(4,4′-Dimethyl-2,2′-bipyridine-$\kappa^2 N,N'$)-bis[2-(2-pyridyl)phenyl-$\kappa^2 N,C^1$]-iridium(III) hexafluoridophosphate

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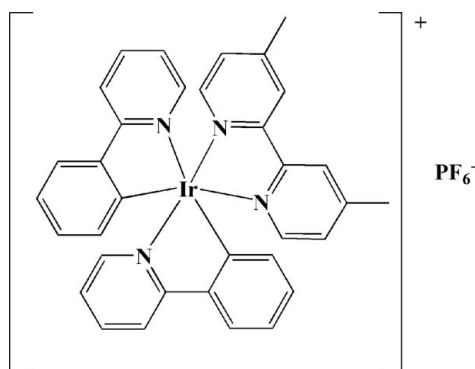
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The title compound, $[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2)]PF_6$, an iridium complex with two cyclometallated 2-phenylpyridine fragments and one 4,4′-dimethyl-2,2′-bipyridine unit, presents a distorted octahedral coordination geometry around the Ir atom. Charge balance is achieved through a hexafluoridophosphate anion. The coordination geometry of the two 2-phenylpyridine ligands around the Ir^{III} centre retains the *cis*-C—C and *trans*-N—N chelate dispositions.

Related literature

For related literature, see: Graces *et al.* (1988); Huo *et al.* (2006); Wong *et al.* (2006); Lo *et al.* (2003); Lamansky *et al.* (2001).

Experimental

Crystal data

$[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2)]PF_6$
$M_r = 829.77$

Orthorhombic, $P2_12_12_1$
$a = 12.5020$ (9) Å
$b = 13.0490$ (9) Å
$c = 19.1980$ (13) Å
$V = 3131.9$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.38$ mm^{-1}
$T = 293$ (2) K
$0.40 \times 0.30 \times 0.25$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.23$, $T_{max} = 0.33$

17622 measured reflections
6124 independent reflections
5760 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.067$
$S = 1.00$
6124 reflections
415 parameters
2 restraints

H-atom parameters constrained
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}
Absolute structure: Flack (1983), with 2663 Friedel pairs
Flack parameter: −0.024 (6)

Table 1
Selected bond lengths (Å).

C13—Ir1	2.057 (4)	N2—Ir1	2.009 (5)
C34—Ir1	2.049 (4)	N3—Ir1	2.140 (4)
N1—Ir1	2.026 (5)	N4—Ir1	2.127 (4)

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2132).

References

Bruker (1997). *SMART*. Version 5.622. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Graces, F. O., King, K. A. & Watts, R. J. (1988). *Inorg. Chem.* **27**, 3464–3471.
Huo, S. Q., Deaton, J. C., Rajeswaran, M. & Lenhart, W. C. (2006). *Inorg. Chem.* **45**, 3155–3157.
Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H., Adachi, C., Burrows, P. E., Forrest, S. R. & Thompson, M. E. (2001). *Inorg. Chem.* **40**, 1704–1711.
Lo, K. K.-W., Chung, C.-K., Lee, T. K.-M., Lui, L.-H., Tsang, K. H.-K. & Zhu, N. (2003). *Inorg. Chem.* **42**, 6886–6897.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instrument Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. Version 2.03. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Wong, W. Y., Zhou, G. J., Yu, X. M., Kwok, H. S. & Tang, B. Z. (2006). *Adv. Funct. Mater.* **16**, 838–846.

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(4,4'-Dimethyl-2,2'-bipyridine-κ^2N,N')bis[2-(2-pyridyl)phenyl-κ^2N,C^1]iridium(III)   hexafluoridophosphate

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Comment

Recently, phosphorescent materials have been extensively studied owing to their applications for organic light-emitting diodes (OLEDs) with high performances. Amongst these materials, Iridium(III) complexes containing phenylpyridine are particularly important and have been thoroughly investigated (Graces *et al.*, 1988) because both singlet and triplet excitons can be harvested for light emission in these complexes, leading to the internal quantum efficiency of phosphorescent emitters theoretically approaching 100% (Huo *et al.*, 2006; Wong *et al.*, 2006). In this contribution, we present the synthesis and crystal structure of [Ir(ppy)$_2$(dMbpy)](PF$_6$) (ppy is 2-phenylpyridine and dMbpy is 4,4'-dimethyl-2,2'-bipyridine). The title compound reveals bright green light under excitation of UV radiation, which implies that it is a candidate for a highly efficient phosphorescent emitter in OLEDs.

The overall structural arrangement is similar to several previously reported examples, including the diketonate complex [(ppy)$_2$Ir(acac)] (Lamansky *et al.*,2001), the diimine complexes such as [Ir(mppz)$_2$(bpy-NH$_2$)](PF$_6$) (Lo *et al.*, 2003). As shown in Fig.1, [Ir(ppy)$_2$(dMbpy)](PF$_6$) has a distorted octahedral coordination geometry with two ppy and one dMbpy around the iridium center, and one hexafluorophosphate (PF$_6^-$) anion providing for charge balance. The coordination geometry of the ppy ligands around the cation is such that the carbon atoms C(13) and C(34) are in a *cis*- orientation, with Ir—C bond lengths of 2.058 (4) Å and 2.055 (4) Å, respectively; on the other side, the nitrogen atoms N(1) and N(2) in ppy reside at *trans*- locations, with Ir—N bond lengths of 2.026 (5) Å and 2.018 (5) Å, respectively. It is to be noted that the Ir—N3 and Ir- N4 bond lengths in the dMbpy ligand are 2.141 (4)Å and 2.127 (4) Å, values which are slightly longer than those in the ppy ligand. Coordination lengths are listed in Table 1.

Experimental

IrCl$_3$·3H$_2$O (0.1784 g, 0.51 mmol), ppy (0.20 ml, 1.29 mmol), 2-ethoxyethanol (9 ml) and water (3 ml) were heated to 120°C for 24 h under nitrogen atmosphere. After cooling to the room temperature, the precipitate was collected by filtration, washed with water and methanol, and then dried in vacuum. The obtained chloro-bridged dimmer(0.1604 g, 0.15 mmol) was mixed with dMbpy (0.0690 g, 0.375 mmol) in methanol/dichloromethane (30 ml, 1: 1, v:v). The mixture was refluxed under nitrogen atmosphere in the dark for 4 h. The title compound was achieved after metathesis with KPF$_6$ and subsequent recrystalllization from dichloromethane /petroleum ether at room temperature.

Refinement

All H-atoms bound to carbon were refined using a riding model with d(C—H) = 0.93 Å, U_{iso} = 1.2U_{eq} (C) for aromatic and 0.96 Å, U_{iso} = 1.5U_{eq} (C) for CH$_3$ atoms.
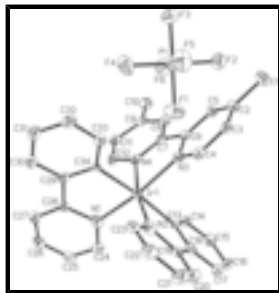
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Figures

Fig. 1. Molecular diagram of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

(4,4'-Dimethyl-2,2'-bipyridine-κ^2N,N')bis[2-(2-pyridyl)phenyl- κ^2N,C]iridium(III) hexafluoridophosphate

Crystal data

$[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2)]PF_6$	$F_{000} = 1624$
$M_r = 829.77$	$D_x = 1.760$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 5760 reflections
$a = 12.5020$ (9) Å	$\theta = 1.9–26.0º$
$b = 13.0490$ (9) Å	$\mu = 4.38$ mm^{-1}
$c = 19.1980$ (13) Å	$T = 293$ (2) K
$V = 3131.9$ (4) Å^3	Block, orange
$Z = 4$	$0.40 \times 0.30 \times 0.25$ mm

Data collection

Bruker APEX CCD area-detector diffractometer	6124 independent reflections
Radiation source: fine-focus sealed tube	5760 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.091$
$T = 293(2)$ K	$\theta_{max} = 26.0º$
ω scans	$\theta_{min} = 1.9º$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 11$
$T_{min} = 0.23$, $T_{max} = 0.33$	$k = -16 \rightarrow 15$
17622 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{max} = 0.002$

$S = 1.00$	$\Delta\rho_{max} = 1.23$ e Å^{-3}
6124 reflections	$\Delta\rho_{min} = -0.76$ e Å^{-3}
415 parameters	Extinction correction: none
2 restraints	Absolute structure: Flack (1983), 2663 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.024 (6)
Secondary atom site location: difference Fourier map	

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}
C1	0.1848 (6)	0.2841 (4)	0.1679 (3)	0.0461 (15)
H1A	0.2140	0.2778	0.1218	0.069*
H1B	0.1125	0.3085	0.1649	0.069*
H1C	0.1856	0.2184	0.1903	0.069*
C2	0.2504 (5)	0.3581 (3)	0.2091 (3)	0.0320 (11)
C3	0.3407 (5)	0.4050 (3)	0.1812 (3)	0.0338 (13)
H3	0.3645	0.3872	0.1369	0.041*
C4	0.3951 (5)	0.4787 (4)	0.2197 (2)	0.0304 (11)
H4	0.4525	0.5125	0.1992	0.037*
C5	0.2253 (4)	0.3823 (4)	0.2777 (2)	0.0316 (10)
H5	0.1666	0.3513	0.2987	0.038*
C6	0.2863 (5)	0.4520 (3)	0.3154 (3)	0.0286 (11)
C7	0.2724 (5)	0.4692 (3)	0.3914 (2)	0.0278 (11)
C8	0.2012 (5)	0.4148 (3)	0.4314 (3)	0.0333 (12)
H8	0.1543	0.3689	0.4105	0.040*
C9	0.1995 (5)	0.4285 (4)	0.5034 (3)	0.0355 (12)
C10	0.1245 (6)	0.3676 (4)	0.5485 (3)	0.0529 (16)
H10A	0.0820	0.3233	0.5197	0.079*
H10B	0.0785	0.4135	0.5736	0.079*
H10C	0.1650	0.3273	0.5808	0.079*
C11	0.2697 (5)	0.4990 (4)	0.5313 (3)	0.0329 (12)
H11	0.2725	0.5088	0.5792	0.039*
C12	0.3352 (5)	0.5546 (4)	0.4882 (3)	0.0328 (12)
H12	0.3796	0.6039	0.5080	0.039*
C13	0.5736 (4)	0.5377 (3)	0.3615 (2)	0.0182 (9)

C14	0.5925 (5)	0.4774 (4)	0.4166 (3)	0.0341 (12)
H14	0.5406	0.4716	0.4511	0.041*
C15	0.6874 (5)	0.4234 (4)	0.4238 (3)	0.0426 (14)
H15	0.6992	0.3818	0.4624	0.051*
C16	0.7637 (6)	0.4329 (4)	0.3725 (3)	0.0466 (15)
H16	0.8275	0.3966	0.3758	0.056*
C17	0.7454 (5)	0.4959 (4)	0.3164 (3)	0.0418 (14)
H17	0.7972	0.5037	0.2820	0.050*
C18	0.6484 (5)	0.5480 (3)	0.3118 (3)	0.0321 (12)
C19	0.6201 (4)	0.6180 (3)	0.2552 (2)	0.0279 (10)
C20	0.6786 (4)	0.6309 (4)	0.1943 (3)	0.0356 (11)
H20	0.7420	0.5947	0.1878	0.043*
C21	0.6428 (5)	0.6974 (4)	0.1434 (3)	0.0387 (13)
H21	0.6801	0.7030	0.1017	0.046*
C22	0.5525 (5)	0.7551 (3)	0.1539 (3)	0.0349 (12)
H22	0.5308	0.8013	0.1198	0.042*
C23	0.4933 (5)	0.7456 (3)	0.2146 (3)	0.0334 (12)
H23	0.4331	0.7864	0.2212	0.040*
C24	0.5684 (5)	0.7350 (3)	0.4616 (2)	0.0347 (11)
H24	0.6222	0.6863	0.4569	0.042*
C25	0.5753 (6)	0.8112 (4)	0.5126 (3)	0.0447 (14)
H25	0.6333	0.8112	0.5429	0.054*
C26	0.4980 (6)	0.8867 (4)	0.5192 (3)	0.0516 (16)
H26	0.5039	0.9366	0.5535	0.062*
C27	0.4131 (5)	0.8868 (4)	0.4746 (3)	0.0464 (14)
H27	0.3616	0.9380	0.4781	0.056*
C28	0.4024 (5)	0.8114 (3)	0.4238 (3)	0.0318 (12)
C29	0.3096 (5)	0.8056 (3)	0.3772 (3)	0.0322 (12)
C30	0.2232 (5)	0.8739 (4)	0.3743 (3)	0.0388 (12)
H30	0.2226	0.9311	0.4032	0.047*
C31	0.1400 (5)	0.8576 (4)	0.3299 (3)	0.0436 (14)
H31	0.0824	0.9027	0.3288	0.052*
C32	0.1422 (5)	0.7725 (4)	0.2858 (3)	0.0388 (13)
H32	0.0868	0.7600	0.2546	0.047*
C33	0.2283 (5)	0.7078 (4)	0.2899 (3)	0.0346 (12)
H33	0.2297	0.6513	0.2605	0.042*
C34	0.3108 (4)	0.7211 (3)	0.33388 (19)	0.0153 (8)
N1	0.4759 (5)	0.7335 (3)	0.4164 (2)	0.0429 (12)
N2	0.5231 (4)	0.6748 (3)	0.2667 (2)	0.0422 (12)
N3	0.3680 (4)	0.5028 (3)	0.28533 (19)	0.0248 (9)
N4	0.3385 (4)	0.5413 (3)	0.4192 (2)	0.0288 (10)
F1	0.4993 (4)	0.4697 (2)	0.59377 (19)	0.0600 (10)
F2	0.6177 (3)	0.3393 (3)	0.5834 (2)	0.0649 (11)
F3	0.5000 (4)	0.2318 (2)	0.6330 (2)	0.0630 (11)
F4	0.3804 (3)	0.3588 (2)	0.64277 (18)	0.0543 (9)
F5	0.4532 (3)	0.3242 (2)	0.53746 (18)	0.0540 (9)
F6	0.5454 (3)	0.3770 (3)	0.68888 (18)	0.0674 (10)
P1	0.49880 (14)	0.35010 (11)	0.61308 (8)	0.0411 (4)
Ir1	0.436483 (15)	0.622344 (12)	0.347270 (9)	0.02485 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.049 (4)	0.042 (3)	0.047 (4)	−0.007 (3)	−0.006 (3)	−0.008 (2)
C2	0.039 (3)	0.023 (2)	0.035 (3)	0.004 (2)	−0.010 (2)	−0.0002 (19)
C3	0.044 (4)	0.028 (2)	0.029 (2)	0.005 (2)	−0.001 (2)	−0.0014 (19)
C4	0.033 (3)	0.033 (2)	0.025 (2)	0.006 (2)	0.004 (2)	0.000 (2)
C5	0.034 (3)	0.026 (2)	0.035 (2)	−0.002 (2)	0.003 (2)	0.003 (2)
C6	0.033 (3)	0.022 (2)	0.030 (3)	0.002 (2)	0.001 (2)	0.0015 (18)
C7	0.034 (3)	0.023 (2)	0.027 (2)	0.004 (2)	−0.001 (2)	−0.0007 (19)
C8	0.035 (3)	0.029 (2)	0.036 (3)	−0.003 (2)	0.009 (3)	−0.0042 (19)
C9	0.040 (3)	0.035 (2)	0.031 (3)	−0.002 (2)	0.008 (3)	0.006 (2)
C10	0.064 (4)	0.054 (3)	0.041 (3)	−0.015 (4)	0.016 (3)	−0.001 (3)
C11	0.037 (3)	0.036 (3)	0.027 (3)	0.007 (2)	0.006 (2)	0.000 (2)
C12	0.035 (3)	0.031 (2)	0.032 (3)	0.005 (2)	−0.001 (2)	−0.003 (2)
C13	0.021 (2)	0.0129 (16)	0.021 (2)	−0.0011 (17)	−0.0028 (19)	0.0044 (14)
C14	0.033 (3)	0.037 (3)	0.033 (3)	0.001 (2)	0.000 (2)	0.000 (2)
C15	0.045 (4)	0.035 (3)	0.048 (3)	0.009 (3)	−0.007 (3)	0.010 (2)
C16	0.039 (4)	0.049 (3)	0.052 (4)	0.014 (3)	0.002 (3)	0.006 (3)
C17	0.027 (3)	0.039 (3)	0.059 (4)	0.007 (2)	0.008 (3)	−0.001 (3)
C18	0.034 (3)	0.021 (2)	0.041 (3)	−0.002 (2)	0.000 (2)	−0.005 (2)
C19	0.027 (3)	0.026 (2)	0.031 (2)	0.001 (2)	0.001 (2)	−0.003 (2)
C20	0.029 (3)	0.034 (2)	0.044 (3)	−0.002 (3)	0.002 (2)	−0.002 (2)
C21	0.042 (3)	0.044 (3)	0.031 (3)	−0.011 (2)	0.005 (3)	−0.001 (2)
C22	0.042 (3)	0.032 (2)	0.031 (2)	−0.011 (2)	−0.001 (3)	0.003 (2)
C23	0.039 (3)	0.025 (2)	0.036 (3)	−0.003 (2)	−0.003 (3)	0.002 (2)
C24	0.037 (3)	0.035 (2)	0.032 (2)	−0.007 (3)	0.002 (3)	0.004 (2)
C25	0.047 (4)	0.047 (3)	0.040 (3)	−0.013 (3)	−0.009 (3)	−0.003 (2)
C26	0.065 (4)	0.043 (3)	0.047 (3)	−0.007 (3)	−0.005 (3)	−0.018 (3)
C27	0.051 (4)	0.038 (3)	0.050 (3)	−0.003 (3)	0.004 (3)	−0.013 (3)
C28	0.037 (3)	0.020 (2)	0.038 (3)	−0.005 (2)	0.002 (2)	−0.0036 (19)
C29	0.035 (3)	0.029 (2)	0.033 (3)	−0.002 (2)	0.006 (3)	0.002 (2)
C30	0.041 (3)	0.027 (2)	0.049 (3)	0.004 (3)	0.006 (3)	−0.005 (2)
C31	0.044 (3)	0.034 (3)	0.053 (3)	0.013 (2)	0.001 (3)	−0.002 (2)
C32	0.033 (3)	0.043 (3)	0.041 (3)	0.003 (3)	−0.005 (3)	0.001 (2)
C33	0.040 (3)	0.029 (2)	0.034 (3)	0.002 (2)	0.006 (3)	−0.003 (2)
C34	0.017 (2)	0.0129 (16)	0.016 (2)	0.0023 (16)	−0.0015 (18)	0.0001 (14)
N1	0.040 (3)	0.048 (3)	0.040 (3)	−0.011 (2)	0.001 (2)	0.001 (2)
N2	0.046 (3)	0.045 (2)	0.036 (3)	−0.005 (2)	0.005 (2)	0.005 (2)
N3	0.030 (2)	0.0235 (18)	0.0209 (19)	0.0058 (17)	−0.0023 (18)	−0.0002 (15)
N4	0.032 (3)	0.028 (2)	0.027 (2)	0.0002 (18)	0.0017 (19)	0.0008 (17)
F1	0.069 (3)	0.0475 (18)	0.063 (2)	−0.014 (2)	−0.014 (2)	0.0061 (17)
F2	0.040 (2)	0.092 (3)	0.063 (2)	−0.003 (2)	0.001 (2)	0.022 (2)
F3	0.060 (3)	0.0452 (18)	0.084 (3)	0.0122 (19)	0.008 (2)	0.0185 (18)
F4	0.042 (2)	0.0624 (19)	0.059 (2)	0.0111 (17)	0.0087 (18)	0.0111 (18)
F5	0.058 (3)	0.0576 (18)	0.0465 (19)	0.0029 (18)	−0.0040 (19)	−0.0062 (16)
F6	0.065 (3)	0.098 (3)	0.0390 (18)	0.005 (3)	−0.0112 (18)	0.005 (2)

supplementary materials

P1	0.0371 (9)	0.0471 (9)	0.0390 (8)	0.0008 (7)	−0.0013 (7)	0.0073 (6)
Ir1	0.02670 (10)	0.02314 (9)	0.02473 (9)	−0.00017 (8)	0.00159 (8)	0.00069 (7)

Geometric parameters (Å, °)

C1—C2	1.495 (7)	C20—C21	1.381 (7)
C1—H1A	0.9600	C20—H20	0.9300
C1—H1B	0.9600	C21—C22	1.372 (8)
C1—H1C	0.9600	C21—H21	0.9300
C2—C5	1.390 (7)	C22—C23	1.388 (8)
C2—C3	1.390 (8)	C22—H22	0.9300
C3—C4	1.390 (7)	C23—N2	1.411 (6)
C3—H3	0.9300	C23—H23	0.9300
C4—N3	1.342 (6)	C24—C25	1.397 (7)
C4—H4	0.9300	C24—N1	1.447 (7)
C5—C6	1.391 (7)	C24—H24	0.9300
C5—H5	0.9300	C25—C26	1.386 (9)
C6—N3	1.347 (7)	C25—H25	0.9300
C6—C7	1.486 (7)	C26—C27	1.364 (9)
C7—N4	1.361 (6)	C26—H26	0.9300
C7—C8	1.373 (7)	C27—C28	1.392 (7)
C8—C9	1.393 (7)	C27—H27	0.9300
C8—H8	0.9300	C28—N1	1.378 (8)
C9—C11	1.380 (8)	C28—C29	1.468 (8)
C9—C10	1.503 (7)	C29—C34	1.380 (6)
C10—H10A	0.9600	C29—C30	1.402 (8)
C10—H10B	0.9600	C30—C31	1.362 (9)
C10—H10C	0.9600	C30—H30	0.9300
C11—C12	1.372 (7)	C31—C32	1.396 (7)
C11—H11	0.9300	C31—H31	0.9300
C12—N4	1.337 (6)	C32—C33	1.369 (8)
C12—H12	0.9300	C32—H32	0.9300
C13—C14	1.340 (6)	C33—C34	1.344 (6)
C13—C18	1.342 (7)	C33—H33	0.9300
C13—Ir1	2.057 (4)	C34—Ir1	2.049 (4)
C14—C15	1.386 (8)	N1—Ir1	2.026 (5)
C14—H14	0.9300	N2—Ir1	2.009 (5)
C15—C16	1.377 (9)	N3—Ir1	2.140 (4)
C15—H15	0.9300	N4—Ir1	2.127 (4)
C16—C17	1.374 (8)	F1—P1	1.604 (4)
C16—H16	0.9300	F2—P1	1.599 (4)
C17—C18	1.394 (8)	F3—P1	1.590 (3)
C17—H17	0.9300	F4—P1	1.590 (4)
C18—C19	1.463 (7)	F5—P1	1.596 (4)
C19—C20	1.389 (7)	F6—P1	1.607 (4)
C19—N2	1.438 (6)		
C2—C1—H1A	109.5	C25—C24—N1	118.6 (6)
C2—C1—H1B	109.5	C25—C24—H24	120.7
H1A—C1—H1B	109.5	N1—C24—H24	120.7

C2—C1—H1C	109.5	C26—C25—C24	121.8 (6)
H1A—C1—H1C	109.5	C26—C25—H25	119.1
H1B—C1—H1C	109.5	C24—C25—H25	119.1
C5—C2—C3	116.7 (5)	C27—C26—C25	119.1 (5)
C5—C2—C1	121.6 (5)	C27—C26—H26	120.5
C3—C2—C1	121.8 (5)	C25—C26—H26	120.5
C4—C3—C2	119.8 (5)	C26—C27—C28	120.9 (6)
C4—C3—H3	120.1	C26—C27—H27	119.6
C2—C3—H3	120.1	C28—C27—H27	119.6
N3—C4—C3	122.5 (5)	N1—C28—C27	122.1 (6)
N3—C4—H4	118.7	N1—C28—C29	115.2 (4)
C3—C4—H4	118.7	C27—C28—C29	122.6 (5)
C2—C5—C6	121.1 (5)	C34—C29—C30	119.5 (5)
C2—C5—H5	119.4	C34—C29—C28	113.6 (5)
C6—C5—H5	119.4	C30—C29—C28	126.9 (5)
N3—C6—C5	121.0 (4)	C31—C30—C29	120.9 (5)
N3—C6—C7	115.8 (4)	C31—C30—H30	119.5
C5—C6—C7	123.0 (5)	C29—C30—H30	119.5
N4—C7—C8	122.0 (4)	C30—C31—C32	119.2 (6)
N4—C7—C6	114.7 (5)	C30—C31—H31	120.4
C8—C7—C6	123.2 (5)	C32—C31—H31	120.4
C7—C8—C9	120.0 (5)	C33—C32—C31	118.1 (6)
C7—C8—H8	120.0	C33—C32—H32	121.0
C9—C8—H8	120.0	C31—C32—H32	121.0
C11—C9—C8	117.4 (5)	C34—C33—C32	124.1 (5)
C11—C9—C10	121.7 (5)	C34—C33—H33	118.0
C8—C9—C10	120.9 (5)	C32—C33—H33	118.0
C9—C10—H10A	109.5	C33—C34—C29	118.2 (5)
C9—C10—H10B	109.5	C33—C34—Ir1	125.9 (3)
H10A—C10—H10B	109.5	C29—C34—Ir1	115.8 (4)
C9—C10—H10C	109.5	C28—N1—C24	117.4 (4)
H10A—C10—H10C	109.5	C28—N1—Ir1	115.7 (4)
H10B—C10—H10C	109.5	C24—N1—Ir1	126.7 (4)
C12—C11—C9	119.9 (5)	C23—N2—C19	116.9 (5)
C12—C11—H11	120.1	C23—N2—Ir1	128.7 (4)
C9—C11—H11	120.1	C19—N2—Ir1	113.4 (3)
N4—C12—C11	123.2 (5)	C4—N3—C6	118.6 (4)
N4—C12—H12	118.4	C4—N3—Ir1	126.3 (4)
C11—C12—H12	118.4	C6—N3—Ir1	115.1 (3)
C14—C13—C18	119.8 (5)	C12—N4—C7	117.4 (4)
C14—C13—Ir1	124.6 (4)	C12—N4—Ir1	126.6 (4)
C18—C13—Ir1	115.6 (3)	C7—N4—Ir1	116.0 (3)
C13—C14—C15	121.9 (5)	F4—P1—F3	89.6 (2)
C13—C14—H14	119.1	F4—P1—F5	90.5 (2)
C15—C14—H14	119.1	F3—P1—F5	90.9 (2)
C16—C15—C14	118.4 (5)	F4—P1—F2	179.1 (2)
C16—C15—H15	120.8	F3—P1—F2	89.5 (2)
C14—C15—H15	120.8	F5—P1—F2	89.4 (2)
C17—C16—C15	120.0 (6)	F4—P1—F1	91.0 (2)

C17—C16—H16	120.0	F3—P1—F1	179.0 (3)
C15—C16—H16	120.0	F5—P1—F1	89.86 (19)
C16—C17—C18	119.1 (6)	F2—P1—F1	90.0 (2)
C16—C17—H17	120.4	F4—P1—F6	89.8 (2)
C18—C17—H17	120.4	F3—P1—F6	89.5 (2)
C13—C18—C17	120.8 (5)	F5—P1—F6	179.4 (3)
C13—C18—C19	115.0 (5)	F2—P1—F6	90.3 (2)
C17—C18—C19	124.2 (5)	F1—P1—F6	89.7 (2)
C20—C19—N2	120.7 (4)	N2—Ir1—N1	97.43 (19)
C20—C19—C18	125.0 (5)	N2—Ir1—C34	95.89 (17)
N2—C19—C18	114.3 (4)	N1—Ir1—C34	79.54 (19)
C21—C20—C19	120.0 (5)	N2—Ir1—C13	80.55 (18)
C21—C20—H20	120.0	N1—Ir1—C13	95.43 (19)
C19—C20—H20	120.0	C34—Ir1—C13	173.47 (15)
C22—C21—C20	120.5 (5)	N2—Ir1—N4	168.43 (17)
C22—C21—H21	119.7	N1—Ir1—N4	94.09 (17)
C20—C21—H21	119.7	C34—Ir1—N4	87.28 (16)
C21—C22—C23	120.9 (5)	C13—Ir1—N4	97.28 (16)
C21—C22—H22	119.6	N2—Ir1—N3	92.06 (17)
C23—C22—H22	119.6	N1—Ir1—N3	169.34 (19)
C22—C23—N2	120.9 (5)	C34—Ir1—N3	94.71 (15)
C22—C23—H23	119.6	C13—Ir1—N3	90.90 (15)
N2—C23—H23	119.6	N4—Ir1—N3	76.57 (15)
C5—C2—C3—C4	−5.4 (7)	C18—C19—N2—Ir1	−12.0 (5)
C1—C2—C3—C4	175.6 (5)	C3—C4—N3—C6	1.4 (7)
C2—C3—C4—N3	4.1 (8)	C3—C4—N3—Ir1	−174.7 (4)
C3—C2—C5—C6	1.6 (7)	C5—C6—N3—C4	−5.4 (7)
C1—C2—C5—C6	−179.4 (5)	C7—C6—N3—C4	169.9 (4)
C2—C5—C6—N3	3.9 (7)	C5—C6—N3—Ir1	171.2 (4)
C2—C5—C6—C7	−171.0 (5)	C7—C6—N3—Ir1	−13.5 (5)
N3—C6—C7—N4	5.6 (6)	C11—C12—N4—C7	0.4 (8)
C5—C6—C7—N4	−179.3 (4)	C11—C12—N4—Ir1	−179.9 (4)
N3—C6—C7—C8	−172.3 (5)	C8—C7—N4—C12	2.9 (7)
C5—C6—C7—C8	2.8 (8)	C6—C7—N4—C12	−175.1 (4)
N4—C7—C8—C9	−3.7 (8)	C8—C7—N4—Ir1	−176.8 (4)
C6—C7—C8—C9	174.1 (5)	C6—C7—N4—Ir1	5.3 (5)
C7—C8—C9—C11	1.1 (8)	C23—N2—Ir1—N1	−88.4 (5)
C7—C8—C9—C10	−178.2 (5)	C19—N2—Ir1—N1	103.5 (4)
C8—C9—C11—C12	2.0 (8)	C23—N2—Ir1—C34	−8.2 (4)
C10—C9—C11—C12	−178.6 (5)	C19—N2—Ir1—C34	−176.3 (3)
C9—C11—C12—N4	−2.9 (8)	C23—N2—Ir1—C13	177.3 (5)
C18—C13—C14—C15	−0.9 (7)	C19—N2—Ir1—C13	9.2 (3)
Ir1—C13—C14—C15	−179.0 (4)	C23—N2—Ir1—N4	97.3 (10)
C13—C14—C15—C16	0.1 (9)	C19—N2—Ir1—N4	−70.9 (11)
C14—C15—C16—C17	1.0 (9)	C23—N2—Ir1—N3	86.8 (4)
C15—C16—C17—C18	−1.3 (9)	C19—N2—Ir1—N3	−81.4 (3)
C14—C13—C18—C17	0.6 (7)	C28—N1—Ir1—N2	98.5 (4)
Ir1—C13—C18—C17	178.9 (4)	C24—N1—Ir1—N2	−86.4 (4)
C14—C13—C18—C19	−178.3 (4)	C28—N1—Ir1—C34	3.9 (4)

Ir1—C13—C18—C19	−0.1 (5)	C24—N1—Ir1—C34	179.0 (4)
C16—C17—C18—C13	0.4 (8)	C28—N1—Ir1—C13	179.6 (4)
C16—C17—C18—C19	179.3 (5)	C24—N1—Ir1—C13	−5.2 (4)
C13—C18—C19—C20	−171.6 (5)	C28—N1—Ir1—N4	−82.6 (4)
C17—C18—C19—C20	9.5 (8)	C24—N1—Ir1—N4	92.5 (4)
C13—C18—C19—N2	7.9 (6)	C28—N1—Ir1—N3	−54.2 (11)
C17—C18—C19—N2	−171.0 (5)	C24—N1—Ir1—N3	120.9 (9)
N2—C19—C20—C21	−1.2 (7)	C33—C34—Ir1—N2	83.9 (4)
C18—C19—C20—C21	178.3 (5)	C29—C34—Ir1—N2	−99.8 (4)
C19—C20—C21—C22	3.4 (8)	C33—C34—Ir1—N1	−179.6 (4)
C20—C21—C22—C23	−2.2 (8)	C29—C34—Ir1—N1	−3.4 (4)
C21—C22—C23—N2	−1.3 (8)	C33—C34—Ir1—N4	−85.0 (4)
N1—C24—C25—C26	−2.2 (8)	C29—C34—Ir1—N4	91.3 (4)
C24—C25—C26—C27	−0.2 (9)	C33—C34—Ir1—N3	−8.7 (4)
C25—C26—C27—C28	1.2 (9)	C29—C34—Ir1—N3	167.6 (3)
C26—C27—C28—N1	0.3 (9)	C14—C13—Ir1—N2	173.0 (4)
C26—C27—C28—C29	176.8 (5)	C18—C13—Ir1—N2	−5.1 (3)
N1—C28—C29—C34	0.9 (7)	C14—C13—Ir1—N1	76.4 (4)
C27—C28—C29—C34	−175.7 (5)	C18—C13—Ir1—N1	−101.8 (3)
N1—C28—C29—C30	179.4 (5)	C14—C13—Ir1—N4	−18.5 (4)
C27—C28—C29—C30	2.8 (8)	C18—C13—Ir1—N4	163.4 (3)
C34—C29—C30—C31	0.6 (8)	C14—C13—Ir1—N3	−95.1 (4)
C28—C29—C30—C31	−177.8 (5)	C18—C13—Ir1—N3	86.8 (3)
C29—C30—C31—C32	−1.1 (9)	C12—N4—Ir1—N2	160.3 (8)
C30—C31—C32—C33	0.7 (8)	C7—N4—Ir1—N2	−20.1 (11)
C31—C32—C33—C34	0.2 (9)	C12—N4—Ir1—N1	−14.1 (5)
C32—C33—C34—C29	−0.7 (8)	C7—N4—Ir1—N1	165.5 (4)
C32—C33—C34—Ir1	175.5 (4)	C12—N4—Ir1—C34	−93.4 (4)
C30—C29—C34—C33	0.3 (7)	C7—N4—Ir1—C34	86.2 (4)
C28—C29—C34—C33	178.9 (4)	C12—N4—Ir1—C13	81.9 (4)
C30—C29—C34—Ir1	−176.3 (4)	C7—N4—Ir1—C13	−98.5 (4)
C28—C29—C34—Ir1	2.3 (5)	C12—N4—Ir1—N3	171.1 (4)
C27—C28—N1—C24	−2.7 (8)	C7—N4—Ir1—N3	−9.3 (4)
C29—C28—N1—C24	−179.4 (4)	C4—N3—Ir1—N2	6.5 (4)
C27—C28—N1—Ir1	172.9 (4)	C6—N3—Ir1—N2	−169.8 (3)
C29—C28—N1—Ir1	−3.8 (6)	C4—N3—Ir1—N1	159.4 (9)
C25—C24—N1—C28	3.6 (7)	C6—N3—Ir1—N1	−16.9 (11)
C25—C24—N1—Ir1	−171.5 (4)	C4—N3—Ir1—C34	102.5 (4)
C22—C23—N2—C19	3.4 (7)	C6—N3—Ir1—C34	−73.7 (3)
C22—C23—N2—Ir1	−164.5 (4)	C4—N3—Ir1—C13	−74.1 (4)
C20—C19—N2—C23	−2.1 (7)	C6—N3—Ir1—C13	109.6 (3)
C18—C19—N2—C23	178.4 (4)	C4—N3—Ir1—N4	−171.4 (4)
C20—C19—N2—Ir1	167.5 (4)	C6—N3—Ir1—N4	12.3 (3)

Fig. 1