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Synthesis and crystal structures of new chiral 3-amino-2*H*-azirines and the Pd complex of one of them

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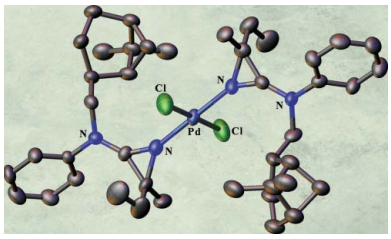
3-Amino-2*H*-azirines are potentially versatile building blocks in heterocyclic and peptide synthesis. Three new 3-amino-2*H*-azirines have been synthesized as racemates or mixtures of diastereoisomers in cases where another chiral residue is incorporated as the exocyclic amine. The crystal structures of two of them, an approximately 1:1 diastereoisomeric mixture of (2*R*)- and (2*S*)-2-ethyl-3-[(2*S*)-2-(1-methoxy-1,1-diphenylmethyl)pyrrolidin-1-yl]-2-methyl-2*H*-azirine, $C_{23}H_{28}N_2O$, **11**, and 2-benzyl-3-(*N*-methyl-*N*-phenylamino)-2-phenyl-2*H*-azirine, $C_{22}H_{20}N_2$, **12**, and the third as its diastereoisomeric *trans*-$PdCl_2$ complex, *trans*-dichlorido[(2*R*)-2-ethyl-2-methyl-3-(*X*)-2*H*-azirine][(2*S*)-2-ethyl-2-methyl-3-(*X*)-2*H*-azirine]palladium(II), where *X* = *N*-{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-methyl}-*N*-phenylamino, $[PdCl_2(C_{21}H_{30}N_2)_2]$, **14**, have been determined and the geometries of the azirine rings compared with those of 11 other 3-amino-2*H*-azirine structures reported in the literature. Most notable is the very long formal N—C single bond, which is, with one exception, around 1.57 Å. Each compound has crystallized in a chiral space group. The Pd atom in the *trans*-$PdCl_2$ complex is coordinated by one of each of the pair of diastereoisomers, while both of the diastereoisomers share the same crystallographic site in the structure of **11**; this property thereby manifesting itself as disorder. The chosen crystal of **12** is either an inversion twin or composed of a pure enantiomorph, but this could not be established specifically.

1. Introduction

Since the first synthesis of 3-amino-2*H*-azirines (Rens & Ghosez, 1970), the chemistry of these three-membered cyclic amidines has been studied intensively (Heimgartner, 1979, 1981, 1986, 1991; Eremeev & Piskunova, 1990). They have been found to be versatile building blocks in heterocyclic and peptide synthesis. In comparison with the better known 3-aryl-2*H*-azirines (three-membered cyclic imines), the 3-amino derivatives are stronger bases and more reactive nucleophiles. For example, 3-phenyl-2*H*-azirine reacts with carboxylic acids in refluxing benzene to give the corresponding *N*-phenacylcarboxamides (Sato *et al.*, 1967; Black & Doyle, 1978), and the reaction of 2,2-dimethyl-3-phenyl-2*H*-azirine with mercaptoacetic acid was performed in acetone at 343 K for 15 h yielding *N*-(1,1-dimethyl-2-oxo-2-phenylethyl)-2-mercaptoacetamide (Él'kinson & Eremeev, 1986). Only 3-alkyl-2*H*-azirine-2-phosphine oxides exhibited a higher reactivity; a slow reaction with carboxylic acids in tetrahydrofuran (THF) occurs already at room temperature within 1–4 days (Palacios *et al.*, 2002). On the other hand, *N*,*N*-disubstituted 3-amino-2*H*-azirines of type **1** react with carboxylic acids (Vittorelli *et al.*, 1974; Obrecht & Heimgartner, 1983) and N-protected amino acids



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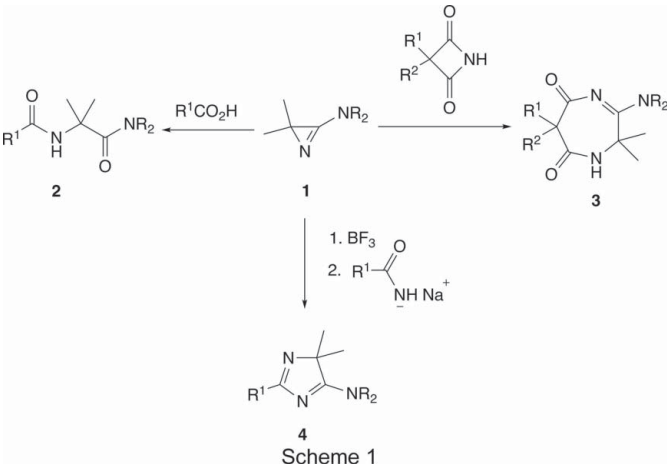
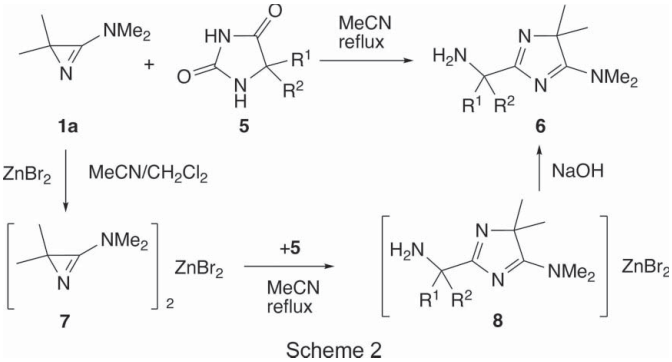
(Obrecht & Heimgartner, 1987; Wipf & Heimgartner, 1988; Dannecker-Dörig *et al.*, 2011) at 273–298 K within a few minutes to give products of type **2** (Scheme 1). The analogous reaction of 3-amino-2-phenylcarbamoyl-2*H*-azirine with acetic acid in acetone was carried out at 323 K within 1 h (Eremeev *et al.*, 1985).



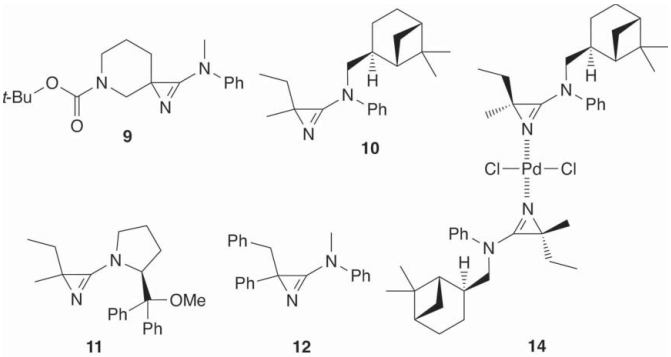
Scheme 1

Furthermore, 3-amino-2*H*-azirines, **1**, react spontaneously with NH-acidic heterocycles if their pK_a value is less than 8 (Chaloupka *et al.*, 1977; Scholl *et al.*, 1978). For example, the reaction with 3,3-disubstituted azetidine-2,4-diones (malonimides) in 2-propanol at room temperature yields 1,4-diazepine derivatives, **3** (Scheme 1). In all of these reactions, **1** has to be activated by protonation to enable the addition of the nucleophilic compound. On the other hand, reactions of **1** with non-acidic N-nucleophiles, such as primary amino compounds (Hugener & Heimgartner, 1995) or sodium amidates (Arnhold *et al.*, 1995), can be performed *via* BF_3 catalysis. In the latter case, 4,4-disubstituted 5-amino-4*H*-imidazoles, **4**, are formed (Scheme 1); the reaction mechanism is explained by the initial complexation of the ring N atom of **1** with BF_3. Similarly, the $ZnCl_2$-catalyzed reaction of 3-aryl-2*H*-azirines with benzimidates has been elaborated as an efficient preparation of imidazoles (Shi *et al.*, 2018).



Scheme 2

Based on these results, we expected that reactions of **1** with nucleophiles may also be catalyzed by complexation of **1** with $ZnBr_2$ or $PdCl_2$. Corresponding complexes of 3-amino-2*H*-azirines **1** are known (Hassner *et al.*, 1978; Dietliker *et al.*, 1978; Dos Santos Filho *et al.*, 1983; Heimgartner, 1991; Villalgordo & Heimgartner, 1993). Unfortunately, attempts to catalyze the reaction of **1a** with imidazolidine-2,4-diones (hydantoins), **5**, by using $ZnBr_2$ (Scheme 2) were only mildly successful (Schläpfer-Dähler *et al.*, 1992). Whereas the formation of the 4*H*-imidazole derivatives, **6**, from **1a** and **5** was achieved in refluxing acetonitrile within two days, the reaction of the azirine complex **7** with **5** was complete after 14–24 h, and after decomplexation of the 4*H*-imidazole complexes, **8**, by treatment with NaOH, compounds **6** were obtained in slightly increased yields.



Scheme 3

On the other hand, we successfully used the complexation of the heterospirocyclic 3-amino-2*H*-azirine, **9**, with $PdCl_2$ for the chromatographic purification of this compound as a racemate (Villalgordo & Heimgartner, 1993). Because 3-amino-2*H*-azirines with two different substituents at the alkyl atom, C2, of the azirine ring, *e.g.* **10**–**12**, are useful building blocks for chiral α,α-disubstituted α-amino acids, the separation of the diastereoisomers or enantiomers is an important issue (Bucher *et al.*, 1995, 1996, 2020; Brun *et al.*, 2001, 2002). Therefore, we synthesized the azirines **10**–**12** with the aim of separating the stereoisomers after their direct crystallization or crystallization of their $PdCl_2$ complexes (Scheme 3).

2. Experimental

2.1. Synthesis and crystallization

The 3-amino-2*H*-azirines **10**–**12** were prepared according to previously described syntheses. In the case of **10**, sequential treatment of 1 g (3.19 mmol) of a diastereomeric mixture of the corresponding 2-methylbutyric acid amide, **13**, bearing the chiral residue derived from (−)-*trans*-myrtanol, in dry THF (15 ml) with lithium diisopropylamide (LDA), diphenylphosphoryl chloride (DPPCl) and NaN_3 in DMF (Scheme 4; Villalgordo, 1992; *cf.* Villalgordo & Heimgartner, 1993) led to the desired product. Chromatographic work-up on SiO_2 (hexane–AcOEt, 9:1 *v*/*v*) gave 712 mg (72%) of **10** as a mixture of diastereoisomers as a slightly yellow oil. To a well-stirred suspension of 156 mg (0.654 mmol) $PdCl_2$ in dry acetonitrile (MeCN, 1.5 ml) at 273 K was added a solution of 200 mg (0.654 mmol) of azirine **10** in MeCN (0.5 ml). After stirring for 10 h, the solvent was partially evaporated and the

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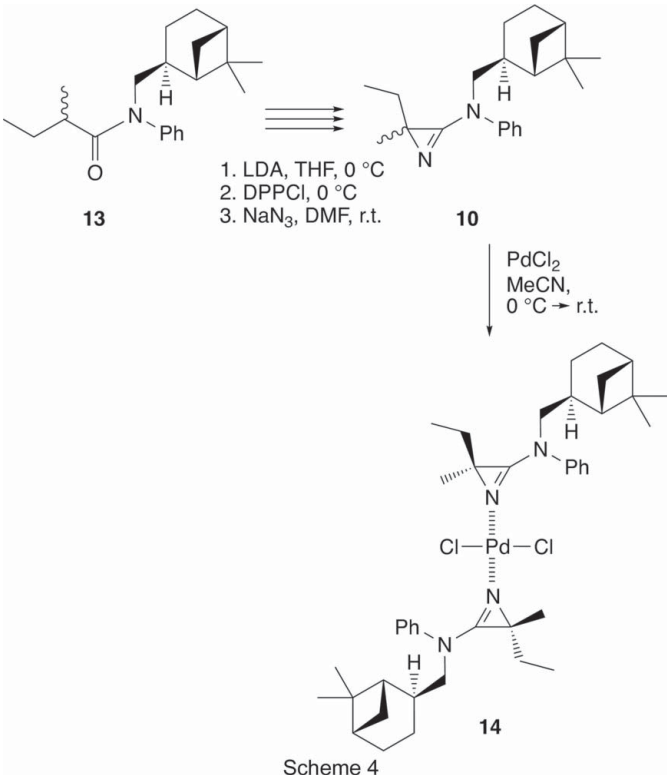
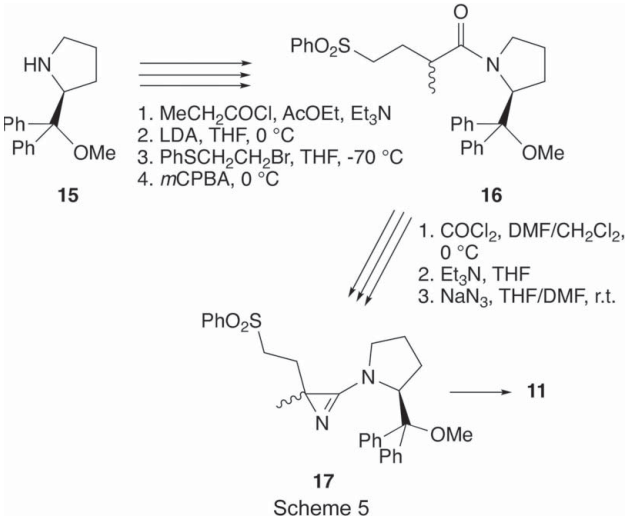
residue was filtered through a short column of SiO_2 (hexane–ethyl acetate, 9:1 *v*/*v*). Evaporation of the solvents gave 475 mg (92%) of the Pd complex, **14**, as a red–orange solid. Recrystallization from MeCN by slow evaporation of the solvent yielded orange crystals of suitable quality for crystal structure analysis. The crystal structure of **14** revealed that one of each of the diastereoisomers of **10** were coordinated to the Pd centre to give a molecule with the absolute stereochemistry shown in Scheme 4.

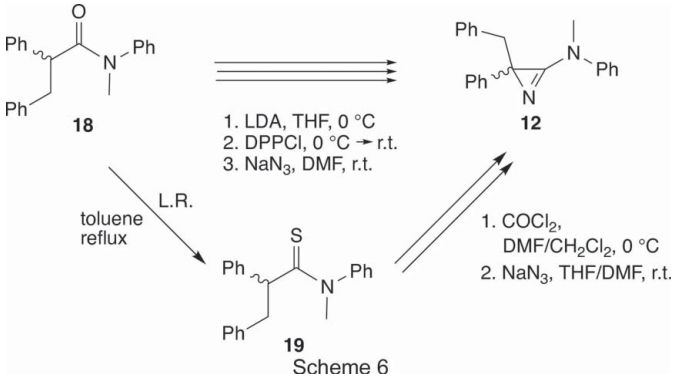


Scheme 4



Scheme 5

Starting with the known (*S*)-pyrrolidine derivative **15** (Enders *et al.*, 1988), the azirine **17** was prepared following procedures described earlier (Scheme 5; Bucher, 1996; *cf.* Bucher & Heimgartner, 1996). Whereas the precursor **16** was obtained in good yield (84%) as a mixture of diastereoisomers, the standard transformation to the aminoazirine led to a *ca* 2:1 mixture of the diastereomeric azirines **17** in only 10% yield. The electrolytical removal of the phenylsulfonyl group (–2.1 V, EtOH, Me_4NCl, 278 K; *cf.* Bucher & Heimgartner, 1996) gave only a few crystals of the desired azirine **11**, which were recrystallized from MeOH/Et_2O, yielding crystals suitable for crystal structure determination.



Scheme 6

3-Amino-2-benzyl-2-phenyl-2*H*-azirine **12** was synthesized either from the amide **18** (*cf.* Villalgordo & Heimgartner, 1993) or the thioamide **19** (*cf.* Bucher *et al.*, 1995; Brun *et al.*, 2002), respectively (Scheme 6). In the first case, starting with 2.50 g (7.9 mmol) of **18**, azirine **12** was obtained in 70% yield (1.74 g) as a slightly yellow oil, which solidified under high vacuum (Gubler, 1996). In the second approach, the amide **18** was transformed into the thioamide **19** in 94% yield, and 19.20 g (57.9 mmol) of the latter were treated with phosgene in DMF/CH_2Cl_2 and then with sodium azide in THF/DMF to give 11.05 g (61%) of azirine **12** as a yellowish solid. Recrystallization of the azirine **12** from Et_2O/hexane yielded colourless crystals of a single enantiomer suitable for a crystal structure analysis.

2.2. Analytical and spectroscopic data

Compound **10** (mixture of diastereoisomers): slightly yellow oil; IR ($CHCl_3$): 2970 (*s*), 2920 (*s*), 2870 (*m*), 1745 (*s*), 1600 (*s*), 1500 (*s*), 1455 (*m*), 1375 (*m*), 1365 (*m*), 1290 (*m*), 1240 (*m*), 1185 (*s*), 1155 (*m*), 1100 (*m*), 965 (*m*), 690 (*m*) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.4–7.0 (*m*, 5 arom. H), 3.72 (*br s*, CH_2N), 2.53 (*br s*, 1H), 2.15–2.05 (*m*, 1H), 1.9–1.55 (*m*, 9H), 1.39, 1.16 (2*s*, 2 Me), 0.74 (*br s*, Me), 0.73 (*s*, Me); ^{13}C NMR ($CDCl_3$): δ 166.6 (*s*, C═N), 150.3, 141.7 (2*s*, 1 arom. C), 129.6, 129.1, 125.3, 123.1, 119.9, 117.3 (6*d*, 5 arom. CH), 63.4, 51.4 (2*t*, CH_2N), 42.6 (*d*, CH), 40.5 (*q*, Me), 38.9 (*s*, Me_2C), 32.5 (*d*, CH), 30.0, 29.9 (2*t*, CH_2), 26.4 (*d*, CH), 23.7, 23.3 (2*t*, 2 CH_2), 19.7 (*q*, Me), 19.0, 18.9 (2*t*, CH_2), 9.6 (*q*, Me); CI–MS: 311 (100, $[M + 1]^+$). Compound **14**: orange solid; m.p. 411–413 K; IR (KBr): 2910 (*s*), 1800 (*s*), 1595 (*s*), 1495 (*s*), 1460 (*m*), 1380 (*m*), 1365 (*m*), 1230 (*m*), 1215 (*m*), 1200 (*m*), 1155 (*m*), 1080 (*m*), 1065 (*m*), 760 (*m*), 690 (*s*) cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.5–7.15 (*m*, 10 arom. H), 4.45–4.25 (*m*, 1H), 4.2–3.95 (*m*, 2H), 3.66 (*br s*, 2H),

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Table 1
Experimental details.

Experiments were carried out at 173 K with Mo $K\alpha$ radiation using a Rigaku AFC-5R diffractometer. H-atom parameters were constrained.

	11	**12**	**14**
Crystal data			
Chemical formula	$C_{23}H_{28}N_2O$	$C_{22}H_{20}N_2$	$[PdCl_2(C_{21}H_{30}N_2)_2]$
M_r	348.47	312.40	798.24
Crystal system, space group	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$	Triclinic, $P1$
a, b, c (Å)	7.792 (4), 14.462 (6), 9.113 (3)	10.642 (2), 15.8762 (18), 10.273 (2)	9.070 (2), 10.504 (6), 11.756 (2)
α, β, γ (°)	90, 105.87 (3), 90	90, 90, 90	80.14 (3), 76.054 (19), 73.67 (2)
V (Å^3)	987.8 (8)	1735.7 (5)	1036.7 (7)
Z	2	4	1
μ (mm^{-1})	0.07	0.07	0.61
Crystal size (mm)	0.38 × 0.23 × 0.23	0.48 × 0.40 × 0.35	0.48 × 0.25 × 0.25
Data collection			
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3163, 2962, 1920	3349, 3238, 2569	6352, 6046, 5673
R_{int}	0.029	0.014	0.015
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.703	0.703	0.704
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.157, 1.02	0.043, 0.118, 1.04	0.033, 0.087, 1.06
No. of reflections	2962	3238	6046
No. of parameters	345	218	600
No. of restraints	398	0	629
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.27	0.22, −0.18	0.73, −0.34
Absolute structure	Absolute structure set to match the known *S*-configuration at atom C9 of the pyrrolidine residue	Absolute structure chosen arbitrarily	Flack parameter determined by classical intensity fit (Flack & Bernardinelli, 1999, 2000)
Absolute structure parameter	−1 (3)	−1.8 (10)	−0.02 (2)

Computer programs: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991), *TEXSAN PROCESS* (Molecular Structure Corporation, 1989), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2020).

2.3–1.9 (*m*, 4H), 1.85–1.45 (*m*, 15H), 1.4–1.25 (*m*, 8H), 1.15–1.05 (*m*, 7H), 0.75–0.55 (*m*, 11H); ^{13}C NMR (DMSO-d_6): δ 164.2, 164.0 (2*s*, 2 C═N), 140.3, 140.2 (2*s*, 2 arom. C), 130.1, 129.7, 125.7, 119.9, 119.7, 119.5 (6*d*, 10 arom. CH), 52.7, 52.5 (2*t*, 2 CH_2N), 49.2, 49.1 (2*s*, 2 C), 40.7, 40.6 (2*d*, 2 CH), 32.5, 32.1 (2*d*, 2 CH), 29.4, 29.3, 28.4, 28.3 (4*t*, 4 CH_2), 26.4, 26.3 (2*q*, 2 Me), 23.6, 23.5 (2*t*, 2 CH_2), 22.8, 22.6 (2*d*, 2 CH), 19.8, 19.6 (2*q*, 2 Me), 18.4, 18.2 (2*t*, 2 CH_2), 9.6, 9.2 (2*q*, 2 Me).

Compound **16** (mixture of diastereoisomers): colourless oil; IR ($CHCl_3$): 3000 (*m*), 1625 (*s*), 1495 (*w*), 1465 (*m*), 1450 (*s*), 1310 (*s*), 1150 (*s*), 1090 (*s*), 1075 (*s*), 705 (*s*), 690 (*m*) cm^{-1}; ^{1}H NMR ($CDCl_3$) (2 diastereoisomers, 1 rotamer): δ 7.95–7.85, 7.7–7.55, 7.45–7.35 (3*m*, 15 arom. H), 5.55, 5.41, 5.00 (3*d*, 1H), 3.7–3.65, 3.6–3.5 (2*m*, 1H), 3.3–2.95 (*m*, 2.5H), 2.9–2.8 (*m* with 3*s* at 2.89, 2.86, and 2.83, 1H and MeO), 2.7–2.6 (*m*, 0.5H), 2.2–1.85 (*m*, 4H), 1.55–1.35 (*m*, 1H), 1.2–1.05 (*m* with 2*d* at 1.18, 1.06, 2.5H), 1.1–0.95 (*m*, 1H), 0.85–0.75 (*m*, 0.5 H); CI–MS: 492 ($[M + H]^+$), 460 ($[M - MeO]^+$). Compound **17** (mixture of diastereoisomers): colourless solid; IR (KBr): 2950 (*m*, broad), 1765 (*s*), 1450 (*s*), 1310 (*s*), 1150 (*s*), 1085 (*m*), 1070 (*m*), 760 (*m*), 705 (*m*), 690 (*m*) cm^{-1}; ESI–MS: 511 ($[M + Na]^+$), 489 ($[M + H]^+$). Compound **11** (mixture of diastereoisomers): colourless crystals.

Compound **12** (mixture of enantiomers): yellowish solid; m.p. 345–348 K; IR ($CHCl_3$): 2985 (*m*), 1760 (*s*, broad), 1600 (*s*), 1498 (*s*), 1452 (*m*), 1390 (*m*), 1326 (*m*), 1283 (*m*), 1110 (*m*), 1075 (*m*), 696 (*m*); ^{1}H NMR (DMSO-d_6): δ 7.4–7.05 (*m*, 15 arom. H), 3.61, 3.49 (AB, J_{AB} = 15.0, $PhCH_2$), 3.26 (*s*, MeN); ^{13}C NMR (DMSO-d_6): δ 159.6 (*s*, C═N), 143.4, 142.7, 138.0 (3*s*, 3 arom. C), 130.1, 129.5, 128.5, 128.1, 126.8, 126.7, 126.3, 123.6, 117.6 (9*d*, 15 arom. CH), 41.3 (*s*, C2), 40.3 (*t*, $PhCH_2$), 36.0 (*q*, CH_3N); EI–MS: 312 ($M^{+\cdot}$), 297 ($[M - CH_3]^+$), 221 ($[M - C_7H_7]^+$), 206, 178, 118, 103, 91, 77.

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For each structure, the methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about the C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.95 (aromatic), 0.99 (methylene) or 1.00 Å (methine) and with U_{iso}(H) = 1.2U_{eq}(C).

The molecule in the crystal structure of compound **11** is disordered in two regions. Atom C7 of the five-membered ring occupies two positions which represent alternate envelope conformations of the ring; the site-occupation factor of the major conformer refined to 0.619 (18). In addition, the azirine ring and its C2-ethyl and methyl substituents required three sets of positions to adequately model the arrangement. These positions indicate that the 2*R* and 2*S* diastereoisomers have crystallized at the same crystallographic site in the crystal and that the 2*S* diastereoisomer is further disordered over two conformations. The site occupation of the 2*R* configuration at atom C2 refined to 0.432 (3), while the site-occupation factors for the two conformations of the 2*S* diastereoisomer refined to

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0.305 (3) and 0.263 (3) for the conformations containing atoms with *A* and *B* suffixes, respectively, in their labels (Fig. 1). Target bond-length restraints were applied to the disordered atoms. In addition, similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while neighbouring atoms within and between each arrangement of the disordered groups were restrained to have similar atomic displacement parameters.

In the structure of **14**, the chiral residue derived from (−)-*trans*-myrtanol in each ligand is conformationally disordered. Two sets of positions were defined for the atoms of each disordered residue and the site-occupation factors of the major conformations of these groups refined to 0.621 (11) and 0.675 (9) for the ligands containing atoms N1 and N21, respectively. Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered C atoms, while neighbouring atoms within and between each conformation of the disordered groups were restrained to have similar atomic displacement parameters.

Table 2
Selected geometric parameters (Å, °) around the Pd atom of **14**.

Pd1—Cl1	2.3049 (19)	Pd1—N1	1.962 (6)
Pd1—Cl2	2.2988 (19)	Pd1—N21	1.999 (5)
Cl1—Pd1—Cl2	179.45 (9)	Cl2—Pd1—N1	89.11 (17)
Cl1—Pd1—N1	90.34 (16)	Cl2—Pd1—N21	90.82 (16)
Cl1—Pd1—N21	9.73 (16)	N1—Pd1—N21	179.6 (3)

3. Results and discussion

The syntheses described in the *Introduction* include nonstereospecific reactions during the azirine ring formation to give 3-amino-2*H*-azirines. Therefore, the products are expected to be either racemic mixtures or, when another residue in the molecule contains one or more invariant stereogenic centres, mixtures of diastereoisomers. The three crystal structures described here are of crystals obtained from the products **11** (Fig. 1), **12** (Fig. 2) and the $PdCl_2$ complex with **10** (**14**; Fig. 3). The chosen crystal in each case had crystallized in a chiral space group, which is a necessity for **11** and **14**, because these molecules contain invariant chiral exocyclic amine residues derived from the known (*S*)-pyrrolidine derivative, **15**, and (−)-*trans*-myrtanol {*i.e.* [(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]-heptan-2-yl]methanol}, respectively. The absolute structure chosen when refining the models for **11** and **14** was thus aligned to match the chirality of the known chiral residues. In the case of **14**, the strong anomalous scattering power imparted by the Pd and Cl atoms allowed the absolute configuration of all stereogenic centres to be confirmed confidently from the diffraction experiment by refinement of the absolute structure parameter (Flack & Bernardinelli, 1999, 2000), which converged to a value of −0.02 (2). The absolute structure of **11** could not be determined independently from the diffraction experiment on account of the weak anomalous scattering power of the compound with the available Mo *Kα* X-ray radiation (the work was carried out in the early 1990s when it was not common to use Cu *Kα* radiation routinely).

In contrast, compound **12** only contains a single stereogenic centre, which is at atom C2 of the azirine ring, so a racemic mixture could conceivably have crystallized in an achiral space group. Given that the synthesis of compound **12** most likely produced a racemic mixture of the product and not a single enantiomer, the fact that compound **12** crystallized in a chiral space group indicates that either a single enantiomer has crystallized in a spontaneous resolution process, or the crystal is an inversion twin and therefore a racemic mixture or another ratio (solid solution) of enantiomers. For the same reasons as given above for compound **11**, the absolute structure of **12** could not be determined. Therefore, the presence of

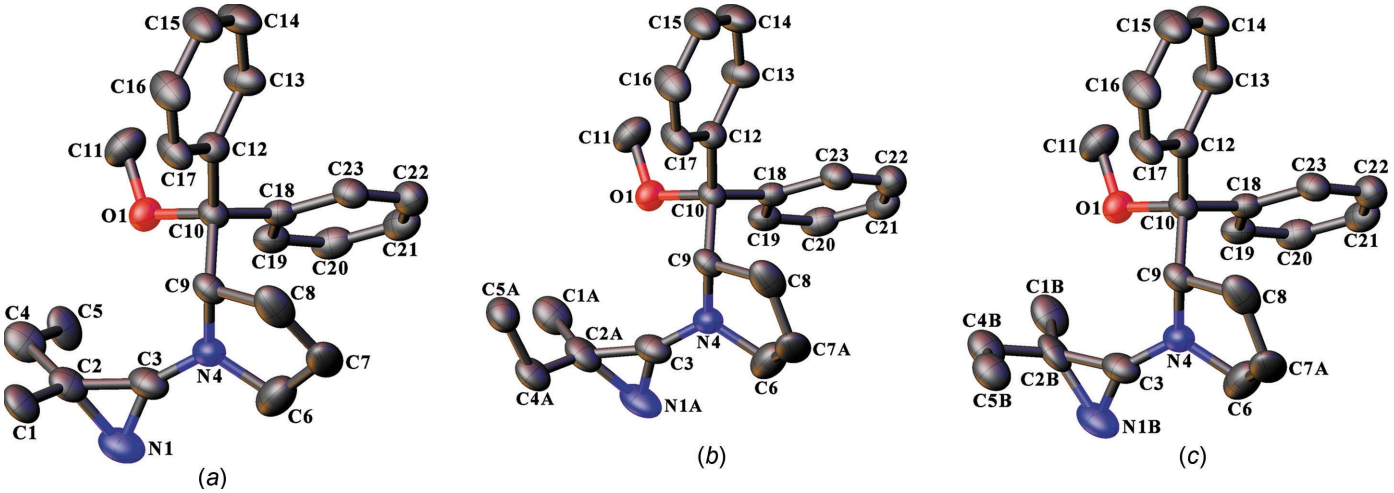

Figure 1
Views and atom-labelling schemes of the individual disordered components in the molecular structure of **11**, showing (*a*) the disorder component composed of the 2*R* diastereoisomer, and (*b*) the major and (*c*) the minor disordered conformations in the component composed of the 2*S* diastereoisomer. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. An overlay of all three disorder components is presented in the supporting information (Fig. S1).

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Table 3
Azirine ring geometry (Å, °) in 3-amino-2*H*-azirines.

CSD refcode/Compound No.	N1═C3	N1—C2	C2—C3	C3—N4	C3═N1—C2	N1═C3—C2	N1—C2—C3	Reference
ABUKUD	1.271 (3)	1.577 (3)	1.436 (3)	1.333 (3)	59.38 (16)	71.01 (19)	49.61 (15)	Brun *et al.* (2001)
ABULAK	1.275 (5)	1.577 (5)	1.436 (5)	1.347 (4)	59.4 (2)	70.9 (3)	49.8 (2)	Brun *et al.* (2001)
ABULEO	1.2712 (13)	1.5766 (16)	1.4290 (16)	1.3401 (12)	59.08 (7)	71.178 (7)	49.74 (7)	Brun *et al.* (2001)
ABULIS	1.277 (3)	1.570 (3)	1.435 (3)	1.340 (2)	59.49 (14)	70.47 (14)	50.05 (12)	Brun *et al.* (2001)
ABULOY	1.290 (8)	1.575 (7)	1.442 (10)	1.327 (9)	59.5 (4)	70.1 (5)	50.4 (4)	Brun *et al.* (2001)
HAGGUR	1.262	1.565	1.454	1.317	60.8	69.9	49.3	Piskunova *et al.* (1993)
JUNJEH	1.264 (3)	1.565 (3)	1.434 (3)	1.342 (3)	59.8 (2)	70.6 (2)	49.6 (1)	Villalgordo & Heimgartner (1992)
LERJUN	1.278 (3)	1.568 (3)	1.435 (4)	1.315 (4)	59.55 (18)	70.3 (2)	50.17 (16)	Peters *et al.* (2000)
MAZRPZ	1.254	1.575	1.428	1.343	59.4	71.6	49.1	Galloy *et al.* (1980)
PXCAZN	1.279	1.490	1.429	1.317	61.6	66.5	51.9	Galloy *et al.* (1974)
TIBFUF	1.283 (3)	1.568 (3)	1.438 (3)	1.322 (3)	59.56 (16)	70.12 (16)	50.32 (14)	Bucher & Heimgartner (1996)
11, 2*R* component	1.280 (6)	1.525 (6)	1.456 (6)	1.323 (5)	61.8 (3)	67.4 (4)	50.8 (3)	This work
11, 2*S* major component	1.281 (6)	1.515 (7)	1.448 (6)	1.323 (5)	61.7 (4)	67.1 (4)	51.1 (3)	This work
11, 2*S* minor component	1.283 (7)	1.517 (7)	1.475 (6)	1.323 (5)	62.9 (4)	66.3 (4)	50.7 (3)	This work
12	1.271 (3)	1.588 (3)	1.446 (3)	1.344 (3)	59.55 (14)	71.20 (16)	49.26 (12)	This work
14 ligand 1	1.294 (8)	1.550 (8)	1.476 (8)	1.326 (8)	61.8 (4)	67.7 (4)	50.5 (4)	This work
14 ligand 2	1.250 (8)	1.519 (8)	1.465 (9)	1.332 (8)	63.0 (4)	67.5 (5)	49.5 (4)	This work

a specific enantiomer or even an inversion twin could not be established and the configuration of the molecule defined in the refinement model and depicted in Fig. 2 was chosen arbitrarily.

The unique molecule in the crystal structure of compound **11** is disordered in two regions (Fig. 1). The five-membered pyrrolidine ring has two distorted envelope conformations, while the azirine ring and its C2-ethyl and methyl substituents are disordered over three arrangements. The disorder model indicates that the 2*R* and 2*S* diastereoisomers are present in the crystal and are distributed randomly at the same crystallographic site. There is a slight excess of the 2*S* diastereoisomer, which is disordered additionally over two conformations (see Section 2.3 for more details).

The crystal structure of compound **14** reveals one symmetry-unique *trans*-$PdCl_2L^1L^2$ complex molecule, where L^1 and L^2 are diastereoisomers of product **10**, which coordinate to the metal *via* their azirine ring N atom (Fig. 3). The diastereoisomers are the 2*S* and 2*R* species which result from interchange of the positions of the ethyl and methyl substituents at atom C2 of the azirine ring, while the configuration of the chiral residue derived from (−)-*trans*-myrtanol remains constant. It is perhaps remarkable that the Pd complex contains one of each of the pair of diastereoisomers, as conceivably the complex could consist of two of the same

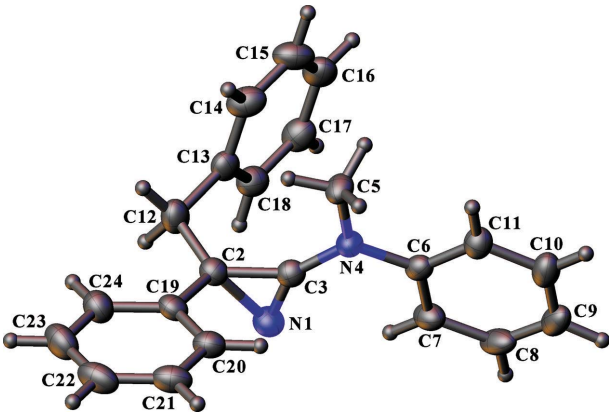

Figure 2
View of the molecule of **12**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

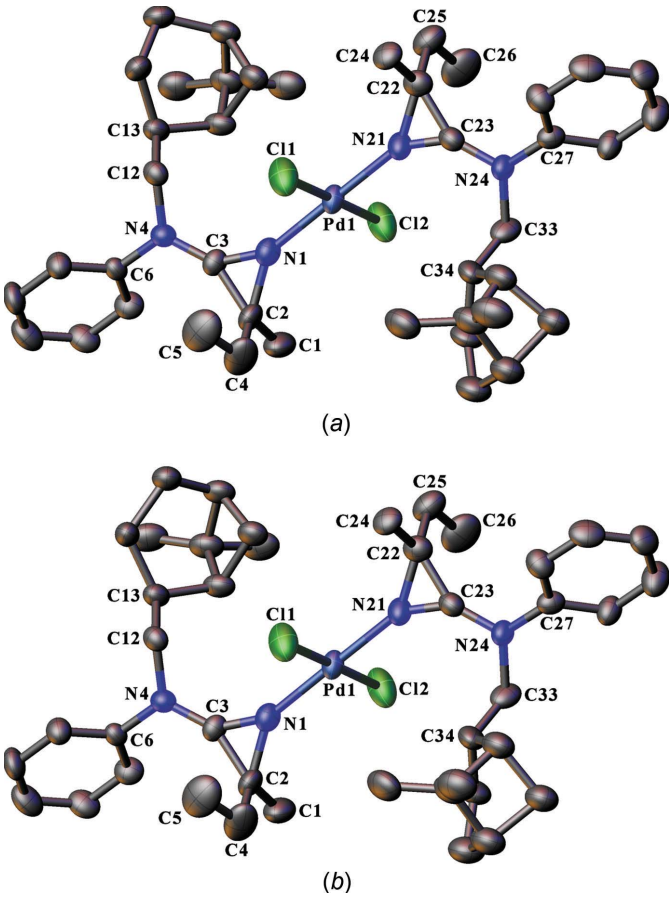

Figure 3
Views of the (*a*) major and (*b*) minor disorder components of the molecule of **14**, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. An overlay of the two disorder components is presented in the supporting information (Fig. S2).

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diastereoisomer or a nonstoichiometric ratio of the two diastereoisomers, which would manifest itself in the same sort of disorder of the ethyl and methyl substitution site that was observed for **11**, as described above. In the structure of **14**, the chiral residue derived from (−)-*trans*-myrtanol in each ligand is conformationally disordered (Fig. 3), but this has no consequence for the unique absolute configuration of the residue. The coordination geometry around the Pd atom is square planar, as usual, and the coordination geometry is listed in Table 2.

Reports of crystal structures of 3-amino-2*H*-azirines are quite rare. The Cambridge Structural Database (CSD; Version 5.43 with November 2022 updates; Groom *et al.*, 2016) lists only 11 structures, of which seven have been reported by the Heimgartner group (Villalgordo & Heimgartner, 1992; Bucher & Heimgartner, 1996; Brun *et al.*, 2001) and the remaining four were reported by Galloy *et al.* (1974, 1980), Piskunova *et al.* (1993) and Peters *et al.* (2000). The geometry of the azirine ring (Table 3) generally shows little variation across all of these structures. Possibly the most remarkable feature is the very long N—C single bond, which is, with one exception, always around 1.57 Å [mean 1.572 (5) Å for 10 structures], compared with N—C distances closer to 1.47 Å usually found for simple imines. This contrasts with the shorter formal C—C single bond with a mean length of 1.437 (7) Å. The short formal C—N single bond to the exocyclic N atom, with a mean value of 1.333 (12) Å, is likely a consequence of electron-pair delocalization between the exocyclic N atom and the ring N═C bond; Galloy *et al.* (1974) described this as the consequence of a contribution from a polar mesomeric form. The biggest ring geometry outlier amongst the 11 structures mentioned above is in the structure of 3-dimethylamino-2-dimethylcarbamoyl-2-phenoxy-2*H*-azirine (3-phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine) (Galloy *et al.*, 1974), in which, in particular, the ring N—C single bond of 1.49 Å is significantly shorter than in the other structures. This might result from the inductive electron-withdrawal properties of the O atom in the phenoxy substituent at the azirine ring sp^3-hybridized C atom, whereas all other structures have C atoms as the first atom of each substituent. The three new crystal structures reported here are no exception, notwithstanding the potential low accuracy for the disordered azirine ring in **11** because of the restraints applied while modelling the disorder; see Section 2.3. The coordination of the azirine rings *via* their N atom to the Pd atom in complex **14** also appears to influence very slightly the geometry of the azirine ring to give marginally shorter N—C and longer C—C single bonds, respectively (Table 3). This is perhaps unsurprising given the change in the electronic properties as a result of the coordination.

4. Conclusion

The 3-amino-2*H*-azirines **10**–**12** were synthesized with the aim of separating the stereoisomers after their direct crystallization or crystallization of their $PdCl_2$ complexes, as exemplified by complex **14**, which incorporates compound **10** as ligands. Unfortunately, this objective was not achieved, as the crystal structures of **11** and **14** revealed the presence of a diastereoisomeric mixture of the azirines in the crystals, and the crystal structure of **12** was inconclusive as to whether the chosen crystal was enantiomerically pure or also a racemic mixture that had crystallized as an inversion twin. Nonetheless, the study has added to the small number of recorded crystal structures of aminoazirines with their unusually long formal ring N—C single bonds.

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supporting information

Acta Cryst. (2023). C**79**, 104-111 [https://doi.org/10.1107/S2053229623001468]

Synthesis and crystal structures of new chiral 3-amino-2*H*-azirines and the Pd complex of one of them

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Computing details

For all structures, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009). Software used to prepare material for publication: *publCIF* (Westrip, 2010) for (11); *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2020) for (12), (14).

(2*R*)- and (2*S*)-2-ethyl-3-[(2*S*)-2-(1-methoxy-1,1-diphenylmethyl)pyrrolidin-1-yl]-2-methyl-2*H*-azirine (11)

Crystal data

$C_{23}H_{28}N_2O$
M_r = 348.47
Monoclinic, $P2_1$
a = 7.792 (4) Å
b = 14.462 (6) Å
c = 9.113 (3) Å
β = 105.87 (3)°
V = 987.8 (8) Å^3
Z = 2
$F(000)$ = 376
D_x = 1.172 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 17.7–19.8°
μ = 0.07 mm^{-1}
T = 173 K
Prism, colorless
0.38 × 0.23 × 0.23 mm

Data collection

Rigaku AFC-5R diffractometer
Radiation source: Rigaku rotating anode generator
Graphite crystal monochromator
ω–θ scans
3163 measured reflections
2962 independent reflections
1920 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 30.0°, θ_{min} = 2.7°
h = 0→10
k = 0→20
l = −12→12
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.157
S = 1.02
2962 reflections
345 parameters
398 restraints
Primary atom site location: dual

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Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.387P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Absolute structure set to match the known S-configuration at atom C9 of the pyrrolidine residue
Absolute structure parameter: −1 (3)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch
Solvent used: MeOH / diethyl ether Crystal mount: on a glass fibre Client: C.b Bucher Sample code: CB P7 (HG9418)

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 structure is disordered in two regions of the molecule. Atom C7 of the 5-membered ring occupies two positions which represent alternate envelope conformations of the ring; the site occupation factor of the major conformer refined to 0.619 (18). In addition, the azirine ring and its C2-ethyl and methyl substituents required three sets of positions to adequately model the arrangement. These positions indicate that the (2R)- and (2S)- diastereoisomers have crystallized at the same crystallographic site in the crystal and that the (2S)- diastereoisomer is further disordered over two conformations. The site occupation of the (2R)- configuration at atom C2 refined to 0.432 (3), while the site occupation factors for the two conformations of the (2S)- diastereoisomer refined to 0.305 (3) for atoms C4A and C5A, and 0.263 (3) for atoms C4B and C5B. Target bond length restraints were applied to the disordered atoms. In addition, similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while neighbouring atoms within and between each arrangement of the disordered groups were restrained to have similar atomic displacement parameters.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.5838 (3)	0.2687 (2)	0.7857 (2)	0.0394 (5)	
N4	0.2761 (4)	0.3773 (2)	0.7412 (3)	0.0391 (7)	
C3	0.3095 (5)	0.4107 (2)	0.6166 (4)	0.0469 (9)	
N1	0.2403 (9)	0.4569 (8)	0.4951 (9)	0.055 (2)	0.432 (3)
C1	0.5347 (14)	0.5438 (6)	0.5956 (12)	0.048 (2)	0.432 (3)
H11	0.490036	0.588250	0.512843	0.073*	0.432 (3)
H12	0.663803	0.536168	0.613321	0.073*	0.432 (3)
H13	0.509689	0.566543	0.688867	0.073*	0.432 (3)
C2	0.4432 (9)	0.4515 (5)	0.5519 (8)	0.0453 (17)	0.432 (3)
C4	0.5470 (12)	0.3901 (6)	0.4717 (10)	0.0509 (19)	0.432 (3)
H41	0.572393	0.425592	0.387164	0.061*	0.432 (3)
H42	0.662872	0.374579	0.544741	0.061*	0.432 (3)
C5	0.4550 (18)	0.3015 (7)	0.4081 (14)	0.049 (2)	0.432 (3)
H51	0.517168	0.273381	0.339185	0.074*	0.432 (3)
H52	0.331141	0.314694	0.351662	0.074*	0.432 (3)
H53	0.456706	0.258730	0.491853	0.074*	0.432 (3)
N1A	0.2141 (11)	0.4320 (11)	0.4828 (10)	0.059 (3)	0.305 (3)
C1A	0.500 (2)	0.3648 (11)	0.4341 (16)	0.057 (2)	0.305 (3)
H14	0.611841	0.343217	0.503556	0.085*	0.305 (3)
H15	0.523523	0.392972	0.343891	0.085*	0.305 (3)
H16	0.418230	0.312352	0.402761	0.085*	0.305 (3)

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C2A	0.4153 (12)	0.4355 (8)	0.5143 (11)	0.053 (2)	0.305 (3)
C4A	0.5117 (14)	0.5276 (8)	0.5362 (13)	0.049 (2)	0.305 (3)
H43	0.517250	0.550989	0.435510	0.059*	0.305 (3)
H44	0.442064	0.572571	0.578529	0.059*	0.305 (3)
C5A	0.6990 (16)	0.5224 (10)	0.6411 (15)	0.053 (3)	0.305 (3)
H54	0.767519	0.476113	0.602354	0.079*	0.305 (3)
H55	0.694080	0.504757	0.743686	0.079*	0.305 (3)
H56	0.756788	0.582874	0.645169	0.079*	0.305 (3)
N1B	0.2371 (12)	0.4361 (12)	0.4788 (10)	0.058 (3)	0.263 (3)
C1B	0.449 (3)	0.3092 (10)	0.438 (2)	0.057 (3)	0.263 (3)
H17	0.367265	0.262781	0.458566	0.086*	0.263 (3)
H18	0.572491	0.287417	0.477881	0.086*	0.263 (3)
H19	0.423465	0.319051	0.327738	0.086*	0.263 (3)
C2B	0.4262 (12)	0.3991 (7)	0.5150 (12)	0.050 (2)	0.263 (3)
C4B	0.5818 (15)	0.4642 (8)	0.5261 (15)	0.051 (2)	0.263 (3)
H45	0.694308	0.429129	0.564163	0.061*	0.263 (3)
H46	0.576978	0.486800	0.422501	0.061*	0.263 (3)
C5B	0.586 (3)	0.5465 (10)	0.629 (2)	0.052 (3)	0.263 (3)
H57	0.657153	0.596011	0.600889	0.078*	0.263 (3)
H58	0.639676	0.528418	0.735093	0.078*	0.263 (3)
H59	0.464160	0.568633	0.617069	0.078*	0.263 (3)
C6	0.0944 (6)	0.3839 (4)	0.7543 (6)	0.0659 (12)	
H61	0.020057	0.332941	0.697830	0.079*	0.619 (18)
H62	0.039791	0.443554	0.712919	0.079*	0.619 (18)
H63	0.036611	0.322403	0.745772	0.079*	0.381 (18)
H64	0.020735	0.425696	0.676014	0.079*	0.381 (18)
C7	0.1097 (8)	0.3770 (8)	0.9210 (7)	0.062 (2)	0.619 (18)
H71	0.071063	0.315196	0.946113	0.074*	0.619 (18)
H72	0.034522	0.424451	0.951486	0.074*	0.619 (18)
C8	0.3074 (6)	0.3929 (3)	1.0036 (5)	0.0570 (11)	
H81	0.344578	0.353592	1.095716	0.068*	0.619 (18)
H82	0.328751	0.458470	1.034533	0.068*	0.619 (18)
H83	0.298139	0.338972	1.067798	0.068*	0.381 (18)
H84	0.369048	0.443515	1.070746	0.068*	0.381 (18)
C7A	0.1251 (14)	0.4237 (12)	0.9132 (10)	0.062 (3)	0.381 (18)
H73	0.118637	0.492019	0.908818	0.074*	0.381 (18)
H74	0.033394	0.400656	0.960903	0.074*	0.381 (18)
C9	0.4115 (5)	0.3667 (2)	0.8881 (3)	0.0344 (7)	
H9	0.507096	0.413855	0.894181	0.041*	
C10	0.4983 (4)	0.2691 (2)	0.9076 (3)	0.0317 (6)	
C11	0.7023 (5)	0.1938 (4)	0.7849 (5)	0.0557 (11)	
H111	0.734010	0.193339	0.688003	0.084*	
H112	0.643836	0.135378	0.796830	0.084*	
H113	0.810578	0.201188	0.869352	0.084*	
C12	0.6416 (4)	0.2600 (3)	1.0622 (3)	0.0349 (7)	
C13	0.6851 (5)	0.1736 (3)	1.1310 (5)	0.0485 (10)	
H131	0.620618	0.120303	1.085823	0.058*	
C14	0.8228 (6)	0.1649 (3)	1.2657 (5)	0.0593 (12)	

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H141	0.849836	0.105971	1.312451	0.071*
C15	0.9193 (5)	0.2411 (3)	1.3310 (5)	0.0552 (11)
H151	1.012633	0.235270	1.422709	0.066*
C16	0.8790 (6)	0.3262 (3)	1.2620 (4)	0.0552 (11)
H161	0.946202	0.378865	1.306325	0.066*
C17	0.7429 (5)	0.3360 (3)	1.1297 (4)	0.0439 (9)
H171	0.717869	0.395255	1.083962	0.053*
C18	0.3539 (4)	0.1949 (2)	0.8815 (4)	0.0325 (7)
C19	0.2780 (5)	0.1600 (3)	0.7344 (4)	0.0371 (8)
H191	0.322535	0.179733	0.652326	0.045*
C20	0.1384 (5)	0.0969 (3)	0.7075 (4)	0.0433 (9)
H20	0.090329	0.073148	0.607439	0.052*
C21	0.0688 (5)	0.0681 (3)	0.8229 (5)	0.0454 (9)
H21	−0.028343	0.025945	0.803003	0.054*
C22	0.1426 (5)	0.1018 (3)	0.9690 (5)	0.0459 (9)
H22	0.096477	0.081816	1.049975	0.055*
C23	0.2823 (5)	0.1639 (3)	0.9981 (4)	0.0382 (8)
H23	0.330980	0.186023	1.099143	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0388 (12)	0.0475 (14)	0.0337 (11)	0.0035 (12)	0.0130 (9)	−0.0018 (12)
N4	0.0347 (15)	0.0380 (16)	0.0420 (17)	0.0017 (13)	0.0060 (12)	0.0072 (14)
C3	0.051 (2)	0.044 (2)	0.0366 (19)	−0.0013 (17)	−0.0027 (16)	0.0074 (15)
N1	0.067 (4)	0.050 (5)	0.036 (3)	−0.002 (3)	−0.007 (3)	0.002 (3)
C1	0.067 (4)	0.055 (4)	0.024 (4)	−0.002 (4)	0.014 (4)	0.007 (3)
C2	0.062 (3)	0.049 (3)	0.023 (3)	0.002 (3)	0.008 (3)	0.004 (3)
C4	0.072 (4)	0.054 (4)	0.024 (3)	−0.003 (3)	0.008 (3)	−0.008 (3)
C5	0.074 (4)	0.056 (4)	0.026 (4)	−0.006 (4)	0.026 (3)	−0.005 (3)
N1A	0.069 (4)	0.055 (5)	0.038 (4)	−0.014 (4)	−0.014 (4)	0.012 (4)
C1A	0.078 (4)	0.058 (4)	0.031 (4)	−0.005 (4)	0.010 (4)	−0.004 (4)
C2A	0.070 (3)	0.055 (4)	0.029 (3)	−0.007 (3)	0.005 (3)	0.010 (3)
C4A	0.066 (4)	0.054 (4)	0.026 (4)	−0.001 (4)	0.009 (4)	0.008 (4)
C5A	0.054 (5)	0.063 (5)	0.039 (4)	−0.006 (5)	0.009 (4)	0.007 (4)
N1B	0.067 (4)	0.056 (5)	0.038 (4)	−0.013 (4)	−0.010 (4)	0.011 (4)
C1B	0.078 (5)	0.065 (5)	0.029 (5)	−0.009 (5)	0.015 (4)	0.002 (4)
C2B	0.067 (3)	0.053 (4)	0.027 (3)	−0.013 (3)	0.009 (3)	0.013 (3)
C4B	0.065 (4)	0.056 (4)	0.030 (4)	−0.006 (4)	0.009 (3)	0.003 (3)
C5B	0.064 (5)	0.055 (5)	0.033 (5)	−0.006 (5)	0.007 (5)	0.002 (4)
C6	0.046 (2)	0.056 (3)	0.098 (3)	0.005 (2)	0.025 (2)	0.000 (3)
C7	0.071 (4)	0.045 (4)	0.086 (4)	0.026 (3)	0.048 (3)	0.020 (3)
C8	0.092 (3)	0.036 (2)	0.053 (2)	0.007 (2)	0.037 (2)	−0.0018 (17)
C7A	0.070 (5)	0.042 (5)	0.087 (5)	0.029 (5)	0.044 (4)	0.017 (5)
C9	0.0445 (18)	0.0312 (16)	0.0252 (15)	−0.0028 (15)	0.0056 (13)	0.0022 (13)
C10	0.0356 (15)	0.0328 (16)	0.0243 (13)	−0.0023 (15)	0.0042 (11)	0.0018 (13)
C11	0.043 (2)	0.062 (3)	0.063 (3)	0.0077 (19)	0.0155 (18)	−0.011 (2)
C12	0.0349 (15)	0.0378 (18)	0.0286 (14)	−0.0024 (15)	0.0028 (12)	0.0007 (14)

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C13	0.047 (2)	0.038 (2)	0.050 (2)	−0.0034 (17)	−0.0056 (17)	0.0050 (17)
C14	0.055 (2)	0.054 (3)	0.056 (2)	−0.002 (2)	−0.0083 (19)	0.021 (2)
C15	0.046 (2)	0.064 (3)	0.044 (2)	−0.0097 (19)	−0.0079 (17)	0.016 (2)
C16	0.055 (2)	0.059 (3)	0.041 (2)	−0.020 (2)	−0.0052 (18)	0.0031 (19)
C17	0.051 (2)	0.040 (2)	0.0331 (17)	−0.0149 (18)	−0.0003 (15)	0.0063 (15)
C18	0.0327 (15)	0.0287 (16)	0.0326 (16)	0.0047 (13)	0.0032 (12)	0.0000 (13)
C19	0.0400 (18)	0.0362 (18)	0.0325 (16)	0.0068 (15)	0.0053 (14)	−0.0014 (15)
C20	0.0391 (18)	0.0384 (19)	0.044 (2)	0.0027 (16)	−0.0024 (15)	−0.0106 (16)
C21	0.0340 (18)	0.0371 (19)	0.059 (2)	−0.0032 (15)	0.0022 (17)	−0.0012 (17)
C22	0.045 (2)	0.042 (2)	0.050 (2)	−0.0017 (18)	0.0125 (17)	0.0040 (18)
C23	0.0408 (17)	0.0354 (17)	0.0331 (16)	0.0001 (15)	0.0013 (14)	0.0028 (15)

Geometric parameters (Å, º)

O1—C11	1.424 (5)	C6—C7	1.494 (6)
O1—C10	1.443 (4)	C6—C7A	1.515 (7)
N4—C3	1.323 (5)	C6—H61	0.9900
N4—C6	1.456 (5)	C6—H62	0.9900
N4—C9	1.469 (4)	C6—H63	0.9900
C3—N1	1.280 (6)	C6—H64	0.9900
C3—N1A	1.281 (6)	C7—C8	1.535 (6)
C3—N1B	1.283 (7)	C7—H71	0.9900
C3—C2A	1.448 (6)	C7—H72	0.9900
C3—C2	1.456 (6)	C8—C7A	1.501 (7)
C3—C2B	1.475 (6)	C8—C9	1.541 (5)
N1—C2	1.525 (6)	C8—H81	0.9900
C1—C2	1.514 (7)	C8—H82	0.9900
C1—H11	0.9800	C8—H83	0.9900
C1—H12	0.9800	C8—H84	0.9900
C1—H13	0.9800	C7A—H73	0.9900
C2—C4	1.517 (6)	C7A—H74	0.9900
C4—C5	1.505 (7)	C9—C10	1.555 (5)
C4—H41	0.9900	C9—H9	1.0000
C4—H42	0.9900	C10—C18	1.526 (5)
C5—H51	0.9800	C10—C12	1.546 (4)
C5—H52	0.9800	C11—H111	0.9800
C5—H53	0.9800	C11—H112	0.9800
N1A—C2A	1.515 (7)	C11—H113	0.9800
C1A—C2A	1.508 (7)	C12—C17	1.395 (5)
C1A—H14	0.9800	C12—C13	1.398 (5)
C1A—H15	0.9800	C13—C14	1.398 (5)
C1A—H16	0.9800	C13—H131	0.9500
C2A—C4A	1.516 (7)	C14—C15	1.375 (6)
C4A—C5A	1.512 (7)	C14—H141	0.9500
C4A—H43	0.9900	C15—C16	1.377 (6)
C4A—H44	0.9900	C15—H151	0.9500
C5A—H54	0.9800	C16—C17	1.378 (5)
C5A—H55	0.9800	C16—H161	0.9500

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C5A—H56	0.9800	C17—H171	0.9500
N1B—C2B	1.517 (7)	C18—C23	1.402 (5)
C1B—C2B	1.511 (7)	C18—C19	1.403 (4)
C1B—H17	0.9800	C19—C20	1.390 (5)
C1B—H18	0.9800	C19—H191	0.9500
C1B—H19	0.9800	C20—C21	1.374 (6)
C2B—C4B	1.517 (7)	C20—H20	0.9500
C4B—C5B	1.509 (7)	C21—C22	1.386 (5)
C4B—H45	0.9900	C21—H21	0.9500
C4B—H46	0.9900	C22—C23	1.380 (5)
C5B—H57	0.9800	C22—H22	0.9500
C5B—H58	0.9800	C23—H23	0.9500
C5B—H59	0.9800		

C11—O1—C10	116.3 (3)	N4—C6—C7A	101.6 (5)
C3—N4—C6	118.0 (3)	N4—C6—H61	110.6
C3—N4—C9	124.0 (3)	C7—C6—H61	110.6
C6—N4—C9	113.8 (3)	N4—C6—H62	110.6
N1—C3—N4	142.9 (5)	C7—C6—H62	110.6
N1A—C3—N4	134.9 (5)	H61—C6—H62	108.7
N1B—C3—N4	143.9 (6)	N4—C6—H63	111.5
N1A—C3—C2A	67.1 (4)	C7A—C6—H63	111.5
N4—C3—C2A	157.3 (6)	N4—C6—H64	111.5
N1—C3—C2	67.4 (4)	C7A—C6—H64	111.5
N4—C3—C2	145.7 (4)	H63—C6—H64	109.3
N1B—C3—C2B	66.3 (4)	C6—C7—C8	106.2 (4)
N4—C3—C2B	142.9 (5)	C6—C7—H71	110.5
C3—N1—C2	61.8 (3)	C8—C7—H71	110.5
C2—C1—H11	109.5	C6—C7—H72	110.5
C2—C1—H12	109.5	C8—C7—H72	110.5
H11—C1—H12	109.5	H71—C7—H72	108.7
C2—C1—H13	109.5	C7A—C8—C9	107.1 (5)
H11—C1—H13	109.5	C7—C8—C9	105.9 (4)
H12—C1—H13	109.5	C7—C8—H81	110.6
C3—C2—C1	126.1 (6)	C9—C8—H81	110.6
C3—C2—C4	119.5 (6)	C7—C8—H82	110.6
C1—C2—C4	111.6 (6)	C9—C8—H82	110.6
C3—C2—N1	50.8 (3)	H81—C8—H82	108.7
C1—C2—N1	114.5 (8)	C7A—C8—H83	110.3
C4—C2—N1	120.4 (6)	C9—C8—H83	110.3
C5—C4—C2	115.1 (7)	C7A—C8—H84	110.3
C5—C4—H41	108.5	C9—C8—H84	110.3
C2—C4—H41	108.5	H83—C8—H84	108.5
C5—C4—H42	108.5	C8—C7A—C6	106.9 (5)
C2—C4—H42	108.5	C8—C7A—H73	110.3
H41—C4—H42	107.5	C6—C7A—H73	110.3
C4—C5—H51	109.5	C8—C7A—H74	110.3
C4—C5—H52	109.5	C6—C7A—H74	110.3

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H51—C5—H52	109.5	H73—C7A—H74	108.6
C4—C5—H53	109.5	N4—C9—C8	102.5 (3)
H51—C5—H53	109.5	N4—C9—C10	112.3 (3)
H52—C5—H53	109.5	C8—C9—C10	116.1 (3)
C3—N1A—C2A	61.7 (4)	N4—C9—H9	108.5
C2A—C1A—H14	109.5	C8—C9—H9	108.5
C2A—C1A—H15	109.5	C10—C9—H9	108.5
H14—C1A—H15	109.5	O1—C10—C18	110.7 (3)
C2A—C1A—H16	109.5	O1—C10—C12	109.4 (2)
H14—C1A—H16	109.5	C18—C10—C12	113.6 (3)
H15—C1A—H16	109.5	O1—C10—C9	101.2 (2)
C3—C2A—C1A	123.0 (8)	C18—C10—C9	109.9 (3)
C3—C2A—N1A	51.1 (3)	C12—C10—C9	111.4 (3)
C1A—C2A—N1A	116.8 (8)	O1—C11—H111	109.5
C3—C2A—C4A	118.8 (7)	O1—C11—H112	109.5
C1A—C2A—C4A	113.2 (7)	H111—C11—H112	109.5
N1A—C2A—C4A	120.3 (8)	O1—C11—H113	109.5
C5A—C4A—C2A	113.4 (7)	H111—C11—H113	109.5
C5A—C4A—H43	108.9	H112—C11—H113	109.5
C2A—C4A—H43	108.9	C17—C12—C13	117.9 (3)
C5A—C4A—H44	108.9	C17—C12—C10	121.0 (3)
C2A—C4A—H44	108.9	C13—C12—C10	120.8 (3)
H43—C4A—H44	107.7	C12—C13—C14	120.6 (4)
C4A—C5A—H54	109.5	C12—C13—H131	119.7
C4A—C5A—H55	109.5	C14—C13—H131	119.7
H54—C5A—H55	109.5	C15—C14—C13	120.4 (4)
C4A—C5A—H56	109.5	C15—C14—H141	119.8
H54—C5A—H56	109.5	C13—C14—H141	119.8
H55—C5A—H56	109.5	C14—C15—C16	119.3 (3)
C3—N1B—C2B	62.9 (4)	C14—C15—H151	120.4
C2B—C1B—H17	109.5	C16—C15—H151	120.4
C2B—C1B—H18	109.5	C15—C16—C17	121.1 (4)
H17—C1B—H18	109.5	C15—C16—H161	119.5
C2B—C1B—H19	109.5	C17—C16—H161	119.5
H17—C1B—H19	109.5	C16—C17—C12	120.8 (4)
H18—C1B—H19	109.5	C16—C17—H171	119.6
C3—C2B—C1B	124.2 (8)	C12—C17—H171	119.6
C3—C2B—C4B	120.4 (6)	C23—C18—C19	117.3 (3)
C1B—C2B—C4B	111.8 (7)	C23—C18—C10	122.4 (3)
C3—C2B—N1B	50.7 (3)	C19—C18—C10	120.1 (3)
C1B—C2B—N1B	115.8 (9)	C20—C19—C18	120.7 (3)
C4B—C2B—N1B	120.4 (8)	C20—C19—H191	119.7
C5B—C4B—C2B	114.4 (8)	C18—C19—H191	119.7
C5B—C4B—H45	108.7	C21—C20—C19	121.2 (3)
C2B—C4B—H45	108.7	C21—C20—H20	119.4
C5B—C4B—H46	108.7	C19—C20—H20	119.4
C2B—C4B—H46	108.7	C20—C21—C22	118.8 (4)
H45—C4B—H46	107.6	C20—C21—H21	120.6

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C4B—C5B—H57	109.5	C22—C21—H21	120.6
C4B—C5B—H58	109.5	C23—C22—C21	120.8 (4)
H57—C5B—H58	109.5	C23—C22—H22	119.6
C4B—C5B—H59	109.5	C21—C22—H22	119.6
H57—C5B—H59	109.5	C22—C23—C18	121.2 (3)
H58—C5B—H59	109.5	C22—C23—H23	119.4
N4—C6—C7	105.6 (4)	C18—C23—H23	119.4

C6—N4—C3—N1	7.5 (12)	N4—C6—C7—C8	15.1 (8)
C9—N4—C3—N1	−148.2 (10)	C6—C7—C8—C9	−24.1 (8)
C6—N4—C3—N1A	−18.2 (12)	C9—C8—C7A—C6	20.6 (13)
C9—N4—C3—N1A	−173.9 (11)	N4—C6—C7A—C8	−28.0 (12)
C6—N4—C3—N1B	−17.6 (15)	C3—N4—C9—C8	142.1 (4)
C9—N4—C3—N1B	−173.3 (14)	C6—N4—C9—C8	−14.5 (4)
C6—N4—C3—C2A	177.5 (13)	C3—N4—C9—C10	−92.6 (4)
C9—N4—C3—C2A	21.8 (15)	C6—N4—C9—C10	110.7 (4)
C6—N4—C3—C2	151.7 (7)	C7A—C8—C9—N4	−4.4 (8)
C9—N4—C3—C2	−4.0 (9)	C7—C8—C9—N4	23.0 (5)
C6—N4—C3—C2B	−150.7 (7)	C7A—C8—C9—C10	−127.2 (8)
C9—N4—C3—C2B	53.5 (9)	C7—C8—C9—C10	−99.8 (5)
N4—C3—N1—C2	159.1 (9)	C11—O1—C10—C18	−73.4 (3)
N1—C3—C2—C1	93.9 (10)	C11—O1—C10—C12	52.5 (4)
N4—C3—C2—C1	−63.7 (12)	C11—O1—C10—C9	170.1 (3)
N1—C3—C2—C4	−106.8 (8)	N4—C9—C10—O1	63.3 (3)
N4—C3—C2—C4	95.7 (9)	C8—C9—C10—O1	−179.3 (3)
N4—C3—C2—N1	−157.5 (10)	N4—C9—C10—C18	−53.8 (3)
C3—N1—C2—C1	−117.6 (7)	C8—C9—C10—C18	63.7 (4)
C3—N1—C2—C4	104.9 (8)	N4—C9—C10—C12	179.4 (3)
C3—C2—C4—C5	24.7 (11)	C8—C9—C10—C12	−63.1 (4)
C1—C2—C4—C5	−173.2 (9)	O1—C10—C12—C17	79.1 (4)
N1—C2—C4—C5	−34.7 (11)	C18—C10—C12—C17	−156.7 (3)
N4—C3—N1A—C2A	−173.5 (9)	C9—C10—C12—C17	−31.9 (4)
N1A—C3—C2A—C1A	−99.7 (11)	O1—C10—C12—C13	−94.6 (4)
N4—C3—C2A—C1A	68.3 (16)	C18—C10—C12—C13	29.6 (5)
N4—C3—C2A—N1A	168.0 (16)	C9—C10—C12—C13	154.4 (3)
N1A—C3—C2A—C4A	107.2 (10)	C17—C12—C13—C14	1.9 (6)
N4—C3—C2A—C4A	−84.9 (16)	C10—C12—C13—C14	175.8 (4)
C3—N1A—C2A—C1A	112.1 (10)	C12—C13—C14—C15	−1.1 (7)
C3—N1A—C2A—C4A	−104.3 (9)	C13—C14—C15—C16	−0.2 (7)
C3—C2A—C4A—C5A	90.7 (11)	C14—C15—C16—C17	0.6 (7)
C1A—C2A—C4A—C5A	−65.0 (13)	C15—C16—C17—C12	0.2 (7)
N1A—C2A—C4A—C5A	150.2 (10)	C13—C12—C17—C16	−1.4 (6)
N4—C3—N1B—C2B	−151.2 (11)	C10—C12—C17—C16	−175.3 (4)
N1B—C3—C2B—C1B	−97.1 (12)	O1—C10—C18—C23	163.1 (3)
N4—C3—C2B—C1B	54.9 (14)	C12—C10—C18—C23	39.6 (4)
N1B—C3—C2B—C4B	106.2 (11)	C9—C10—C18—C23	−85.9 (3)
N4—C3—C2B—C4B	−101.8 (11)	O1—C10—C18—C19	−21.7 (4)
N4—C3—C2B—N1B	152.0 (11)	C12—C10—C18—C19	−145.1 (3)

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C3—N1B—C2B—C1B	114.3 (10)	C9—C10—C18—C19	89.3 (3)
C3—N1B—C2B—C4B	−106.2 (9)	C23—C18—C19—C20	−0.4 (5)
C3—C2B—C4B—C5B	−8.9 (17)	C10—C18—C19—C20	−175.8 (3)
C1B—C2B—C4B—C5B	−168.3 (15)	C18—C19—C20—C21	1.2 (5)
N1B—C2B—C4B—C5B	50.7 (16)	C19—C20—C21—C22	−1.3 (6)
C3—N4—C6—C7	−158.3 (6)	C20—C21—C22—C23	0.8 (6)
C9—N4—C6—C7	−0.2 (6)	C21—C22—C23—C18	0.0 (6)
C3—N4—C6—C7A	−131.3 (8)	C19—C18—C23—C22	−0.2 (5)
C9—N4—C6—C7A	26.9 (8)	C10—C18—C23—C22	175.1 (3)

2-Benzyl-3-(*N*-methyl-*N*-phenylamino)-2-phenyl-2*H*-azirine (12)

Crystal data

$C_{22}H_{20}N_2$
M_r = 312.40
Orthorhombic, $P2_12_12_1$
a = 10.642 (2) Å
b = 15.8762 (18) Å
c = 10.273 (2) Å
V = 1735.7 (5) Å^3
Z = 4
$F(000)$ = 664
D_x = 1.196 Mg m^{-3}
Melting point: 346.5 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 18.4–19.7°
μ = 0.07 mm^{-1}
T = 173 K
Prism, colorless
0.48 × 0.40 × 0.35 mm

Data collection

Rigaku AFC-5R diffractometer
Radiation source: Rigaku rotating anode generator
Graphite crystal monochromator
ω–θ scans
3349 measured reflections
3238 independent reflections
2569 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 30.0°, θ_{min} = 2.6°
h = 0→14
k = −1→22
l = −1→14
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.118
S = 1.03
3238 reflections
218 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Absolute structure chosen arbitrarily
Absolute structure parameter: −1.8 (10)

Special details

Experimental. Solvent used: diethyl ether / hexane Crystal mount: on a glass fibre Client: R. Gubler Sample code: RG007 (HG9516)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.47471 (16)	0.55930 (11)	0.17401 (19)	0.0357 (4)
N4	0.48045 (16)	0.68242 (10)	0.02403 (17)	0.0298 (3)
C2	0.57272 (19)	0.61965 (12)	0.2438 (2)	0.0317 (4)
C3	0.50191 (18)	0.63046 (12)	0.1249 (2)	0.0299 (4)
C5	0.5554 (2)	0.76023 (13)	0.0159 (2)	0.0365 (5)
H51	0.608698	0.765053	0.093327	0.055*
H52	0.498972	0.808935	0.011182	0.055*
H53	0.608236	0.758474	−0.062126	0.055*
C6	0.39484 (18)	0.66107 (12)	−0.0765 (2)	0.0300 (4)
C7	0.3172 (2)	0.59000 (13)	−0.0653 (3)	0.0390 (5)
H7	0.318047	0.556987	0.011846	0.047*
C8	0.2388 (2)	0.56850 (14)	−0.1689 (3)	0.0476 (6)
H8	0.185136	0.520959	−0.160892	0.057*
C9	0.2373 (2)	0.61471 (16)	−0.2827 (3)	0.0460 (6)
H9	0.186946	0.597330	−0.354103	0.055*
C10	0.3103 (2)	0.68671 (17)	−0.2914 (2)	0.0437 (5)
H10	0.307541	0.720062	−0.368088	0.052*
C11	0.38768 (19)	0.71060 (15)	−0.1884 (2)	0.0358 (4)
H11	0.435803	0.760841	−0.194485	0.043*
C12	0.5270 (2)	0.66084 (16)	0.3694 (2)	0.0402 (5)
H121	0.510181	0.616303	0.434584	0.048*
H122	0.594692	0.697215	0.404212	0.048*
C13	0.4093 (2)	0.71334 (14)	0.35199 (19)	0.0345 (4)
C14	0.4185 (2)	0.79880 (15)	0.3213 (3)	0.0448 (6)
H14	0.499045	0.824068	0.313687	0.054*
C15	0.3118 (3)	0.84738 (15)	0.3016 (3)	0.0495 (6)
H15	0.320085	0.905244	0.279667	0.059*
C16	0.1941 (2)	0.81229 (16)	0.3138 (3)	0.0456 (6)
H16	0.121156	0.845694	0.300424	0.055*
C17	0.1830 (2)	0.72775 (16)	0.3456 (2)	0.0433 (5)
H17	0.102127	0.703224	0.355470	0.052*
C18	0.2898 (2)	0.67890 (15)	0.3632 (2)	0.0388 (5)
H18	0.281019	0.620780	0.383250	0.047*
C19	0.7071 (2)	0.59151 (12)	0.2360 (2)	0.0322 (4)
C20	0.7617 (2)	0.57313 (13)	0.1152 (2)	0.0368 (5)
H20	0.713755	0.579707	0.037893	0.044*
C21	0.8853 (2)	0.54538 (14)	0.1074 (3)	0.0439 (6)
H21	0.921138	0.533303	0.024830	0.053*
C22	0.9567 (2)	0.53517 (15)	0.2190 (3)	0.0506 (7)
H22	1.041028	0.515982	0.213240	0.061*
C23	0.9042 (2)	0.55311 (16)	0.3387 (3)	0.0501 (6)
H23	0.952904	0.546391	0.415487	0.060*
C24	0.7801 (2)	0.58105 (14)	0.3480 (3)	0.0410 (5)
H24	0.745023	0.593033	0.430960	0.049*

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Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0336 (8)	0.0332 (8)	0.0403 (9)	−0.0035 (7)	0.0002 (8)	0.0031 (8)
N4	0.0320 (8)	0.0265 (7)	0.0310 (8)	−0.0025 (7)	−0.0036 (7)	−0.0004 (7)
C2	0.0325 (9)	0.0295 (9)	0.0330 (10)	0.0007 (8)	0.0004 (8)	0.0025 (8)
C3	0.0270 (8)	0.0304 (9)	0.0322 (9)	0.0001 (8)	0.0020 (8)	−0.0019 (8)
C5	0.0425 (11)	0.0315 (10)	0.0355 (10)	−0.0107 (9)	−0.0085 (9)	0.0010 (9)
C6	0.0250 (9)	0.0296 (9)	0.0355 (10)	0.0036 (7)	−0.0025 (8)	−0.0063 (8)
C7	0.0352 (10)	0.0288 (9)	0.0529 (13)	0.0003 (8)	−0.0091 (10)	−0.0024 (10)
C8	0.0361 (11)	0.0311 (10)	0.0756 (18)	0.0026 (9)	−0.0168 (12)	−0.0155 (12)
C9	0.0366 (11)	0.0497 (13)	0.0517 (14)	0.0120 (10)	−0.0171 (11)	−0.0201 (12)
C10	0.0406 (11)	0.0553 (14)	0.0351 (11)	0.0095 (11)	−0.0069 (10)	−0.0074 (11)
C11	0.0314 (10)	0.0422 (11)	0.0338 (10)	0.0007 (9)	−0.0019 (8)	−0.0023 (9)
C12	0.0401 (11)	0.0500 (12)	0.0304 (10)	0.0077 (10)	−0.0013 (9)	0.0002 (10)
C13	0.0376 (10)	0.0390 (10)	0.0267 (9)	0.0047 (9)	0.0017 (9)	−0.0031 (9)
C14	0.0403 (11)	0.0398 (12)	0.0544 (14)	−0.0056 (10)	0.0097 (11)	−0.0089 (11)
C15	0.0576 (14)	0.0321 (11)	0.0588 (16)	0.0035 (10)	0.0106 (13)	−0.0047 (11)
C16	0.0453 (12)	0.0432 (12)	0.0484 (13)	0.0117 (10)	−0.0017 (11)	−0.0103 (11)
C17	0.0357 (11)	0.0487 (13)	0.0456 (13)	−0.0003 (10)	0.0012 (10)	−0.0078 (11)
C18	0.0437 (12)	0.0361 (11)	0.0366 (11)	−0.0018 (9)	0.0026 (10)	−0.0006 (9)
C19	0.0343 (9)	0.0244 (8)	0.0380 (10)	0.0024 (7)	−0.0010 (9)	0.0045 (8)
C20	0.0383 (11)	0.0294 (10)	0.0429 (12)	0.0032 (9)	0.0014 (10)	−0.0017 (9)
C21	0.0420 (12)	0.0314 (10)	0.0584 (15)	0.0036 (10)	0.0104 (11)	−0.0036 (11)
C22	0.0358 (11)	0.0367 (11)	0.079 (2)	0.0076 (9)	0.0005 (13)	0.0038 (13)
C23	0.0406 (12)	0.0453 (13)	0.0643 (17)	0.0058 (11)	−0.0112 (13)	0.0095 (13)
C24	0.0412 (12)	0.0394 (12)	0.0424 (13)	0.0033 (9)	−0.0044 (10)	0.0049 (10)

Geometric parameters (Å, º)

N1—C3	1.271 (3)	C12—H122	0.9900
N1—C2	1.588 (3)	C13—C18	1.389 (3)
N4—C3	1.344 (3)	C13—C14	1.396 (3)
N4—C6	1.418 (2)	C14—C15	1.387 (4)
N4—C5	1.472 (3)	C14—H14	0.9500
C2—C3	1.446 (3)	C15—C16	1.377 (4)
C2—C19	1.500 (3)	C15—H15	0.9500
C2—C12	1.526 (3)	C16—C17	1.387 (4)
C5—H51	0.9800	C16—H16	0.9500
C5—H52	0.9800	C17—C18	1.388 (3)
C5—H53	0.9800	C17—H17	0.9500
C6—C11	1.395 (3)	C18—H18	0.9500
C6—C7	1.403 (3)	C19—C24	1.398 (3)
C7—C8	1.395 (3)	C19—C20	1.401 (3)
C7—H7	0.9500	C20—C21	1.390 (3)
C8—C9	1.380 (4)	C20—H20	0.9500
C8—H8	0.9500	C21—C22	1.384 (4)
C9—C10	1.385 (4)	C21—H21	0.9500

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C9—H9	0.9500	C22—C23	1.380 (4)
C10—C11	1.393 (3)	C22—H22	0.9500
C10—H10	0.9500	C23—C24	1.396 (3)
C11—H11	0.9500	C23—H23	0.9500
C12—C13	1.515 (3)	C24—H24	0.9500
C12—H121	0.9900		

C3—N1—C2	59.55 (14)	C13—C12—H122	108.9
C3—N4—C6	121.59 (17)	C2—C12—H122	108.9
C3—N4—C5	117.81 (17)	H121—C12—H122	107.7
C6—N4—C5	120.47 (17)	C18—C13—C14	117.7 (2)
C3—C2—C19	119.13 (18)	C18—C13—C12	122.0 (2)
C3—C2—C12	119.83 (17)	C14—C13—C12	120.2 (2)
C19—C2—C12	118.48 (18)	C15—C14—C13	121.1 (2)
C3—C2—N1	49.26 (12)	C15—C14—H14	119.5
C19—C2—N1	114.98 (16)	C13—C14—H14	119.5
C12—C2—N1	115.54 (17)	C16—C15—C14	120.4 (2)
N1—C3—N4	144.4 (2)	C16—C15—H15	119.8
N1—C3—C2	71.20 (16)	C14—C15—H15	119.8
N4—C3—C2	144.39 (19)	C15—C16—C17	119.4 (2)
N4—C5—H51	109.5	C15—C16—H16	120.3
N4—C5—H52	109.5	C17—C16—H16	120.3
H51—C5—H52	109.5	C16—C17—C18	120.1 (2)
N4—C5—H53	109.5	C16—C17—H17	119.9
H51—C5—H53	109.5	C18—C17—H17	119.9
H52—C5—H53	109.5	C17—C18—C13	121.3 (2)
C11—C6—C7	119.27 (19)	C17—C18—H18	119.4
C11—C6—N4	120.03 (18)	C13—C18—H18	119.4
C7—C6—N4	120.69 (19)	C24—C19—C20	118.24 (19)
C8—C7—C6	119.1 (2)	C24—C19—C2	121.4 (2)
C8—C7—H7	120.5	C20—C19—C2	120.34 (19)
C6—C7—H7	120.5	C21—C20—C19	120.7 (2)
C9—C8—C7	121.5 (2)	C21—C20—H20	119.7
C9—C8—H8	119.2	C19—C20—H20	119.7
C7—C8—H8	119.2	C22—C21—C20	120.6 (3)
C8—C9—C10	119.2 (2)	C22—C21—H21	119.7
C8—C9—H9	120.4	C20—C21—H21	119.7
C10—C9—H9	120.4	C23—C22—C21	119.4 (2)
C9—C10—C11	120.5 (2)	C23—C22—H22	120.3
C9—C10—H10	119.8	C21—C22—H22	120.3
C11—C10—H10	119.8	C22—C23—C24	120.6 (2)
C10—C11—C6	120.3 (2)	C22—C23—H23	119.7
C10—C11—H11	119.9	C24—C23—H23	119.7
C6—C11—H11	119.9	C23—C24—C19	120.5 (2)
C13—C12—C2	113.54 (17)	C23—C24—H24	119.8
C13—C12—H121	108.9	C19—C24—H24	119.8
C2—C12—H121	108.9		

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C3—N1—C2—C19	−107.9 (2)	N1—C2—C12—C13	−58.1 (2)
C3—N1—C2—C12	108.4 (2)	C2—C12—C13—C18	88.6 (3)
C2—N1—C3—N4	178.6 (4)	C2—C12—C13—C14	−90.1 (3)
C6—N4—C3—N1	1.6 (4)	C18—C13—C14—C15	−0.5 (4)
C5—N4—C3—N1	−174.2 (3)	C12—C13—C14—C15	178.3 (2)
C6—N4—C3—C2	179.3 (3)	C13—C14—C15—C16	0.8 (4)
C5—N4—C3—C2	3.5 (4)	C14—C15—C16—C17	−0.1 (4)
C19—C2—C3—N1	99.1 (2)	C15—C16—C17—C18	−0.9 (4)
C12—C2—C3—N1	−99.3 (2)	C16—C17—C18—C13	1.3 (4)
C19—C2—C3—N4	−79.5 (4)	C14—C13—C18—C17	−0.6 (3)
C12—C2—C3—N4	82.1 (4)	C12—C13—C18—C17	−179.3 (2)
N1—C2—C3—N4	−178.6 (4)	C3—C2—C19—C24	179.25 (19)
C3—N4—C6—C11	−171.07 (19)	C12—C2—C19—C24	17.4 (3)
C5—N4—C6—C11	4.7 (3)	N1—C2—C19—C24	−125.1 (2)
C3—N4—C6—C7	8.5 (3)	C3—C2—C19—C20	−2.2 (3)
C5—N4—C6—C7	−175.7 (2)	C12—C2—C19—C20	−164.1 (2)
C11—C6—C7—C8	2.8 (3)	N1—C2—C19—C20	53.4 (3)
N4—C6—C7—C8	−176.8 (2)	C24—C19—C20—C21	−0.1 (3)
C6—C7—C8—C9	1.0 (3)	C2—C19—C20—C21	−178.67 (19)
C7—C8—C9—C10	−3.6 (3)	C19—C20—C21—C22	0.2 (3)
C8—C9—C10—C11	2.3 (3)	C20—C21—C22—C23	−0.2 (4)
C9—C10—C11—C6	1.5 (3)	C21—C22—C23—C24	0.2 (4)
C7—C6—C11—C10	−4.1 (3)	C22—C23—C24—C19	−0.2 (4)
N4—C6—C11—C10	175.48 (19)	C20—C19—C24—C23	0.1 (3)
C3—C2—C12—C13	−2.2 (3)	C2—C19—C24—C23	178.7 (2)
C19—C2—C12—C13	159.53 (19)		

trans-Dichlorido[(2*R*)-2-ethyl-2-methyl-3-(*N*-{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl}-*N*-phenylamino)-2*H*-azirine][(2*S*)-2-ethyl-2-methyl-3-(*N*-{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl}-*N*-phenylamino)-2*H*-azirine]palladium(II) (14)

Crystal data

$[PdCl_2(C_{21}H_{30}N_2)_2]$
M_r = 798.24
Triclinic, *P*1
a = 9.070 (2) Å
b = 10.504 (6) Å
c = 11.756 (2) Å
α = 80.14 (3)°
β = 76.054 (19)°
γ = 73.67 (2)°
V = 1036.7 (7) Å^3
Z = 1
F(000) = 420
D_x = 1.279 Mg m^{-3}
Melting point: 412 K
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 22 reflections
θ = 23.1–23.5°
μ = 0.61 mm^{-1}
T = 173 K
Prism, orange
0.48 × 0.25 × 0.25 mm

Data collection

Rigaku AFC-5R diffractometer
Radiation source: Rigaku rotating anode generator
Graphite crystal monochromator
ω–*θ* scans
6352 measured reflections
6046 independent reflections
5673 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30.0°, θ_{min} = 2.6°
h = −12→11

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$k = -14 \rightarrow 0$
$l = -16 \rightarrow 16$

3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.06$
6046 reflections
600 parameters
629 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1903P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack parameter determined by classical intensity fit (Flack & Bernardinelli, 1999, 2000)
Absolute structure parameter: −0.02 (2)

Special details

Experimental. Solvent used: MeCN Crystal mount: on a glass fibre Client: Jose Vollalgordo Sample code: HG9208

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. Both of the fused-ring substituents are disordered. Two sets of positions were defined for the atoms of each disordered group and the site occupation factors of the major conformations of these groups refined to 0.621 (11) and 0.675 (9). Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered C-atoms, while neighbouring atoms within and between each conformation of the disordered groups were restrained to have similar atomic displacement parameters.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Pd1	−0.00133 (6)	0.00002 (5)	0.00194 (6)	0.03619 (7)	
Cl1	−0.2121 (2)	−0.0604 (2)	0.13095 (17)	0.0610 (5)	
Cl2	0.2083 (2)	0.0595 (2)	−0.12815 (17)	0.0609 (5)	
N1	−0.0314 (6)	−0.0904 (5)	−0.1205 (5)	0.0403 (12)	
N4	−0.2372 (6)	−0.0475 (4)	−0.2366 (5)	0.0336 (10)	
N21	0.0306 (6)	0.0909 (5)	0.1270 (5)	0.0407 (12)	
N24	0.2425 (6)	0.0399 (5)	0.2356 (5)	0.0354 (11)	
C1	0.1882 (9)	−0.1991 (7)	−0.2842 (7)	0.063 (2)	
H11	0.182715	−0.105831	−0.316298	0.095*	
H12	0.200772	−0.252239	−0.348347	0.095*	
H13	0.278032	−0.233819	−0.245320	0.095*	
C2	0.0419 (8)	−0.2074 (6)	−0.1974 (7)	0.0453 (15)	
C3	−0.1039 (6)	−0.1007 (5)	−0.1994 (5)	0.0335 (12)	
C4	0.0328 (10)	−0.3439 (6)	−0.1371 (9)	0.074 (2)	
H41	0.066502	−0.407197	−0.197348	0.089*	
H42	0.107449	−0.373030	−0.083028	0.089*	
C5	−0.1243 (11)	−0.3514 (9)	−0.0694 (9)	0.080 (3)	
H51	−0.201354	−0.313373	−0.119829	0.121*	
H52	−0.151666	−0.300829	−0.001299	0.121*	
H53	−0.124602	−0.444837	−0.042070	0.121*	

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C6	−0.2586 (7)	−0.0945 (5)	−0.3376 (5)	0.0300 (10)	
C7	−0.3964 (7)	−0.1225 (6)	−0.3399 (6)	0.0411 (12)	
H7	−0.480473	−0.113452	−0.273167	0.049*	
C8	−0.4110 (8)	−0.1648 (7)	−0.4425 (6)	0.0510 (14)	
H8	−0.507408	−0.181334	−0.446112	0.061*	
C9	−0.2897 (10)	−0.1825 (7)	−0.5366 (6)	0.0547 (16)	
H9	−0.301066	−0.214085	−0.604305	0.066*	
C10	−0.1511 (9)	−0.1552 (7)	−0.5353 (6)	0.0471 (13)	
H10	−0.066965	−0.166669	−0.601953	0.057*	
C11	−0.1349 (8)	−0.1105 (6)	−0.4348 (6)	0.0418 (13)	
H111	−0.039535	−0.090944	−0.432861	0.050*	
C12	−0.3610 (6)	0.0529 (5)	−0.1708 (5)	0.0349 (11)	
H121	−0.337955	0.050247	−0.092160	0.042*	
H122	−0.462593	0.029689	−0.158714	0.042*	
C13	−0.3763 (3)	0.1954 (3)	−0.2338 (3)	0.0412 (6)	
H131	−0.386030	0.198786	−0.317243	0.049*	0.621 (11)
H132	−0.368273	0.188529	−0.318957	0.049*	0.379 (11)
C14	−0.2348 (9)	0.2472 (9)	−0.2287 (10)	0.0435 (11)	0.621 (11)
H141	−0.131024	0.180881	−0.245899	0.052*	0.621 (11)
C15	−0.2702 (14)	0.3043 (8)	−0.1091 (10)	0.0457 (12)	0.621 (11)
H151	−0.176529	0.311229	−0.083834	0.055*	0.621 (11)
H152	−0.339589	0.262143	−0.044490	0.055*	0.621 (11)
C16	−0.3562 (8)	0.4344 (8)	−0.1756 (7)	0.0487 (11)	0.621 (11)
H161	−0.349790	0.518353	−0.149872	0.058*	0.621 (11)
C17	−0.5238 (9)	0.4342 (7)	−0.1868 (9)	0.0520 (13)	0.621 (11)
H171	−0.542006	0.471697	−0.266916	0.062*	0.621 (11)
H172	−0.604935	0.487204	−0.128402	0.062*	0.621 (11)
C18	−0.5271 (7)	0.2833 (6)	−0.1621 (7)	0.0489 (14)	0.621 (11)
H181	−0.533984	0.253534	−0.076789	0.059*	0.621 (11)
H182	−0.620984	0.272309	−0.184363	0.059*	0.621 (11)
C19	−0.2356 (9)	0.3921 (8)	−0.2914 (7)	0.0494 (11)	0.621 (11)
C20	−0.2853 (13)	0.4231 (8)	−0.4105 (8)	0.0604 (16)	0.621 (11)
H201	−0.197632	0.382755	−0.471093	0.091*	0.621 (11)
H202	−0.314991	0.520028	−0.431114	0.091*	0.621 (11)
H203	−0.375029	0.386486	−0.405601	0.091*	0.621 (11)
C21	−0.0816 (11)	0.4305 (9)	−0.3046 (10)	0.0608 (17)	0.621 (11)
H211	−0.099949	0.527861	−0.319194	0.091*	0.621 (11)
H212	−0.004986	0.389864	−0.370974	0.091*	0.621 (11)
H213	−0.040903	0.398549	−0.232010	0.091*	0.621 (11)
C14A	−0.2410 (15)	0.2559 (14)	−0.2287 (17)	0.0453 (14)	0.379 (11)
H142	−0.132626	0.196861	−0.247600	0.054*	0.379 (11)
C15A	−0.278 (2)	0.3325 (14)	−0.1192 (17)	0.0460 (15)	0.379 (11)
H153	−0.346445	0.296534	−0.049345	0.055*	0.379 (11)
H154	−0.184700	0.345971	−0.098389	0.055*	0.379 (11)
C16A	−0.3669 (14)	0.4546 (13)	−0.1925 (12)	0.0489 (14)	0.379 (11)
H162	−0.358037	0.545007	−0.183478	0.059*	0.379 (11)
C17A	−0.5303 (15)	0.4232 (12)	−0.1469 (14)	0.0495 (15)	0.379 (11)
H173	−0.612055	0.499578	−0.173167	0.059*	0.379 (11)

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H174	−0.553371	0.411458	−0.059617	0.059*	0.379 (11)
C18A	−0.5361 (9)	0.2943 (11)	−0.1932 (13)	0.0459 (16)	0.379 (11)
H183	−0.600715	0.246207	−0.129885	0.055*	0.379 (11)
H184	−0.590576	0.321577	−0.260343	0.055*	0.379 (11)
C19A	−0.2744 (14)	0.3924 (14)	−0.3092 (11)	0.0516 (14)	0.379 (11)
C20A	−0.3734 (19)	0.4330 (12)	−0.4038 (12)	0.062 (2)	0.379 (11)
H204	−0.312181	0.395238	−0.476495	0.093*	0.379 (11)
H205	−0.403953	0.530543	−0.419075	0.093*	0.379 (11)
H206	−0.467794	0.399251	−0.376427	0.093*	0.379 (11)
C21A	−0.1293 (17)	0.4479 (13)	−0.3420 (15)	0.058 (2)	0.379 (11)
H214	−0.064650	0.417082	−0.416569	0.088*	0.379 (11)
H215	−0.068304	0.416582	−0.279714	0.088*	0.379 (11)
H216	−0.161823	0.545669	−0.350680	0.088*	0.379 (11)
C22	−0.0410 (8)	0.1990 (6)	0.2093 (6)	0.0430 (14)	
C23	0.1067 (7)	0.0951 (5)	0.2012 (6)	0.0376 (14)	
C24	−0.1913 (6)	0.1886 (6)	0.2983 (5)	0.0436 (13)	
H241	−0.281045	0.222421	0.259331	0.065*	
H242	−0.205119	0.241695	0.362792	0.065*	
H243	−0.184416	0.095054	0.330097	0.065*	
C25	−0.0367 (8)	0.3391 (7)	0.1589 (7)	0.0581 (16)	
H251	−0.051639	0.392507	0.224356	0.070*	
H252	−0.125534	0.378254	0.118135	0.070*	
C26	0.1150 (10)	0.3502 (8)	0.0725 (8)	0.075 (3)	
H261	0.129011	0.300452	0.005693	0.113*	
H262	0.203723	0.312954	0.112245	0.113*	
H263	0.110117	0.444252	0.043808	0.113*	
C27	0.2687 (7)	0.0792 (5)	0.3380 (6)	0.0363 (12)	
C28	0.1482 (9)	0.1022 (7)	0.4350 (6)	0.0451 (15)	
H28	0.048412	0.090196	0.434494	0.054*	
C29	0.1732 (9)	0.1429 (7)	0.5332 (7)	0.0524 (17)	
H29	0.089145	0.158397	0.599523	0.063*	
C30	0.3134 (9)	0.1615 (7)	0.5380 (6)	0.0505 (14)	
H30	0.327842	0.188624	0.606726	0.061*	
C31	0.4364 (9)	0.1399 (8)	0.4399 (7)	0.0590 (17)	
H311	0.534929	0.153752	0.441423	0.071*	
C32	0.4156 (8)	0.0980 (7)	0.3394 (6)	0.0440 (13)	
H321	0.499562	0.082535	0.273036	0.053*	
C33	0.3591 (8)	−0.0615 (6)	0.1641 (6)	0.0462 (15)	
H331	0.462519	−0.076465	0.185067	0.055*	
H332	0.369420	−0.026056	0.079687	0.055*	
C34	0.3167 (5)	−0.1938 (4)	0.1812 (3)	0.0514 (8)	
H342	0.206461	−0.176571	0.170339	0.062*	0.675 (9)
H341	0.209343	−0.179035	0.165231	0.062*	0.325 (9)
C35	0.3261 (13)	−0.2654 (8)	0.3067 (6)	0.0560 (11)	0.675 (9)
H351	0.274101	−0.205459	0.370112	0.067*	0.675 (9)
C36	0.4993 (12)	−0.3386 (8)	0.3120 (10)	0.0586 (13)	0.675 (9)
H361	0.577857	−0.300628	0.252599	0.070*	0.675 (9)
H362	0.523119	−0.352628	0.391796	0.070*	0.675 (9)

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C37	0.4636 (8)	−0.4606 (7)	0.2760 (7)	0.0637 (13)	0.675 (9)
H371	0.518509	−0.550219	0.310325	0.076*	0.675 (9)
C38	0.4770 (12)	−0.4422 (7)	0.1405 (7)	0.0655 (15)	0.675 (9)
H381	0.410040	−0.491577	0.120629	0.079*	0.675 (9)
H382	0.586920	−0.480159	0.101777	0.079*	0.675 (9)
C39	0.4258 (10)	−0.2921 (7)	0.0928 (7)	0.0610 (14)	0.675 (9)
H391	0.521912	−0.260445	0.058820	0.073*	0.675 (9)
H392	0.371964	−0.285953	0.027403	0.073*	0.675 (9)
C40	0.2883 (8)	−0.4063 (7)	0.3370 (7)	0.0620 (12)	0.675 (9)
C41	0.1575 (10)	−0.4264 (9)	0.2865 (9)	0.0682 (15)	0.675 (9)
H411	0.055482	−0.384320	0.333049	0.102*	0.675 (9)
H412	0.166999	−0.522089	0.289452	0.102*	0.675 (9)
H413	0.166118	−0.385600	0.204444	0.102*	0.675 (9)
C42	0.2614 (12)	−0.4558 (8)	0.4684 (8)	0.0733 (18)	0.675 (9)
H421	0.345961	−0.445493	0.501782	0.110*	0.675 (9)
H422	0.260452	−0.550225	0.479225	0.110*	0.675 (9)
H423	0.160472	−0.403566	0.508654	0.110*	0.675 (9)
C35A	0.324 (3)	−0.2710 (16)	0.3051 (9)	0.0582 (15)	0.325 (9)
H352	0.272633	−0.224050	0.377154	0.070*	0.325 (9)
C36A	0.494 (3)	−0.360 (2)	0.293 (2)	0.0608 (17)	0.325 (9)
H363	0.574195	−0.316146	0.242437	0.073*	0.325 (9)
H364	0.523985	−0.399664	0.369754	0.073*	0.325 (9)
C37A	0.4482 (16)	−0.4574 (15)	0.2307 (14)	0.0637 (16)	0.325 (9)
H372	0.490146	−0.554920	0.253271	0.076*	0.325 (9)
C38A	0.478 (3)	−0.4082 (14)	0.0965 (14)	0.0658 (19)	0.325 (9)
H383	0.410723	−0.439576	0.058174	0.079*	0.325 (9)
H384	0.588848	−0.446632	0.060184	0.079*	0.325 (9)
C39A	0.442 (2)	−0.2529 (14)	0.0752 (12)	0.059 (2)	0.325 (9)
H393	0.538765	−0.223697	0.067213	0.071*	0.325 (9)
H394	0.401823	−0.220690	0.001381	0.071*	0.325 (9)
C40A	0.2717 (16)	−0.3953 (16)	0.2863 (13)	0.0623 (14)	0.325 (9)
C41A	0.1466 (19)	−0.3853 (17)	0.2161 (17)	0.065 (2)	0.325 (9)
H414	0.173837	−0.338056	0.137617	0.098*	0.325 (9)
H415	0.044470	−0.336213	0.257429	0.098*	0.325 (9)
H416	0.141316	−0.475170	0.208153	0.098*	0.325 (9)
C42A	0.217 (2)	−0.4583 (17)	0.4110 (16)	0.0720 (19)	0.325 (9)
H424	0.183197	−0.537819	0.406715	0.108*	0.325 (9)
H425	0.128925	−0.393801	0.453003	0.108*	0.325 (9)
H426	0.303634	−0.483574	0.453199	0.108*	0.325 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02889 (9)	0.05094 (12)	0.03025 (9)	−0.01255 (7)	−0.00740 (6)	−0.00235 (7)
Cl1	0.0464 (10)	0.0986 (14)	0.0444 (11)	−0.0366 (10)	0.0074 (9)	−0.0178 (11)
Cl2	0.0590 (12)	0.0948 (13)	0.0412 (11)	−0.0482 (11)	0.0062 (9)	−0.0157 (10)
N1	0.036 (3)	0.047 (3)	0.037 (3)	−0.009 (2)	−0.010 (2)	−0.002 (2)
N4	0.034 (2)	0.0322 (19)	0.034 (2)	−0.0070 (17)	−0.0041 (19)	−0.0070 (17)

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N21	0.031 (2)	0.055 (3)	0.038 (3)	−0.010 (2)	−0.006 (2)	−0.013 (2)
N24	0.031 (2)	0.044 (2)	0.033 (2)	−0.0055 (18)	−0.0096 (18)	−0.0087 (18)
C1	0.052 (4)	0.064 (4)	0.072 (5)	0.009 (3)	−0.016 (3)	−0.035 (3)
C2	0.034 (3)	0.047 (3)	0.056 (4)	0.001 (2)	−0.021 (2)	−0.008 (2)
C3	0.031 (3)	0.038 (2)	0.030 (3)	−0.008 (2)	−0.007 (2)	0.002 (2)
C4	0.074 (5)	0.038 (3)	0.114 (6)	−0.017 (3)	−0.046 (4)	0.024 (3)
C5	0.068 (5)	0.069 (5)	0.102 (7)	−0.038 (4)	−0.008 (5)	0.021 (5)
C6	0.036 (2)	0.0268 (18)	0.030 (2)	−0.0083 (16)	−0.0108 (18)	−0.0037 (15)
C7	0.035 (2)	0.050 (2)	0.040 (3)	−0.0110 (18)	−0.0046 (18)	−0.0133 (18)
C8	0.049 (3)	0.067 (3)	0.051 (3)	−0.021 (2)	−0.020 (2)	−0.018 (2)
C9	0.077 (4)	0.056 (3)	0.040 (3)	−0.025 (3)	−0.015 (3)	−0.010 (2)
C10	0.055 (3)	0.051 (3)	0.034 (3)	−0.018 (2)	0.002 (2)	−0.011 (2)
C11	0.040 (3)	0.046 (3)	0.037 (3)	−0.013 (2)	0.001 (2)	−0.005 (2)
C12	0.035 (2)	0.036 (2)	0.037 (2)	−0.0138 (18)	−0.0034 (19)	−0.0081 (17)
C13	0.0455 (15)	0.0321 (13)	0.0477 (16)	−0.0021 (12)	−0.0168 (13)	−0.0115 (12)
C14	0.0450 (18)	0.0287 (18)	0.0530 (19)	−0.0082 (17)	−0.0002 (17)	−0.0096 (17)
C15	0.048 (2)	0.034 (3)	0.059 (2)	−0.013 (2)	−0.010 (2)	−0.012 (2)
C16	0.0523 (19)	0.031 (2)	0.063 (2)	−0.0078 (17)	−0.0096 (18)	−0.0146 (18)
C17	0.048 (2)	0.036 (2)	0.069 (3)	0.0013 (17)	−0.013 (2)	−0.016 (2)
C18	0.040 (2)	0.040 (2)	0.069 (3)	0.0007 (17)	−0.021 (2)	−0.014 (2)
C19	0.056 (2)	0.0293 (16)	0.062 (2)	−0.0134 (19)	−0.0057 (19)	−0.0085 (17)
C20	0.071 (3)	0.039 (2)	0.065 (3)	−0.011 (3)	−0.009 (3)	0.000 (2)
C21	0.063 (3)	0.040 (3)	0.073 (4)	−0.018 (3)	0.002 (3)	−0.005 (3)
C14A	0.047 (2)	0.030 (2)	0.055 (2)	−0.007 (2)	−0.003 (2)	−0.009 (2)
C15A	0.049 (2)	0.032 (3)	0.058 (2)	−0.010 (2)	−0.009 (2)	−0.010 (2)
C16A	0.052 (2)	0.029 (2)	0.063 (3)	−0.005 (2)	−0.010 (2)	−0.011 (2)
C17A	0.048 (2)	0.037 (2)	0.065 (3)	−0.002 (2)	−0.016 (2)	−0.016 (2)
C18A	0.041 (2)	0.037 (2)	0.065 (3)	−0.002 (2)	−0.023 (3)	−0.016 (2)
C19A	0.057 (2)	0.0315 (19)	0.062 (2)	−0.009 (2)	−0.004 (2)	−0.007 (2)
C20A	0.071 (4)	0.038 (3)	0.065 (4)	−0.006 (4)	−0.004 (4)	0.001 (3)
C21A	0.061 (3)	0.036 (3)	0.069 (3)	−0.013 (3)	−0.001 (3)	0.002 (3)
C22	0.045 (3)	0.037 (2)	0.046 (3)	−0.013 (2)	−0.005 (2)	−0.004 (2)
C23	0.038 (3)	0.037 (2)	0.040 (3)	−0.012 (2)	−0.004 (3)	−0.012 (2)
C24	0.030 (2)	0.050 (3)	0.045 (3)	−0.010 (2)	0.004 (2)	−0.007 (2)
C25	0.043 (3)	0.056 (3)	0.066 (3)	−0.003 (2)	−0.010 (2)	−0.002 (3)
C26	0.076 (5)	0.062 (4)	0.076 (6)	−0.009 (4)	−0.025 (5)	0.024 (4)
C27	0.038 (2)	0.034 (2)	0.032 (3)	−0.0032 (17)	−0.0045 (19)	−0.0037 (17)
C28	0.049 (3)	0.051 (3)	0.038 (3)	−0.020 (2)	−0.004 (2)	−0.009 (2)
C29	0.060 (3)	0.054 (3)	0.034 (3)	−0.009 (2)	0.006 (2)	−0.012 (2)
C30	0.059 (3)	0.058 (3)	0.037 (3)	−0.010 (2)	−0.016 (2)	−0.013 (2)
C31	0.042 (3)	0.091 (4)	0.045 (3)	−0.015 (3)	−0.006 (2)	−0.018 (3)
C32	0.033 (2)	0.061 (3)	0.038 (2)	−0.008 (2)	−0.0077 (18)	−0.010 (2)
C33	0.039 (3)	0.056 (3)	0.034 (2)	0.004 (2)	−0.001 (2)	−0.016 (2)
C34	0.0448 (16)	0.0529 (17)	0.0630 (19)	−0.0032 (14)	−0.0140 (15)	−0.0346 (15)
C35	0.0542 (19)	0.0442 (19)	0.073 (2)	−0.0138 (17)	−0.0061 (19)	−0.0233 (18)
C36	0.058 (2)	0.046 (2)	0.076 (3)	−0.009 (2)	−0.015 (2)	−0.022 (2)
C37	0.064 (2)	0.050 (2)	0.080 (3)	−0.0092 (18)	−0.013 (2)	−0.026 (2)
C38	0.065 (3)	0.054 (3)	0.077 (3)	−0.006 (2)	−0.008 (3)	−0.033 (2)

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C39	0.061 (2)	0.057 (3)	0.066 (3)	−0.002 (2)	−0.008 (2)	−0.039 (2)
C40	0.064 (2)	0.0469 (19)	0.079 (3)	−0.0185 (17)	−0.003 (2)	−0.025 (2)
C41	0.067 (3)	0.055 (3)	0.087 (3)	−0.024 (2)	−0.004 (3)	−0.025 (3)
C42	0.080 (3)	0.051 (3)	0.085 (4)	−0.024 (3)	0.004 (3)	−0.015 (3)
C35A	0.056 (2)	0.047 (2)	0.074 (3)	−0.012 (2)	−0.007 (2)	−0.024 (2)
C36A	0.060 (3)	0.047 (3)	0.076 (3)	−0.008 (2)	−0.012 (3)	−0.023 (3)
C37A	0.064 (2)	0.049 (2)	0.079 (3)	−0.011 (2)	−0.009 (3)	−0.024 (3)
C38A	0.065 (3)	0.055 (3)	0.075 (3)	−0.004 (3)	−0.007 (3)	−0.028 (3)
C39A	0.060 (3)	0.053 (3)	0.067 (3)	−0.005 (3)	−0.010 (3)	−0.033 (3)
C40A	0.062 (2)	0.048 (2)	0.081 (3)	−0.019 (2)	−0.006 (2)	−0.024 (2)
C41A	0.064 (4)	0.052 (4)	0.089 (4)	−0.027 (3)	−0.006 (4)	−0.023 (4)
C42A	0.072 (3)	0.054 (3)	0.088 (3)	−0.022 (3)	0.000 (3)	−0.015 (3)

Geometric parameters (Å, º)

Pd1—Cl1	2.3049 (19)	C19A—C20A	1.526 (6)
Pd1—Cl2	2.2988 (19)	C20A—H204	0.9800
Pd1—N1	1.962 (6)	C20A—H205	0.9800
Pd1—N21	1.999 (5)	C20A—H206	0.9800
N1—C3	1.294 (8)	C21A—H214	0.9800
N1—C2	1.550 (8)	C21A—H215	0.9800
N4—C3	1.326 (8)	C21A—H216	0.9800
N4—C6	1.434 (7)	C22—C23	1.465 (9)
N4—C12	1.472 (7)	C22—C25	1.497 (9)
N21—C23	1.250 (8)	C22—C24	1.524 (8)
N21—C22	1.519 (8)	C24—H241	0.9800
N24—C23	1.332 (8)	C24—H242	0.9800
N24—C27	1.427 (8)	C24—H243	0.9800
N24—C33	1.485 (7)	C25—C26	1.521 (11)
C1—C2	1.481 (11)	C25—H251	0.9900
C1—H11	0.9800	C25—H252	0.9900
C1—H12	0.9800	C26—H261	0.9800
C1—H13	0.9800	C26—H262	0.9800
C2—C3	1.476 (8)	C26—H263	0.9800
C2—C4	1.502 (9)	C27—C28	1.378 (9)
C4—C5	1.471 (12)	C27—C32	1.406 (9)
C4—H41	0.9900	C28—C29	1.385 (10)
C4—H42	0.9900	C28—H28	0.9500
C5—H51	0.9800	C29—C30	1.355 (11)
C5—H52	0.9800	C29—H29	0.9500
C5—H53	0.9800	C30—C31	1.398 (10)
C6—C7	1.369 (8)	C30—H30	0.9500
C6—C11	1.391 (9)	C31—C32	1.399 (10)
C7—C8	1.401 (9)	C31—H311	0.9500
C7—H7	0.9500	C32—H321	0.9500
C8—C9	1.356 (10)	C33—C34	1.513 (8)
C8—H8	0.9500	C33—H331	0.9900
C9—C10	1.370 (10)	C33—H332	0.9900

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C9—H9	0.9500	C34—C35	1.547 (4)
C10—C11	1.397 (10)	C34—C35A	1.548 (5)
C10—H10	0.9500	C34—C39A	1.553 (5)
C11—H111	0.9500	C34—C39	1.556 (4)
C12—C13	1.536 (6)	C34—H342	1.0000
C12—H121	0.9900	C34—H341	1.0000
C12—H122	0.9900	C35—C36	1.554 (5)
C13—C14	1.545 (4)	C35—C40	1.575 (5)
C13—C18A	1.548 (4)	C35—H351	1.0000
C13—C14A	1.549 (4)	C36—C37	1.552 (5)
C13—C18	1.560 (4)	C36—H361	0.9900
C13—H131	1.0000	C36—H362	0.9900
C13—H132	1.0000	C37—C38	1.550 (5)
C14—C15	1.550 (5)	C37—C40	1.565 (5)
C14—C19	1.572 (5)	C37—H371	1.0000
C14—H141	1.0000	C38—C39	1.558 (5)
C15—C16	1.554 (5)	C38—H381	0.9900
C15—H151	0.9900	C38—H382	0.9900
C15—H152	0.9900	C39—H391	0.9900
C16—C17	1.558 (5)	C39—H392	0.9900
C16—C19	1.570 (5)	C40—C41	1.525 (6)
C16—H161	1.0000	C40—C42	1.527 (6)
C17—C18	1.570 (5)	C41—H411	0.9800
C17—H171	0.9900	C41—H412	0.9800
C17—H172	0.9900	C41—H413	0.9800
C18—H181	0.9900	C42—H421	0.9800
C18—H182	0.9900	C42—H422	0.9800
C19—C21	1.527 (5)	C42—H423	0.9800
C19—C20	1.528 (6)	C35A—C36A	1.553 (5)
C20—H201	0.9800	C35A—C40A	1.572 (5)
C20—H202	0.9800	C35A—H352	1.0000
C20—H203	0.9800	C36A—C37A	1.552 (5)
C21—H211	0.9800	C36A—H363	0.9900
C21—H212	0.9800	C36A—H364	0.9900
C21—H213	0.9800	C37A—C38A	1.557 (5)
C14A—C15A	1.553 (5)	C37A—C40A	1.572 (5)
C14A—C19A	1.572 (5)	C37A—H372	1.0000
C14A—H142	1.0000	C38A—C39A	1.558 (5)
C15A—C16A	1.552 (5)	C38A—H383	0.9900
C15A—H153	0.9900	C38A—H384	0.9900
C15A—H154	0.9900	C39A—H393	0.9900
C16A—C17A	1.557 (5)	C39A—H394	0.9900
C16A—C19A	1.567 (5)	C40A—C42A	1.527 (6)
C16A—H162	1.0000	C40A—C41A	1.528 (6)
C17A—C18A	1.562 (5)	C41A—H414	0.9800
C17A—H173	0.9900	C41A—H415	0.9800
C17A—H174	0.9900	C41A—H416	0.9800
C18A—H183	0.9900	C42A—H424	0.9800

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C18A—H184	0.9900	C42A—H425	0.9800
C19A—C21A	1.526 (6)	C42A—H426	0.9800
Cl1—Pd1—Cl2	179.45 (9)	C19A—C20A—H206	109.5
Cl1—Pd1—N1	90.34 (16)	H204—C20A—H206	109.5
Cl1—Pd1—N21	89.73 (16)	H205—C20A—H206	109.5
Cl2—Pd1—N1	89.11 (17)	C19A—C21A—H214	109.5
Cl2—Pd1—N21	90.82 (16)	C19A—C21A—H215	109.5
N1—Pd1—N21	179.6 (3)	H214—C21A—H215	109.5
C3—N1—C2	61.8 (4)	C19A—C21A—H216	109.5
C3—N1—Pd1	153.3 (4)	H214—C21A—H216	109.5
C2—N1—Pd1	144.7 (4)	H215—C21A—H216	109.5
C3—N4—C6	118.4 (5)	C23—C22—C25	118.9 (6)
C3—N4—C12	119.5 (5)	C23—C22—N21	49.5 (4)
C6—N4—C12	122.0 (5)	C25—C22—N21	117.4 (6)
C23—N21—C22	63.0 (4)	C23—C22—C24	124.2 (6)
C23—N21—Pd1	150.5 (4)	C25—C22—C24	113.8 (5)
C22—N21—Pd1	146.1 (5)	N21—C22—C24	117.3 (5)
C23—N24—C27	119.4 (5)	N21—C23—N24	142.6 (6)
C23—N24—C33	117.1 (5)	N21—C23—C22	67.5 (5)
C27—N24—C33	123.5 (5)	N24—C23—C22	149.6 (6)
C2—C1—H11	109.5	C22—C24—H241	109.5
C2—C1—H12	109.5	C22—C24—H242	109.5
H11—C1—H12	109.5	H241—C24—H242	109.5
C2—C1—H13	109.5	C22—C24—H243	109.5
H11—C1—H13	109.5	H241—C24—H243	109.5
H12—C1—H13	109.5	H242—C24—H243	109.5
C3—C2—C1	121.0 (6)	C22—C25—C26	113.9 (6)
C3—C2—C4	119.5 (6)	C22—C25—H251	108.8
C1—C2—C4	116.4 (6)	C26—C25—H251	108.8
C3—C2—N1	50.5 (4)	C22—C25—H252	108.8
C1—C2—N1	115.9 (6)	C26—C25—H252	108.8
C4—C2—N1	116.3 (7)	H251—C25—H252	107.7
N1—C3—N4	141.0 (6)	C25—C26—H261	109.5
N1—C3—C2	67.7 (4)	C25—C26—H262	109.5
N4—C3—C2	150.7 (6)	H261—C26—H262	109.5
C5—C4—C2	114.2 (7)	C25—C26—H263	109.5
C5—C4—H41	108.7	H261—C26—H263	109.5
C2—C4—H41	108.7	H262—C26—H263	109.5
C5—C4—H42	108.7	C28—C27—C32	119.6 (6)
C2—C4—H42	108.7	C28—C27—N24	119.9 (6)
H41—C4—H42	107.6	C32—C27—N24	120.4 (6)
C4—C5—H51	109.5	C27—C28—C29	119.8 (7)
C4—C5—H52	109.5	C27—C28—H28	120.1
H51—C5—H52	109.5	C29—C28—H28	120.1
C4—C5—H53	109.5	C30—C29—C28	122.2 (7)
H51—C5—H53	109.5	C30—C29—H29	118.9
H52—C5—H53	109.5	C28—C29—H29	118.9

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C7—C6—C11	120.3 (6)	C29—C30—C31	118.7 (7)
C7—C6—N4	121.6 (6)	C29—C30—H30	120.6
C11—C6—N4	118.1 (5)	C31—C30—H30	120.6
C6—C7—C8	118.8 (6)	C30—C31—C32	120.5 (7)
C6—C7—H7	120.6	C30—C31—H311	119.7
C8—C7—H7	120.6	C32—C31—H311	119.7
C9—C8—C7	121.0 (6)	C31—C32—C27	119.1 (7)
C9—C8—H8	119.5	C31—C32—H321	120.5
C7—C8—H8	119.5	C27—C32—H321	120.5
C8—C9—C10	120.8 (6)	N24—C33—C34	113.6 (5)
C8—C9—H9	119.6	N24—C33—H331	108.9
C10—C9—H9	119.6	C34—C33—H331	108.9
C9—C10—C11	119.2 (7)	N24—C33—H332	108.9
C9—C10—H10	120.4	C34—C33—H332	108.9
C11—C10—H10	120.4	H331—C33—H332	107.7
C6—C11—C10	120.0 (6)	C33—C34—C35	111.2 (4)
C6—C11—H111	120.0	C33—C34—C35A	114.0 (7)
C10—C11—H111	120.0	C33—C34—C39A	96.0 (7)
N4—C12—C13	113.1 (4)	C35A—C34—C39A	117.5 (11)
N4—C12—H121	109.0	C33—C34—C39	113.2 (5)
C13—C12—H121	109.0	C35—C34—C39	106.9 (6)
N4—C12—H122	109.0	C33—C34—H342	108.5
C13—C12—H122	109.0	C35—C34—H342	108.5
H121—C12—H122	107.8	C39—C34—H342	108.5
C12—C13—C14	110.4 (4)	C33—C34—H341	109.5
C12—C13—C18A	114.5 (6)	C35A—C34—H341	109.5
C12—C13—C14A	113.3 (6)	C39A—C34—H341	109.5
C18A—C13—C14A	109.7 (9)	C34—C35—C36	109.8 (7)
C12—C13—C18	105.7 (4)	C34—C35—C40	117.2 (6)
C14—C13—C18	108.1 (6)	C36—C35—C40	87.5 (5)
C12—C13—H131	110.8	C34—C35—H351	113.3
C14—C13—H131	110.8	C36—C35—H351	113.3
C18—C13—H131	110.8	C40—C35—H351	113.3
C12—C13—H132	106.2	C37—C36—C35	86.0 (6)
C18A—C13—H132	106.2	C37—C36—H361	114.3
C14A—C13—H132	106.2	C35—C36—H361	114.3
C13—C14—C15	107.8 (8)	C37—C36—H362	114.3
C13—C14—C19	115.4 (6)	C35—C36—H362	114.3
C15—C14—C19	88.0 (6)	H361—C36—H362	111.5
C13—C14—H141	114.2	C38—C37—C36	108.7 (7)
C15—C14—H141	114.2	C38—C37—C40	109.0 (6)
C19—C14—H141	114.2	C36—C37—C40	87.9 (5)
C14—C15—C16	84.3 (6)	C38—C37—H371	115.9
C14—C15—H151	114.6	C36—C37—H371	115.9
C16—C15—H151	114.6	C40—C37—H371	115.9
C14—C15—H152	114.6	C37—C38—C39	111.4 (6)
C16—C15—H152	114.6	C37—C38—H381	109.3
H151—C15—H152	111.7	C39—C38—H381	109.3

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C15—C16—C17	113.9 (8)	C37—C38—H382	109.3
C15—C16—C19	87.9 (6)	C39—C38—H382	109.3
C17—C16—C19	109.5 (7)	H381—C38—H382	108.0
C15—C16—H161	114.2	C34—C39—C38	117.8 (5)
C17—C16—H161	114.2	C34—C39—H391	107.9
C19—C16—H161	114.2	C38—C39—H391	107.9
C16—C17—C18	104.7 (7)	C34—C39—H392	107.9
C16—C17—H171	110.8	C38—C39—H392	107.9
C18—C17—H171	110.8	H391—C39—H392	107.2
C16—C17—H172	110.8	C41—C40—C42	108.5 (7)
C18—C17—H172	110.8	C41—C40—C37	119.7 (6)
H171—C17—H172	108.9	C42—C40—C37	110.7 (6)
C13—C18—C17	110.6 (5)	C41—C40—C35	117.4 (7)
C13—C18—H181	109.5	C42—C40—C35	114.1 (5)
C17—C18—H181	109.5	C37—C40—C35	84.9 (6)
C13—C18—H182	109.5	C40—C41—H411	109.5
C17—C18—H182	109.5	C40—C41—H412	109.5
H181—C18—H182	108.1	H411—C41—H412	109.5
C21—C19—C20	109.1 (7)	C40—C41—H413	109.5
C21—C19—C16	112.8 (6)	H411—C41—H413	109.5
C20—C19—C16	121.0 (7)	H412—C41—H413	109.5
C21—C19—C14	114.0 (5)	C40—C42—H421	109.5
C20—C19—C14	115.0 (7)	C40—C42—H422	109.5
C16—C19—C14	83.1 (6)	H421—C42—H422	109.5
C19—C20—H201	109.5	C40—C42—H423	109.5
C19—C20—H202	109.5	H421—C42—H423	109.5
H201—C20—H202	109.5	H422—C42—H423	109.5
C19—C20—H203	109.5	C34—C35A—C36A	104.7 (15)
H201—C20—H203	109.5	C34—C35A—C40A	97.7 (9)
H202—C20—H203	109.5	C36A—C35A—C40A	88.2 (12)
C19—C21—H211	109.5	C34—C35A—H352	120.0
C19—C21—H212	109.5	C36A—C35A—H352	120.0
H211—C21—H212	109.5	C40A—C35A—H352	120.0
C19—C21—H213	109.5	C37A—C36A—C35A	89.1 (13)
H211—C21—H213	109.5	C37A—C36A—H363	113.8
H212—C21—H213	109.5	C35A—C36A—H363	113.8
C13—C14A—C15A	112.4 (13)	C37A—C36A—H364	113.8
C13—C14A—C19A	103.1 (9)	C35A—C36A—H364	113.8
C15A—C14A—C19A	89.9 (10)	H363—C36A—H364	111.0
C13—C14A—H142	116.0	C36A—C37A—C38A	106.9 (15)
C15A—C14A—H142	116.0	C36A—C37A—C40A	88.2 (12)
C19A—C14A—H142	116.0	C38A—C37A—C40A	108.5 (13)
C16A—C15A—C14A	87.1 (11)	C36A—C37A—H372	116.5
C16A—C15A—H153	114.1	C38A—C37A—H372	116.5
C14A—C15A—H153	114.1	C40A—C37A—H372	116.5
C16A—C15A—H154	114.1	C37A—C38A—C39A	111.1 (12)
C14A—C15A—H154	114.1	C37A—C38A—H383	109.4
H153—C15A—H154	111.3	C39A—C38A—H383	109.4

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C15A—C16A—C17A	95.1 (13)	C37A—C38A—H384	109.4
C15A—C16A—C19A	90.1 (10)	C39A—C38A—H384	109.4
C17A—C16A—C19A	113.0 (11)	H383—C38A—H384	108.0
C15A—C16A—H162	117.7	C34—C39A—C38A	109.0 (9)
C17A—C16A—H162	117.7	C34—C39A—H393	109.9
C19A—C16A—H162	117.7	C38A—C39A—H393	109.9
C16A—C17A—C18A	111.7 (11)	C34—C39A—H394	109.9
C16A—C17A—H173	109.3	C38A—C39A—H394	109.9
C18A—C17A—H173	109.3	H393—C39A—H394	108.3
C16A—C17A—H174	109.3	C42A—C40A—C41A	107.5 (14)
C18A—C17A—H174	109.3	C42A—C40A—C37A	113.9 (13)
H173—C17A—H174	107.9	C41A—C40A—C37A	118.6 (12)
C13—C18A—C17A	116.4 (8)	C42A—C40A—C35A	104.5 (11)
C13—C18A—H183	108.2	C41A—C40A—C35A	123.3 (13)
C17A—C18A—H183	108.2	C37A—C40A—C35A	87.7 (12)
C13—C18A—H184	108.2	C40A—C41A—H414	109.5
C17A—C18A—H184	108.2	C40A—C41A—H415	109.5
H183—C18A—H184	107.3	H414—C41A—H415	109.5
C21A—C19A—C20A	112.8 (12)	C40A—C41A—H416	109.5
C21A—C19A—C16A	103.1 (10)	H414—C41A—H416	109.5
C20A—C19A—C16A	110.9 (11)	H415—C41A—H416	109.5
C21A—C19A—C14A	110.1 (8)	C40A—C42A—H424	109.5
C20A—C19A—C14A	128.1 (11)	C40A—C42A—H425	109.5
C16A—C19A—C14A	85.8 (11)	H424—C42A—H425	109.5
C19A—C20A—H204	109.5	C40A—C42A—H426	109.5
C19A—C20A—H205	109.5	H424—C42A—H426	109.5
H204—C20A—H205	109.5	H425—C42A—H426	109.5

Pd1—N1—C2—C3	−175.6 (8)	Pd1—N21—C22—C23	172.8 (9)
C3—N1—C2—C1	110.0 (7)	C23—N21—C22—C25	105.9 (7)
Pd1—N1—C2—C1	−65.6 (10)	Pd1—N21—C22—C25	−81.4 (10)
C3—N1—C2—C4	−107.7 (7)	C23—N21—C22—C24	−113.0 (7)
Pd1—N1—C2—C4	76.7 (10)	Pd1—N21—C22—C24	59.8 (10)
C2—N1—C3—N4	172.9 (9)	C22—N21—C23—N24	−175.3 (11)
Pd1—N1—C3—N4	−12.8 (16)	Pd1—N21—C23—N24	13.0 (17)
Pd1—N1—C3—C2	174.3 (10)	Pd1—N21—C23—C22	−171.8 (10)
C6—N4—C3—N1	177.2 (7)	C27—N24—C23—N21	−175.9 (8)
C12—N4—C3—N1	−5.5 (11)	C33—N24—C23—N21	3.6 (13)
C6—N4—C3—C2	−16.3 (14)	C27—N24—C23—C22	12.7 (15)
C12—N4—C3—C2	160.9 (10)	C33—N24—C23—C22	−167.7 (10)
C1—C2—C3—N1	−99.5 (7)	C25—C22—C23—N21	−102.7 (7)
C4—C2—C3—N1	101.2 (8)	C24—C22—C23—N21	98.5 (7)
C1—C2—C3—N4	89.6 (13)	C25—C22—C23—N24	71.6 (14)
C4—C2—C3—N4	−69.6 (14)	N21—C22—C23—N24	174.3 (13)
N1—C2—C3—N4	−170.8 (12)	C24—C22—C23—N24	−87.2 (13)
C3—C2—C4—C5	−8.7 (12)	C23—C22—C25—C26	17.5 (10)
C1—C2—C4—C5	−168.9 (8)	N21—C22—C25—C26	−39.1 (10)
N1—C2—C4—C5	49.0 (10)	C24—C22—C25—C26	178.5 (6)

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C3—N4—C6—C7	135.4 (6)	C23—N24—C27—C28	39.0 (9)
C12—N4—C6—C7	−41.8 (8)	C33—N24—C27—C28	−140.5 (7)
C3—N4—C6—C11	−45.0 (8)	C23—N24—C27—C32	−139.3 (6)
C12—N4—C6—C11	137.8 (6)	C33—N24—C27—C32	41.2 (9)
C11—C6—C7—C8	−1.3 (10)	C32—C27—C28—C29	−0.4 (10)
N4—C6—C7—C8	178.4 (6)	N24—C27—C28—C29	−178.7 (6)
C6—C7—C8—C9	2.3 (11)	C27—C28—C29—C30	0.0 (11)
C7—C8—C9—C10	−2.1 (11)	C28—C29—C30—C31	0.6 (11)
C8—C9—C10—C11	0.8 (11)	C29—C30—C31—C32	−0.9 (11)
C7—C6—C11—C10	0.0 (9)	C30—C31—C32—C27	0.6 (12)
N4—C6—C11—C10	−179.6 (6)	C28—C27—C32—C31	0.1 (11)
C9—C10—C11—C6	0.2 (10)	N24—C27—C32—C31	178.3 (6)
C3—N4—C12—C13	106.1 (6)	C23—N24—C33—C34	−73.5 (7)
C6—N4—C12—C13	−76.7 (6)	C27—N24—C33—C34	106.0 (7)
N4—C12—C13—C14	−71.7 (7)	N24—C33—C34—C35	−68.1 (7)
N4—C12—C13—C18A	159.6 (6)	N24—C33—C34—C35A	−68.1 (11)
N4—C12—C13—C14A	−73.6 (10)	N24—C33—C34—C39A	168.1 (10)
N4—C12—C13—C18	171.6 (5)	N24—C33—C34—C39	171.5 (6)
C12—C13—C14—C15	−84.1 (6)	C33—C34—C35—C36	−81.2 (6)
C18—C13—C14—C15	31.1 (7)	C39—C34—C35—C36	42.8 (7)
C12—C13—C14—C19	179.4 (6)	C33—C34—C35—C40	−178.8 (6)
C18—C13—C14—C19	−65.3 (9)	C39—C34—C35—C40	−54.8 (9)
C13—C14—C15—C16	−85.8 (7)	C34—C35—C36—C37	−90.4 (7)
C19—C14—C15—C16	30.3 (6)	C40—C35—C36—C37	27.7 (6)
C14—C15—C16—C17	80.1 (8)	C35—C36—C37—C38	81.6 (7)
C14—C15—C16—C19	−30.4 (6)	C35—C36—C37—C40	−27.8 (6)
C15—C16—C17—C18	−17.8 (10)	C36—C37—C38—C39	−32.8 (10)
C19—C16—C17—C18	78.8 (9)	C40—C37—C38—C39	61.6 (9)
C12—C13—C18—C17	159.4 (7)	C33—C34—C39—C38	139.8 (8)
C14—C13—C18—C17	41.1 (9)	C35—C34—C39—C38	17.0 (10)
C16—C17—C18—C13	−47.0 (10)	C37—C38—C39—C34	−22.0 (11)
C15—C16—C19—C21	−83.2 (7)	C38—C37—C40—C41	37.1 (9)
C17—C16—C19—C21	162.1 (6)	C36—C37—C40—C41	146.2 (8)
C15—C16—C19—C20	145.0 (8)	C38—C37—C40—C42	164.5 (6)
C17—C16—C19—C20	30.3 (9)	C36—C37—C40—C42	−86.4 (7)
C15—C16—C19—C14	30.0 (5)	C38—C37—C40—C35	−81.6 (6)
C17—C16—C19—C14	−84.7 (6)	C36—C37—C40—C35	27.5 (6)
C13—C14—C19—C21	−169.4 (8)	C34—C35—C40—C41	−37.5 (11)
C15—C14—C19—C21	81.8 (8)	C36—C35—C40—C41	−148.4 (7)
C13—C14—C19—C20	−42.3 (11)	C34—C35—C40—C42	−166.1 (7)
C15—C14—C19—C20	−151.1 (8)	C36—C35—C40—C42	82.9 (8)
C13—C14—C19—C16	78.7 (9)	C34—C35—C40—C37	83.5 (8)
C15—C14—C19—C16	−30.1 (6)	C36—C35—C40—C37	−27.5 (6)
C12—C13—C14A—C15A	−90.3 (10)	C33—C34—C35A—C36A	−90.5 (11)
C18A—C13—C14A—C15A	39.0 (12)	C39A—C34—C35A—C36A	20.6 (15)
C12—C13—C14A—C19A	174.3 (8)	C33—C34—C35A—C40A	179.3 (8)
C18A—C13—C14A—C19A	−56.4 (14)	C39A—C34—C35A—C40A	−69.5 (15)
C13—C14A—C15A—C16A	−84.2 (12)	C34—C35A—C36A—C37A	−77.7 (14)

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C19A—C14A—C15A—C16A	19.9 (10)	C40A—C35A—C36A—C37A	19.7 (12)
C14A—C15A—C16A—C17A	93.1 (11)	C35A—C36A—C37A—C38A	89.1 (14)
C14A—C15A—C16A—C19A	−20.0 (10)	C35A—C36A—C37A—C40A	−19.7 (12)
C15A—C16A—C17A—C18A	−68.5 (16)	C36A—C37A—C38A—C39A	−35 (2)
C19A—C16A—C17A—C18A	23.8 (18)	C40A—C37A—C38A—C39A	59.1 (19)
C12—C13—C18A—C17A	123.7 (12)	C33—C34—C39A—C38A	156.6 (14)
C14A—C13—C18A—C17A	−5.0 (17)	C35A—C34—C39A—C38A	35.6 (19)
C16A—C17A—C18A—C13	21 (2)	C37A—C38A—C39A—C34	−27 (2)
C15A—C16A—C19A—C21A	−89.9 (12)	C36A—C37A—C40A—C42A	−85.4 (16)
C17A—C16A—C19A—C21A	174.5 (11)	C38A—C37A—C40A—C42A	167.4 (14)
C15A—C16A—C19A—C20A	149.1 (12)	C36A—C37A—C40A—C41A	146.6 (16)
C17A—C16A—C19A—C20A	53.5 (14)	C38A—C37A—C40A—C41A	39.4 (18)
C15A—C16A—C19A—C14A	19.8 (10)	C36A—C37A—C40A—C35A	19.5 (12)
C17A—C16A—C19A—C14A	−75.9 (11)	C38A—C37A—C40A—C35A	−87.7 (12)
C13—C14A—C19A—C21A	−164.4 (12)	C34—C35A—C40A—C42A	−160.7 (13)
C15A—C14A—C19A—C21A	82.6 (13)	C36A—C35A—C40A—C42A	94.6 (15)
C13—C14A—C19A—C20A	−20.2 (19)	C34—C35A—C40A—C41A	−37.9 (19)
C15A—C14A—C19A—C20A	−133.2 (14)	C36A—C35A—C40A—C41A	−142.6 (15)
C13—C14A—C19A—C16A	93.2 (12)	C34—C35A—C40A—C37A	85.2 (13)
C15A—C14A—C19A—C16A	−19.8 (10)	C36A—C35A—C40A—C37A	−19.5 (12)

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