IUCrData

ISSN 2414-3146

# [(1,2,5,6-$\eta$)-Cycloocta-1,5-diene](1-ethyl-3-isopropyl-1,3-imidazol-2-ylidene-$\kappa C^2$)(triphenylphosphane-$\kappa P$)iridium(I) tetrafluoridoborate

Karam B. Idrees,[a] William J. Rutledge,[a] Sue A. Roberts[b] and Edward Rajaseelan[a]*

[a]Department of Chemistry, Millersville University, Millersville, PA 17551, USA, and [b]Department of Chemistry and Biochemistry, The University of Arizona, Tuscon, AZ 85716, USA. *Correspondence e-mail: edward.rajaseelan@millersville.edu

Received 27 September 2017
Accepted 30 September 2017

Edited by J. Simpson, University of Otago, New Zealand

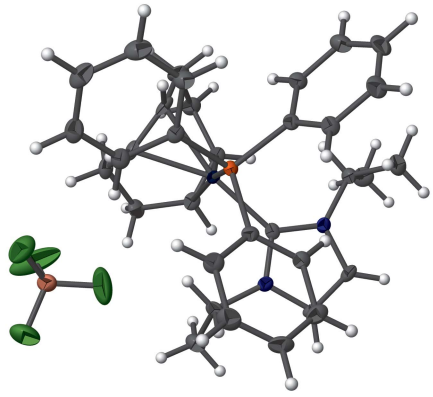
**Keywords:** crystal structure; iridium complex; imidazole; cycloocta-1,5-diene.

**CCDC reference**: 1577406

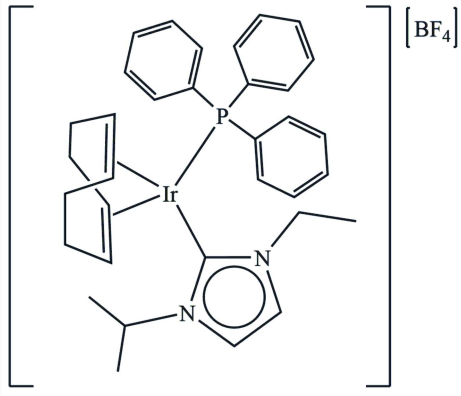
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title compound, $[Ir(C_8H_{12})(C_8H_{14}N_2)(C_{18}H_{15}P)]BF_4$, the cationic complex has the anticipated square-planar geometry. The asymmetric unit comprises the iridium complex and one tetrafluoridoborate anion. The space group is non-centrosymmetric, with the Flack parameter of 0.007 (3) well determined, and confirms the hand for the complex cation. This compound shows promising catalytic activity in transfer hydrogenation reactions.

**3D view**



**Chemical scheme**




## Structure description

N-heterocyclic carbene complexes are of interest because of their catalytic properties in transfer hydrogenation reactions. Transfer hydrogenation of ketones and imines is an encouraging example of an efficient and benign chemical transformation that exemplifies some of the key aspects of green chemistry (Ruff *et al.*, 2016; Zuo *et al.*, 2014). The N-heterocyclic carbene (NHC) ligands can be tuned sterically and electronically by having different alkyl groups on the nitrogen atoms (Gusev, 2009). Many related NHC rhodium and iridium complexes have been synthesized and structurally characterized (Köcher & Herrmann 1997; Wang & Lin 1998; Chianese *et al.*, 2004; Herrmann *et al.* 2006; Nichol *et al.*, 2009, 2010, 2011, 2012; Lu *et al.*, 2011; Huttenstine *et al.*, 2011, Idrees *et al.*, 2017). Their catalytic activity in transfer hydrogenation reactions has also been studied and reported (Hillier *et al.*, 2001; Albrecht *et al.*, 2002; Gnanamgari *et al.*, 2007).

The title complex comprises an $Ir^I$ cation, a cyclooctadiene ligand, an N-heterocyclic carbene ligand, a phosphane ligand, and a tetrafluoridoborate counter-anion, Fig. 1. The coordination sphere of the $Ir^I$ cation is completed through bonds to the phosphane, cyclooctadiene and the carbene, resulting in a distorted square-planar geometry. Charge

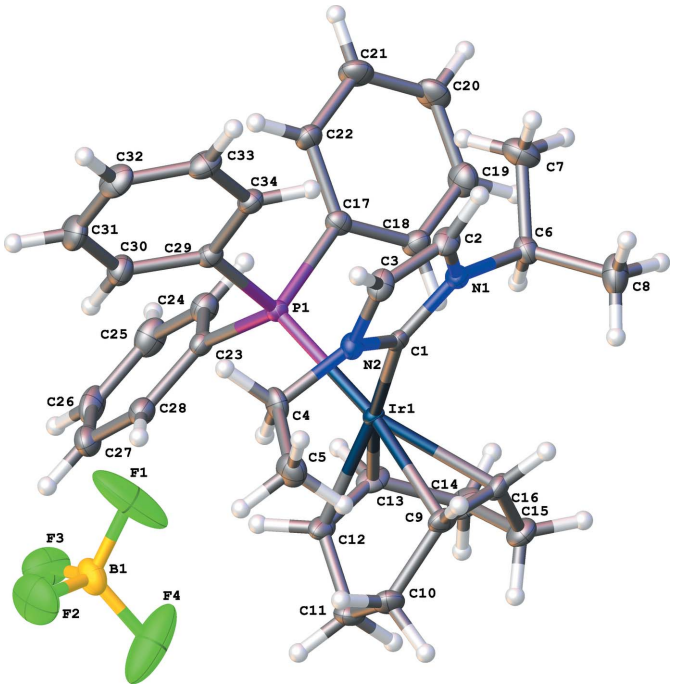



**Figure 1**
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level.

balance is achieved with a non-coordinating tetrafluoridoborate anion. The carbene atom, C1, deviates from the expected $sp^2$ hybridization in that the N1—C1—N2 bond angle is 105.1 (5)°. Other selected bond lengths and angles in the structure are: Ir1—P1 2.3232 (11), Ir1—C1 2.049 (7) Å, and C1—Ir1—P1 89.72 (16)°.

In the crystal structure, the cations and anions are arranged in chains along the *a*-axis direction through C–H···F hydrogen bonds, Fig. 2 and Table 1. The individual chains are arranged into layers in the *ac* plane.

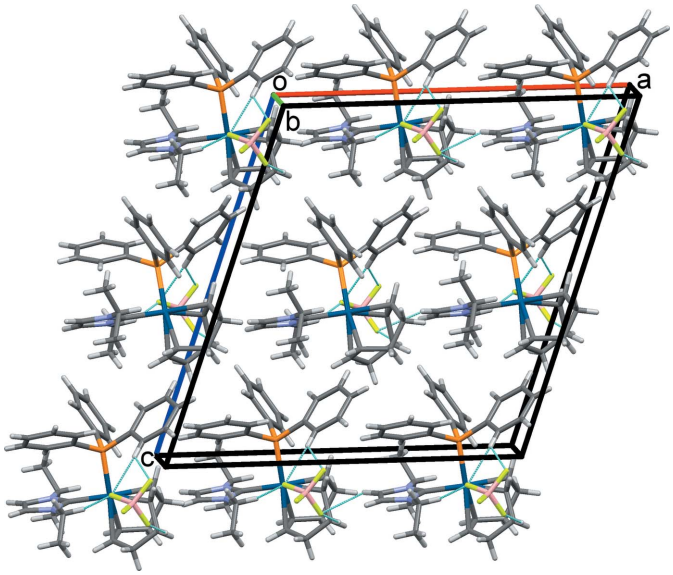



**Figure 2**
The unit cell viewed along the crystallographic *b* axis.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4*A*···F1 | 0.99 | 2.43 | 3.153 (5) | 130 |
| C28—H28···F3 | 0.95 | 2.58 | 3.265 (4) | 130 |
| C28—H28···F1 | 0.95 | 2.52 | 3.474 (6) | 178 |
| C11—H11*B*···F4 | 0.99 | 2.60 | 3.357 (5) | 134 |
| C19—H19···F3$^{i}$ | 0.95 | 2.60 | 3.390 (5) | 141 |
| C16—H16···F2$^{i}$ | 1.00 | 2.66 | 3.134 (4) | 109 |
| C16—H16···F2$^{i}$ | 1.00 | 2.66 | 3.134 (4) | 109 |
| C2—H2···F4$^{ii}$ | 0.95 | 2.56 | 3.116 (5) | 117 |

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

## Synthesis and crystallization

Unless otherwise stated, all chemicals were purchased from Sigma–Aldrich and used without further purification, in the dark, and under a nitrogen atmosphere. 1-Ethyl imidazole (4.99 g, 51.91 mmol) and 2-bromopropane (7.39 g, 60 mmol) were refluxed in toluene (10 ml) for 24 h. After cooling in an ice bath for 30 min, the top toluene layer was decanted and the bottom light-brown layer was washed with ether. $N_2$ was purged throughout the product and the imidazolium salt **1** (Fig. 3) was recrystallized in $CH_2Cl_2$/ pentane (96%). Transmetallation in $CH_2Cl_2$ (10 ml) with **1** (0.1305 g, 0.5958 mmol), $Ag_2O$ (0.0691 g, 0.2979 mmol), and $[Ir(cod)Cl]_2$ (0.200 g, 0.2979 mmol), gave a dark-red solid (**2**) (92%). In a round-bottom flask, **2** (0.2277 g, 0.4805 mmol), triphenylphosphine (0.1258 g, 0.4801 mmol), and $AgBF_4$ (0.0942 g, 0.4801 mmol) were dissolved in $CH_2Cl_2$ (15 ml) and stirred for 2 h to obtain a bright orange–red complex (**3**) (94%) (Fig. 3). X-ray quality crystals of **3** were grown from $CH_2Cl_2$/ pentane by slow diffusion.

## Refinement

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

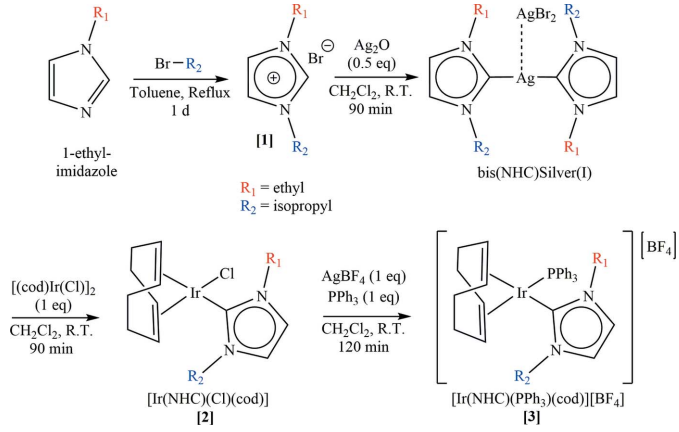



**Figure 3**
A scheme showing the various steps in the synthesis of the title compound

## Acknowledgements

KI gratefully acknowledges the financial support donated to the MU Chemistry Student Research Grant by Ms Karen A. Murley and a Neimeyer–Hodgson Research Grant.

## References

Albrecht, M., Miecznikowski, J. R., Samuel, A., Faller, J. W. & Crabtree, R. H. (2002). *Organometallics*, **21**, 3596–3604.
Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.
Bruker (2012). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2013). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chianese, A. R., Kovacevic, A., Zeglis, B. M., Faller, J. W. & Crabtree, R. H. (2004). *Organometallics*, **23**, 2461–2468.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Gnanamgari, D., Moores, A., Rajaseelan, E. & Crabtree, R. H. (2007). *Organometallics*, **26**, 1226–1230.
Gusev, D. G. (2009). *Organometallics*, **28**, 6458–6461.
Herrmann, W. A., Schütz, J., Frey, G. D. & Herdtweck, E. (2006). *Organometallics*, **25**, 2437–2448.
Hillier, A. C., Lee, H. M., Stevens, E. D. & Nolan, S. P. (2001). *Organometallics*, **20**, 4246–4252.
Huttenstine, A. L., Rajaseelan, E., Oliver, A. G. & Rood, J. A. (2011). *Acta Cryst.* E**67**, m1274–m1275.
Idrees, K. B., Astashkin, A. V. & Rajaseelan, E. (2017). *IUCrData*, **2**, x171081.
Köcher, C. & Herrmann, W. A. (1997). *J. Organomet. Chem.* **532**, 261–265.
Lu, W. Y., Cavell, K. J., Wixey, J. S. & Kariuki, B. (2011). *Organometallics*, **30**, 5649–5655.
Nichol, G. S., Rajaseelan, J., Anna, L. J. & Rajaseelan, E. (2009). *Eur. J. Inorg. Chem.* pp. 4320–4328.
Nichol, G. S., Rajaseelan, J., Walton, D. P. & Rajaseelan, E. (2011). *Acta Cryst.* E**67**, m1860–m1861.
Nichol, G. S., Stasiw, D., Anna, L. J. & Rajaseelan, E. (2010). *Acta Cryst.* E**66**, m1114.
Nichol, G. S., Walton, D. P., Anna, L. J. & Rajaseelan, E. (2012). *Acta Cryst.* E**68**, m158–m159.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{34}H_{41}IrN_2P^+\cdot BF_4^-$ |
| $M_r$ | 787.67 |
| Crystal system, space group | Monoclinic, *Cc* |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 17.4915 (13), 10.2653 (8), 18.644 (2) |
| $\beta$ (°) | 109.6047 (16) |
| $V$ (Å$^3$) | 3153.5 (5) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 4.34 |
| Crystal size (mm) | 0.3 × 0.2 × 0.12 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2012) |
| $T_{min}$, $T_{max}$ | 0.576, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 25634, 6517, 6410 |
| $R_{int}$ | 0.026 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.667 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.015, 0.033, 1.01 |
| No. of reflections | 6517 |
| No. of parameters | 391 |
| No. of restraints | 2 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.81, −0.57 |
| Absolute structure | Flack *x* determined using 2467 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al*, 2013) |
| Absolute structure parameter | 0.007 (3) |

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *Olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Ruff, A., Kirby, C., Chan, B. C. & O'Connor, A. R. (2016). *Organometallics*, **35**, 327–335.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Wang, H. M. J. & Lin, I. J. B. (1998). *Organometallics*, **17**, 972–975.
Zuo, W., Tauer, S., Prokopchuk, D. E. & Morris, R. H. (2014). *Organometallics*, **33**, 5791–5801.

# full crystallographic data

*IUCrData* (2017). **2**, x171411 [https://doi.org/10.1107/S2414314617014110]

## [(1,2,5,6-$\eta$)-Cycloocta-1,5-diene](1-ethyl-3-isopropyl-1,3-imidazol-2-ylidene-$\kappa C^2$)(triphenylphosphane-$\kappa P$)iridium(I) tetrafluoridoborate

**Karam B. Idrees, William J. Rutledge, Sue A. Roberts and Edward Rajaseelan**

**[(1,2,5,6-$\eta$)-Cycloocta-1,5-diene](1-ethyl-3-isopropyl-1,3-imidazol-2-ylidene-$\kappa C^2$)(triphenylphosphane-$\kappa P$)iridium(I) tetrafluoridoborate**

*Crystal data*

$C_{34}H_{41}IrN_2P^+\cdot BF_4^-$
$M_r$ = 787.67
Monoclinic, *Cc*
*a* = 17.4915 (13) Å
*b* = 10.2653 (8) Å
*c* = 18.644 (2) Å
$\beta$ = 109.6047 (16)°
*V* = 3153.5 (5) Å$^3$
*Z* = 4
*F*(000) = 1568
$D_x$ = 1.659 Mg m$^{-3}$
Mo *K*$\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9729 reflections
$\theta$ = 2.3–28.3°
$\mu$ = 4.34 mm$^{-1}$
*T* = 150 K
Plate, clear orange
0.3 × 0.2 × 0.12 mm

*Data collection*

Bruker APEXII CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{min}$ = 0.576, $T_{max}$ = 0.746
25634 measured reflections
6517 independent reflections
6410 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
$\theta_{max}$ = 28.3°, $\theta_{min}$ = 2.3°
*h* = −23→13
*k* = −13→13
*l* = −24→24

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.015
$wR(F^2)$ = 0.033
*S* = 1.01
6517 reflections
391 parameters
2 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.81 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.57 e Å$^{-3}$
Absolute structure: Flack *x* determined using 2467 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al*, 2013)
Absolute structure parameter: 0.007 (3)

*Special details*

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

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ir1 | 0.38107 (2) | 0.82129 (2) | 0.58767 (2) | 0.01181 (3) |
| C1 | 0.2700 (4) | 0.8408 (4) | 0.6009 (3) | 0.0148 (11) |
| C13 | 0.4968 (4) | 0.8485 (6) | 0.5689 (4) | 0.0219 (11) |
| H13 | 0.4929 | 0.8445 | 0.5142 | 0.026* |
| C14 | 0.5403 (3) | 0.9684 (4) | 0.6107 (2) | 0.0275 (10) |
| H14A | 0.5199 | 1.0462 | 0.5786 | 0.033* |
| H14B | 0.5990 | 0.9603 | 0.6190 | 0.033* |
| N1 | 0.2213 (2) | 0.9453 (3) | 0.59388 (18) | 0.0161 (7) |
| N2 | 0.22893 (16) | 0.7402 (3) | 0.61841 (16) | 0.0164 (5) |
| C4 | 0.2575 (2) | 0.6041 (3) | 0.6270 (2) | 0.0220 (7) |
| H4A | 0.3089 | 0.5989 | 0.6157 | 0.026* |
| H4B | 0.2169 | 0.5491 | 0.5894 | 0.026* |
| C3 | 0.1544 (2) | 0.7809 (3) | 0.6207 (2) | 0.0204 (7) |
| H3 | 0.1146 | 0.7286 | 0.6312 | 0.024* |
| C12 | 0.49705 (19) | 0.7269 (3) | 0.60237 (19) | 0.0193 (7) |
| H12 | 0.4931 | 0.6521 | 0.5669 | 0.023* |
| C6 | 0.2415 (2) | 1.0805 (3) | 0.57994 (19) | 0.0189 (7) |
| H6 | 0.2945 | 1.0796 | 0.5706 | 0.023* |
| P1 | 0.31715 (7) | 0.77862 (11) | 0.45900 (6) | 0.0133 (2) |
| C9 | 0.4315 (3) | 0.8179 (3) | 0.7132 (3) | 0.0198 (11) |
| H9 | 0.3896 | 0.8169 | 0.7388 | 0.024* |
| C10 | 0.4914 (3) | 0.7073 (4) | 0.7358 (2) | 0.0232 (8) |
| H10A | 0.4615 | 0.6247 | 0.7335 | 0.028* |
| H10B | 0.5271 | 0.7203 | 0.7892 | 0.028* |
| C29 | 0.2240 (3) | 0.6807 (3) | 0.4333 (2) | 0.0163 (7) |
| C23 | 0.3788 (2) | 0.7051 (3) | 0.40747 (19) | 0.0171 (6) |
| C22 | 0.2172 (2) | 0.9413 (3) | 0.34318 (18) | 0.0194 (7) |
| H22 | 0.1847 | 0.8664 | 0.3245 | 0.023* |
| C34 | 0.1553 (2) | 0.7331 (3) | 0.44541 (18) | 0.0184 (7) |
| H34 | 0.1563 | 0.8210 | 0.4617 | 0.022* |
| C18 | 0.3319 (2) | 1.0435 (3) | 0.43574 (19) | 0.0200 (7) |
| H18 | 0.3779 | 1.0383 | 0.4809 | 0.024* |
| C19 | 0.3123 (3) | 1.1609 (3) | 0.3976 (2) | 0.0270 (8) |
| H19 | 0.3449 | 1.2357 | 0.4161 | 0.032* |
| C28 | 0.4147 (2) | 0.5825 (3) | 0.43037 (19) | 0.0215 (7) |
| H28 | 0.4041 | 0.5363 | 0.4702 | 0.026* |
| C17 | 0.28505 (19) | 0.9328 (3) | 0.40866 (18) | 0.0166 (6) |
| C21 | 0.1968 (2) | 1.0597 (3) | 0.3051 (2) | 0.0262 (8) |
| H21 | 0.1502 | 1.0656 | 0.2606 | 0.031* |
| C16 | 0.4456 (2) | 0.9395 (3) | 0.68829 (18) | 0.0193 (7) |
| H16 | 0.4113 | 1.0097 | 0.6990 | 0.023* |
| C30 | 0.2198 (2) | 0.5519 (3) | 0.40753 (19) | 0.0237 (7) |
| H30 | 0.2651 | 0.5144 | 0.3980 | 0.028* |
| C2 | 0.1494 (2) | 0.9095 (3) | 0.6053 (2) | 0.0200 (7) |
| H2 | 0.1052 | 0.9653 | 0.6027 | 0.024* |

| | | | | |
|---|---|---|---|---|
| C33 | 0.0858 (2) | 0.6591 (3) | 0.4341 (2) | 0.0247 (8) |
| H33 | 0.0401 | 0.6959 | 0.4432 | 0.030* |
| C32 | 0.0835 (2) | 0.5312 (4) | 0.4095 (2) | 0.0275 (8) |
| H32 | 0.0363 | 0.4799 | 0.4021 | 0.033* |
| C24 | 0.3962 (2) | 0.7705 (3) | 0.3494 (2) | 0.0215 (7) |
| H24 | 0.3727 | 0.8536 | 0.3335 | 0.026* |
| C11 | 0.5439 (2) | 0.6955 (3) | 0.6852 (2) | 0.0249 (8) |
| H11A | 0.5907 | 0.7555 | 0.7040 | 0.030* |
| H11B | 0.5654 | 0.6056 | 0.6886 | 0.030* |
| C20 | 0.2444 (3) | 1.1690 (3) | 0.3321 (2) | 0.0282 (9) |
| H20 | 0.2307 | 1.2496 | 0.3057 | 0.034* |
| C26 | 0.4826 (2) | 0.5959 (4) | 0.3378 (2) | 0.0290 (8) |
| H26 | 0.5183 | 0.5593 | 0.3145 | 0.035* |
| C5 | 0.2714 (2) | 0.5513 (3) | 0.7060 (2) | 0.0276 (8) |
| H5A | 0.2924 | 0.4622 | 0.7094 | 0.041* |
| H5B | 0.2201 | 0.5512 | 0.7163 | 0.041* |
| H5C | 0.3109 | 0.6064 | 0.7435 | 0.041* |
| C27 | 0.4655 (2) | 0.5290 (4) | 0.3950 (2) | 0.0265 (8) |
| H27 | 0.4890 | 0.4457 | 0.4103 | 0.032* |
| C8 | 0.2512 (3) | 1.1643 (3) | 0.6500 (3) | 0.0315 (9) |
| H8A | 0.1988 | 1.1719 | 0.6580 | 0.047* |
| H8B | 0.2704 | 1.2512 | 0.6424 | 0.047* |
| H8C | 0.2907 | 1.1237 | 0.6948 | 0.047* |
| C31 | 0.1498 (2) | 0.4784 (3) | 0.3958 (2) | 0.0295 (8) |
| H31 | 0.1476 | 0.3912 | 0.3783 | 0.035* |
| C15 | 0.5280 (2) | 0.9876 (4) | 0.6880 (2) | 0.0247 (8) |
| H15A | 0.5713 | 0.9404 | 0.7277 | 0.030* |
| H15B | 0.5334 | 1.0814 | 0.7012 | 0.030* |
| C25 | 0.4471 (2) | 0.7169 (4) | 0.3144 (2) | 0.0296 (8) |
| H25 | 0.4579 | 0.7625 | 0.2745 | 0.036* |
| C7 | 0.1775 (2) | 1.1369 (4) | 0.5098 (2) | 0.0303 (8) |
| H7A | 0.1716 | 1.0805 | 0.4659 | 0.045* |
| H7B | 0.1941 | 1.2242 | 0.4997 | 0.045* |
| H7C | 0.1255 | 1.1424 | 0.5188 | 0.045* |
| F3 | 0.46323 (17) | 0.3183 (2) | 0.53320 (17) | 0.0442 (7) |
| F4 | 0.4980 (2) | 0.3779 (4) | 0.6562 (2) | 0.0893 (14) |
| B1 | 0.4349 (3) | 0.3333 (4) | 0.5942 (3) | 0.0272 (9) |
| F1 | 0.3696 (3) | 0.4149 (3) | 0.5731 (3) | 0.0969 (17) |
| F2 | 0.41140 (18) | 0.2160 (3) | 0.61307 (19) | 0.0560 (8) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ir1 | 0.01033 (5) | 0.01332 (5) | 0.01119 (5) | −0.00084 (8) | 0.00286 (3) | −0.00066 (7) |
| C1 | 0.016 (3) | 0.0157 (18) | 0.010 (2) | −0.0001 (16) | 0.0005 (18) | −0.0021 (15) |
| C13 | 0.009 (2) | 0.036 (2) | 0.022 (3) | 0.000 (2) | 0.0065 (19) | −0.004 (2) |
| C14 | 0.0154 (18) | 0.033 (2) | 0.032 (2) | −0.0116 (16) | 0.0040 (18) | −0.0027 (18) |
| N1 | 0.0129 (14) | 0.0152 (13) | 0.0190 (16) | −0.0006 (11) | 0.0036 (13) | −0.0018 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2 | 0.0157 (13) | 0.0160 (13) | 0.0184 (14) | −0.0017 (11) | 0.0070 (11) | −0.0029 (10) |
| C4 | 0.0278 (18) | 0.0119 (14) | 0.0289 (18) | −0.0015 (13) | 0.0131 (15) | −0.0013 (13) |
| C3 | 0.0181 (16) | 0.0232 (16) | 0.0236 (17) | −0.0061 (14) | 0.0120 (14) | −0.0045 (14) |
| C12 | 0.0126 (15) | 0.0258 (16) | 0.0183 (16) | 0.0042 (13) | 0.0036 (13) | −0.0049 (14) |
| C6 | 0.0192 (16) | 0.0154 (15) | 0.0235 (17) | 0.0005 (12) | 0.0088 (14) | −0.0011 (12) |
| P1 | 0.0140 (5) | 0.0135 (5) | 0.0117 (4) | 0.0006 (4) | 0.0033 (4) | 0.0000 (4) |
| C9 | 0.019 (2) | 0.027 (3) | 0.0121 (18) | 0.0011 (16) | 0.0029 (16) | −0.0018 (15) |
| C10 | 0.024 (2) | 0.0253 (17) | 0.0158 (17) | 0.0038 (17) | 0.0011 (16) | 0.0042 (14) |
| C29 | 0.0156 (18) | 0.0178 (16) | 0.0142 (16) | −0.0023 (12) | 0.0034 (14) | 0.0018 (12) |
| C23 | 0.0153 (16) | 0.0201 (15) | 0.0148 (15) | −0.0015 (12) | 0.0035 (13) | −0.0043 (12) |
| C22 | 0.0212 (16) | 0.0210 (16) | 0.0139 (15) | 0.0003 (13) | 0.0031 (13) | −0.0007 (12) |
| C34 | 0.0162 (16) | 0.0190 (15) | 0.0177 (16) | −0.0016 (13) | 0.0028 (13) | −0.0009 (12) |
| C18 | 0.0201 (16) | 0.0208 (15) | 0.0171 (15) | −0.0021 (13) | 0.0036 (13) | 0.0011 (13) |
| C19 | 0.031 (2) | 0.0208 (17) | 0.030 (2) | −0.0049 (14) | 0.0110 (17) | 0.0008 (14) |
| C28 | 0.0204 (17) | 0.0221 (16) | 0.0202 (17) | −0.0004 (13) | 0.0043 (14) | −0.0037 (13) |
| C17 | 0.0186 (15) | 0.0178 (15) | 0.0145 (15) | 0.0017 (12) | 0.0070 (13) | 0.0021 (12) |
| C21 | 0.0293 (19) | 0.0294 (18) | 0.0173 (16) | 0.0044 (15) | 0.0041 (14) | 0.0074 (14) |
| C16 | 0.0179 (15) | 0.0213 (16) | 0.0162 (15) | −0.0030 (13) | 0.0022 (13) | −0.0064 (12) |
| C30 | 0.0227 (17) | 0.0225 (16) | 0.0245 (17) | −0.0029 (14) | 0.0061 (15) | −0.0048 (14) |
| C2 | 0.0133 (14) | 0.0246 (16) | 0.0239 (17) | −0.0006 (13) | 0.0087 (13) | −0.0053 (13) |
| C33 | 0.0170 (17) | 0.0339 (19) | 0.0218 (18) | −0.0033 (14) | 0.0045 (15) | −0.0009 (14) |
| C32 | 0.0233 (18) | 0.0285 (18) | 0.0285 (19) | −0.0127 (15) | 0.0059 (15) | 0.0004 (15) |
| C24 | 0.0227 (17) | 0.0229 (17) | 0.0194 (17) | −0.0026 (14) | 0.0077 (14) | −0.0016 (13) |
| C11 | 0.0190 (18) | 0.0278 (18) | 0.0234 (19) | 0.0072 (14) | 0.0013 (15) | 0.0001 (14) |
| C20 | 0.036 (2) | 0.0231 (18) | 0.025 (2) | 0.0043 (15) | 0.0107 (18) | 0.0105 (14) |
| C26 | 0.0237 (18) | 0.036 (2) | 0.031 (2) | −0.0038 (16) | 0.0133 (16) | −0.0181 (16) |
| C5 | 0.033 (2) | 0.0200 (16) | 0.0297 (19) | −0.0013 (15) | 0.0107 (16) | 0.0023 (14) |
| C27 | 0.0246 (18) | 0.0244 (17) | 0.0292 (19) | 0.0036 (15) | 0.0073 (15) | −0.0075 (15) |
| C8 | 0.036 (2) | 0.0240 (18) | 0.039 (2) | −0.0057 (15) | 0.018 (2) | −0.0114 (15) |
| C31 | 0.0302 (19) | 0.0208 (17) | 0.034 (2) | −0.0077 (15) | 0.0057 (16) | −0.0062 (15) |
| C15 | 0.0182 (16) | 0.0266 (18) | 0.0251 (18) | −0.0053 (14) | 0.0017 (14) | −0.0041 (14) |
| C25 | 0.032 (2) | 0.036 (2) | 0.0244 (19) | −0.0092 (17) | 0.0146 (17) | −0.0064 (16) |
| C7 | 0.029 (2) | 0.0283 (18) | 0.034 (2) | 0.0080 (16) | 0.0104 (17) | 0.0092 (16) |
| F3 | 0.0328 (15) | 0.0667 (19) | 0.0371 (15) | 0.0054 (11) | 0.0172 (12) | 0.0015 (11) |
| F4 | 0.077 (2) | 0.137 (3) | 0.074 (2) | −0.074 (2) | 0.053 (2) | −0.067 (2) |
| B1 | 0.028 (2) | 0.0185 (19) | 0.040 (3) | −0.0021 (16) | 0.017 (2) | −0.0008 (16) |
| F1 | 0.110 (3) | 0.083 (2) | 0.134 (4) | 0.073 (3) | 0.087 (3) | 0.062 (3) |
| F2 | 0.059 (2) | 0.0327 (13) | 0.079 (2) | −0.0114 (13) | 0.0269 (17) | 0.0123 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ir1—C1 | 2.049 (7) | C34—H34 | 0.9500 |
| Ir1—C12 | 2.181 (3) | C18—C19 | 1.382 (5) |
| Ir1—C13 | 2.185 (7) | C18—C17 | 1.394 (4) |
| Ir1—C16 | 2.201 (3) | C18—H18 | 0.9500 |
| Ir1—C9 | 2.207 (5) | C19—C20 | 1.391 (6) |
| Ir1—P1 | 2.3232 (11) | C19—H19 | 0.9500 |
| C1—N1 | 1.349 (6) | C28—C27 | 1.385 (5) |

| | | | |
|---|---|---|---|
| C1—N2 | 1.359 (6) | C28—H28 | 0.9500 |
| C13—C12 | 1.395 (7) | C21—C20 | 1.388 (5) |
| C13—C14 | 1.517 (7) | C21—H21 | 0.9500 |
| C13—H13 | 1.0000 | C16—C15 | 1.526 (5) |
| C14—C15 | 1.540 (6) | C16—H16 | 1.0000 |
| C14—H14A | 0.9900 | C30—C31 | 1.392 (5) |
| C14—H14B | 0.9900 | C30—H30 | 0.9500 |
| N1—C2 | 1.393 (5) | C2—H2 | 0.9500 |
| N1—C6 | 1.477 (4) | C33—C32 | 1.387 (5) |
| N2—C3 | 1.384 (4) | C33—H33 | 0.9500 |
| N2—C4 | 1.474 (4) | C32—C31 | 1.378 (5) |
| C4—C5 | 1.511 (5) | C32—H32 | 0.9500 |
| C4—H4A | 0.9900 | C24—C25 | 1.382 (5) |
| C4—H4B | 0.9900 | C24—H24 | 0.9500 |
| C3—C2 | 1.348 (5) | C11—H11A | 0.9900 |
| C3—H3 | 0.9500 | C11—H11B | 0.9900 |
| C12—C11 | 1.520 (5) | C20—H20 | 0.9500 |
| C12—H12 | 1.0000 | C26—C27 | 1.383 (5) |
| C6—C7 | 1.521 (5) | C26—C25 | 1.391 (6) |
| C6—C8 | 1.526 (5) | C26—H26 | 0.9500 |
| C6—H6 | 1.0000 | C5—H5A | 0.9800 |
| P1—C17 | 1.829 (3) | C5—H5B | 0.9800 |
| P1—C23 | 1.830 (4) | C5—H5C | 0.9800 |
| P1—C29 | 1.837 (4) | C27—H27 | 0.9500 |
| C9—C16 | 1.383 (5) | C8—H8A | 0.9800 |
| C9—C10 | 1.507 (6) | C8—H8B | 0.9800 |
| C9—H9 | 1.0000 | C8—H8C | 0.9800 |
| C10—C11 | 1.526 (6) | C31—H31 | 0.9500 |
| C10—H10A | 0.9900 | C15—H15A | 0.9900 |
| C10—H10B | 0.9900 | C15—H15B | 0.9900 |
| C29—C30 | 1.400 (4) | C25—H25 | 0.9500 |
| C29—C34 | 1.402 (5) | C7—H7A | 0.9800 |
| C23—C24 | 1.392 (5) | C7—H7B | 0.9800 |
| C23—C28 | 1.408 (4) | C7—H7C | 0.9800 |
| C22—C17 | 1.391 (4) | F3—B1 | 1.393 (6) |
| C22—C21 | 1.392 (5) | F4—B1 | 1.381 (6) |
| C22—H22 | 0.9500 | B1—F2 | 1.356 (5) |
| C34—C33 | 1.387 (5) | B1—F1 | 1.363 (6) |

| | | | |
|---|---|---|---|
| C1—Ir1—C12 | 155.25 (16) | C19—C18—C17 | 120.7 (3) |
| C1—Ir1—C13 | 166.86 (13) | C19—C18—H18 | 119.7 |
| C12—Ir1—C13 | 37.26 (17) | C17—C18—H18 | 119.7 |
| C1—Ir1—C16 | 94.56 (17) | C18—C19—C20 | 119.7 (3) |
| C12—Ir1—C16 | 87.05 (13) | C18—C19—H19 | 120.1 |
| C13—Ir1—C16 | 80.12 (19) | C20—C19—H19 | 120.1 |
| C1—Ir1—C9 | 86.1 (2) | C27—C28—C23 | 120.2 (3) |
| C12—Ir1—C9 | 80.55 (17) | C27—C28—H28 | 119.9 |
| C13—Ir1—C9 | 96.3 (2) | C23—C28—H28 | 119.9 |

| | | | |
|---|---|---|---|
| C16—Ir1—C9 | 36.56 (13) | C22—C17—C18 | 119.5 (3) |
| C1—Ir1—P1 | 89.72 (16) | C22—C17—P1 | 122.0 (2) |
| C12—Ir1—P1 | 98.70 (9) | C18—C17—P1 | 118.5 (2) |
| C13—Ir1—P1 | 90.55 (17) | C20—C21—C22 | 120.1 (3) |
| C16—Ir1—P1 | 156.29 (9) | C20—C21—H21 | 120.0 |
| C9—Ir1—P1 | 167.06 (11) | C22—C21—H21 | 120.0 |
| N1—C1—N2 | 105.1 (5) | C9—C16—C15 | 124.7 (4) |
| N1—C1—Ir1 | 131.3 (4) | C9—C16—Ir1 | 72.0 (2) |
| N2—C1—Ir1 | 123.6 (3) | C15—C16—Ir1 | 113.0 (2) |
| C12—C13—C14 | 124.8 (5) | C9—C16—H16 | 113.4 |
| C12—C13—Ir1 | 71.2 (3) | C15—C16—H16 | 113.4 |
| C14—C13—Ir1 | 110.7 (4) | Ir1—C16—H16 | 113.4 |
| C12—C13—H13 | 114.1 | C31—C30—C29 | 120.5 (3) |
| C14—C13—H13 | 114.1 | C31—C30—H30 | 119.8 |
| Ir1—C13—H13 | 114.1 | C29—C30—H30 | 119.8 |
| C13—C14—C15 | 112.4 (4) | C3—C2—N1 | 107.1 (3) |
| C13—C14—H14A | 109.1 | C3—C2—H2 | 126.5 |
| C15—C14—H14A | 109.1 | N1—C2—H2 | 126.5 |
| C13—C14—H14B | 109.1 | C32—C33—C34 | 119.7 (4) |
| C15—C14—H14B | 109.1 | C32—C33—H33 | 120.2 |
| H14A—C14—H14B | 107.9 | C34—C33—H33 | 120.2 |
| C1—N1—C2 | 110.4 (3) | C31—C32—C33 | 120.0 (3) |
| C1—N1—C6 | 125.7 (4) | C31—C32—H32 | 120.0 |
| C2—N1—C6 | 123.8 (3) | C33—C32—H32 | 120.0 |
| C1—N2—C3 | 110.9 (3) | C25—C24—C23 | 121.3 (3) |
| C1—N2—C4 | 124.0 (3) | C25—C24—H24 | 119.4 |
| C3—N2—C4 | 124.9 (3) | C23—C24—H24 | 119.4 |
| N2—C4—C5 | 112.5 (3) | C12—C11—C10 | 112.3 (3) |
| N2—C4—H4A | 109.1 | C12—C11—H11A | 109.1 |
| C5—C4—H4A | 109.1 | C10—C11—H11A | 109.1 |
| N2—C4—H4B | 109.1 | C12—C11—H11B | 109.1 |
| C5—C4—H4B | 109.1 | C10—C11—H11B | 109.1 |
| H4A—C4—H4B | 107.8 | H11A—C11—H11B | 107.9 |
| C2—C3—N2 | 106.5 (3) | C21—C20—C19 | 120.1 (3) |
| C2—C3—H3 | 126.8 | C21—C20—H20 | 120.0 |
| N2—C3—H3 | 126.8 | C19—C20—H20 | 120.0 |
| C13—C12—C11 | 124.3 (4) | C27—C26—C25 | 119.7 (3) |
| C13—C12—Ir1 | 71.5 (3) | C27—C26—H26 | 120.1 |
| C11—C12—Ir1 | 112.6 (2) | C25—C26—H26 | 120.1 |
| C13—C12—H12 | 113.7 | C4—C5—H5A | 109.5 |
| C11—C12—H12 | 113.7 | C4—C5—H5B | 109.5 |
| Ir1—C12—H12 | 113.7 | H5A—C5—H5B | 109.5 |
| N1—C6—C7 | 111.0 (3) | C4—C5—H5C | 109.5 |
| N1—C6—C8 | 110.1 (3) | H5A—C5—H5C | 109.5 |
| C7—C6—C8 | 111.1 (3) | H5B—C5—H5C | 109.5 |
| N1—C6—H6 | 108.2 | C26—C27—C28 | 120.6 (3) |
| C7—C6—H6 | 108.2 | C26—C27—H27 | 119.7 |
| C8—C6—H6 | 108.2 | C28—C27—H27 | 119.7 |

| | | | |
|---|---|---|---|
| C17—P1—C23 | 102.75 (16) | C6—C8—H8A | 109.5 |
| C17—P1—C29 | 104.30 (16) | C6—C8—H8B | 109.5 |
| C23—P1—C29 | 105.38 (16) | H8A—C8—H8B | 109.5 |
| C17—P1—Ir1 | 108.98 (11) | C6—C8—H8C | 109.5 |
| C23—P1—Ir1 | 117.10 (12) | H8A—C8—H8C | 109.5 |
| C29—P1—Ir1 | 116.74 (13) | H8B—C8—H8C | 109.5 |
| C16—C9—C10 | 126.1 (5) | C32—C31—C30 | 120.6 (3) |
| C16—C9—Ir1 | 71.5 (2) | C32—C31—H31 | 119.7 |
| C10—C9—Ir1 | 107.6 (3) | C30—C31—H31 | 119.7 |
| C16—C9—H9 | 114.3 | C16—C15—C14 | 113.0 (3) |
| C10—C9—H9 | 114.3 | C16—C15—H15A | 109.0 |
| Ir1—C9—H9 | 114.3 | C14—C15—H15A | 109.0 |
| C9—C10—C11 | 113.2 (3) | C16—C15—H15B | 109.0 |
| C9—C10—H10A | 108.9 | C14—C15—H15B | 109.0 |
| C11—C10—H10A | 108.9 | H15A—C15—H15B | 107.8 |
| C9—C10—H10B | 108.9 | C24—C25—C26 | 119.8 (4) |
| C11—C10—H10B | 108.9 | C24—C25—H25 | 120.1 |
| H10A—C10—H10B | 107.8 | C26—C25—H25 | 120.1 |
| C30—C29—C34 | 118.0 (3) | C6—C7—H7A | 109.5 |
| C30—C29—P1 | 123.1 (3) | C6—C7—H7B | 109.5 |
| C34—C29—P1 | 118.8 (2) | H7A—C7—H7B | 109.5 |
| C24—C23—C28 | 118.3 (3) | C6—C7—H7C | 109.5 |
| C24—C23—P1 | 122.1 (3) | H7A—C7—H7C | 109.5 |
| C28—C23—P1 | 119.4 (3) | H7B—C7—H7C | 109.5 |
| C17—C22—C21 | 120.0 (3) | F2—B1—F1 | 108.8 (4) |
| C17—C22—H22 | 120.0 | F2—B1—F4 | 107.6 (4) |
| C21—C22—H22 | 120.0 | F1—B1—F4 | 113.2 (4) |
| C33—C34—C29 | 121.3 (3) | F2—B1—F3 | 109.6 (3) |
| C33—C34—H34 | 119.4 | F1—B1—F3 | 109.0 (4) |
| C29—C34—H34 | 119.4 | F4—B1—F3 | 108.5 (4) |

| | | | |
|---|---|---|---|
| C12—C13—C14—C15 | −44.5 (7) | P1—C23—C28—C27 | −176.1 (3) |
| Ir1—C13—C14—C15 | 36.4 (5) | C21—C22—C17—C18 | 0.3 (5) |
| N2—C1—N1—C2 | −1.4 (5) | C21—C22—C17—P1 | −177.5 (3) |
| Ir1—C1—N1—C2 | 177.5 (4) | C19—C18—C17—C22 | −0.9 (5) |
| N2—C1—N1—C6 | 175.8 (3) | C19—C18—C17—P1 | 177.0 (3) |
| Ir1—C1—N1—C6 | −5.4 (7) | C23—P1—C17—C22 | 85.0 (3) |
| N1—C1—N2—C3 | 1.3 (5) | C29—P1—C17—C22 | −24.8 (3) |
| Ir1—C1—N2—C3 | −177.6 (3) | Ir1—P1—C17—C22 | −150.1 (3) |
| N1—C1—N2—C4 | 176.3 (3) | C23—P1—C17—C18 | −92.8 (3) |
| Ir1—C1—N2—C4 | −2.7 (6) | C29—P1—C17—C18 | 157.4 (3) |
| C1—N2—C4—C5 | 118.7 (4) | Ir1—P1—C17—C18 | 32.0 (3) |
| C3—N2—C4—C5 | −67.0 (4) | C17—C22—C21—C20 | 0.4 (5) |
| C1—N2—C3—C2 | −0.8 (4) | C10—C9—C16—C15 | −7.2 (7) |
| C4—N2—C3—C2 | −175.7 (3) | Ir1—C9—C16—C15 | −105.9 (3) |
| C14—C13—C12—C11 | −2.6 (8) | C10—C9—C16—Ir1 | 98.6 (4) |
| Ir1—C13—C12—C11 | −105.2 (4) | C34—C29—C30—C31 | −1.2 (5) |
| C14—C13—C12—Ir1 | 102.6 (6) | P1—C29—C30—C31 | 173.9 (3) |

| | | | |
|---|---|---|---|
| C1—N1—C6—C7 | 125.0 (4) | N2—C3—C2—N1 | −0.1 (4) |
| C2—N1—C6—C7 | −58.1 (4) | C1—N1—C2—C3 | 0.9 (4) |
| C1—N1—C6—C8 | −111.6 (4) | C6—N1—C2—C3 | −176.3 (3) |
| C2—N1—C6—C8 | 65.2 (4) | C29—C34—C33—C32 | −0.8 (5) |
| C16—C9—C10—C11 | −38.8 (6) | C34—C33—C32—C31 | −0.5 (6) |
| Ir1—C9—C10—C11 | 40.8 (4) | C28—C23—C24—C25 | 0.4 (5) |
| C17—P1—C29—C30 | 131.1 (3) | P1—C23—C24—C25 | 175.8 (3) |
| C23—P1—C29—C30 | 23.3 (3) | C13—C12—C11—C10 | 95.9 (5) |
| Ir1—P1—C29—C30 | −108.6 (3) | Ir1—C12—C11—C10 | 13.5 (4) |
| C17—P1—C29—C34 | −53.9 (3) | C9—C10—C11—C12 | −36.7 (5) |
| C23—P1—C29—C34 | −161.7 (3) | C22—C21—C20—C19 | −0.6 (6) |
| Ir1—P1—C29—C34 | 66.4 (3) | C18—C19—C20—C21 | 0.0 (6) |
| C17—P1—C23—C24 | 4.7 (3) | C25—C26—C27—C28 | −1.2 (5) |
| C29—P1—C23—C24 | 113.6 (3) | C23—C28—C27—C26 | 0.9 (5) |
| Ir1—P1—C23—C24 | −114.7 (3) | C33—C32—C31—C30 | 0.9 (6) |
| C17—P1—C23—C28 | −179.9 (3) | C29—C30—C31—C32 | −0.1 (6) |
| C29—P1—C23—C28 | −71.0 (3) | C9—C16—C15—C14 | 95.5 (4) |
| Ir1—P1—C23—C28 | 60.7 (3) | Ir1—C16—C15—C14 | 12.2 (4) |
| C30—C29—C34—C33 | 1.6 (5) | C13—C14—C15—C16 | −32.1 (5) |
| P1—C29—C34—C33 | −173.6 (3) | C23—C24—C25—C26 | −0.7 (6) |
| C17—C18—C19—C20 | 0.8 (6) | C27—C26—C25—C24 | 1.1 (6) |
| C24—C23—C28—C27 | −0.5 (5) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4*A*···F1 | 0.99 | 2.43 | 3.153 (5) | 130 |
| C28—H28···F3 | 0.95 | 2.58 | 3.265 (4) | 130 |
| C28—H28···F1 | 0.95 | 2.52 | 3.474 (6) | 178 |
| C11—H11*B*···F4 | 0.99 | 2.60 | 3.357 (5) | 134 |
| C19—H19···F3$^{i}$ | 0.95 | 2.60 | 3.390 (5) | 141 |
| C16—H16···F2$^{i}$ | 1.00 | 2.66 | 3.134 (4) | 109 |
| C16—H16···F2$^{i}$ | 1.00 | 2.66 | 3.134 (4) | 109 |
| C2—H2···F4$^{ii}$ | 0.95 | 2.56 | 3.116 (5) | 117 |

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