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***mer*-Hydridotris(trimethylphosphane- κ P)(D-valinato- κ^2 N,O)iridium hexafluoridophosphate dichloromethane 0.675-solvate**

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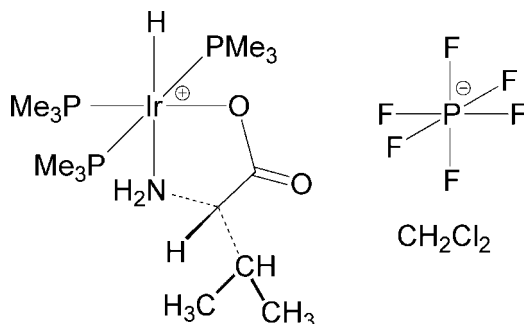
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; disorder in solvent or counterion; R factor = 0.031; wR factor = 0.046; data-to-parameter ratio = 31.1.

The title compound, $[\text{Ir}(\text{C}_5\text{H}_{10}\text{NO}_2)\text{H}(\text{C}_3\text{H}_9\text{P})_3]\text{PF}_6 \cdot 0.675\text{CH}_2\text{Cl}_2$, an iridium compound with a meridional arrangement of PMe_3 groups, O,N -bidentate coordination of D-valine and with a hydride ligand *trans* to the N atom is compared with the L-valine complex reported previously. As expected, the complexes from the corresponding L and D isomers of valine crystallize in enantiomorphous space groups ($P4_3$ and $P4_1$, respectively). In the crystal, $\text{N}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{F}$ hydrogen bonding is observed, the $\text{N}-\text{H}$ to carbonyl oxygen hydrogen bond producing a helical motif that proceeds along the 4_1 screw of the c axis.

Related literature

The structure of the related L-valine complex has been described by Roy *et al.* (2006). For studies of hydrogen-bonded lattice systems that lose crystallinity on loss of solvent and an analogous one that retains crystallinity, see: Parkin & Behrman (2009, 2011). An analysis of the geometric parameters for hydrogen bonds is given by Wood *et al.* (2009).



Experimental

Crystal data

$[\text{Ir}(\text{C}_5\text{H}_{10}\text{NO}_2)\text{H}(\text{C}_3\text{H}_9\text{P})_3]\text{PF}_6 \cdot 0.675\text{CH}_2\text{Cl}_2$
 $M_r = 739.86$
 Tetragonal, $P4_1$
 $a = 14.04454$ (17) Å
 $c = 14.2657$ (3) Å

$V = 2813.89$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.15$ mm⁻¹
 $T = 100$ K
 $0.17 \times 0.05 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur2 (Eos, Gemini ultra) diffractometer
 Absorption correction: gaussian (*CrysAlis PRO*; Oxford Diffraction, 2010)
 $T_{\min} = 0.449$, $T_{\max} = 0.774$

39354 measured reflections
 9371 independent reflections
 7266 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.046$
 $S = 0.81$
 9371 reflections
 301 parameters
 2 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.61$ e Å⁻³
 Absolute structure: Flack
 parameter determined using 3004 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: -0.021 (4)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{N1}-\text{H1A} \cdots \text{F1}$ | 0.92 (6) | 2.39 (6) | 3.157 (7) | 140 (5) |
| $\text{N1}-\text{H1B} \cdots \text{O2}^{\dagger}$ | 0.83 (6) | 2.02 (6) | 2.848 (7) | 172 (6) |

Symmetry code: (i) $y, -x, z - \frac{1}{4}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

We thank the National Science Foundation for funds (grant CHE-01311288) for the purchase of the Oxford Diffraction Xcalibur2 single-crystal diffractometer.

Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2516).

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supplementary materials

Acta Cryst. (2014). E70, m82 [doi:10.1107/S1600536814002165]

***mer*-Hydridotris(trimethylphosphane- κ P)(D-valinato- κ^2 N,O)iridium hexafluoridophosphate dichloromethane 0.675-solvate**

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1. Comment

Both the *D*- and *L*-Valine complexes of the type [HIr(AA)(PMe₃)₃][PF₆] crystallize in primitive tetragonal space groups, with the *L*-valine complex in P4₃ and the *D*-valine complex in the enantiomorphic group P4₁. The former structure was measured at room temperature on a Siemens P4 diffractometer while the latter was measured on an Oxford Diffraction instrument at 100 K. Accounting for room temperature vs. 100 K, the unit-cell parameters are essentially the same. Figure 1 shows a thermal ellipsoid plot of the asymmetric unit of the title compound. N—H to carbonyl oxygen hydrogen bonding produces a helical motif that proceeds along the 4₁ screw of the *c* axis. The helical motif for the H-bonding is shown in figure 2. Hydrogen bonding also occurs between the second N—H atom and a fluorine atom of the PF₆⁻ anion. Table 1 lists the hydrogen bonding parameters for the hydrogen bonds N1—H1A···F1 and N1—H1B···O2. With an H···O distance of 2.02 (6) Å and an N—H···O angle of 172 (6)°, the N1—H1B···O bond is a strong hydrogen bond while the N—H···F bond is not as strong based on geometric parameters, but still not a "weak" H-bond (Wood *et al.*, 2009).

In addition to the overall quality improvement of the structure of the *D* compound reported here at 100 K compared with the *L*-valine compound at RT, the issue of lattice solvent is an interesting one. In the previous report, the crystals were isolated and handled in air at room temperature for a period of days before mounting them and collecting data at room temperature. The *L*-valine complex showed very large voids (573 Å³) with negligible residual electron density. The current *D*-valine complex clearly shows dichloromethane within the structure, but each dichloromethane site is only ~68% occupied. Here, it would appear that dichloromethane of solvation is partially lost.

Often, for molecular compounds, loss of solvent of crystallization results in the collapse of the crystal lattice. The *D*-valine complex with partial loss and the *L*-valine with complete solvent loss maintain the crystal lattice structural integrity. Figure 3 shows a view of both the *D*- and *L*-valine space filling packing diagrams that show, the CH₂Cl₂ in the title compound and the empty space in the *L*-valine structure reported previously. The loss of solvent with preservation of the crystal lattice is the norm for metal-organic framework (MOF) compounds, but those involve strong coordination bonds between metals and linking ligands. Maintaining the crystal lattice solely with hydrogen bonding is not new, but it is somewhat rare. For another example, see Parkin and Behrman (2011).

2. Experimental

For a detailed description of the synthetic procedure for all of the tris-trimethylphosphine iridium amino acid complexes, see (Roy *et al.*, 2006). The title compound was recrystallized by the layering of diethyl ether over a dichloromethane solution. After several days of slow diffusion, suitable single crystals grew at the interface.

3. Refinement

The H-atoms on the amine nitrogen were located from the residual electron density map and the positions refined independently. The N—H bonds are 0.92 (6) and 0.83 (6) Å. The displacement parameters were fixed at $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{N1})$. The hydride was located in the residual electron density map, the distance restrained to 1.57 (2) Å, and the displacement parameter fixed at $U_{\text{iso}}(\text{H1})=1.5U_{\text{eq}}(\text{Ir1})$. After locating the iridium hydride salt, additional strong residual electron density peaks were modeled as a partially occupied CH_2Cl_2 molecule with occupancy that refined to 0.675 (6).

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2010); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

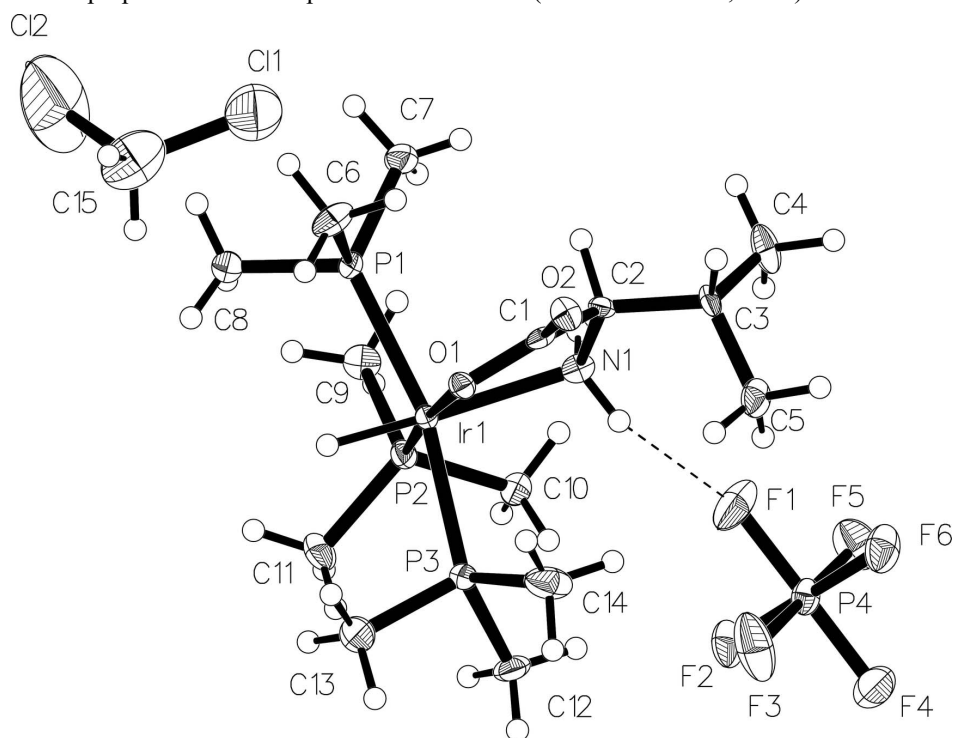
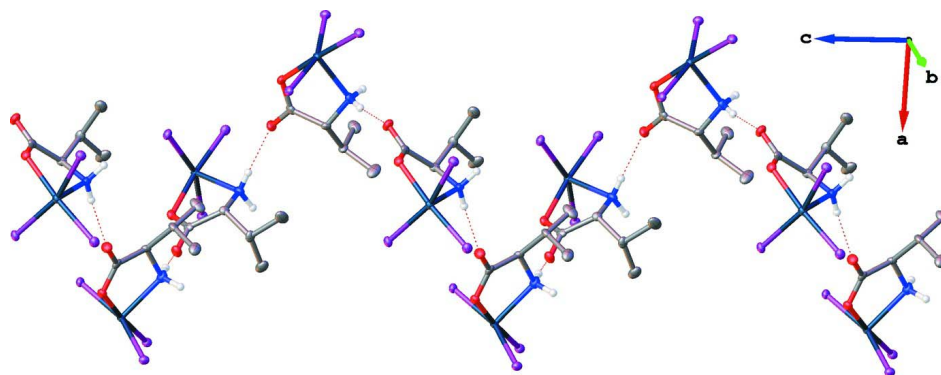
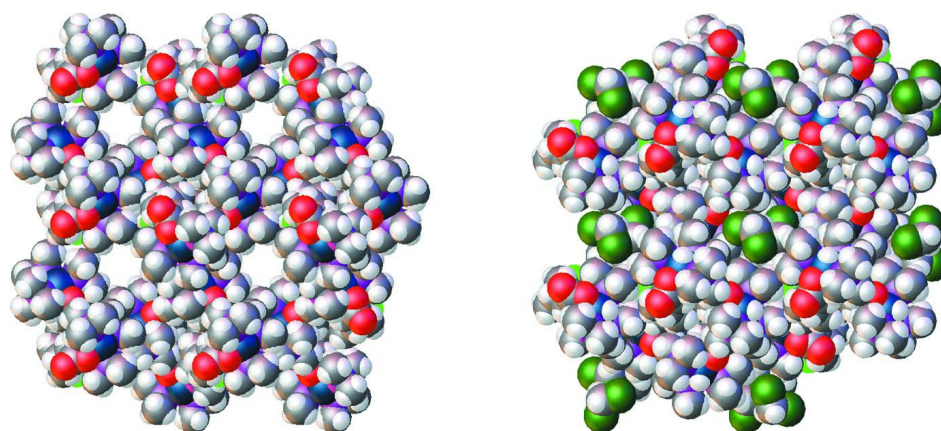


Figure 1

Thermal ellipsoid plot of the title compound showing the ellipsoids at the 50% probability level. The dichloromethane of solvation has a site occupancy of ~68%.


Figure 2

A view of the hydrogen-bonded extended helical lattice of the title compound. Ellipsoids are shown at the 50% probability level and hydrogen atoms as well as phosphorus methyl atoms are omitted for clarity.


Figure 3

A space filling model of both the *D*- and *L*-valine iridium complexes packed from $-0.5 \rightarrow 1.0$ along *a*, $-0.5 \rightarrow 1.0$ along *b*, and $-0.5 \rightarrow 1.0$ along *c*. The *L*-valine structure (left) shows a void while the *D*-valine structure (right) shows the dichloromethane in the lattice (68% occupancy). Spheres are shown at full van der Waals radii.

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$M_r = 739.86$

Tetragonal, $P4_1$

$a = 14.04454(17) \text{ \AA}$

$c = 14.2657(3) \text{ \AA}$

$V = 2813.89(9) \text{ \AA}^3$

$Z = 4$

$F(000) = 1457$

$D_x = 1.746 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 12856 reflections

$\theta = 3.5\text{--}31.4^\circ$

$\mu = 5.15 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Needle, colourless

$0.17 \times 0.05 \times 0.05 \text{ mm}$

Data collection

| | |
|--|--|
| Oxford Diffraction Xcalibur2 (Eos, Gemini ultra) diffractometer | $T_{\min} = 0.449$, $T_{\max} = 0.774$ |
| Radiation source: Enhance (Mo) X-ray Source | 39354 measured reflections |
| Graphite monochromator | 9371 independent reflections |
| Detector resolution: 16.0122 pixels mm ⁻¹ | 7266 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{\text{int}} = 0.069$ |
| Absorption correction: gaussian (CrysAlis PRO; Oxford Diffraction, 2010) | $\theta_{\max} = 31.5^\circ$, $\theta_{\min} = 3.5^\circ$ |
| | $h = -19 \rightarrow 20$ |
| | $k = -20 \rightarrow 20$ |
| | $l = -20 \rightarrow 20$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0129P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.046$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| $S = 0.81$ | $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$ |
| 9371 reflections | $\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$ |
| 301 parameters | Absolute structure: Flack parameter determined using 3004 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013) |
| 2 restraints | Absolute structure parameter: $-0.021(4)$ |
| Hydrogen site location: mixed | |

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.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|-------------|----------------------------------|-----------|
| Ir1 | 0.35067 (2) | 0.06307 (2) | 0.87490 (2) | 0.01215 (4) | |
| H | 0.423 (3) | 0.057 (4) | 0.946 (3) | 0.018* | |
| O1 | 0.2567 (3) | 0.1552 (3) | 0.9483 (3) | 0.0147 (9) | |
| O2 | 0.1109 (3) | 0.2137 (3) | 0.9557 (3) | 0.0185 (9) | |
| N1 | 0.2309 (4) | 0.0780 (4) | 0.7763 (4) | 0.0167 (11) | |
| H1A | 0.243 (4) | 0.127 (4) | 0.735 (4) | 0.020* | |
| H1B | 0.221 (4) | 0.023 (5) | 0.758 (4) | 0.020* | |
| C1 | 0.1714 (4) | 0.1635 (4) | 0.9161 (4) | 0.0139 (12) | |
| C2 | 0.1437 (4) | 0.1072 (4) | 0.8295 (4) | 0.0131 (12) | |
| H2 | 0.1141 | 0.0469 | 0.8529 | 0.016* | |
| C3 | 0.0677 (4) | 0.1561 (4) | 0.7699 (4) | 0.0161 (12) | |
| H3 | 0.0145 | 0.1728 | 0.8134 | 0.019* | |
| C4 | 0.0260 (5) | 0.0889 (5) | 0.6968 (4) | 0.0288 (16) | |
| H4A | 0.0754 | 0.0717 | 0.6512 | 0.043* | |
| H4B | -0.0268 | 0.1205 | 0.6643 | 0.043* | |
| H4C | 0.0026 | 0.0312 | 0.7277 | 0.043* | |
| C5 | 0.1009 (4) | 0.2493 (4) | 0.7263 (4) | 0.0249 (15) | |
| H5A | 0.1337 | 0.2876 | 0.7737 | 0.037* | |
| H5B | 0.0456 | 0.2845 | 0.7026 | 0.037* | |

| | | | | | |
|------|--------------|---------------|--------------|-------------|-----------|
| H5C | 0.1446 | 0.2358 | 0.6744 | 0.037* | |
| P1 | 0.28924 (11) | -0.05993 (12) | 0.96794 (11) | 0.0148 (3) | |
| C6 | 0.2254 (5) | -0.0111 (5) | 1.0676 (4) | 0.0281 (17) | |
| H6A | 0.2641 | 0.0385 | 1.0973 | 0.042* | |
| H6B | 0.2126 | -0.0619 | 1.1130 | 0.042* | |
| H6C | 0.1651 | 0.0165 | 1.0463 | 0.042* | |
| C7 | 0.2042 (5) | -0.1472 (4) | 0.9273 (4) | 0.0255 (15) | |
| H7A | 0.1438 | -0.1156 | 0.9126 | 0.038* | |
| H7B | 0.1938 | -0.1949 | 0.9764 | 0.038* | |
| H7C | 0.2289 | -0.1785 | 0.8709 | 0.038* | |
| C8 | 0.3778 (4) | -0.1308 (5) | 1.0273 (4) | 0.0287 (16) | |
| H8A | 0.4116 | -0.1703 | 0.9815 | 0.043* | |
| H8B | 0.3467 | -0.1718 | 1.0737 | 0.043* | |
| H8C | 0.4233 | -0.0888 | 1.0590 | 0.043* | |
| P2 | 0.44500 (11) | -0.02850 (12) | 0.78431 (11) | 0.0161 (3) | |
| C9 | 0.4335 (5) | -0.1576 (4) | 0.7880 (4) | 0.0230 (13) | |
| H9A | 0.4649 | -0.1853 | 0.7330 | 0.034* | |
| H9B | 0.3660 | -0.1749 | 0.7877 | 0.034* | |
| H9C | 0.4636 | -0.1819 | 0.8451 | 0.034* | |
| C10 | 0.4244 (4) | -0.0090 (4) | 0.6599 (4) | 0.0190 (14) | |
| H10A | 0.4285 | 0.0592 | 0.6461 | 0.028* | |
| H10B | 0.3609 | -0.0325 | 0.6430 | 0.028* | |
| H10C | 0.4726 | -0.0433 | 0.6234 | 0.028* | |
| C11 | 0.5723 (4) | -0.0150 (5) | 0.8001 (4) | 0.0252 (15) | |
| H11A | 0.6059 | -0.0491 | 0.7502 | 0.038* | |
| H11B | 0.5908 | -0.0412 | 0.8611 | 0.038* | |
| H11C | 0.5889 | 0.0527 | 0.7976 | 0.038* | |
| P3 | 0.42554 (11) | 0.20679 (11) | 0.83341 (11) | 0.0156 (3) | |
| C12 | 0.4899 (4) | 0.2255 (5) | 0.7248 (4) | 0.0246 (15) | |
| H12A | 0.5181 | 0.2893 | 0.7249 | 0.037* | |
| H12B | 0.4460 | 0.2196 | 0.6717 | 0.037* | |
| H12C | 0.5405 | 0.1778 | 0.7190 | 0.037* | |
| C13 | 0.5114 (5) | 0.2398 (5) | 0.9217 (4) | 0.0294 (17) | |
| H13A | 0.5631 | 0.1929 | 0.9228 | 0.044* | |
| H13B | 0.4803 | 0.2416 | 0.9832 | 0.044* | |
| H13C | 0.5375 | 0.3028 | 0.9071 | 0.044* | |
| C14 | 0.3453 (5) | 0.3082 (5) | 0.8334 (6) | 0.037 (2) | |
| H14A | 0.3821 | 0.3670 | 0.8259 | 0.056* | |
| H14B | 0.3104 | 0.3102 | 0.8928 | 0.056* | |
| H14C | 0.3001 | 0.3020 | 0.7814 | 0.056* | |
| P4 | 0.29616 (12) | 0.22465 (12) | 0.48790 (11) | 0.0201 (4) | |
| F1 | 0.2682 (3) | 0.1526 (3) | 0.5708 (3) | 0.0469 (12) | |
| F2 | 0.4001 (3) | 0.1782 (3) | 0.4853 (3) | 0.0322 (9) | |
| F3 | 0.3308 (3) | 0.2988 (3) | 0.5639 (3) | 0.0554 (14) | |
| F4 | 0.3246 (3) | 0.2950 (3) | 0.4063 (3) | 0.0439 (12) | |
| F5 | 0.2601 (3) | 0.1496 (3) | 0.4133 (3) | 0.0426 (11) | |
| F6 | 0.1918 (3) | 0.2709 (3) | 0.4920 (3) | 0.0353 (10) | |
| C15 | 0.5610 (11) | 0.3894 (9) | 0.4795 (10) | 0.066 (4) | 0.675 (6) |
| H15A | 0.5070 | 0.3578 | 0.4475 | 0.080* | 0.675 (6) |

| | | | | | |
|------|------------|------------|------------|-------------|-----------|
| H15B | 0.5730 | 0.3546 | 0.5387 | 0.080* | 0.675 (6) |
| Cl1 | 0.6642 (3) | 0.3794 (2) | 0.4068 (3) | 0.0708 (15) | 0.675 (6) |
| Cl2 | 0.5294 (4) | 0.4995 (4) | 0.5055 (7) | 0.157 (3) | 0.675 (6) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|-------------|---------------|---------------|--------------|
| Ir1 | 0.01075 (12) | 0.01395 (12) | 0.01177 (7) | -0.00014 (11) | -0.00084 (10) | 0.00094 (10) |
| O1 | 0.015 (2) | 0.015 (2) | 0.014 (2) | -0.0025 (18) | -0.0022 (17) | -0.0019 (16) |
| O2 | 0.016 (2) | 0.023 (2) | 0.017 (2) | 0.0037 (19) | 0.0020 (17) | -0.0052 (18) |
| N1 | 0.020 (3) | 0.013 (3) | 0.017 (3) | 0.001 (2) | 0.004 (2) | -0.002 (2) |
| C1 | 0.016 (3) | 0.012 (3) | 0.014 (3) | -0.001 (2) | 0.005 (2) | 0.004 (2) |
| C2 | 0.010 (3) | 0.012 (3) | 0.017 (3) | -0.003 (2) | 0.000 (2) | 0.000 (2) |
| C3 | 0.010 (3) | 0.024 (3) | 0.015 (3) | 0.003 (2) | -0.003 (2) | -0.001 (3) |
| C4 | 0.022 (4) | 0.032 (4) | 0.033 (4) | 0.015 (3) | -0.010 (3) | -0.010 (3) |
| C5 | 0.020 (4) | 0.029 (4) | 0.025 (3) | 0.011 (3) | 0.002 (3) | 0.006 (3) |
| P1 | 0.0151 (9) | 0.0175 (9) | 0.0118 (7) | -0.0009 (7) | -0.0008 (6) | 0.0031 (6) |
| C6 | 0.037 (4) | 0.024 (4) | 0.023 (4) | 0.001 (3) | 0.011 (3) | 0.006 (3) |
| C7 | 0.029 (4) | 0.025 (4) | 0.023 (3) | -0.010 (3) | -0.005 (3) | 0.004 (3) |
| C8 | 0.020 (4) | 0.038 (4) | 0.029 (4) | -0.004 (3) | -0.003 (3) | 0.013 (3) |
| P2 | 0.0127 (8) | 0.0188 (9) | 0.0166 (8) | 0.0015 (7) | -0.0005 (6) | 0.0011 (7) |
| C9 | 0.026 (4) | 0.019 (4) | 0.024 (3) | 0.000 (3) | 0.002 (3) | -0.006 (3) |
| C10 | 0.018 (3) | 0.021 (3) | 0.017 (3) | 0.006 (3) | 0.005 (2) | 0.001 (2) |
| C11 | 0.014 (3) | 0.034 (4) | 0.027 (4) | 0.004 (3) | -0.002 (3) | -0.002 (3) |
| P3 | 0.0137 (8) | 0.0155 (8) | 0.0177 (8) | -0.0013 (7) | -0.0004 (6) | 0.0013 (6) |
| C12 | 0.028 (4) | 0.026 (4) | 0.019 (3) | -0.011 (3) | 0.003 (3) | 0.006 (3) |
| C13 | 0.036 (4) | 0.027 (4) | 0.025 (4) | -0.010 (3) | -0.010 (3) | -0.001 (3) |
| C14 | 0.023 (4) | 0.018 (4) | 0.072 (6) | 0.000 (3) | 0.005 (4) | 0.004 (4) |
| P4 | 0.0213 (9) | 0.0208 (9) | 0.0180 (8) | 0.0069 (7) | -0.0001 (7) | 0.0002 (7) |
| F1 | 0.049 (3) | 0.049 (3) | 0.043 (3) | 0.026 (2) | 0.021 (2) | 0.025 (2) |
| F2 | 0.026 (2) | 0.039 (3) | 0.031 (2) | 0.0158 (19) | -0.0018 (17) | 0.0012 (19) |
| F3 | 0.061 (3) | 0.048 (3) | 0.058 (3) | 0.019 (2) | -0.034 (3) | -0.028 (2) |
| F4 | 0.040 (3) | 0.046 (3) | 0.046 (3) | 0.002 (2) | 0.004 (2) | 0.021 (2) |
| F5 | 0.039 (3) | 0.039 (3) | 0.049 (3) | 0.003 (2) | -0.008 (2) | -0.015 (2) |
| F6 | 0.032 (2) | 0.042 (3) | 0.031 (2) | 0.017 (2) | 0.0028 (18) | 0.0063 (19) |
| C15 | 0.089 (12) | 0.036 (8) | 0.074 (11) | 0.011 (7) | -0.013 (9) | 0.001 (7) |
| Cl1 | 0.084 (3) | 0.047 (2) | 0.082 (3) | -0.0090 (19) | 0.017 (2) | -0.0030 (18) |
| Cl2 | 0.140 (5) | 0.061 (4) | 0.270 (8) | 0.039 (4) | 0.095 (7) | 0.018 (4) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|----------|-----------|
| Ir1—H | 1.44 (3) | P2—C9 | 1.821 (6) |
| Ir1—O1 | 2.124 (4) | P2—C10 | 1.820 (5) |
| Ir1—N1 | 2.203 (6) | P2—C11 | 1.811 (6) |
| Ir1—P1 | 2.3430 (16) | C9—H9A | 0.9800 |
| Ir1—P2 | 2.2537 (16) | C9—H9B | 0.9800 |
| Ir1—P3 | 2.3517 (16) | C9—H9C | 0.9800 |
| O1—C1 | 1.288 (7) | C10—H10A | 0.9800 |
| O2—C1 | 1.240 (6) | C10—H10B | 0.9800 |

| | | | |
|------------|-------------|---------------|------------|
| N1—H1A | 0.92 (6) | C10—H10C | 0.9800 |
| N1—H1B | 0.83 (6) | C11—H11A | 0.9800 |
| N1—C2 | 1.499 (7) | C11—H11B | 0.9800 |
| C1—C2 | 1.518 (7) | C11—H11C | 0.9800 |
| C2—H2 | 1.0000 | P3—C12 | 1.813 (6) |
| C2—C3 | 1.528 (7) | P3—C13 | 1.805 (6) |
| C3—H3 | 1.0000 | P3—C14 | 1.816 (7) |
| C3—C4 | 1.524 (8) | C12—H12A | 0.9800 |
| C3—C5 | 1.522 (8) | C12—H12B | 0.9800 |
| C4—H4A | 0.9800 | C12—H12C | 0.9800 |
| C4—H4B | 0.9800 | C13—H13A | 0.9800 |
| C4—H4C | 0.9800 | C13—H13B | 0.9800 |
| C5—H5A | 0.9800 | C13—H13C | 0.9800 |
| C5—H5B | 0.9800 | C14—H14A | 0.9800 |
| C5—H5C | 0.9800 | C14—H14B | 0.9800 |
| P1—C6 | 1.815 (6) | C14—H14C | 0.9800 |
| P1—C7 | 1.807 (6) | P4—F1 | 1.605 (4) |
| P1—C8 | 1.805 (6) | P4—F2 | 1.599 (4) |
| C6—H6A | 0.9800 | P4—F3 | 1.580 (4) |
| C6—H6B | 0.9800 | P4—F4 | 1.578 (4) |
| C6—H6C | 0.9800 | P4—F5 | 1.582 (4) |
| C7—H7A | 0.9800 | P4—F6 | 1.604 (4) |
| C7—H7B | 0.9800 | C15—H15A | 0.9900 |
| C7—H7C | 0.9800 | C15—H15B | 0.9900 |
| C8—H8A | 0.9800 | C15—C11 | 1.789 (15) |
| C8—H8B | 0.9800 | C15—C12 | 1.651 (13) |
| C8—H8C | 0.9800 | | |
| O1—Ir1—H | 97 (2) | H8A—C8—H8C | 109.5 |
| O1—Ir1—N1 | 77.43 (17) | H8B—C8—H8C | 109.5 |
| O1—Ir1—P1 | 86.61 (11) | C9—P2—Ir1 | 120.0 (2) |
| O1—Ir1—P2 | 174.55 (11) | C10—P2—Ir1 | 112.3 (2) |
| O1—Ir1—P3 | 83.06 (11) | C10—P2—C9 | 99.4 (3) |
| N1—Ir1—H | 174 (2) | C11—P2—Ir1 | 116.7 (2) |
| N1—Ir1—P1 | 98.66 (15) | C11—P2—C9 | 100.9 (3) |
| N1—Ir1—P2 | 97.88 (14) | C11—P2—C10 | 105.2 (3) |
| N1—Ir1—P3 | 95.69 (15) | P2—C9—H9A | 109.5 |
| P1—Ir1—H | 80 (2) | P2—C9—H9B | 109.5 |
| P1—Ir1—P3 | 160.05 (5) | P2—C9—H9C | 109.5 |
| P2—Ir1—H | 88 (2) | H9A—C9—H9B | 109.5 |
| P2—Ir1—P1 | 96.93 (5) | H9A—C9—H9C | 109.5 |
| P2—Ir1—P3 | 94.74 (6) | H9B—C9—H9C | 109.5 |
| P3—Ir1—H | 85 (2) | P2—C10—H10A | 109.5 |
| C1—O1—Ir1 | 117.2 (3) | P2—C10—H10B | 109.5 |
| Ir1—N1—H1A | 110 (4) | P2—C10—H10C | 109.5 |
| Ir1—N1—H1B | 104 (4) | H10A—C10—H10B | 109.5 |
| H1A—N1—H1B | 122 (6) | H10A—C10—H10C | 109.5 |
| C2—N1—Ir1 | 109.1 (4) | H10B—C10—H10C | 109.5 |
| C2—N1—H1A | 106 (4) | P2—C11—H11A | 109.5 |

| | | | |
|------------|-----------|---------------|-----------|
| C2—N1—H1B | 106 (4) | P2—C11—H11B | 109.5 |
| O1—C1—C2 | 118.8 (5) | P2—C11—H11C | 109.5 |
| O2—C1—O1 | 121.8 (5) | H11A—C11—H11B | 109.5 |
| O2—C1—C2 | 119.4 (5) | H11A—C11—H11C | 109.5 |
| N1—C2—C1 | 110.2 (5) | H11B—C11—H11C | 109.5 |
| N1—C2—H2 | 106.1 | C12—P3—Ir1 | 124.2 (2) |
| N1—C2—C3 | 114.3 (5) | C12—P3—C14 | 101.3 (3) |
| C1—C2—H2 | 106.1 | C13—P3—Ir1 | 110.1 (2) |
| C1—C2—C3 | 113.5 (5) | C13—P3—C12 | 103.1 (3) |
| C3—C2—H2 | 106.1 | C13—P3—C14 | 102.3 (3) |
| C2—C3—H3 | 106.3 | C14—P3—Ir1 | 113.3 (2) |
| C4—C3—C2 | 111.8 (5) | P3—C12—H12A | 109.5 |
| C4—C3—H3 | 106.3 | P3—C12—H12B | 109.5 |
| C5—C3—C2 | 113.7 (5) | P3—C12—H12C | 109.5 |
| C5—C3—H3 | 106.3 | H12A—C12—H12B | 109.5 |
| C5—C3—C4 | 111.8 (5) | H12A—C12—H12C | 109.5 |
| C3—C4—H4A | 109.5 | H12B—C12—H12C | 109.5 |
| C3—C4—H4B | 109.5 | P3—C13—H13A | 109.5 |
| C3—C4—H4C | 109.5 | P3—C13—H13B | 109.5 |
| H4A—C4—H4B | 109.5 | P3—C13—H13C | 109.5 |
| H4A—C4—H4C | 109.5 | H13A—C13—H13B | 109.5 |
| H4B—C4—H4C | 109.5 | H13A—C13—H13C | 109.5 |
| C3—C5—H5A | 109.5 | H13B—C13—H13C | 109.5 |
| C3—C5—H5B | 109.5 | P3—C14—H14A | 109.5 |
| C3—C5—H5C | 109.5 | P3—C14—H14B | 109.5 |
| H5A—C5—H5B | 109.5 | P3—C14—H14C | 109.5 |
| H5A—C5—H5C | 109.5 | H14A—C14—H14B | 109.5 |
| H5B—C5—H5C | 109.5 | H14A—C14—H14C | 109.5 |
| C6—P1—Ir1 | 110.3 (2) | H14B—C14—H14C | 109.5 |
| C7—P1—Ir1 | 124.2 (2) | F2—P4—F1 | 89.1 (2) |
| C7—P1—C6 | 100.4 (3) | F2—P4—F6 | 179.2 (2) |
| C8—P1—Ir1 | 114.8 (2) | F3—P4—F1 | 89.1 (3) |
| C8—P1—C6 | 100.5 (3) | F3—P4—F2 | 90.2 (2) |
| C8—P1—C7 | 103.4 (3) | F3—P4—F5 | 178.9 (3) |
| P1—C6—H6A | 109.5 | F3—P4—F6 | 89.4 (2) |
| P1—C6—H6B | 109.5 | F4—P4—F1 | 179.5 (2) |
| P1—C6—H6C | 109.5 | F4—P4—F2 | 90.4 (2) |
| H6A—C6—H6B | 109.5 | F4—P4—F3 | 90.9 (3) |
| H6A—C6—H6C | 109.5 | F4—P4—F5 | 90.1 (2) |
| H6B—C6—H6C | 109.5 | F4—P4—F6 | 90.3 (2) |
| P1—C7—H7A | 109.5 | F5—P4—F1 | 89.8 (2) |
| P1—C7—H7B | 109.5 | F5—P4—F2 | 90.3 (2) |
| P1—C7—H7C | 109.5 | F5—P4—F6 | 90.1 (2) |
| H7A—C7—H7B | 109.5 | F6—P4—F1 | 90.3 (2) |
| H7A—C7—H7C | 109.5 | H15A—C15—H15B | 107.5 |
| H7B—C7—H7C | 109.5 | C11—C15—H15A | 108.5 |
| P1—C8—H8A | 109.5 | C11—C15—H15B | 108.5 |
| P1—C8—H8B | 109.5 | C12—C15—H15A | 108.5 |
| P1—C8—H8C | 109.5 | C12—C15—H15B | 108.5 |

| | | | |
|------------|-------|-------------|-----------|
| H8A—C8—H8B | 109.5 | Cl2—C15—C11 | 115.0 (8) |
|------------|-------|-------------|-----------|

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|--------------------------|------------|--------------|--------------|----------------|
| N1—H1A...F1 | 0.92 (6) | 2.39 (6) | 3.157 (7) | 140 (5) |
| N1—H1B...O2 ⁱ | 0.83 (6) | 2.02 (6) | 2.848 (7) | 172 (6) |

Symmetry code: (i) $y, -x, z-1/4$.