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Bis(μ-4-benzyl-3,5-diphenylpyrazolato-κ^2N:N')bis[(4,4′-dimethyl-2,2′-bipyridine-κ^2N,N')palladium(II)] bis(hexafluorophosphate) diethyl ether monosolvate monohydrate

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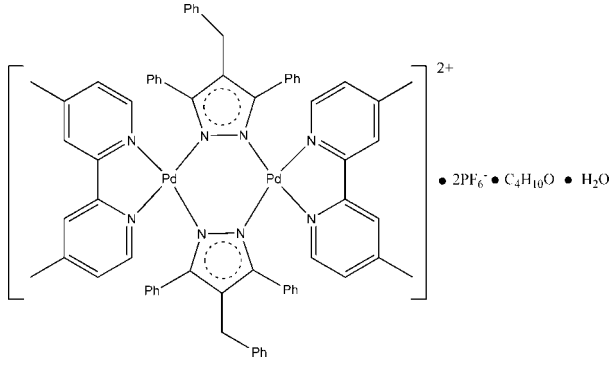
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.011 Å; disorder in solvent or counterion; R factor = 0.045; wR factor = 0.144; data-to-parameter ratio = 19.3.

In the crystal structure of the title compound, $[Pd_2(C_{22}H_{17}N_2)_2(C_{12}H_{12}N_2)_2](PF_6)_2\cdot C_4H_{10}O\cdot H_2O$, two Pd(dmbpy) units (dmbpy is 4,4′-dimethyl-2,2′-bipyridine) are bridged by 4-benzyl-3,5-diphenylpyrazolate ligands in an exodentate fashion, which results in a clip-like cavity between the two Pd(dmbpy)Pd planes. A disordered hexafluoridophosphate anion is held in the cavity by an anion–π interaction [P—F$\cdots Cg1$ = 3.435 (15) Å ($Cg1$ is the centroid of the Pd–dmbpy chelate ring system) and P—F$\cdots Cg2$ = 3.187 (15) Å ($Cg2$ is the centroid of a pyridine ring)]. A crystallographic twofold rotation axis passes through an F atom of the disordered anion and the mid-point of the two Pd atoms. The P and two F atoms of the second anion also lie on a twofold rotation axis, as do the O atom of the diethyl ether and the water O atom. The crystal structure is stabilized by electrostatic forces between the cations and anions, and intermolecular hydrogen bonds involving hexafluoridophosphate anions (C—H$\cdots$F), the solvent diethyl ether molecules and water molecules (C—H$\cdots$O).

Related literature

For related literature, see: Huang *et al.* (2005); Huang, Wu, Liu & Song (2007); Huang, Wu, Liu & Sun (2007).



Experimental

Crystal data

$[Pd_2(C_{22}H_{17}N_2)_2(C_{12}H_{12}N_2)_2](PF_6)_2\cdot C_4H_{10}O\cdot H_2O$
M_r = 1582.10
Trigonal, $P3_121$
a = 22.1138 (3) Å
c = 12.8884 (2) Å
V = 5458.29 (13) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 0.62 mm^{-1}
T = 291 (2) K
0.48 × 0.42 × 0.36 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.756, T_{max} = 0.808
47040 measured reflections
9007 independent reflections
8156 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.144
S = 1.10
9007 reflections
466 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}
Absolute structure: Flack (1983), with 4168 Friedel pairs
Flack parameter: −0.02 (3)

Table 1
Selected geometric parameters (Å, °).

N1—Pd1	2.002 (3)	N3—Pd1	2.033 (3)
N2—Pd1	2.010 (3)	N4—Pd1	2.017 (3)
N3—N4^{i}	1.352 (5)	Pd1$\cdots$Pd1^{i}	2.9989 (6)
N4^{i}—N3—Pd1	114.1 (3)	N1—Pd1—N2	80.8 (1)
N3^{i}—N4—Pd1	113.9 (3)	N4—Pd1—N3	86.8 (1)

Symmetry code: (i) $x-y+1, -y+2, -z+\frac{5}{3}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$F1^{i}	0.93	2.50	3.228 (8)	135
C12—H12$\cdots$F1	0.93	2.44	3.200 (8)	139
C36—H36$A\cdots$O2	0.96	2.45	3.25 (3)	141
C36—H36$B\cdots$F7^{ii}	0.96	2.31	3.04 (4)	133
C36—H36$C\cdots$F9^{ii}	0.96	2.19	2.95 (3)	135

Symmetry codes: (i) $x-y+1, -y+2, -z+\frac{5}{3}$; (ii) $-x+y, -x+1, z-\frac{1}{3}$.

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Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by Renmin University of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2018).

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supplementary materials

Acta Cryst. (2007). E**63**, m1875-m1876 [**doi:10.1107/S1600536807028401**]

Bis(μ-4-benzyl-3,5-diphenylpyrazolato-κ^2N:N')bis[(4,4'-dimethyl-2,2'-bipyridine-κ^2N,N')palladium(II)] bis(hexafluorophosphate) diethyl ether monosolvate monohydrate

H.-P. Huang and L.-X. Liu

Comment

In our previous publictions, we reported a 3,5-diphenylpyrazolate-bridged dinuclear Pd(II) complex having an inorganic anion as the charge-balancing species (Huang *et al.*, 2005 and 2007). Recently, we reported a 4-benzyl substituted 3,5-diphenylpyrazole ligand (Huang *et al.*, 2007). In the present paper, we report the crytal structure of a dinuclear palladium(II) complex based on 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4-benzyl-3,5-diphenylpyrazolate (Fig. 1). In the cation, a crystallographic twofold rotation axis passes through F6 and the mid-point of the Pd1—Pd1^{i} atoms (Fig. 1)·The distance of two palladium atoms is 2.9989 (6) Å which are shorter than that of our previous dipalladium complexes (Table 1). The Pd^{II} center has a *cis*-square-planar geometry defined by a *N*,*N*'-bidentate pyrazolate ligand and a chelating 4,4'-dimethyl-2,2'-bipyridine ligand. This conformation creates an 'open book' disposition for the square-planar environment of the two Pd atoms. The dihedral angle between the two coordination planes around the Pd atoms is 61.0 (1)°. The two Pd(dmbpy)Pd planes form a cleft with a cavity of approximately 180 Å^3. An interesting feature of the structure is the presence of a disordered hexafluorophosphate anion in the clip-like cavity formed by the Pd(dmbpy)Pd1 and Pd(dmbpy)Pd^{i} planes. This disordered hexafluorophosphate anions is generated by a twofold rotation axis and held in the cavity by an anion–π interaction (P2—F8···*Cg*1 3.435 (15) Å, *Cg*1 is the centroid of the ring system Pd1, N1, C6, C7, N2; P2—F8···*Cg*2 3.187 (15) Å, *Cg*2 is the centroid of the ring system N1, C1, C2, C3, C5, C6). Atoms P1, F3 and F4 of the second anion lie also on a twofold rotation axis (Wyckoff letter a) and is located near the cation by C—H···F intermolecular hydrogen bonds. The compound packs by elestrostatic interactions, C—H···F intermolecular hydrogen bonds between the cations and anions, and C—H···O intermolecular hydrogen bonds between the solvent diethyl ether molecules and water molecules. The non-classical hydrogen bonds that connect cations and anions are detailed in Table 2.

Experimental

A mixture of [4,4'-dimethyl-2,2'-bipyridine]dinitratopalladium (83.0 mg, 0.20 mmol) and 4-benzyl-3,5-diphenylpyrazole (31.0 mg, 0.10 mmol) was dissolved in water (5 ml) and stirred 2 h resulting in a clear yellow solution. To the mixture was added a tenfold excess of potassium hexafluorophosphate, which resulted in the immediate deposition of yellow microcrystals·The crystals were filtered, washed with a minimum amount of cold water and dried under vacuum (quantative yield, of 129.6 mg). Crystals were obtained by the vapor diffusion of diethyl ether into a 1 m*M* solution of in acetonitrile. ^{1}H NMR (400 MHz, [D$_3$] acetonitrile): δ 2.45 (12*H*, s, dmbpy-CH$_3$), 4.09 (4*H*, s, CH$_2$), 6.82 (4*H*, m, Ph—H), 7.03 (6*H*, m, Ph—H), 7.20 (4*H*, d, J=5.9 Hz, dmbpy-H$_{5,5'}$), 7.26 (8*H*, t, J = 7.5 Hz, Ph—H), 7.33 (4*H*, t, J = 7.3 Hz, Ph—H), 7.53 (8*H*, d, J = 7.5 Hz, Ph—H), 7.77 (4*H*, d, J = 5.9 Hz, dmbpy-H$_{6,6'}$), 7.99 (4*H*, s, dmbpy-H$_{3,3'}$) p.p.m.

Refinement

The value −0.02 (3) of the Flack parameter (Flack, 1983) indicates the absolute structure of the measured crystal was correctly determined. The water O atoms were refined with anisotropic displacement parameters. The H atoms of water molecules were located in a difference Fourier map and refined as riding, with O—H distances of 0.97 Å and U_{iso}(H) = 1.2U_{eq}(O). The aromatic H atoms were constrained to an ideal geometry, with C—H distances of 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). The methyl H atoms were rotated to fit the electron density, with C—H distances of 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C). The methylene H atoms were constrained to ideal geometry, with C—H distances of 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). Both PF_6^- anions and ether molecule were disordered about twofold rotation axis. The largest peak and deepest hole on the final difference Fourier map corresponds to 1.05 and −0.720 e Å^{-3}, and were located 1.15 and 0.16 Å from the F3 and C35 atoms, respectively.

Figures

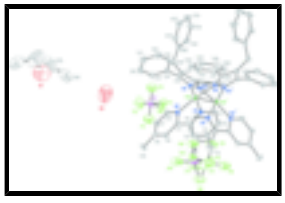

Fig. 1. A view of the title compound, showing 30% probability displacement ellipsoids and the atom numbering scheme.

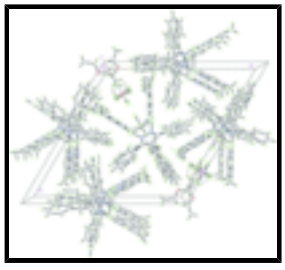

Fig. 2. Crystal packing of the title compound.

Bis(μ-4-benzyl-3,5-diphenylpyrazolato-κ^2*N*:*N*')bis[(4,4'-\ dimethyl-2,2'-bipyridine-κ^2*N*,*N*')palladium(II)] bis(hexafluoridophosphate) diethyl ether monosolvate monohydrate

Crystal data

$[Pd_2(C_{22}H_{17}N_2)_2(C_{12}H_{12}N_2)_2](PF_6)_2{\cdot}C_4H_{10}O{\cdot}H_2O$	Z = 3
M_r = 1582.10	F_{000} = 2412
Trigonal, $P3_121$	D_x = 1.444 Mg m^{-3}
Hall symbol: P 31 2"	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 22.1138 (3) Å	Cell parameters from 9974 reflections
b = 22.1138 (3) Å	θ = 2.4–27.9º
c = 12.8884 (2) Å	μ = 0.62 mm^{-1}
α = 90º	T = 291 (2) K
β = 90º	Block, yellow
γ = 120º	0.48 × 0.42 × 0.36 mm

V = 5458.29 (13) Å^3

Data collection

Bruker SMART CCD area-detector diffractometer	9007 independent reflections
Radiation source: sealed tube	8156 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.028
T = 291(2) K	θ_{max} = 28.3º
φ and ω scans	θ_{min} = 1.1º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	h = −29→29
T_{min} = 0.756, T_{max} = 0.808	k = −29→29
47040 measured reflections	l = −16→16

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2 + 2.0829P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.144	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.10	$\Delta\rho_{max}$ = 1.05 e Å^{-3}
9007 reflections	$\Delta\rho_{min}$ = −0.74 e Å^{-3}
466 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 4168 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.02 (3)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.5436 (3)	0.8913 (3)	1.0360 (4)	0.0499 (10)	
H1	0.5219	0.9138	1.0659	0.060*	
C2	0.5767 (3)	0.8665 (3)	1.0993 (4)	0.0590 (13)	

H2	0.5777	0.8732	1.1706	0.071*
C3	0.6080 (3)	0.8319 (3)	1.0572 (4)	0.0600 (13)
C4	0.6420 (5)	0.8022 (5)	1.1256 (6)	0.095 (3)
H4A	0.6909	0.8355	1.1322	0.142*
H4B	0.6362	0.7600	1.0952	0.142*
H4C	0.6206	0.7921	1.1929	0.142*
C5	0.6071 (3)	0.8259 (3)	0.9514 (5)	0.0577 (12)
H5	0.6284	0.8033	0.9208	0.069*
C6	0.5751 (2)	0.8527 (2)	0.8887 (4)	0.0439 (9)
C7	0.5768 (2)	0.8544 (2)	0.7752 (4)	0.0422 (9)
C8	0.6115 (3)	0.8291 (3)	0.7153 (4)	0.0525 (11)
H8	0.6319	0.8060	0.7471	0.063*
C9	0.6160 (3)	0.8379 (3)	0.6094 (4)	0.0580 (13)
C10	0.6557 (5)	0.8132 (5)	0.5452 (6)	0.089 (2)
H10A	0.6379	0.7643	0.5576	0.133*
H10B	0.7042	0.8389	0.5637	0.133*
H10C	0.6505	0.8204	0.4731	0.133*
C11	0.5847 (3)	0.8732 (3)	0.5659 (4)	0.0591 (13)
H11	0.5870	0.8809	0.4947	0.071*
C12	0.5500 (3)	0.8965 (3)	0.6292 (4)	0.0508 (11)
H12	0.5295	0.9201	0.5992	0.061*
C13	0.4209 (2)	0.9453 (2)	0.6460 (4)	0.0422 (9)
C14	0.3722 (2)	0.8706 (2)	0.6242 (4)	0.0468 (10)
C15	0.3780 (3)	0.8400 (3)	0.5326 (5)	0.0652 (14)
H15	0.4128	0.8663	0.4847	0.078*
C16	0.3309 (5)	0.7694 (4)	0.5139 (7)	0.084 (2)
H16	0.3354	0.7484	0.4542	0.101*
C17	0.2784 (5)	0.7310 (3)	0.5822 (7)	0.088 (2)
H17	0.2472	0.6841	0.5685	0.106*
C18	0.2716 (4)	0.7611 (4)	0.6711 (8)	0.086 (2)
H18	0.2352	0.7349	0.7169	0.103*
C19	0.3187 (3)	0.8307 (3)	0.6929 (5)	0.0620 (12)
H19	0.3143	0.8506	0.7539	0.074*
C20	0.4195 (2)	0.9389 (2)	1.0197 (4)	0.0403 (9)
C21	0.3762 (2)	0.8629 (2)	1.0408 (4)	0.0455 (10)
C22	0.3518 (3)	0.8147 (3)	0.9600 (5)	0.0589 (13)
H22	0.3615	0.8299	0.8916	0.071*
C23	0.3129 (3)	0.7436 (3)	0.9820 (6)	0.0715 (17)
H23	0.2971	0.7116	0.9278	0.086*
C24	0.2976 (3)	0.7204 (3)	1.0813 (7)	0.082 (2)
H24	0.2704	0.6728	1.0944	0.098*
C25	0.3214 (3)	0.7660 (4)	1.1609 (6)	0.0725 (18)
H25	0.3114	0.7495	1.2287	0.087*
C26	0.3609 (3)	0.8374 (3)	1.1428 (5)	0.0591 (13)
H26	0.3772	0.8683	1.1984	0.071*
C27	0.4274 (2)	1.0032 (3)	0.5939 (3)	0.0429 (8)
C28	0.3809 (3)	1.0019 (3)	0.5084 (4)	0.0528 (11)
H28A	0.3642	0.9587	0.4699	0.063*
H28B	0.4085	1.0401	0.4613	0.063*

C29	0.3190 (3)	1.0073 (2)	0.5424 (4)	0.0498 (11)	
C30	0.2880 (3)	0.9856 (3)	0.6380 (5)	0.0644 (14)	
H30	0.3081	0.9699	0.6865	0.077*	
C31	0.2275 (4)	0.9864 (5)	0.6643 (9)	0.096 (3)	
H31	0.2067	0.9696	0.7286	0.115*	
C32	0.1984 (5)	1.0118 (6)	0.5953 (11)	0.117 (4)	
H32	0.1591	1.0145	0.6138	0.140*	
C33	0.2280 (5)	1.0335 (5)	0.4983 (11)	0.108 (4)	
H33	0.2079	1.0494	0.4501	0.130*	
C34	0.2877 (4)	1.0314 (3)	0.4731 (6)	0.0742 (19)	
H34	0.3075	1.0466	0.4078	0.089*	
C35	0.0657 (19)	0.0584 (18)	0.794 (3)	0.282 (17)	
H35A	0.0256	0.0564	0.8277	0.338*	
H35B	0.0548	0.0504	0.7204	0.338*	
C36	0.1279 (17)	0.1337 (17)	0.806 (2)	0.267 (14)	
H36A	0.1342	0.1462	0.8782	0.401*	
H36B	0.1185	0.1654	0.7682	0.401*	
H36C	0.1696	0.1359	0.7795	0.401*	
F1	0.5517 (4)	1.0008 (4)	0.4557 (3)	0.1223 (19)	
F2	0.5204 (7)	0.9199 (4)	0.3331 (6)	0.185 (4)	
F3	0.4871 (6)	1.0000	0.3333	0.220 (9)	
F4	0.6205 (7)	1.0000	0.3333	0.218 (7)	
F5	0.8020 (4)	1.0593 (5)	0.8395 (10)	0.098 (3)	0.50
F6	0.8550 (5)	1.0000	0.8333	0.174 (5)	
F7	0.7642 (6)	0.9347 (7)	0.9591 (14)	0.270 (7)	
F8	0.7129 (6)	0.9957 (7)	0.9187 (15)	0.158 (6)	0.50
F9	0.8204 (7)	1.0540 (8)	0.9732 (17)	0.173 (7)	0.50
N1	0.5419 (2)	0.8839 (2)	0.9324 (3)	0.0409 (7)	
N2	0.5449 (2)	0.8865 (2)	0.7307 (3)	0.0405 (7)	
N3	0.46707 (19)	0.96654 (19)	0.7249 (3)	0.0386 (7)	
N4	0.46601 (18)	0.96287 (19)	0.9408 (3)	0.0384 (7)	
O1	0.0732 (17)	0.0000	0.8333	0.290 (15)	
O2	0.2246 (11)	0.2246 (11)	1.0000	0.332 (17)	
H2A	0.2470	0.2505	0.9373	0.398*	
P1	0.55322 (12)	1.0000	0.3333	0.0683 (6)	
P2	0.7837 (3)	0.9967 (3)	0.8965 (6)	0.122 (2)	0.50
Pd1	0.500203 (16)	0.921712 (16)	0.83157 (2)	0.03555 (10)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.058 (3)	0.064 (3)	0.040 (2)	0.040 (2)	0.004 (2)	0.003 (2)
C2	0.067 (3)	0.078 (4)	0.046 (3)	0.047 (3)	0.000 (2)	0.009 (3)
C3	0.069 (3)	0.071 (4)	0.056 (3)	0.047 (3)	0.001 (3)	0.016 (3)
C4	0.129 (7)	0.135 (7)	0.072 (4)	0.105 (6)	0.011 (5)	0.035 (5)
C5	0.066 (3)	0.063 (3)	0.066 (3)	0.049 (3)	0.003 (3)	0.008 (3)
C6	0.042 (2)	0.041 (2)	0.052 (3)	0.0235 (17)	0.0037 (19)	0.0088 (19)
C7	0.043 (2)	0.042 (2)	0.047 (2)	0.0253 (17)	−0.0012 (19)	−0.0018 (18)

C8	0.055 (3)	0.057 (3)	0.058 (3)	0.038 (2)	0.000 (2)	−0.005 (2)
C9	0.056 (3)	0.068 (3)	0.060 (3)	0.038 (3)	0.000 (2)	−0.013 (2)
C10	0.104 (6)	0.130 (7)	0.071 (4)	0.088 (6)	−0.001 (4)	−0.027 (4)
C11	0.061 (3)	0.079 (4)	0.048 (3)	0.043 (3)	0.003 (2)	−0.006 (3)
C12	0.060 (3)	0.065 (3)	0.042 (2)	0.043 (3)	0.001 (2)	0.001 (2)
C13	0.0375 (19)	0.049 (2)	0.042 (2)	0.0227 (18)	−0.0035 (17)	−0.0047 (18)
C14	0.045 (2)	0.043 (2)	0.053 (3)	0.0231 (18)	−0.009 (2)	−0.0076 (19)
C15	0.069 (3)	0.066 (3)	0.061 (3)	0.035 (3)	−0.011 (3)	−0.020 (3)
C16	0.103 (5)	0.066 (4)	0.093 (5)	0.050 (4)	−0.031 (5)	−0.034 (4)
C17	0.086 (5)	0.048 (3)	0.125 (7)	0.029 (3)	−0.038 (5)	−0.016 (4)
C18	0.062 (4)	0.050 (3)	0.130 (7)	0.017 (3)	−0.003 (4)	0.006 (4)
C19	0.058 (3)	0.051 (3)	0.070 (3)	0.023 (2)	0.002 (3)	0.001 (3)
C20	0.0340 (19)	0.044 (2)	0.045 (2)	0.0209 (17)	0.0018 (17)	0.0033 (18)
C21	0.0374 (19)	0.048 (2)	0.056 (3)	0.0251 (19)	0.0064 (18)	0.008 (2)
C22	0.054 (3)	0.051 (3)	0.067 (3)	0.024 (2)	0.006 (3)	0.000 (2)
C23	0.060 (3)	0.046 (3)	0.102 (5)	0.022 (2)	0.007 (3)	−0.002 (3)
C24	0.054 (3)	0.051 (3)	0.135 (7)	0.022 (3)	0.015 (4)	0.024 (4)
C25	0.059 (3)	0.073 (4)	0.083 (5)	0.031 (3)	0.018 (3)	0.039 (4)
C26	0.051 (2)	0.058 (3)	0.061 (3)	0.023 (2)	0.006 (2)	0.017 (3)
C27	0.0407 (19)	0.049 (2)	0.041 (2)	0.0238 (18)	−0.0036 (17)	−0.0006 (19)
C28	0.050 (2)	0.058 (3)	0.044 (3)	0.022 (2)	−0.007 (2)	0.003 (2)
C29	0.048 (2)	0.0312 (18)	0.065 (3)	0.0159 (17)	−0.018 (2)	−0.0006 (19)
C30	0.060 (3)	0.062 (3)	0.080 (4)	0.037 (3)	−0.005 (3)	0.000 (3)
C31	0.064 (4)	0.087 (5)	0.141 (8)	0.040 (4)	0.008 (4)	−0.011 (5)
C32	0.080 (5)	0.103 (7)	0.196 (12)	0.068 (5)	−0.033 (7)	−0.033 (8)
C33	0.095 (6)	0.083 (5)	0.173 (10)	0.064 (5)	−0.070 (7)	−0.025 (6)
C34	0.078 (4)	0.046 (3)	0.098 (5)	0.031 (3)	−0.036 (4)	0.002 (3)
C35	0.28 (3)	0.27 (4)	0.29 (3)	0.13 (3)	0.15 (3)	0.00 (3)
C36	0.27 (3)	0.28 (3)	0.33 (3)	0.20 (3)	−0.01 (3)	−0.09 (3)
F1	0.160 (5)	0.157 (5)	0.047 (2)	0.077 (4)	−0.004 (3)	0.002 (3)
F2	0.282 (12)	0.118 (5)	0.138 (6)	0.087 (6)	0.020 (6)	0.015 (5)
F3	0.197 (9)	0.37 (3)	0.149 (10)	0.186 (14)	0.000 (6)	0.000 (12)
F4	0.188 (8)	0.30 (2)	0.200 (12)	0.152 (11)	0.013 (7)	0.026 (13)
F5	0.050 (4)	0.068 (5)	0.160 (10)	0.016 (4)	0.000 (5)	0.007 (5)
F6	0.110 (5)	0.099 (6)	0.309 (16)	0.049 (3)	0.009 (4)	0.018 (8)
F7	0.150 (8)	0.208 (11)	0.42 (2)	0.066 (9)	−0.013 (11)	0.086 (12)
F8	0.088 (7)	0.095 (8)	0.291 (19)	0.045 (6)	0.021 (9)	0.024 (10)
F9	0.097 (8)	0.120 (10)	0.28 (2)	0.040 (8)	0.038 (11)	0.061 (12)
N1	0.0424 (18)	0.0435 (18)	0.0425 (19)	0.0258 (15)	0.0024 (16)	0.0035 (16)
N2	0.0427 (18)	0.0451 (18)	0.0409 (19)	0.0273 (15)	0.0031 (15)	0.0001 (16)
N3	0.0353 (16)	0.0387 (17)	0.0426 (19)	0.0192 (14)	−0.0027 (14)	−0.0017 (15)
N4	0.0343 (16)	0.0369 (16)	0.046 (2)	0.0195 (13)	0.0048 (15)	0.0013 (15)
O1	0.29 (3)	0.30 (4)	0.28 (3)	0.15 (2)	0.025 (15)	0.05 (3)
O2	0.278 (18)	0.278 (18)	0.29 (3)	0.03 (3)	0.056 (16)	−0.056 (16)
P1	0.0776 (11)	0.0938 (17)	0.0389 (10)	0.0469 (8)	0.0025 (5)	0.0049 (10)
P2	0.061 (2)	0.078 (3)	0.219 (7)	0.029 (2)	0.013 (3)	0.010 (4)
Pd1	0.03531 (15)	0.03791 (16)	0.03836 (16)	0.02200 (12)	0.00096 (12)	0.00067 (12)

Geometric parameters (Å, °)

C1—N1	1.343 (6)	C24—H24	0.9300
C1—C2	1.378 (7)	C25—C26	1.390 (9)
C1—H1	0.9300	C25—H25	0.9300
C2—C3	1.375 (8)	C26—H26	0.9300
C2—H2	0.9300	C27—C20^{i}	1.409 (6)
C3—C5	1.370 (8)	C27—C28	1.497 (6)
C3—C4	1.506 (7)	C28—C29	1.499 (8)
C4—H4A	0.9600	C28—H28A	0.9700
C4—H4B	0.9600	C28—H28B	0.9700
C4—H4C	0.9600	C29—C30	1.375 (9)
C5—C6	1.388 (6)	C29—C34	1.389 (7)
C5—H5	0.9300	C30—C31	1.387 (9)
C6—N1	1.356 (6)	C30—H30	0.9300
C6—C7	1.464 (7)	C31—C32	1.373 (14)
C7—N2	1.355 (5)	C31—H31	0.9300
C7—C8	1.387 (6)	C32—C33	1.382 (16)
C8—C9	1.375 (8)	C32—H32	0.9300
C8—H8	0.9300	C33—C34	1.382 (13)
C9—C11	1.394 (8)	C33—H33	0.9300
C9—C10	1.495 (8)	C34—H34	0.9300
C10—H10A	0.9600	C35—O1	1.47 (4)
C10—H10B	0.9600	C35—C36	1.55 (4)
C10—H10C	0.9600	C35—H35A	0.9700
C11—C12	1.384 (7)	C35—H35B	0.9700
C11—H11	0.9300	C36—H36A	0.9600
C12—N2	1.321 (6)	C36—H36B	0.9600
C12—H12	0.9300	C36—H36C	0.9600
C13—N3	1.349 (6)	P1—F3	1.462 (15)
C13—C27	1.388 (7)	P1—F4	1.489 (15)
C13—C14	1.480 (6)	P1—F2	1.542 (8)
C14—C19	1.385 (8)	P1—F2^{ii}	1.542 (8)
C14—C15	1.397 (8)	P1—F1^{ii}	1.577 (4)
C15—C16	1.398 (10)	P1—F1	1.577 (4)
C15—H15	0.9300	P2—F5^{i}	1.425 (13)
C16—C17	1.362 (12)	P2—F5	1.436 (12)
C16—H16	0.9300	P2—F7	1.458 (13)
C17—C18	1.372 (12)	P2—F9	1.49 (2)
C17—H17	0.9300	P2—F8	1.582 (13)
C18—C19	1.389 (9)	P2—P2^{i}	1.634 (15)
C18—H18	0.9300	P2—F6	1.744 (11)
C19—H19	0.9300	F5—P2^{i}	1.425 (12)
C20—N4	1.352 (6)	F6—P2^{i}	1.744 (11)
C20—C27^{i}	1.409 (6)	N1—Pd1	2.002 (3)
C20—C21	1.484 (6)	N2—Pd1	2.010 (3)

C21—C22	1.392 (8)	N3—N4^{i}	1.352 (5)
C21—C26	1.403 (7)	N3—Pd1	2.033 (3)
C22—C23	1.392 (8)	N4—N3^{i}	1.352 (5)
C22—H22	0.9300	N4—Pd1	2.017 (3)
C23—C24	1.356 (11)	O1—C35^{iii}	1.47 (4)
C23—H23	0.9300	O2—H2A	0.9713
C24—C25	1.348 (12)	Pd1—Pd1^{i}	2.9989 (6)
N1—C1—C2	121.9 (4)	C30—C29—C34	116.9 (6)
N1—C1—H1	119.0	C30—C29—C28	123.3 (5)
C2—C1—H1	119.0	C34—C29—C28	119.6 (6)
C3—C2—C1	120.2 (5)	C29—C30—C31	122.0 (7)
C3—C2—H2	119.9	C29—C30—H30	119.0
C1—C2—H2	119.9	C31—C30—H30	119.0
C5—C3—C2	117.3 (5)	C32—C31—C30	120.0 (10)
C5—C3—C4	121.8 (5)	C32—C31—H31	120.0
C2—C3—C4	120.9 (6)	C30—C31—H31	120.0
C3—C4—H4A	109.5	C31—C32—C33	119.3 (8)
C3—C4—H4B	109.5	C31—C32—H32	120.4
H4A—C4—H4B	109.5	C33—C32—H32	120.4
C3—C4—H4C	109.5	C34—C33—C32	119.8 (7)
H4A—C4—H4C	109.5	C34—C33—H33	120.1
H4B—C4—H4C	109.5	C32—C33—H33	120.1
C3—C5—C6	121.6 (5)	C33—C34—C29	121.9 (8)
C3—C5—H5	119.2	C33—C34—H34	119.0
C6—C5—H5	119.2	C29—C34—H34	119.0
N1—C6—C5	119.8 (5)	O1—C35—C36	119 (4)
N1—C6—C7	114.6 (4)	O1—C35—H35A	107.7
C5—C6—C7	125.5 (4)	C36—C35—H35A	107.7
N2—C7—C8	121.0 (4)	O1—C35—H35B	107.7
N2—C7—C6	115.0 (4)	C36—C35—H35B	107.7
C8—C7—C6	124.0 (4)	H35A—C35—H35B	107.1
C9—C8—C7	120.7 (5)	C35—C36—H36A	109.5
C9—C8—H8	119.7	C35—C36—H36B	109.5
C7—C8—H8	119.7	H36A—C36—H36B	109.5
C8—C9—C11	117.2 (5)	C35—C36—H36C	109.5
C8—C9—C10	120.8 (6)	H36A—C36—H36C	109.5
C11—C9—C10	121.9 (6)	H36B—C36—H36C	109.5
C9—C10—H10A	109.5	F3—P1—F4	180.000 (4)
C9—C10—H10B	109.5	F3—P1—F2	95.9 (5)
H10A—C10—H10B	109.5	F4—P1—F2	84.1 (5)
C9—C10—H10C	109.5	F3—P1—F2^{ii}	95.9 (5)
H10A—C10—H10C	109.5	F4—P1—F2^{ii}	84.1 (5)
H10B—C10—H10C	109.5	F2—P1—F2^{ii}	168.1 (10)
C12—C11—C9	119.6 (5)	F3—P1—F1^{ii}	88.5 (3)
C12—C11—H11	120.2	F4—P1—F1^{ii}	91.5 (3)
C9—C11—H11	120.2	F2—P1—F1^{ii}	89.5 (4)

N2—C12—C11	122.6 (5)	F2^{ii}—P1—F1^{ii}	90.8 (4)
N2—C12—H12	118.7	F3—P1—F1	88.5 (3)
C11—C12—H12	118.7	F4—P1—F1	91.5 (3)
N3—C13—C27	109.4 (4)	F2—P1—F1	90.8 (4)
N3—C13—C14	122.2 (4)	F2^{ii}—P1—F1	89.5 (4)
C27—C13—C14	128.4 (4)	F1^{ii}—P1—F1	177.0 (6)
C19—C14—C15	119.2 (5)	F5^{i}—P2—F5	105.5 (7)
C19—C14—C13	120.1 (5)	F5^{i}—P2—F7	76.7 (8)
C15—C14—C13	120.6 (5)	F5—P2—F7	177.0 (10)
C14—C15—C16	119.2 (7)	F5^{i}—P2—F9	174.8 (8)
C14—C15—H15	120.4	F5—P2—F9	75.4 (8)
C16—C15—H15	120.4	F7—P2—F9	102.3 (11)
C17—C16—C15	120.8 (7)	F5^{i}—P2—F8	84.6 (8)
C17—C16—H16	119.6	F5—P2—F8	84.6 (7)
C15—C16—H16	119.6	F7—P2—F8	93.6 (8)
C16—C17—C18	120.2 (6)	F9—P2—F8	90.4 (9)
C16—C17—H17	119.9	F5^{i}—P2—P2^{i}	55.5 (6)
C18—C17—H17	119.9	F5—P2—P2^{i}	54.8 (6)
C17—C18—C19	120.2 (7)	F7—P2—P2^{i}	128.0 (10)
C17—C18—H18	119.9	F9—P2—P2^{i}	127.2 (8)
C19—C18—H18	119.9	F8—P2—P2^{i}	100.4 (7)
C14—C19—C18	120.3 (6)	F5^{i}—P2—F6	85.0 (5)
C14—C19—H19	119.9	F5—P2—F6	84.7 (5)
C18—C19—H19	119.9	F7—P2—F6	97.7 (7)
N4—C20—C27^{i}	108.2 (4)	F9—P2—F6	100.2 (6)
N4—C20—C21	121.0 (4)	F8—P2—F6	162.5 (9)
C27^{i}—C20—C21	130.7 (4)	P2^{i}—P2—F6	62.1 (3)
C22—C21—C26	117.9 (5)	P2^{i}—F5—P2	69.7 (7)
C22—C21—C20	120.9 (5)	P2^{i}—F6—P2	55.9 (6)
C26—C21—C20	121.1 (5)	C1—N1—C6	119.0 (4)
C21—C22—C23	119.8 (6)	C1—N1—Pd1	125.9 (3)
C21—C22—H22	120.1	C6—N1—Pd1	115.0 (3)
C23—C22—H22	120.1	C12—N2—C7	118.8 (4)
C24—C23—C22	121.0 (7)	C12—N2—Pd1	126.4 (3)
C24—C23—H23	119.5	C7—N2—Pd1	114.5 (3)
C22—C23—H23	119.5	C13—N3—N4^{i}	108.4 (3)
C25—C24—C23	120.4 (6)	C13—N3—Pd1	137.3 (3)
C25—C24—H24	119.8	N4^{i}—N3—Pd1	114.1 (3)
C23—C24—H24	119.8	N3^{i}—N4—C20	109.0 (3)
C24—C25—C26	120.6 (6)	N3^{i}—N4—Pd1	113.9 (3)
C24—C25—H25	119.7	C20—N4—Pd1	137.0 (3)
C26—C25—H25	119.7	C35—O1—C35^{iii}	113 (4)
C25—C26—C21	120.2 (6)	H2A—O2—H2A^{iv}	113.3 (1)
C25—C26—H26	119.9	N1—Pd1—N2	80.8 (1)

C21—C26—H26	119.9	N1—Pd1—N4	95.2 (1)
C13—C27—C20^{i}	105.0 (4)	N2—Pd1—N4	173.5 (2)
C13—C27—C28	125.7 (4)	N1—Pd1—N3	174.7 (2)
C20^{i}—C27—C28	129.0 (4)	N2—Pd1—N3	96.8 (1)
C27—C28—C29	115.5 (4)	N4—Pd1—N3	86.8 (1)
C27—C28—H28A	108.4	N1—Pd1—Pd1^{i}	110.59 (12)
C29—C28—H28A	108.4	N2—Pd1—Pd1^{i}	110.18 (11)
C27—C28—H28B	108.4	N4—Pd1—Pd1^{i}	66.34 (11)
C29—C28—H28B	108.4	N3—Pd1—Pd1^{i}	65.68 (11)
H28A—C28—H28B	107.5		
N1—C1—C2—C3	−1.2 (10)	C30—C29—C34—C33	−0.2 (9)
C1—C2—C3—C5	2.4 (10)	C28—C29—C34—C33	176.0 (6)
C1—C2—C3—C4	−177.7 (7)	F5^{i}—P2—F5—P2^{i}	−23.9 (8)
C2—C3—C5—C6	−0.8 (9)	F9—P2—F5—P2^{i}	161.4 (7)
C4—C3—C5—C6	179.3 (7)	F8—P2—F5—P2^{i}	−106.8 (8)
C3—C5—C6—N1	−2.0 (9)	F6—P2—F5—P2^{i}	59.4 (4)
C3—C5—C6—C7	174.2 (6)	F5^{i}—P2—F6—P2^{i}	53.3 (5)
N1—C6—C7—N2	−0.3 (6)	F5—P2—F6—P2^{i}	−52.8 (5)
C5—C6—C7—N2	−176.6 (5)	F7—P2—F6—P2^{i}	129.1 (9)
N1—C6—C7—C8	176.2 (5)	F9—P2—F6—P2^{i}	−126.9 (8)
C5—C6—C7—C8	−0.2 (8)	F8—P2—F6—P2^{i}	−0.5 (18)
N2—C7—C8—C9	1.9 (8)	C2—C1—N1—C6	−1.7 (8)
C6—C7—C8—C9	−174.3 (5)	C2—C1—N1—Pd1	−176.6 (4)
C7—C8—C9—C11	0.2 (8)	C5—C6—N1—C1	3.3 (7)
C7—C8—C9—C10	177.6 (6)	C7—C6—N1—C1	−173.3 (4)
C8—C9—C11—C12	−1.0 (9)	C5—C6—N1—Pd1	178.7 (4)
C10—C9—C11—C12	−178.4 (6)	C7—C6—N1—Pd1	2.1 (5)
C9—C11—C12—N2	−0.3 (9)	C11—C12—N2—C7	2.4 (8)
N3—C13—C14—C19	68.4 (6)	C11—C12—N2—Pd1	176.8 (4)
C27—C13—C14—C19	−111.3 (6)	C8—C7—N2—C12	−3.2 (7)
N3—C13—C14—C15	−114.1 (6)	C6—C7—N2—C12	173.4 (4)
C27—C13—C14—C15	66.2 (7)	C8—C7—N2—Pd1	−178.3 (4)
C19—C14—C15—C16	−1.9 (9)	C6—C7—N2—Pd1	−1.7 (5)
C13—C14—C15—C16	−179.4 (6)	C27—C13—N3—N4^{i}	0.6 (5)
C14—C15—C16—C17	2.1 (11)	C14—C13—N3—N4^{i}	−179.1 (4)
C15—C16—C17—C18	−0.6 (12)	C27—C13—N3—Pd1	−173.7 (3)
C16—C17—C18—C19	−1.0 (12)	C14—C13—N3—Pd1	6.6 (7)
C15—C14—C19—C18	0.3 (9)	C27^{i}—C20—N4—N3^{i}	0.5 (5)
C13—C14—C19—C18	177.9 (6)	C21—C20—N4—N3^{i}	−177.2 (4)
C17—C18—C19—C14	1.2 (11)	C27^{i}—C20—N4—Pd1	175.6 (3)
N4—C20—C21—C22	−35.4 (7)	C21—C20—N4—Pd1	−2.0 (7)
C27^{i}—C20—C21—C22	147.6 (5)	C36—C35—O1—C35^{iii}	147 (3)
N4—C20—C21—C26	142.2 (5)	C1—N1—Pd1—N2	172.7 (5)
C27^{i}—C20—C21—C26	−34.9 (7)	C6—N1—Pd1—N2	−2.4 (3)

C26—C21—C22—C23	0.7 (8)	C1—N1—Pd1—N4	−2.1 (4)
C20—C21—C22—C23	178.3 (5)	C6—N1—Pd1—N4	−177.2 (3)
C21—C22—C23—C24	0.7 (9)	C1—N1—Pd1—Pd1^{i}	64.5 (4)
C22—C23—C24—C25	−1.7 (10)	C6—N1—Pd1—Pd1^{i}	−110.6 (3)
C23—C24—C25—C26	1.3 (10)	C12—N2—Pd1—N1	−172.4 (5)
C24—C25—C26—C21	0.1 (9)	C7—N2—Pd1—N1	2.2 (3)
C22—C21—C26—C25	−1.1 (8)	C12—N2—Pd1—N3	2.8 (5)
C20—C21—C26—C25	−178.7 (5)	C7—N2—Pd1—N3	177.4 (3)
N3—C13—C27—C20^{i}	−0.3 (5)	C12—N2—Pd1—Pd1^{i}	−63.7 (4)
C14—C13—C27—C20^{i}	179.4 (5)	C7—N2—Pd1—Pd1^{i}	110.9 (3)
N3—C13—C27—C28	−173.6 (4)	N3^{i}—N4—Pd1—N1	111.1 (3)
C14—C13—C27—C28	6.1 (8)	C20—N4—Pd1—N1	−63.9 (5)
C13—C27—C28—C29	90.3 (6)	N3^{i}—N4—Pd1—N3	−63.9 (3)
C20^{i}—C27—C28—C29	−81.4 (6)	C20—N4—Pd1—N3	121.1 (4)
C27—C28—C29—C30	−27.2 (7)	N3^{i}—N4—Pd1—Pd1^{i}	0.9 (2)
C27—C28—C29—C34	156.9 (5)	C20—N4—Pd1—Pd1^{i}	−174.1 (5)
C34—C29—C30—C31	1.1 (9)	C13—N3—Pd1—N2	65.8 (5)
C28—C29—C30—C31	−175.0 (6)	N4^{i}—N3—Pd1—N2	−108.3 (3)
C29—C30—C31—C32	−2.5 (12)	C13—N3—Pd1—N4	−119.6 (5)
C30—C31—C32—C33	3.0 (14)	N4^{i}—N3—Pd1—N4	66.3 (3)
C31—C32—C33—C34	−2.2 (14)	C13—N3—Pd1—Pd1^{i}	174.9 (5)
C32—C33—C34—C29	0.8 (12)	N4^{i}—N3—Pd1—Pd1^{i}	0.9 (2)

Symmetry codes: (i) *x*−*y*+1, −*y*+2, −*z*+5/3; (ii) *x*−*y*+1, −*y*+2, −*z*+2/3; (iii) *x*−*y*, −*y*, −*z*+5/3; (iv) *y*, *x*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···F1^{i}	0.93	2.50	3.228 (8)	135
C12—H12···F1	0.93	2.44	3.200 (8)	139
C36—H36A···O2	0.96	2.45	3.25 (3)	141
C36—H36B···F7^{v}	0.96	2.31	3.04 (4)	133
C36—H36C···F9^{v}	0.96	2.19	2.95 (3)	135

Symmetry codes: (i) *x*−*y*+1, −*y*+2, −*z*+5/3; (v) −*x*+*y*, −*x*+1, *z*−1/3.

Fig. 1

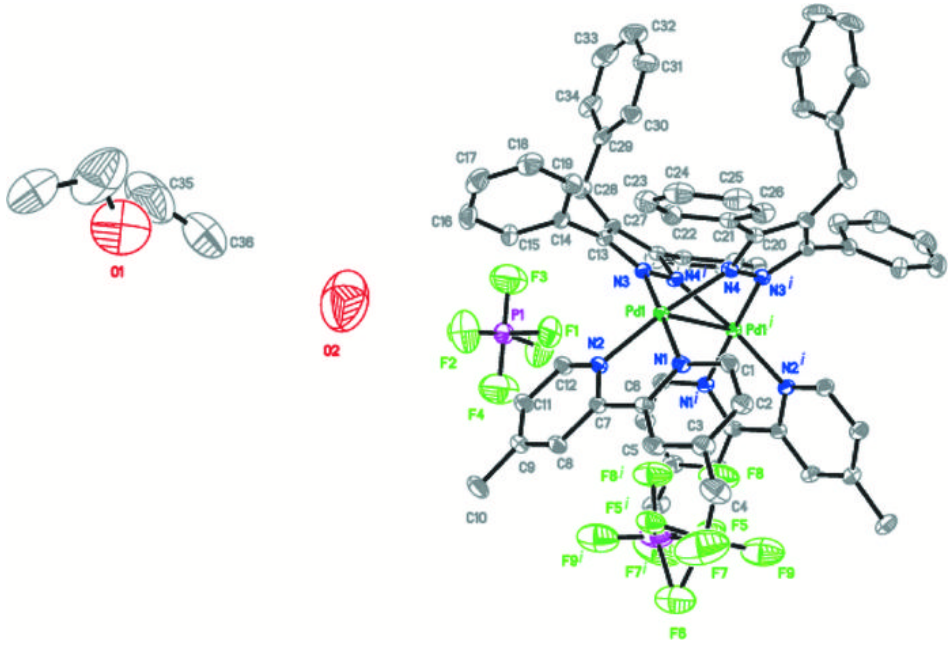
C35
C36
O1
O2
C32
C33
C31
C34
C30
C29
C18
C17
C19
C28
C23
C24
C25
C26
C16
C27
C22
C21
C15
C14
C13
C20
F3
N3
N4
N3i
P1
F1
Pd1
Pd1i
F2
N2
N1
C1
N2i
C12
C6
N1i
C2
F4
C11
C7
C3
C5
C9
C8
F8i
F8
F5i
C4
C10
F5
F9i
F7i
F7
F9
F6

Fig. 2