0.0178 (13) | −0.0081 (10) | −0.0056 (11) | 0.0005 (10) |
| C5    | 0.0224 (13) | 0.0167 (12) | 0.0198 (13) | −0.0055 (10) | −0.0075 (11) | −0.0003 (10) |
| C6    | 0.0196 (13) | 0.0165 (12) | 0.0222 (14) | −0.0061 (10) | −0.0089 (11) | 0.0022 (10) |
| C7    | 0.0232 (14) | 0.0246 (14) | 0.0227 (14) | −0.0104 (11) | −0.0066 (12) | −0.0026 (11) |
| C8    | 0.0229 (14) | 0.0250 (14) | 0.0215 (14) | −0.0082 (11) | −0.0035 (12) | −0.0024 (11) |
| C9    | 0.0189 (13) | 0.0171 (12) | 0.0296 (15) | −0.0052 (10) | −0.0069 (12) | 0.0002 (11) |
| C10   | 0.0300 (15) | 0.0237 (14) | 0.0287 (16) | −0.0128 (12) | −0.0105 (13) | −0.0021 (11) |
| C11   | 0.0280 (15) | 0.0282 (14) | 0.0194 (14) | −0.0127 (12) | −0.0092 (12) | 0.0007 (11) |
| C12   | 0.0258 (15) | 0.0242 (14) | 0.0398 (18) | −0.0128 (12) | −0.0059 (14) | 0.0010 (13) |
| C13   | 0.0224 (13) | 0.0169 (12) | 0.0200 (13) | −0.0059 (10) | −0.0096 (11) | 0.0034 (10) |
| C14   | 0.0253 (14) | 0.0191 (13) | 0.0202 (14) | −0.0061 (11) | −0.0068 (12) | 0.0013 (10) |
| C15   | 0.0293 (15) | 0.0194 (13) | 0.0265 (15) | −0.0089 (11) | −0.0127 (13) | 0.0011 (11) |
| C16   | 0.0211 (13) | 0.0239 (14) | 0.0301 (16) | −0.0059 (11) | −0.0118 (13) | 0.0075 (11) |
| C17   | 0.0262 (15) | 0.0281 (15) | 0.0234 (15) | −0.0030 (12) | −0.0036 (13) | 0.0030 (12) |
| C18   | 0.0314 (15) | 0.0232 (14) | 0.0210 (14) | −0.0081 (12) | −0.0080 (13) | −0.0029 (11) |
| C19   | 0.0290 (16) | 0.0328 (17) | 0.0409 (19) | −0.0140 (13) | −0.0093 (15) | 0.0073 (14) |

#### Geometric parameters (Å, °)

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| Pd1—N1 | 2.015 (2) | C8—H8A | 0.9500 |
| Pd1—N2 | 2.040 (2) | C9—C10 | 1.394 (4) |
| Pd1—Cl1 | 2.3067 (7) | C9—C12 | 1.507 (4) |
| Pd1—Cl2 | 2.3082 (7) | C10—C11 | 1.384 (4) |
| S1—C1 | 1.702 (3) | C10—H10A | 0.9500 |
| S1—C4 | 1.721 (3) | C11—H11A | 0.9500 |
| N1—C5 | 1.291 (3) | C12—H12A | 0.9800 |
| N1—C6 | 1.442 (3) | C12—H12B | 0.9800 |
| N2—C13 | 1.446 (3) | C12—H12C | 0.9800 |
| N2—H2N1 | 0.868 (16) | C13—C18 | 1.372 (4) |
# Supporting Information

| Bond  | Length (A)  | Bond  | Length (A)  | Bond  | Length (A)  |
|-------|-------------|-------|-------------|-------|-------------|
| N2—H2N2 | 0.848 (16)  | C13—C14 | 1.382 (4)  | N1—Pd1—N2 | 176.02 (9)  |
| C1—C2  | 1.358 (4)   | C14—C15 | 1.383 (4)  | N1—Pd1—Cl1 | 90.55 (6)   |
| C1—H1A | 0.9500      | C14—H14A | 0.9500     | N2—Pd1—Cl1 | 86.64 (7)   |
| C2—C3  | 1.410 (4)   | C15—C16 | 1.384 (4)  | N1—Pd1—Cl2 | 92.04 (6)   |
| C2—H2A | 0.9500      | C15—H15A | 0.9500     | N2—Pd1—Cl2 | 91.00 (7)   |
| C3—C4  | 1.417 (4)   | C16—C17 | 1.392 (4)  | Cl1—Pd1—Cl1 | 174.53 (2) |
| C3—H3A | 0.9500      | C17—C18 | 1.386 (4)  | Cl1—Pd1—Cl2 | 113.09 (16) |
| C4—C5  | 1.429 (3)   | C17—H17A | 0.9500     | C1—S1—C4 | 91.29 (14)  |
| C5—H5A | 0.9500      | C18—C19 | 0.9800     | C5—N1—C6 | 118.0 (2)   |
| C6—C7  | 1.386 (4)   | C18—H18A | 0.9500     | C11—Pd1—N1 | 124.71 (18) |
| C6—C11 | 1.388 (4)   | C19—H19A | 0.9800     | C6—N1—Pd1 | 116.66 (15) |
| C7—C8  | 1.376 (4)   | C19—H19B | 0.9800     | C13—N2—Pd1 | 113.09 (16) |
| C7—H7A | 0.9500      | C19—H19C | 0.9800     | H2N1—N2—H2N2 | 112 (2) |
| C8—C9  | 1.383 (4)   | C8—C9—C10 | 118.0 (2)  | Pd1—N2—H2N1 | 106 (2)   |
| C10—C9—C12 | 120.7 (3) | C9—C12—H12A | 109.5     | C13—N2—H2N2 | 110 (2)   |
| C11—C10—C9 | 121.1 (3) | C9—C12—H12B | 109.5     | Pd1—N2—H2N2 | 113 (2)   |
| C11—C10—H10A | 119.5 | C9—C12—H12C | 109.5     | H2N1—N2—H2N2 | 102 (2) |
| C9—C10—H10A | 119.5 | C8—C13—C14 | 120.4 (3) | C2—C1—S1 | 113.1 (2)   |
| C9—C12—H12A | 109.5 | C8—C13—N2 | 120.1 (2) | C2—C1—H1A | 123.4       |
| C9—C12—H12B | 109.5 | C14—C13—N2 | 119.5 (2) | S1—C1—H1A | 123.4       |
| C9—C12—H12C | 109.5 | C14—C13—C14 | 119.7 (3) | C1—C2—C3 | 113.4 (3)   |
| C11—C10—H10A | 119.5 | C13—C14—C15 | 119.7 (3) | C1—C2—H2A | 123.3       |
| C9—C10—H10A | 119.5 | C13—C14—H14A | 120.1 | C3—C2—H2A | 123.3       |
| C11—C10—H10A | 119.5 | C15—C14—H14A | 120.1 | C2—C3—C4 | 110.5 (2)   |
| C9—C10—H10A | 119.5 | C14—C15—C16 | 121.1 (3) | C2—C3—H3A | 124.7       |
| C11—C10—H10A | 119.5 | C14—C15—H15A | 119.4 | C4—C3—H3A | 124.7       |
| C11—C10—H10A | 119.5 | C16—C17—C16 | 121.2 (3) | C3—C4—C5 | 122.3 (2)   |
| C11—C10—H10A | 119.5 | C18—C17—C16 | 121.2 (3) | C3—C4—S1 | 111.66 (19) |
| C11—C10—H10A | 119.5 | C18—C17—H17A | 119.4 | C5—C4—S1 | 126.0 (2)   |
| C11—C10—H10A | 119.5 | C18—C17—H17A | 119.4 | N1—C5—C4 | 128.2 (2)   |
| C11—C10—H10A | 119.5 | C13—C18—C17 | 119.5 (3) | N1—C5—H5A | 115.9       |
| C11—C10—H10A | 119.5 | C13—C18—H18A | 120.3 | C4—C5—H5A | 115.9       |
| C11—C10—H10A | 119.5 | C19—C18—H18A | 120.3 | C7—C6—C11 | 119.9 (2)   |
| C11—C10—H10A | 119.5 | C17—C18—H18A | 120.3 | C7—C6—N1 | 120.8 (2)   |

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Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| N2—H2N2···Cl2' | 0.85 (2) | 2.45 (2) | 3.273 (2) | 163 (2) |
| C2—H2A···Cl1ii | 0.95 | 2.97 | 3.779 (3) | 144 |
| C5—H5A···Cl1iii | 0.95 | 2.98 | 3.759 (3) | 140 |
| C7—H7A···Cl1iii | 0.95 | 2.80 | 3.629 (3) | 147 |
| C11—H11A···Cl12 | 0.95 | 2.96 | 3.711 (3) | 137 |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) x+1, y, z; (iii) −x+1, −y+1, −z+2.

C11—C6—N1 119.3 (2) C16—C19—H19A 109.5
C8—C7—C6 119.6 (3) C16—C19—H19B 109.5
C8—C7—H7A 120.2 C19A—C19—H19B 109.5
C6—C7—H7A 120.2 C16—C19—H19C 109.5
C7—C8—C9 121.8 (3) H19A—C19—H19C 109.5
C7—C8—H8A 119.1 H19B—C19—H19C 109.5
C9—C8—H8A 119.1

C4—S1—C1—C2 −0.2 (3) C7—C8—C9—C12 −177.2 (2)
S1—C1—C2—C3 0.4 (3) C8—C9—C10—C11 −2.2 (4)
C1—C2—C3—C4 −0.4 (3) C12—C9—C10—C11 176.6 (3)
C2—C3—C4—C5 179.1 (2) C9—C10—C11—C6 1.2 (4)
C2—C3—C4—S1 0.3 (3) C7—C6—C11—C10 0.3 (4)
C1—S1—C4—C3 −0.1 (2) N1—C6—C11—C10 −179.4 (2)
C1—S1—C4—C5 −178.9 (3) Pd1—N2—C13—C18 102.6 (2)
C6—N1—C5—C4 −178.6 (2) Pd1—N2—C13—C14 −76.9 (3)
Pd1—N1—C5—C4 −7.9 (4) C18—C13—C14—C15 2.1 (4)
C3—C4—C5—N1 175.2 (3) N2—C13—C14—C15 −178.3 (2)
S1—C4—C5—N1 −6.2 (4) C13—C14—C15—C16 −0.6 (4)
C5—N1—C6—C7 43.1 (3) C14—C15—C16—C17 −0.6 (4)
Pd1—N1—C6—C7 −128.3 (2) C14—C15—C16—C19 178.9 (2)
C5—N1—C6—C11 −137.2 (2) C15—C16—C17—C18 0.3 (4)
Pd1—N1—C6—C11 51.4 (3) C19—C16—C17—C18 −179.1 (3)
C11—C6—C7—C8 −0.9 (4) C14—C13—C18—C17 −2.4 (4)
N1—C6—C7—C8 178.8 (2) N2—C13—C18—C17 178.1 (2)
C6—C7—C8—C9 −0.1 (4) C16—C17—C18—C13 1.1 (4)
C7—C8—C9—C10 1.6 (4)