IUCrData

ISSN 2414-3146

(S_C,R_S)-Bromido(N-{4-methyl-1-[(4-methylphenyl)-sulfanyl]pentan-2-yl}-N'-(pyridin-2-yl)imidazol-2-ylidene)palladium(II) bromide

Xianggui Zeng, Yanze Xu, Shuling Guo, Yongmei Xiao, Jinwei Yuan and Liangru Yang*

School of Chemistry & Chemical Engineering, Henan University of Technology, Zhengzhou 450001, People's Republic of China. *Correspondence e-mail: lryang@haut.edu.cn

Received 25 March 2024
Accepted 21 April 2024

Edited by M. Zeller, Purdue University, USA

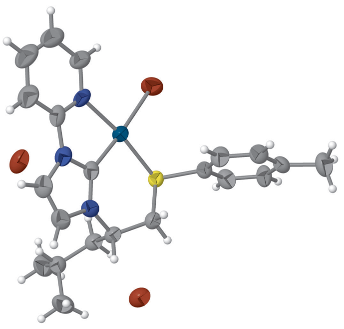
Keywords: crystal structure; *N*-heterocyclic carbene; palladium(II); hydrogen bonds.

CCDC reference: 2312031

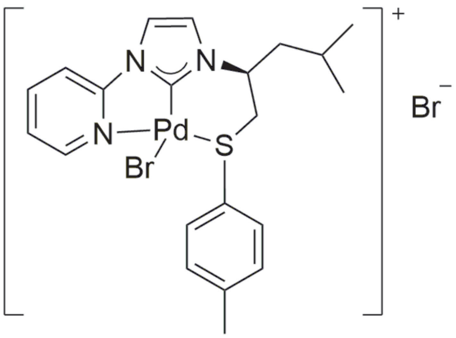
Structural data: full structural data are available from iucrdata.iucr.org

The molecule of the title $NC_{NHC}S$ pincer *N*-heterocyclic carbene palladium(II) complex, $[PdBr(C_{21}H_{25}N_3S)]Br$, exhibits a slightly distorted square-planar coordination at the palladium(II) atom, with the five-membered chelate ring nearly planar. The six-membered chelate ring adopts an envelope conformation. Upon chelation, the sulfur atom becomes a stereogenic centre with an R_S configuration induced by the chiral carbon of the precursor imidazolium salt. There are intramolecular C—H···Br—Pd hydrogen bonds in the structure. The two interstitial Br atoms, as the counter-anion of the structure, are both located on crystallographic twofold axes and are connected to the complex cations *via* C—H···Br hydrogen bonds.

3D view



Chemical scheme



Structure description

N-Heterocyclic carbenes (NHCs) have been widely used as ancillary ligands in coordination chemistry and organic catalysis due to their characteristic electronic properties and easy structural modification (Hopkinson *et al.*, 2014; Gardiner *et al.*, 2018). Introduction of a coordinating heteroatom functional group to the N-atom substituents of the NHCs leads to the formation of a potentially chelating ligand, and facilitates the formation of stable pincer NHC–metal complexes that can possess catalytic activities. Metal complexes containing heteroatom donors, such as P, N, O and S, have been synthesized, characterized and employed extensively as catalysts for a variety of organic transformations (Ahrens *et al.*, 2006; Bierenstiel & Cross, 2011; Meyer *et al.*, 2012; Peris & Crabtree, 2004). Our group has investigated the synthesis and catalytic performance of a series of chelating NHC–palladium complexes derived from natural amino alcohols (Yang *et al.*, 2015, 2023; Yang, Zhang, Xiao & Mao, 2016; Yang, Zhang, Yuan *et al.*, 2016; Meng *et al.*, 2022). As part of our work on the study of NHC–metal complexes containing

https://doi.org/10.1107/S2414314624003602

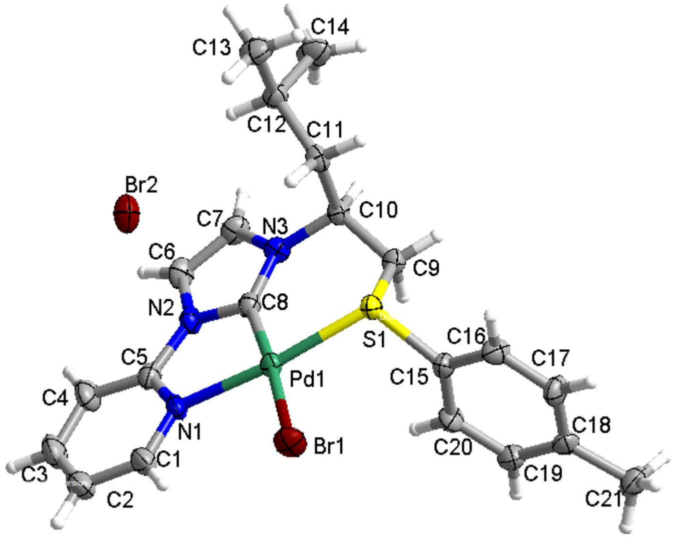


Figure 1
The molecular structure of the title complex, shown with 50% probability displacement ellipsoids.

heteroatom-functionalized N-atom substituents, we present here the crystal structure of the title $NC_{NHC}S$ pincer NHC palladium(II) complex (Fig. 1).

In the title complex, the palladium(II) atom is coordinated to C8, N1, Br1, and S1, resulting in a slightly distorted square-planar coordination. The Pd1—C8, Pd1—N1, Pd1—Br1 and Pd1—S1 bond lengths are 1.946 (8), 2.093 (6), 2.4663 (10), and 2.2603 (17) Å, respectively. The five-membered chelate ring (C8/Pd1/N1/C5/N2) is almost planar, with Pd1—N1—C5—N2 and C5—N2—C8—Pd1 torsion angles of −0.3 (8) and 2.0 (8)°, respectively. The six-membered chelate ring (C8/Pd1/S1/C9/C10/N3) adopts an envelope conformation with puckering parameters of θ = 51.6 (6)° and φ= 125.4 (8)°, which are close to the expected values for this conformation (Boeyens, 1978).

Upon chelation, the sulfur atom becomes a stereogenic centre, resulting in the formation of molecules with an R_S configuration. This can be attributed to the chiral induction of the chiral carbon C(5), which retains the same *S* configuration as in the precursor imidazolium salt. The environment of the sulfur atoms of the molecule is approximately triangular pyramidal. This is indicated by the bond angles C9—S1—Pd1, C15—S1—Pd1 and C9—S1–15, which were found to be 106.2 (2), 111.0 (2), and 97.2 (3)°, respectively, with an average of 105.0°. In the crystal, intra- and intermolecular C—H⋯Br hydrogen bonds occur (Table 1, Fig. 2).

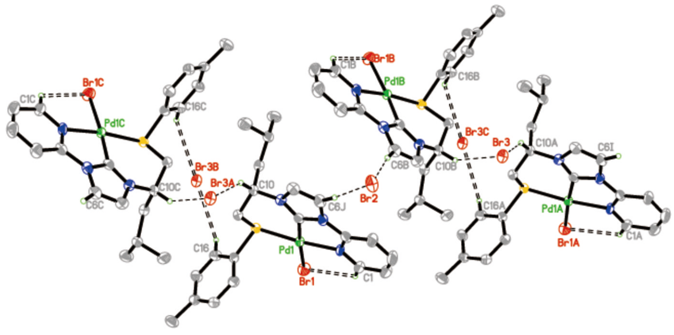


Figure 2
The C—H⋯Br interactions in the structure.

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C1—H1⋯Br1	0.93	2.90	3.510 (10)	124
C6—H6⋯Br2^{i}	0.93	2.74	3.661 (9)	173
C10—H10⋯Br3	0.98	2.78	3.624 (7)	144
C16—H16⋯Br3^{ii}	0.93	3.11	3.742 (7)	127

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[PdBr(C_{21}H_{25}N_3S)]Br$
M_r	617.72
Crystal system, space group	Monoclinic, *C*2
Temperature (K)	293
a, *b*, *c* (Å)	25.8993 (7), 6.6206 (2), 13.4938 (3)
β (°)	96.425 (2)
V (Å^3)	2299.23 (12)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	11.52
Crystal size (mm)	0.14 × 0.1 × 0.03
Data collection	
Diffractometer	Xcalibur, Eos, Gemini
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.419, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20069, 3950, 3693
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.072, 1.04
No. of reflections	3950
No. of parameters	258
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.38
Absolute structure	Flack *x* determined using 1371 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.030 (7)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

A mixture of (*S*)-*N*-(4-methyl-1-(*p*-tolylthio)pentan-2-yl)-*N*′-(pyridin-2-yl)-1*H*-imidazolium bromide (1.0 mmol, 0.43 g), $PdCl_2$ (1.0 mmol, 0.18 g), NaOAc (1.0 mmol, 0.10 g), and NaBr (4 mmol, 0.41 g) in CH_3CN (10 ml) was heated at 80°C for 24 h, and then the volatiles were evaporated. Purification of the residue by column chromatography (silica gel, CH_2Cl_2/MeOH 15/1 ∼1:1, *v*/*v*) produced the title complex as a yellow solid (0.32 g, 60%). Crystallization of the solid from CH_3CN afforded the title complex as yellow crystals, m.p. 269–277°C. HR—MS (ESI) *m*/*z* calculated for $C_{21}H_{25}BrN_3PdS^+$ $(M - Br)^+$

535.9987, found 535.9998. F T–IR (ATR mode): $\nu = 3388, 3012, 2910, 1681, 1496, 1376, 1316, 1144, 1014, 914, 806, 780, 738, 666, 448$ cm$^{-1.}$ $[\alpha]^{15}{}_{589}$: 8.3 (1.00, CH_2Cl_2).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank Ms Y. Zhu for technical assistance.

Funding information

Funding for this research was provided by: the Natural Science Foundation of Henan Province (grant No. 242300420186).

References

Ahrens, S., Zeller, A., Taige, M. & Strassner, T. (2006). *Organometallics*, **25**, 5409–5415.

Bierenstiel, M. & Cross, E. D. (2011). *Coord. Chem. Rev.* **255**, 574–590.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Gardiner, M. G. & Ho, C. C. (2018). *Coord. Chem. Rev.* **375**, 373–388.

Hopkinson, M. N., Richter, C., Schedler, M. & Glorius, F. (2014). *Nature*, **510**, 485–496.

Meng, X., Yang, L., Liu, Q., Dong, Z., Yuan, J., Xiao, Y. & Mao, P. (2022). *Chin. J. Org. Chem.* **42**, 3747–3756.

Meyer, D., Zeller, A. & Strassner, T. (2012). *J. Organomet. Chem.* **701**, 56–61.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Peris, E. & Crabtree, R. H. (2004). *Coord. Chem. Rev.* **248**, 2239–2246.

Rigaku OD (2023). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

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

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Yang, L., Guo, M., Yuan, J., Wangx, J., Xia, Y., Xiao, Y. & Mao, P. (2023). *Chin. J. Org. Chem.* **43**, 2002–2025.

Yang, L., Yuan, J., Mao, P. & Guo, Q. (2015). *RSC Adv.* **5**, 107601–107607.

Yang, L., Zhang, W., Xiao, Y. & Mao, P. (2016). *ChemistrySelect*, **4**, 680–684.

Yang, L., Zhang, X., Yuan, J., Xiao, Y. & Mao, P. (2016). *J. Organomet. Chem.* **818**, 179–184.

full crystallographic data

IUCrData (2024). **9**, x240360 [https://doi.org/10.1107/S2414314624003602]

(S_C,R_S)-Bromido(*N*-{4-methyl-1-[(4-methylphenyl)sulfanyl]pentan-2-yl}-*N*′-(pyridin-2-yl)imidazol-2-ylidene)palladium(II) bromide

Xianggui Zeng, Yanze Xu, Shuling Guo, Yongmei Xiao, Jinwei Yuan and Liangru Yang

(S_C,R_S)-Bromido(*N*-{4-methyl-1-[(4-methylphenyl)sulfanyl]pentan-2-yl}-*N*′-(pyridin-2-yl)imidazol-2-ylidene)palladium(II) bromide

Crystal data

[PdBr($C_{21}H_{25}N_3S$)]Br
M_r = 617.72
Monoclinic, *C*2
a = 25.8993 (7) Å
b = 6.6206 (2) Å
c = 13.4938 (3) Å
β = 96.425 (2)°
V = 2299.23 (12) Å^3
Z = 4
F(000) = 1216
D_x = 1.785 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 8595 reflections
θ = 4.5–70.1°
μ = 11.52 mm^{-1}
T = 293 K
Plate, colourless
0.14 × 0.1 × 0.03 mm

Data collection

Xcalibur, Eos, Gemini diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.2312 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2023)
$T_{\min}$ = 0.419, $T_{\max}$ = 1.000
20069 measured reflections
3950 independent reflections
3693 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
$\theta_{\max}$ = 70.5°, $\theta_{\min}$ = 3.4°
h = −31→31
k = −8→6
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.072
S = 1.04
3950 reflections
258 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 2.7656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ < 0.001
$\Delta\rho_{\max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\min}$ = −0.38 e Å^{-3}
Extinction correction: SHELXL-2014/7 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00034 (4)
Absolute structure: Flack *x* determined using 1371 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.030 (7)

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.

Refinement. The H atoms on the carbons were positioned geometrically and constrained to ride on their parent atoms. C—H bond distances were constrained to 0.93 Å for aromatic and alkene C—H moieties, and to 0.98, 0.91 and 0.96 Å for aliphatic C—H, CH$_2$ and CH$_3$ moieties, respectively. Methyl CH$_3$ H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\rm iso}$(H) values were set to a multiple of $U_{\rm eq}$(C) with 1.5 for CH$_3$, and 1.2 for C—H and CH$_2$ units, respectively.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Pd1	0.37598 (2)	0.06095 (8)	0.28758 (3)	0.03701 (15)
S1	0.40637 (6)	−0.0902 (3)	0.15555 (12)	0.0381 (4)
N1	0.3574 (2)	0.2356 (11)	0.4079 (4)	0.0443 (16)
N2	0.4255 (2)	0.4165 (10)	0.3607 (4)	0.0413 (14)
N3	0.4680 (2)	0.3203 (10)	0.2419 (4)	0.0381 (13)
C1	0.3187 (3)	0.2026 (16)	0.4635 (6)	0.057 (2)
H1	0.2972	0.0912	0.4501	0.069*
C2	0.3100 (4)	0.3329 (18)	0.5414 (7)	0.069 (3)
H2	0.2832	0.3085	0.5804	0.083*
C3	0.3414 (4)	0.4954 (18)	0.5587 (7)	0.074 (3)
H3	0.3359	0.5840	0.6099	0.089*
C4	0.3813 (3)	0.5318 (18)	0.5021 (6)	0.061 (2)
H4	0.4033	0.6422	0.5144	0.073*
C5	0.3873 (3)	0.3975 (13)	0.4263 (5)	0.0450 (18)
C6	0.4650 (3)	0.5562 (15)	0.3556 (5)	0.0478 (16)
H6	0.4719	0.6686	0.3963	0.057*
C7	0.4911 (3)	0.4978 (13)	0.2812 (6)	0.049 (2)
H7	0.5195	0.5632	0.2593	0.059*
C8	0.4280 (2)	0.2737 (13)	0.2911 (5)	0.0393 (16)
C9	0.4434 (2)	0.1033 (12)	0.0964 (5)	0.0415 (18)
H9A	0.4574	0.0439	0.0394	0.050*
H9B	0.4199	0.2108	0.0720	0.050*
C10	0.4877 (3)	0.1938 (11)	0.1649 (5)	0.0366 (15)
H10	0.5072	0.2821	0.1242	0.044*
C11	0.5255 (2)	0.0360 (13)	0.2122 (5)	0.0397 (16)
H11A	0.5325	−0.0599	0.1610	0.048*
H11B	0.5085	−0.0373	0.2617	0.048*
C12	0.5777 (3)	0.1161 (12)	0.2623 (5)	0.0441 (19)
H12	0.5707	0.2109	0.3150	0.053*
C13	0.6081 (3)	−0.0612 (16)	0.3099 (7)	0.065 (3)
H13A	0.5892	−0.1208	0.3598	0.097*
H13B	0.6413	−0.0150	0.3404	0.097*
H13C	0.6132	−0.1599	0.2598	0.097*
C14	0.6090 (3)	0.2258 (18)	0.1894 (7)	0.072 (3)

H14A	0.6092	0.1467	0.1298	0.108*
H14B	0.6440	0.2448	0.2196	0.108*
H14C	0.5935	0.3549	0.1729	0.108*
C15	0.3558 (3)	−0.1214 (13)	0.0549 (5)	0.0428 (18)
C16	0.3572 (3)	−0.2944 (13)	−0.0012 (6)	0.0494 (19)
H16	0.3814	−0.3949	0.0174	0.059*
C17	0.3221 (3)	−0.3171 (14)	−0.0853 (6)	0.054 (2)
H17	0.3225	−0.4353	−0.1224	0.064*
C18	0.2862 (3)	−0.1665 (14)	−0.1157 (5)	0.048 (2)
C19	0.2848 (3)	0.0021 (14)	−0.0560 (5)	0.051 (2)
H19	0.2601	0.1015	−0.0734	0.061*
C20	0.3190 (3)	0.0263 (14)	0.0282 (5)	0.049 (2)
H20	0.3176	0.1415	0.0672	0.059*
C21	0.2512 (3)	−0.1845 (17)	−0.2126 (6)	0.067 (3)
H21A	0.2684	−0.1290	−0.2659	0.101*
H21B	0.2195	−0.1116	−0.2075	0.101*
H21C	0.2433	−0.3242	−0.2261	0.101*
Br1	0.30979 (4)	−0.20451 (15)	0.29589 (7)	0.0603 (3)
Br2	0.5000	0.0140 (2)	0.5000	0.0609 (4)
Br3	0.5000	0.61892 (17)	0.0000	0.0480 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0397 (2)	0.0390 (3)	0.0327 (2)	−0.0004 (2)	0.00594 (15)	−0.0005 (2)
S1	0.0391 (8)	0.0388 (11)	0.0362 (8)	0.0001 (7)	0.0032 (6)	−0.0042 (8)
N1	0.050 (3)	0.054 (5)	0.030 (3)	0.012 (3)	0.009 (2)	−0.007 (3)
N2	0.050 (3)	0.036 (4)	0.038 (3)	0.007 (3)	0.003 (2)	−0.007 (3)
N3	0.042 (3)	0.031 (4)	0.042 (3)	−0.003 (3)	0.006 (2)	0.002 (3)
C1	0.054 (4)	0.073 (7)	0.047 (4)	0.009 (4)	0.015 (3)	−0.002 (4)
C2	0.063 (5)	0.091 (9)	0.055 (5)	0.018 (5)	0.019 (4)	0.003 (5)
C3	0.089 (7)	0.087 (9)	0.050 (4)	0.020 (6)	0.019 (4)	−0.017 (5)
C4	0.071 (5)	0.058 (7)	0.054 (4)	0.012 (5)	0.010 (3)	−0.019 (5)
C5	0.051 (4)	0.043 (5)	0.038 (4)	0.010 (4)	−0.006 (3)	−0.007 (4)
C6	0.061 (4)	0.030 (4)	0.050 (4)	−0.001 (4)	−0.001 (3)	−0.008 (4)
C7	0.052 (4)	0.038 (5)	0.055 (4)	−0.011 (3)	0.003 (3)	0.000 (4)
C8	0.042 (3)	0.037 (5)	0.036 (3)	0.005 (3)	−0.003 (3)	−0.002 (3)
C9	0.042 (3)	0.047 (6)	0.035 (3)	0.001 (3)	0.003 (2)	−0.001 (3)
C10	0.045 (3)	0.031 (4)	0.034 (3)	−0.002 (3)	0.008 (3)	−0.001 (3)
C11	0.049 (3)	0.032 (4)	0.039 (3)	0.002 (3)	0.009 (2)	0.000 (4)
C12	0.043 (3)	0.048 (6)	0.041 (3)	−0.005 (3)	0.004 (3)	−0.001 (3)
C13	0.051 (4)	0.073 (7)	0.068 (5)	0.007 (4)	−0.005 (4)	0.010 (5)
C14	0.051 (5)	0.096 (9)	0.069 (6)	−0.019 (5)	0.006 (4)	0.022 (6)
C15	0.038 (3)	0.051 (5)	0.039 (3)	−0.001 (3)	0.003 (3)	−0.009 (4)
C16	0.047 (4)	0.038 (5)	0.062 (5)	0.003 (3)	0.001 (3)	−0.009 (4)
C17	0.056 (4)	0.051 (6)	0.051 (4)	−0.001 (4)	−0.006 (3)	−0.020 (4)
C18	0.036 (3)	0.058 (6)	0.048 (4)	−0.011 (3)	0.004 (3)	−0.006 (4)
C19	0.042 (4)	0.060 (7)	0.050 (4)	0.007 (3)	0.002 (3)	0.000 (4)

C20	0.051 (4)	0.046 (6)	0.051 (4)	0.014 (4)	0.004 (3)	−0.011 (4)
C21	0.058 (5)	0.079 (8)	0.061 (5)	−0.003 (5)	−0.014 (4)	−0.006 (5)
Br1	0.0612 (5)	0.0547 (7)	0.0674 (5)	−0.0142 (4)	0.0173 (4)	0.0042 (5)
Br2	0.0953 (9)	0.0421 (9)	0.0444 (5)	0.000	0.0037 (5)	0.000
Br3	0.0607 (6)	0.0392 (8)	0.0460 (5)	0.000	0.0141 (4)	0.000

Geometric parameters (Å, º)

Pd1—S1	2.2603 (17)	C10—H10	0.9800
Pd1—N1	2.093 (6)	C10—C11	1.522 (10)
Pd1—C8	1.946 (8)	C11—H11A	0.9700
Pd1—Br1	2.4663 (10)	C11—H11B	0.9700
S1—C9	1.836 (7)	C11—C12	1.537 (9)
S1—C15	1.789 (7)	C12—H12	0.9800
N1—C1	1.335 (9)	C12—C13	1.517 (11)
N1—C5	1.330 (10)	C12—C14	1.527 (10)
N2—C5	1.405 (9)	C13—H13A	0.9600
N2—C6	1.387 (10)	C13—H13B	0.9600
N2—C8	1.340 (9)	C13—H13C	0.9600
N3—C7	1.396 (10)	C14—H14A	0.9600
N3—C8	1.328 (9)	C14—H14B	0.9600
N3—C10	1.470 (9)	C14—H14C	0.9600
C1—H1	0.9300	C15—C16	1.376 (11)
C1—C2	1.397 (13)	C15—C20	1.384 (11)
C2—H2	0.9300	C16—H16	0.9300
C2—C3	1.354 (15)	C16—C17	1.380 (11)
C3—H3	0.9300	C17—H17	0.9300
C3—C4	1.373 (12)	C17—C18	1.393 (12)
C4—H4	0.9300	C18—C19	1.379 (11)
C4—C5	1.376 (11)	C18—C21	1.511 (10)
C6—H6	0.9300	C19—H19	0.9300
C6—C7	1.329 (10)	C19—C20	1.370 (10)
C7—H7	0.9300	C20—H20	0.9300
C9—H9A	0.9700	C21—H21A	0.9600
C9—H9B	0.9700	C21—H21B	0.9600
C9—C10	1.513 (9)	C21—H21C	0.9600

S1—Pd1—Br1	91.46 (5)	C9—C10—H10	107.3
N1—Pd1—S1	170.64 (19)	C9—C10—C11	113.1 (6)
N1—Pd1—Br1	97.90 (19)	C11—C10—H10	107.3
C8—Pd1—S1	92.2 (2)	C10—C11—H11A	108.3
C8—Pd1—N1	78.4 (3)	C10—C11—H11B	108.3
C8—Pd1—Br1	175.9 (2)	C10—C11—C12	116.1 (7)
C9—S1—Pd1	106.2 (2)	H11A—C11—H11B	107.4
C15—S1—Pd1	111.0 (2)	C12—C11—H11A	108.3
C15—S1—C9	97.2 (3)	C12—C11—H11B	108.3
C1—N1—Pd1	126.7 (6)	C11—C12—H12	108.5
C5—N1—Pd1	114.3 (5)	C13—C12—C11	108.0 (7)

C5—N1—C1	119.0 (7)	C13—C12—H12	108.5
C6—N2—C5	131.8 (6)	C13—C12—C14	110.6 (7)
C8—N2—C5	118.1 (7)	C14—C12—C11	112.7 (6)
C8—N2—C6	110.0 (6)	C14—C12—H12	108.5
C7—N3—C10	125.5 (6)	C12—C13—H13A	109.5
C8—N3—C7	109.3 (6)	C12—C13—H13B	109.5
C8—N3—C10	124.9 (6)	C12—C13—H13C	109.5
N1—C1—H1	119.5	H13A—C13—H13B	109.5
N1—C1—C2	121.1 (9)	H13A—C13—H13C	109.5
C2—C1—H1	119.5	H13B—C13—H13C	109.5
C1—C2—H2	120.8	C12—C14—H14A	109.5
C3—C2—C1	118.4 (8)	C12—C14—H14B	109.5
C3—C2—H2	120.8	C12—C14—H14C	109.5
C2—C3—H3	119.4	H14A—C14—H14B	109.5
C2—C3—C4	121.3 (9)	H14A—C14—H14C	109.5
C4—C3—H3	119.4	H14B—C14—H14C	109.5
C3—C4—H4	121.5	C16—C15—S1	116.9 (6)
C3—C4—C5	117.0 (10)	C16—C15—C20	120.2 (7)
C5—C4—H4	121.5	C20—C15—S1	122.7 (6)
N1—C5—N2	113.0 (6)	C15—C16—H16	120.4
N1—C5—C4	123.2 (8)	C15—C16—C17	119.2 (8)
C4—C5—N2	123.8 (8)	C17—C16—H16	120.4
N2—C6—H6	126.8	C16—C17—H17	119.3
C7—C6—N2	106.5 (7)	C16—C17—C18	121.4 (8)
C7—C6—H6	126.8	C18—C17—H17	119.3
N3—C7—H7	126.3	C17—C18—C21	121.0 (8)
C6—C7—N3	107.4 (7)	C19—C18—C17	117.9 (7)
C6—C7—H7	126.3	C19—C18—C21	121.1 (8)
N2—C8—Pd1	116.1 (5)	C18—C19—H19	119.3
N3—C8—Pd1	137.2 (6)	C20—C19—C18	121.5 (8)
N3—C8—N2	106.7 (7)	C20—C19—H19	119.3
S1—C9—H9A	108.7	C15—C20—H20	120.1
S1—C9—H9B	108.7	C19—C20—C15	119.7 (8)
H9A—C9—H9B	107.6	C19—C20—H20	120.1
C10—C9—S1	114.1 (5)	C18—C21—H21A	109.5
C10—C9—H9A	108.7	C18—C21—H21B	109.5
C10—C9—H9B	108.7	C18—C21—H21C	109.5
N3—C10—C9	111.0 (5)	H21A—C21—H21B	109.5
N3—C10—H10	107.3	H21A—C21—H21C	109.5
N3—C10—C11	110.6 (5)	H21B—C21—H21C	109.5

Pd1—S1—C9—C10	58.1 (5)	C7—N3—C8—Pd1	−179.7 (6)
Pd1—S1—C15—C16	−143.9 (5)	C7—N3—C8—N2	−0.4 (8)
Pd1—S1—C15—C20	41.2 (7)	C7—N3—C10—C9	−144.6 (7)
Pd1—N1—C1—C2	−179.1 (6)	C7—N3—C10—C11	89.0 (8)
Pd1—N1—C5—N2	−0.3 (8)	C8—N2—C5—N1	−1.1 (9)
Pd1—N1—C5—C4	179.8 (6)	C8—N2—C5—C4	178.8 (8)
S1—C9—C10—N3	−69.7 (7)	C8—N2—C6—C7	0.8 (9)

S1—C9—C10—C11	55.2 (7)	C8—N3—C7—C6	0.9 (9)
S1—C15—C16—C17	−173.9 (6)	C8—N3—C10—C9	41.5 (9)
S1—C15—C20—C19	173.0 (6)	C8—N3—C10—C11	−84.8 (8)
N1—C1—C2—C3	0.7 (14)	C9—S1—C15—C16	105.7 (6)
N2—C6—C7—N3	−1.0 (9)	C9—S1—C15—C20	−69.3 (7)
N3—C10—C11—C12	−68.7 (7)	C9—C10—C11—C12	166.1 (5)
C1—N1—C5—N2	−178.3 (7)	C10—N3—C7—C6	−173.7 (7)
C1—N1—C5—C4	1.8 (12)	C10—N3—C8—Pd1	−5.0 (11)
C1—C2—C3—C4	−0.5 (15)	C10—N3—C8—N2	174.3 (6)
C2—C3—C4—C5	0.9 (15)	C10—C11—C12—C13	176.6 (6)
C3—C4—C5—N1	−1.6 (13)	C10—C11—C12—C14	−60.9 (9)
C3—C4—C5—N2	178.6 (8)	C15—S1—C9—C10	172.5 (5)
C5—N1—C1—C2	−1.3 (12)	C15—C16—C17—C18	1.5 (13)
C5—N2—C6—C7	177.4 (7)	C16—C15—C20—C19	−1.8 (12)
C5—N2—C8—Pd1	2.0 (8)	C16—C17—C18—C19	−3.5 (12)
C5—N2—C8—N3	−177.4 (6)	C16—C17—C18—C21	174.6 (8)
C6—N2—C5—N1	−177.5 (7)	C17—C18—C19—C20	2.9 (12)
C6—N2—C5—C4	2.4 (13)	C18—C19—C20—C15	−0.3 (12)
C6—N2—C8—Pd1	179.2 (5)	C20—C15—C16—C17	1.2 (12)
C6—N2—C8—N3	−0.2 (8)	C21—C18—C19—C20	−175.2 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br1	0.93	2.90	3.510 (10)	124
C6—H6···Br2$^{\text{i}}$	0.93	2.74	3.661 (9)	173
C10—H10···Br3	0.98	2.78	3.624 (7)	144
C16—H16···Br3$^{\text{ii}}$	0.93	3.11	3.742 (7)	127

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