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(4-Butyl-1-methyl-1,2,4-triazol-5-ylidene)[(1,2,5,6-η)-cycloocta-1,5-diene](triphenylphosphane)-iridium(I) tetrafluoridoborate

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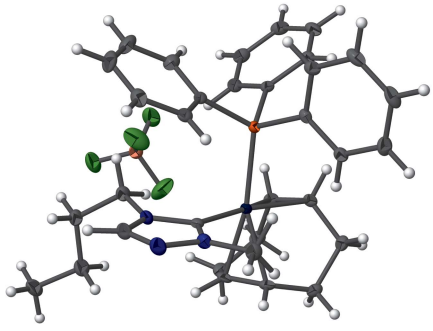
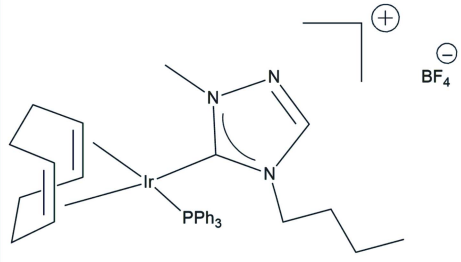
A new triazole-based N-heterocyclic cationic carbene iridium(I) complex with a tetrafluoridoborate counter-anion, $[Ir(C_8H_{12})(C_7H_{13}N_3)(C_{18}H_{15}P)]BF_4$, has been synthesized and structurally characterized. The Ir^I atom of the cationic complex has an expected square-planar coordination environment with unexceptional bond lengths. There are several close F···H contacts between the cations and the anions in the range 2.36–2.58 Å, stabilizing the orientation of the out-sphere [BF_4^-] counter-anion. In the crystal, C—H···π(ring) interactions are observed that orient the phenyl rings of the triphenylphosphane ligands.

3D view



Chemical scheme



Structure description

N-heterocyclic carbenes (NHC) have become important alternatives to phosphanes as ancillary ligands in transition-metal chemistry, synthesis, and in homogeneous catalysis (Cazin, 2013; Díez-Gonzáles *et al.*, 2009; Rovis & Nolan, 2013; Ruff *et al.*, 2016; Zuo *et al.*, 2014). Their catalytic activities in the transfer hydrogenation of ketones and imines have also been studied and reported (Albrecht *et al.*, 2002; Gnanamgari *et al.*, 2007). NHC ligands can be tuned sterically and electronically by having different substituents on the nitrogen atoms (Gusev, 2009). Although many imidazole- and triazole-based NHC rhodium and iridium complexes have been prepared and structurally characterized (Herrmann *et al.*, 2006; Wang & Lin, 1998; Chianese *et al.*, 2004), new imidazole and triazole-based NHC complexes of rhodium and iridium are still being synthesized to study the effect of different substituents on NHC ligands and other ligands coordinating

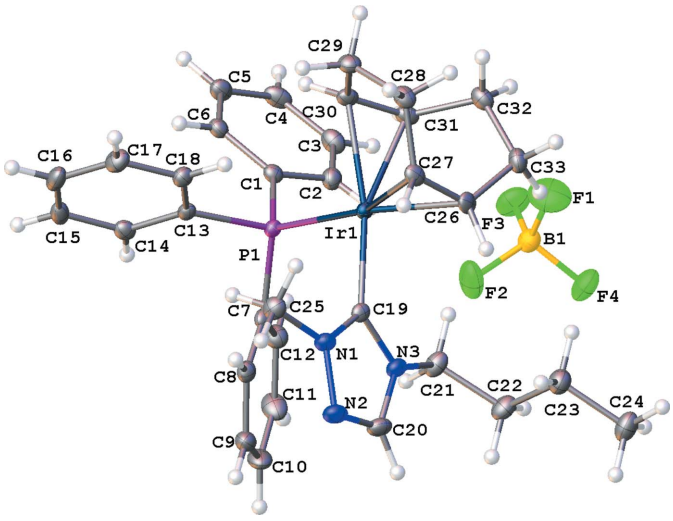


Figure 1
The molecular entities in the crystal structure of the title compound (**4**). Displacement ellipsoids are drawn at the 50% probability level.

to the metal in transfer hydrogenation reactions (Nichol *et al.*, 2009, 2010, 2011, 2012; Idrees *et al.*, 2017*a*,*b*; Rood *et al.*, 2021; Rushlow *et al.*, 2021; Newman *et al.*, 2021).

The molecular structure of the title complex, $[Ir(C_8H_{12})(C_{18}H_{15}P)(C_7H_{13}N_3)][BF_4]$ (**4**), comprises an Ir^I cationic complex and a tetrafluoridoborate counter-anion, illustrated in Fig. 1. The coordination sphere around the Ir^I atom, formed by the bidentate cycloocta-1,5-diene (COD), the carbene C atom of the NHC, and the P atom of the triphenylphosphane ligand, exhibits a distorted square-planar geometry. The carbene atom, C19, deviates from the expected sp^2 hybridization in that the N1—C19—N3 bond angle in the triazole-based carbene is 103.41 (18)°. Other selected bond lengths and angles in the structure are: Ir1—$C19_{(NHC)}$ = 2.043 (2) Å, Ir1—P1 = 2.3330 (6) Å, and C19—Ir1—P1 = 91.94 (6)°. Fig. 2 shows the molecular packing diagram of the complex (**4**). There are several close F···H contacts (likely, non-standard hydrogen bonds between the cation and anion), stabilizing the orientation of the $[BF_4^-]$ group as reported in Table 1 and shown as dotted green lines in Fig. 2. An intramolecular C—H···π(ring) interaction is observed between a hydrogen atom on the butyl wingtip of the NHC (H21*B*) and a phenyl phosphane ring (C7–C12) with an H···centroid distance of 2.84 Å and a C—H···centroid angle of 139°. Intermolecular C—H···π(ring) interactions are observed between phenyl phosphane rings on adjacent moieties with a hydrogen atom of a phenyl ring (H9) interacting with a phenyl phosphane ring (C13–C18). The intermolecular C—H···π(ring) interaction has an H···centroid distance of 2.77 Å and a C—H···centroid angle of 159°. The interaction

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···F2	0.95	2.36	3.285 (3)	165
C20—H20···F1^{i}	0.95	2.47	3.329 (3)	150
C25—H25*B*···F4^{ii}	0.98	2.37	3.245 (3)	149

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

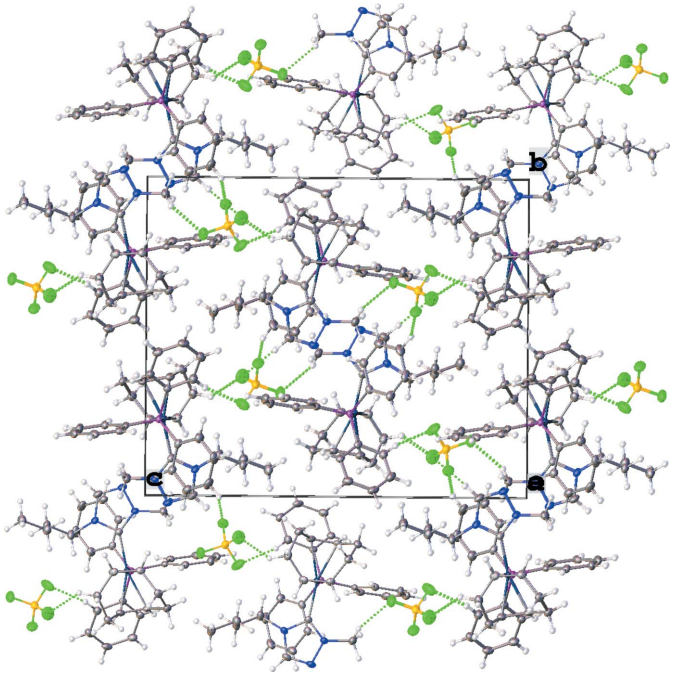


Figure 2
Crystal packing unit-cell diagram of the title compound (**4**) shown along the *a* axis. Hydrogen-bonding interactions between F and H atoms are shown as dotted green lines. **Add axis labels**

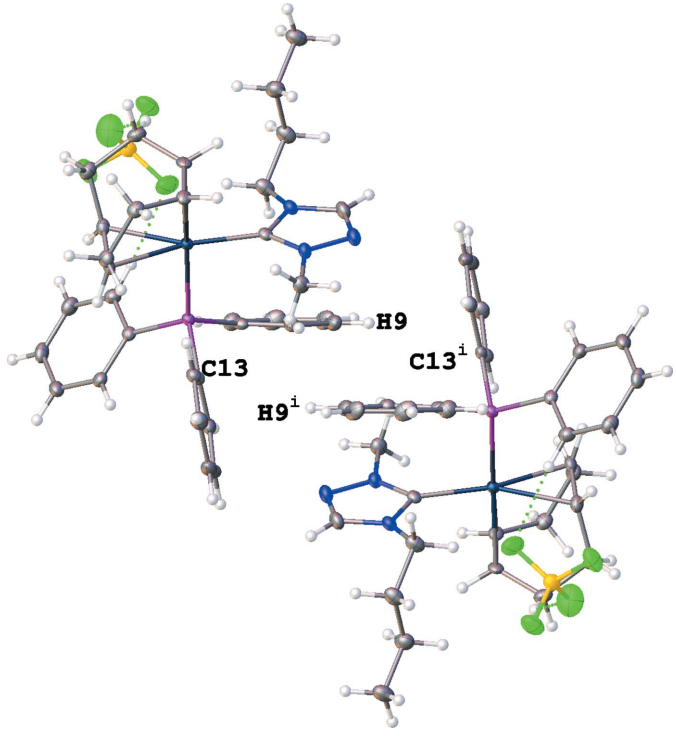


Figure 3
View of the title compound (**4**) showing T-shaped distorted perpendicular interactions arising from C—H···π(ring) interactions between a hydrogen atom on a phenyl ring (H9) and a phenyl ring (C13–C18) of triphenylphosphane. [Symmetry code: (i) $-x+2, -y+1, -z+1$].

results in nearly perpendicular T-shaped orientations of the phenyl rings (C7–C12 and C13–C18), as seen in Fig. 3, with a dihedral angle of 80.43 (11)° between the ring planes.

Synthesis and crystallization

1-Methyl-1,2,4-triazole (**1**) was purchased from Matrix Scientific. All other compounds used in the syntheses, shown in Fig. 4, were obtained from Sigma–Aldrich and Strem and used as received; all syntheses were performed under a nitrogen atmosphere. NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz (operating at 162 MHz for ^{31}P) Varian spectrometer and referenced to the residual solvent peak (δ in ppm).

4-Butyl-1-methyl-1,2,4-triazolium bromide (2): 1-Methyl-1,2,4-triazole (**1**) (1.231 g, 14.82 mmol) and 1-bromobutane (3.393 g, 24.76 mmol) were added to toluene (10 mL), and the mixture was refluxed in the dark for 24 h. After the mixture was cooled, the off-white solid was filtered, washed with ether, and dried under vacuum. Yield: 2.228 g (68%). ^1H NMR: δ 11.42 (*s*, 1 H, N—C_5H—N), 9.01 (*s*, 1 H, N—C_3H—N), 4.56 (*t*, 2 H, N—CH_2 of *n*-Bu), 4.25 (*s*, 3 H, N—CH_3), 1.95 (*m*, 2 H, CH_2 of *n*-Bu), 1.40 (*m*, 2 H, CH_2 of *n*-Bu), 0.96 (*t*, 3 H, CH_3 of *n*-Bu). ^{13}C NMR: δ 143.77 (N—C_5—N), 143.35 (N—C_3—N), 48.60 (N—CH_3), 39.55 (N-CH_2 of *n*-Bu), 31.90 (CH_2 of *n*-Bu), 19.43 (CH_2 of *n*-Bu), 13.39 (CH_3 of *n*-Bu).

[(1,2,5,6-η)-Cycloocta-1,5-diene](4-butyl-1-methyl-1,2,4-triazol-5-ylidene)chloroiridium (3): Triazolium bromide (**2**) (0.066 g, 0.300 mmol) and Ag_2O (0.035 g, 0.151 mmol) were stirred at room temperature in the dark for 1 h in CH_2Cl_2 (10 mL). The mixture was then filtered through Celite into $[Ir(cod)Cl]_2$ (0.100 g, 0.149 mmol), and stirred again in the dark for 1.5 h. The resulting solution was filtered through Celite and the solvent was removed at reduced pressure. The yellow solid product (**3**) was dried under vacuum. Yield: 0.134g (94%). ^1H NMR: δ 7.85 (*s*, 1 H, N—C_3H—N), 4.78 (*t*, 2 H, N—CH_2 of *n*-Bu), 4.46 (*m*, 2 H, CH of COD), 4.35 (*m*, 2H of COD), 4.14 (*s*, 3 H, N—CH_3), 3.01, 2.91 (*m*, 4 H, CH_2 of COD), 2.25,2.09 (*m*, 4 H, CH_2 of COD), 1.80 (*m*, 2 H, CH_2 of *n*-Bu), 1.43 (*m*, 2 H, CH_2 of *n*-Bu), 1.02 (*t*, 3 H, CH_2 of *n*-Bu). ^{13}C NMR: δ 178.56 (Ir—C), 143.73 (N—C_3H—N), 86.06,85.48, 52.50, 52.10 (CH of COD), 48.80 (N—CH_3), 48.59 (N- CH_2 of *n*-Bu), 33.77,33.20,32.65,32.50 (CH_2 of COD), 31.35 (CH_2 of *n*-Bu), 19.95 (CH_2 of *n*-Bu), 13.76 (CH_3 of *n*-Bu).

[(1,2,5,6-η)-Cycloocta-1,5-diene](4-butyl-1-methyl-1,2,4-triazol-5-ylidene)(triphenylphosphane)iridium(I) tetrafluoridoborate (4): Triphenylphosphane (0.074 g, 0.282 mmol) and $AgBF_4$ (0.055 g, 0.282 mmol) were added to (**3**) (0.134 g, 0.282 mmol) in CH_2Cl_2 (10 mL). The solution was stirred in the dark for 1.5 h. The resulting mixture was filtered through Celite and the solvent was removed at reduced pressure. The bright-orange solid product (**4**) was dried under vacuum. Yield: 0.220 g (99%). ^1H NMR: δ 8.14 (*s*, 1 H, N-C_3H-N), 7.26–

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ir(C_8H_{12})(C_7H_{13}N_3)(C_{18}H_{15}P)]BF_4$
M_r	788.66
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	9.8966 (9), 16.3247 (17), 20.0560 (19)
β (°)	102.285 (4)
V (Å^3)	3166.0 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.32
Crystal size (mm)	0.31 × 0.21 × 0.19
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.668, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34219, 6457, 5986
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.039, 1.02
No. of reflections	6457
No. of parameters	390
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, −0.46

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

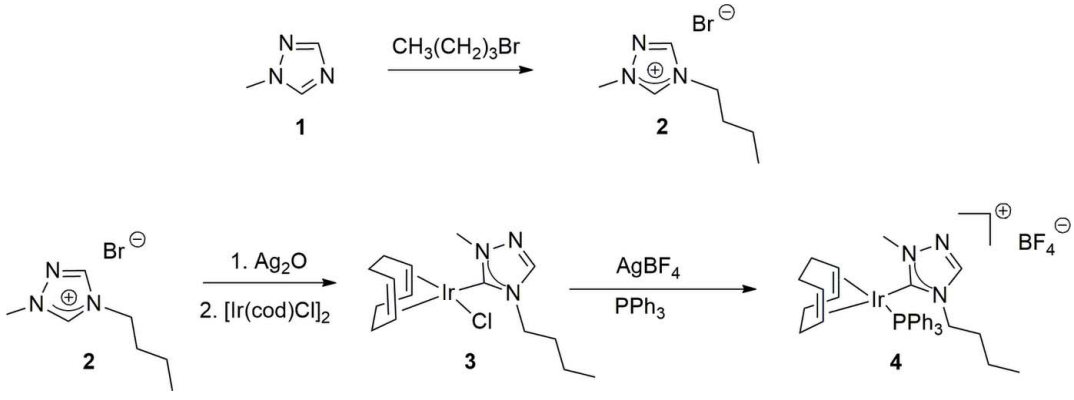


Figure 4
Reaction scheme for the synthesis of the N-heterocyclic carbene (**2**) and subsequent formation of the title compound (**4**).

7.45 (*m*, 15 H, H_{ar}), 4.84 (*s*, 3H, N—CH_3), 4.76 (*t*, 2 H, N—CH_2 of CH_2 of *n*-Bu), 4.52 (*m*, 2 H, CH of COD), 4.36 (*m*, 2H, CH of COD), 3.95 (*m*, 2 H, CH_2 of COD), 3.84 (*m*, 2 H, CH_2 of COD), 2.43 (*m*, 2 H, CH_2 of COD), 2.17 (*m*, 2 H, CH_2 of COD), 1.55 (*m*, CH_2 of *n*-Bu), 1.32 (*m*, 2 H, CH_2 of *n*-Bu), 0.91 (*t*, 3 H, CH_3 of *n*-Bu). ^{13}C NMR: δ 178.27 (Ir—C), 143.44 (N—C_3H—N), 133.57–129.04 (C arom), 87.66, 87.26, 86.06, 85.18 (CH of COD), 48.48 (N—CH_3), 39.44 (N—CH_2 of *n*-Bu), 33.35, 31.78, 31.18, 30.60 (CH_2 of COD), 26.23 (CH_2 of *n*-Bu), 19.98 (CH_2 of *n*-Bu), 13.65 (CH_3 of *n*-Bu).^{31}P NMR: δ 17.40.

The title compound (**4**) was crystallized by slow diffusion of pentane into a CH_2Cl_2 solution.

Refinement

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

Funding information

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full crystallographic data

IUCrData (2021). **6**, x211142 [https://doi.org/10.1107/S2414314621011421]

(4-Butyl-1-methyl-1,2,4-triazol-5-ylidene)[(1,2,5,6-η)-cycloocta-1,5-diene](triphenylphosphane)iridium(I) tetrafluoridoborate

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Crystal data

$[Ir(C_8H_{12})(C_7H_{13}N_3)(C_{18}H_{15}P)]BF_4$
M_r = 788.66
Monoclinic, $P2_1/c$
a = 9.8966 (9) Å
b = 16.3247 (17) Å
c = 20.0560 (19) Å
β = 102.285 (4)°
V = 3166.0 (5) Å^3
Z = 4
$F(000)$ = 1568
D_x = 1.655 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9226 reflections
θ = 2.4–26.4°
μ = 4.32 mm^{-1}
T = 100 K
Irregular, clear light pink
0.31 × 0.21 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.668, T_{max} = 0.745
34219 measured reflections
6457 independent reflections
5986 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.4°, θ_{min} = 1.6°
h = −9→12
k = −20→20
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.039
S = 1.02
6457 reflections
390 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2 + 3.1892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-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	0.65716 (2)	0.26151 (2)	0.45405 (2)	0.01160 (3)
P1	0.89650 (6)	0.26064 (3)	0.46457 (3)	0.01218 (11)
F3	0.71162 (17)	0.08389 (9)	0.20651 (8)	0.0358 (4)
F4	0.55953 (16)	0.17666 (10)	0.14868 (7)	0.0353 (4)
F1	0.5266 (2)	0.12606 (12)	0.24796 (9)	0.0503 (5)
F2	0.70664 (17)	0.21312 (10)	0.24647 (9)	0.0433 (4)
N1	0.65074 (19)	0.44904 (11)	0.47394 (9)	0.0162 (4)
N3	0.63018 (19)	0.41838 (11)	0.36915 (9)	0.0161 (4)
N2	0.6419 (2)	0.52330 (12)	0.44004 (10)	0.0211 (4)
C19	0.6459 (2)	0.38401 (13)	0.43264 (11)	0.0133 (4)
C14	1.1314 (2)	0.29788 (13)	0.56684 (11)	0.0173 (5)
H14	1.179953	0.300731	0.530836	0.021*
C1	0.9725 (2)	0.16434 (13)	0.44288 (11)	0.0142 (4)
C7	0.9666 (2)	0.33788 (14)	0.41425 (11)	0.0153 (4)
C30	0.6753 (2)	0.14351 (13)	0.50736 (11)	0.0164 (4)
H30	0.772530	0.124875	0.525058	0.020*
C13	0.9890 (2)	0.28236 (13)	0.55206 (10)	0.0140 (4)
C27	0.4612 (2)	0.26324 (14)	0.49000 (12)	0.0165 (4)
H27	0.439383	0.317551	0.508224	0.020*
C18	0.9175 (2)	0.28029 (14)	0.60557 (11)	0.0169 (4)
H18	0.820762	0.270299	0.596020	0.020*
C6	1.0729 (2)	0.12075 (13)	0.48883 (11)	0.0166 (4)
H6	1.102300	0.139853	0.534351	0.020*
C2	0.9277 (2)	0.13410 (14)	0.37611 (11)	0.0189 (5)
H2	0.856611	0.161719	0.344911	0.023*
C29	0.5865 (2)	0.14483 (14)	0.56032 (11)	0.0191 (5)
H29A	0.639649	0.170571	0.602525	0.023*
H29B	0.565779	0.087741	0.571466	0.023*
C31	0.6252 (2)	0.12923 (13)	0.43760 (11)	0.0173 (5)
H31	0.694465	0.102954	0.414647	0.021*
C33	0.3877 (2)	0.18133 (15)	0.37746 (12)	0.0208 (5)
H33A	0.396562	0.191149	0.329864	0.025*
H33B	0.289372	0.169226	0.376674	0.025*
C26	0.4292 (2)	0.25843 (14)	0.41893 (12)	0.0175 (5)
H26	0.388874	0.309840	0.395824	0.021*
C10	1.0450 (3)	0.46222 (16)	0.33383 (12)	0.0271 (6)
H10	1.070139	0.504338	0.306101	0.033*
C8	0.9513 (2)	0.42037 (14)	0.42979 (11)	0.0174 (5)
H8	0.914969	0.434381	0.468486	0.021*
C28	0.4490 (2)	0.19174 (14)	0.53677 (11)	0.0190 (5)
H28A	0.377662	0.153371	0.512567	0.023*
H28B	0.417828	0.212455	0.577402	0.023*
C20	0.6288 (2)	0.50151 (14)	0.37636 (12)	0.0209 (5)
H20	0.619314	0.539019	0.339443	0.025*
C21	0.6380 (2)	0.37261 (15)	0.30676 (11)	0.0211 (5)

H21A	0.619985	0.313956	0.313919	0.025*
H21B	0.733011	0.377231	0.298694	0.025*
C12	1.0261 (2)	0.31863 (15)	0.35861 (12)	0.0215 (5)
H12	1.040077	0.262983	0.347945	0.026*
C11	1.0647 (3)	0.38084 (17)	0.31903 (12)	0.0275 (6)
H11	1.105034	0.367323	0.281487	0.033*
C9	0.9881 (2)	0.48205 (15)	0.38964 (12)	0.0220 (5)
H9	0.974646	0.537806	0.400139	0.026*
C4	1.0889 (2)	0.02184 (14)	0.40176 (13)	0.0224 (5)
H4	1.130025	−0.025843	0.387538	0.027*
C3	0.9873 (2)	0.06395 (14)	0.35580 (12)	0.0214 (5)
H3	0.958607	0.044591	0.310313	0.026*
C25	0.6757 (2)	0.44862 (14)	0.54844 (11)	0.0201 (5)
H25A	0.770805	0.430993	0.567206	0.030*
H25B	0.611083	0.410699	0.563228	0.030*
H25C	0.661787	0.503904	0.564823	0.030*
C5	1.1299 (2)	0.04971 (14)	0.46846 (12)	0.0208 (5)
H5	1.197231	0.020093	0.500216	0.025*
C22	0.5356 (2)	0.40274 (16)	0.24331 (11)	0.0227 (5)
H22A	0.550364	0.462150	0.237934	0.027*
H22B	0.556200	0.374777	0.202807	0.027*
C24	0.2888 (3)	0.41824 (17)	0.17845 (12)	0.0273 (6)
H24A	0.312914	0.390240	0.139350	0.041*
H24B	0.299661	0.477499	0.173758	0.041*
H24C	0.192680	0.405874	0.180060	0.041*
C15	1.2020 (2)	0.30915 (14)	0.63392 (12)	0.0213 (5)
H15	1.299068	0.318279	0.643787	0.026*
C23	0.3847 (2)	0.38868 (16)	0.24451 (12)	0.0246 (5)
H23A	0.361964	0.418257	0.283794	0.029*
H23B	0.369070	0.329525	0.250673	0.029*
C16	1.1305 (3)	0.30704 (15)	0.68664 (12)	0.0242 (5)
H16	1.178888	0.315308	0.732387	0.029*
C32	0.4761 (2)	0.10623 (14)	0.40586 (12)	0.0200 (5)
H32A	0.434297	0.079092	0.440757	0.024*
H32B	0.475337	0.066578	0.368436	0.024*
B1	0.6273 (3)	0.15018 (17)	0.21277 (13)	0.0199 (5)
C17	0.9887 (3)	0.29291 (15)	0.67276 (11)	0.0224 (5)
H17	0.940288	0.291852	0.708901	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.01031 (5)	0.01204 (5)	0.01236 (4)	0.00107 (3)	0.00225 (3)	0.00077 (3)
P1	0.0116 (3)	0.0132 (3)	0.0115 (2)	0.0014 (2)	0.0020 (2)	0.00072 (19)
F3	0.0445 (10)	0.0277 (8)	0.0356 (9)	0.0155 (7)	0.0094 (7)	0.0015 (7)
F4	0.0410 (9)	0.0387 (9)	0.0223 (8)	0.0116 (7)	−0.0024 (6)	0.0008 (6)
F1	0.0625 (12)	0.0533 (12)	0.0466 (11)	−0.0028 (9)	0.0373 (9)	−0.0002 (8)
F2	0.0370 (9)	0.0358 (9)	0.0489 (10)	0.0014 (8)	−0.0092 (8)	−0.0191 (8)

N1	0.0179 (10)	0.0126 (9)	0.0182 (9)	0.0020 (7)	0.0040 (7)	0.0012 (7)
N3	0.0155 (9)	0.0157 (10)	0.0168 (9)	0.0030 (7)	0.0025 (7)	0.0034 (7)
N2	0.0226 (11)	0.0141 (10)	0.0263 (11)	0.0025 (8)	0.0046 (8)	0.0044 (8)
C19	0.0094 (10)	0.0155 (11)	0.0155 (10)	0.0022 (8)	0.0038 (8)	0.0015 (8)
C14	0.0164 (11)	0.0128 (11)	0.0228 (11)	0.0017 (9)	0.0044 (9)	−0.0002 (9)
C1	0.0118 (10)	0.0141 (11)	0.0176 (11)	−0.0007 (8)	0.0050 (8)	−0.0002 (8)
C7	0.0096 (10)	0.0203 (12)	0.0157 (10)	−0.0006 (9)	0.0017 (8)	0.0036 (8)
C30	0.0156 (11)	0.0113 (11)	0.0223 (11)	0.0026 (9)	0.0042 (9)	0.0024 (8)
C13	0.0154 (11)	0.0108 (10)	0.0145 (10)	0.0013 (8)	0.0005 (8)	0.0008 (8)
C27	0.0100 (10)	0.0167 (11)	0.0237 (11)	0.0015 (9)	0.0053 (9)	−0.0009 (9)
C18	0.0158 (11)	0.0165 (11)	0.0180 (11)	0.0022 (9)	0.0023 (9)	0.0014 (8)
C6	0.0151 (11)	0.0153 (11)	0.0190 (11)	−0.0028 (9)	0.0032 (9)	−0.0004 (8)
C2	0.0159 (11)	0.0210 (12)	0.0191 (11)	−0.0009 (9)	0.0023 (9)	0.0002 (9)
C29	0.0213 (12)	0.0177 (12)	0.0190 (11)	−0.0022 (9)	0.0060 (9)	0.0031 (9)
C31	0.0177 (12)	0.0125 (11)	0.0232 (12)	0.0009 (9)	0.0075 (9)	−0.0003 (8)
C33	0.0164 (12)	0.0255 (13)	0.0192 (11)	−0.0038 (10)	0.0009 (9)	−0.0027 (9)
C26	0.0076 (10)	0.0182 (11)	0.0251 (12)	0.0016 (8)	0.0000 (9)	0.0020 (9)
C10	0.0295 (14)	0.0295 (14)	0.0220 (12)	−0.0114 (11)	0.0045 (10)	0.0085 (10)
C8	0.0130 (11)	0.0202 (12)	0.0182 (11)	0.0002 (9)	0.0015 (8)	0.0011 (9)
C28	0.0172 (12)	0.0213 (12)	0.0201 (11)	−0.0028 (9)	0.0078 (9)	−0.0019 (9)
C20	0.0211 (12)	0.0162 (12)	0.0254 (12)	0.0031 (9)	0.0051 (10)	0.0070 (9)
C21	0.0222 (12)	0.0264 (13)	0.0151 (11)	0.0065 (10)	0.0046 (9)	0.0004 (9)
C12	0.0212 (12)	0.0238 (12)	0.0207 (12)	−0.0019 (10)	0.0073 (9)	−0.0010 (9)
C11	0.0288 (14)	0.0375 (15)	0.0188 (12)	−0.0090 (12)	0.0109 (10)	−0.0013 (10)
C9	0.0203 (12)	0.0191 (12)	0.0244 (12)	−0.0036 (10)	−0.0002 (9)	0.0038 (9)
C4	0.0231 (13)	0.0139 (11)	0.0333 (13)	0.0004 (9)	0.0131 (10)	−0.0039 (9)
C3	0.0228 (12)	0.0207 (12)	0.0222 (12)	−0.0034 (10)	0.0082 (10)	−0.0063 (9)
C25	0.0235 (12)	0.0193 (12)	0.0176 (11)	0.0017 (10)	0.0048 (9)	−0.0024 (9)
C5	0.0154 (11)	0.0166 (12)	0.0295 (13)	0.0019 (9)	0.0028 (9)	0.0016 (9)
C22	0.0255 (13)	0.0276 (13)	0.0152 (11)	0.0055 (10)	0.0051 (9)	0.0029 (9)
C24	0.0248 (13)	0.0332 (15)	0.0214 (12)	0.0077 (11)	−0.0006 (10)	−0.0011 (10)
C15	0.0176 (12)	0.0147 (11)	0.0274 (12)	0.0014 (9)	−0.0048 (9)	−0.0019 (9)
C23	0.0234 (13)	0.0278 (14)	0.0211 (12)	−0.0003 (10)	0.0016 (10)	0.0019 (10)
C16	0.0282 (13)	0.0193 (12)	0.0196 (11)	0.0029 (10)	−0.0067 (10)	−0.0008 (9)
C32	0.0208 (12)	0.0185 (12)	0.0214 (12)	−0.0039 (9)	0.0064 (9)	−0.0053 (9)
B1	0.0218 (14)	0.0206 (13)	0.0173 (12)	0.0026 (11)	0.0043 (10)	−0.0017 (10)
C17	0.0282 (13)	0.0232 (12)	0.0154 (11)	0.0021 (10)	0.0040 (9)	0.0006 (9)

Geometric parameters (Å, º)

Ir1—P1	2.3330 (6)	C33—H33A	0.9900
Ir1—C19	2.043 (2)	C33—H33B	0.9900
Ir1—C30	2.192 (2)	C33—C26	1.516 (3)
Ir1—C27	2.208 (2)	C33—C32	1.543 (3)
Ir1—C31	2.197 (2)	C26—H26	1.0000
Ir1—C26	2.216 (2)	C10—H10	0.9500
P1—C1	1.834 (2)	C10—C11	1.384 (4)
P1—C7	1.841 (2)	C10—C9	1.394 (4)

P1—C13	1.833 (2)	C8—H8	0.9500
F3—B1	1.389 (3)	C8—C9	1.386 (3)
F4—B1	1.386 (3)	C28—H28A	0.9900
F1—B1	1.394 (3)	C28—H28B	0.9900
F2—B1	1.380 (3)	C20—H20	0.9500
N1—N2	1.384 (3)	C21—H21A	0.9900
N1—C19	1.341 (3)	C21—H21B	0.9900
N1—C25	1.462 (3)	C21—C22	1.530 (3)
N3—C19	1.370 (3)	C12—H12	0.9500
N3—C20	1.365 (3)	C12—C11	1.392 (3)
N3—C21	1.474 (3)	C11—H11	0.9500
N2—C20	1.305 (3)	C9—H9	0.9500
C14—H14	0.9500	C4—H4	0.9500
C14—C13	1.400 (3)	C4—C3	1.392 (3)
C14—C15	1.390 (3)	C4—C5	1.389 (3)
C1—C6	1.398 (3)	C3—H3	0.9500
C1—C2	1.407 (3)	C25—H25A	0.9800
C7—C8	1.398 (3)	C25—H25B	0.9800
C7—C12	1.404 (3)	C25—H25C	0.9800
C30—H30	1.0000	C5—H5	0.9500
C30—C29	1.515 (3)	C22—H22A	0.9900
C30—C31	1.401 (3)	C22—H22B	0.9900
C13—C18	1.406 (3)	C22—C23	1.516 (3)
C27—H27	1.0000	C24—H24A	0.9800
C27—C26	1.395 (3)	C24—H24B	0.9800
C27—C28	1.518 (3)	C24—H24C	0.9800
C18—H18	0.9500	C24—C23	1.534 (3)
C18—C17	1.396 (3)	C15—H15	0.9500
C6—H6	0.9500	C15—C16	1.392 (4)
C6—C5	1.389 (3)	C23—H23A	0.9900
C2—H2	0.9500	C23—H23B	0.9900
C2—C3	1.388 (3)	C16—H16	0.9500
C29—H29A	0.9900	C16—C17	1.391 (3)
C29—H29B	0.9900	C32—H32A	0.9900
C29—C28	1.546 (3)	C32—H32B	0.9900
C31—H31	1.0000	C17—H17	0.9500
C31—C32	1.525 (3)		

C19—Ir1—P1	91.94 (6)	C33—C26—Ir1	109.39 (15)
C19—Ir1—C30	163.28 (8)	C33—C26—H26	114.1
C19—Ir1—C27	92.51 (8)	C11—C10—H10	120.2
C19—Ir1—C31	158.53 (9)	C11—C10—C9	119.6 (2)
C19—Ir1—C26	87.09 (8)	C9—C10—H10	120.2
C30—Ir1—P1	88.54 (6)	C7—C8—H8	119.5
C30—Ir1—C27	80.69 (8)	C9—C8—C7	121.1 (2)
C30—Ir1—C31	37.22 (8)	C9—C8—H8	119.5
C30—Ir1—C26	96.15 (8)	C27—C28—C29	112.87 (18)
C27—Ir1—P1	156.32 (6)	C27—C28—H28A	109.0

C27—Ir1—C26	36.76 (8)	C27—C28—H28B	109.0
C31—Ir1—P1	96.80 (6)	C29—C28—H28A	109.0
C31—Ir1—C27	87.32 (8)	C29—C28—H28B	109.0
C31—Ir1—C26	79.96 (8)	H28A—C28—H28B	107.8
C26—Ir1—P1	166.86 (6)	N3—C20—H20	124.0
C1—P1—Ir1	116.32 (7)	N2—C20—N3	111.9 (2)
C1—P1—C7	103.62 (10)	N2—C20—H20	124.0
C7—P1—Ir1	116.12 (7)	N3—C21—H21A	108.9
C13—P1—Ir1	112.09 (7)	N3—C21—H21B	108.9
C13—P1—C1	104.27 (10)	N3—C21—C22	113.45 (19)
C13—P1—C7	102.86 (10)	H21A—C21—H21B	107.7
N2—N1—C25	119.05 (18)	C22—C21—H21A	108.9
C19—N1—N2	113.57 (18)	C22—C21—H21B	108.9
C19—N1—C25	127.14 (19)	C7—C12—H12	119.9
C19—N3—C21	124.44 (19)	C11—C12—C7	120.2 (2)
C20—N3—C19	108.08 (18)	C11—C12—H12	119.9
C20—N3—C21	126.70 (19)	C10—C11—C12	120.7 (2)
C20—N2—N1	102.98 (18)	C10—C11—H11	119.7
N1—C19—Ir1	130.67 (16)	C12—C11—H11	119.7
N1—C19—N3	103.41 (18)	C10—C9—H9	120.0
N3—C19—Ir1	125.92 (16)	C8—C9—C10	119.9 (2)
C13—C14—H14	119.8	C8—C9—H9	120.0
C15—C14—H14	119.8	C3—C4—H4	120.1
C15—C14—C13	120.4 (2)	C5—C4—H4	120.1
C6—C1—P1	123.34 (16)	C5—C4—C3	119.9 (2)
C6—C1—C2	119.0 (2)	C2—C3—C4	120.3 (2)
C2—C1—P1	117.67 (16)	C2—C3—H3	119.8
C8—C7—P1	117.78 (17)	C4—C3—H3	119.8
C8—C7—C12	118.5 (2)	N1—C25—H25A	109.5
C12—C7—P1	123.60 (18)	N1—C25—H25B	109.5
Ir1—C30—H30	114.4	N1—C25—H25C	109.5
C29—C30—Ir1	109.27 (14)	H25A—C25—H25B	109.5
C29—C30—H30	114.4	H25A—C25—H25C	109.5
C31—C30—Ir1	71.60 (12)	H25B—C25—H25C	109.5
C31—C30—H30	114.4	C6—C5—C4	120.2 (2)
C31—C30—C29	124.6 (2)	C6—C5—H5	119.9
C14—C13—P1	120.85 (16)	C4—C5—H5	119.9
C14—C13—C18	119.33 (19)	C21—C22—H22A	108.6
C18—C13—P1	119.76 (16)	C21—C22—H22B	108.6
Ir1—C27—H27	113.8	H22A—C22—H22B	107.6
C26—C27—Ir1	71.92 (13)	C23—C22—C21	114.7 (2)
C26—C27—H27	113.8	C23—C22—H22A	108.6
C26—C27—C28	123.9 (2)	C23—C22—H22B	108.6
C28—C27—Ir1	112.53 (14)	H24A—C24—H24B	109.5
C28—C27—H27	113.8	H24A—C24—H24C	109.5
C13—C18—H18	120.0	H24B—C24—H24C	109.5
C17—C18—C13	120.1 (2)	C23—C24—H24A	109.5
C17—C18—H18	120.0	C23—C24—H24B	109.5

C1—C6—H6	119.7	C23—C24—H24C	109.5
C5—C6—C1	120.5 (2)	C14—C15—H15	120.0
C5—C6—H6	119.7	C14—C15—C16	119.9 (2)
C1—C2—H2	120.0	C16—C15—H15	120.0
C3—C2—C1	120.1 (2)	C22—C23—C24	111.7 (2)
C3—C2—H2	120.0	C22—C23—H23A	109.3
C30—C29—H29A	108.9	C22—C23—H23B	109.3
C30—C29—H29B	108.9	C24—C23—H23A	109.3
C30—C29—C28	113.38 (18)	C24—C23—H23B	109.3
H29A—C29—H29B	107.7	H23A—C23—H23B	108.0
C28—C29—H29A	108.9	C15—C16—H16	119.8
C28—C29—H29B	108.9	C17—C16—C15	120.4 (2)
Ir1—C31—H31	113.6	C17—C16—H16	119.8
C30—C31—Ir1	71.18 (12)	C31—C32—C33	112.38 (19)
C30—C31—H31	113.6	C31—C32—H32A	109.1
C30—C31—C32	124.3 (2)	C31—C32—H32B	109.1
C32—C31—Ir1	113.60 (15)	C33—C32—H32A	109.1
C32—C31—H31	113.6	C33—C32—H32B	109.1
H33A—C33—H33B	107.8	H32A—C32—H32B	107.9
C26—C33—H33A	109.0	F3—B1—F1	109.5 (2)
C26—C33—H33B	109.0	F4—B1—F3	109.9 (2)
C26—C33—C32	113.01 (18)	F4—B1—F1	107.5 (2)
C32—C33—H33A	109.0	F2—B1—F3	109.5 (2)
C32—C33—H33B	109.0	F2—B1—F4	109.5 (2)
Ir1—C26—H26	114.1	F2—B1—F1	110.8 (2)
C27—C26—Ir1	71.32 (12)	C18—C17—H17	120.1
C27—C26—C33	125.7 (2)	C16—C17—C18	119.8 (2)
C27—C26—H26	114.1	C16—C17—H17	120.1

Ir1—P1—C1—C6	−120.92 (17)	C30—C31—C32—C33	95.6 (3)
Ir1—P1—C1—C2	59.92 (19)	C13—P1—C1—C6	3.0 (2)
Ir1—P1—C7—C8	64.05 (18)	C13—P1—C1—C2	−176.11 (17)
Ir1—P1—C7—C12	−111.60 (18)	C13—P1—C7—C8	−58.73 (19)
Ir1—P1—C13—C14	−169.45 (15)	C13—P1—C7—C12	125.61 (19)
Ir1—P1—C13—C18	13.1 (2)	C13—C14—C15—C16	−1.6 (3)
Ir1—C30—C29—C28	37.1 (2)	C13—C18—C17—C16	−0.4 (4)
Ir1—C30—C31—C32	−106.2 (2)	C6—C1—C2—C3	−2.8 (3)
Ir1—C27—C26—C33	100.9 (2)	C2—C1—C6—C5	1.5 (3)
Ir1—C27—C28—C29	11.8 (2)	C29—C30—C31—Ir1	101.1 (2)
Ir1—C31—C32—C33	13.0 (2)	C29—C30—C31—C32	−5.1 (3)
P1—C1—C6—C5	−177.65 (17)	C31—C30—C29—C28	−43.4 (3)
P1—C1—C2—C3	176.41 (18)	C26—C27—C28—C29	94.6 (3)
P1—C7—C8—C9	−173.12 (17)	C26—C33—C32—C31	−33.8 (3)
P1—C7—C12—C11	173.78 (18)	C8—C7—C12—C11	−1.8 (3)
P1—C13—C18—C17	176.94 (17)	C28—C27—C26—Ir1	−105.4 (2)
N1—N2—C20—N3	−0.5 (2)	C28—C27—C26—C33	−4.6 (3)
N3—C21—C22—C23	−66.4 (3)	C20—N3—C19—Ir1	−179.37 (16)
N2—N1—C19—Ir1	178.98 (15)	C20—N3—C19—N1	1.0 (2)

N2—N1—C19—N3	−1.4 (2)	C20—N3—C21—C22	−48.3 (3)
C19—N1—N2—C20	1.2 (2)	C21—N3—C19—Ir1	−8.9 (3)
C19—N3—C20—N2	−0.3 (3)	C21—N3—C19—N1	171.45 (19)
C19—N3—C21—C22	143.0 (2)	C21—N3—C20—N2	−170.5 (2)
C14—C13—C18—C17	−0.6 (3)	C21—C22—C23—C24	−178.4 (2)
C14—C15—C16—C17	0.6 (4)	C12—C7—C8—C9	2.8 (3)
C1—P1—C7—C8	−167.13 (17)	C11—C10—C9—C8	−0.2 (4)
C1—P1—C7—C12	17.2 (2)	C9—C10—C11—C12	1.1 (4)
C1—P1—C13—C14	63.90 (19)	C3—C4—C5—C6	−1.9 (4)
C1—P1—C13—C18	−113.56 (18)	C25—N1—N2—C20	176.05 (19)
C1—C6—C5—C4	0.8 (3)	C25—N1—C19—Ir1	4.7 (3)
C1—C2—C3—C4	1.8 (3)	C25—N1—C19—N3	−175.69 (19)
C7—P1—C1—C6	110.38 (19)	C5—C4—C3—C2	0.6 (4)
C7—P1—C1—C2	−68.78 (19)	C15—C14—C13—P1	−175.91 (17)
C7—P1—C13—C14	−44.0 (2)	C15—C14—C13—C18	1.6 (3)
C7—P1—C13—C18	138.53 (18)	C15—C16—C17—C18	0.4 (4)
C7—C8—C9—C10	−1.8 (3)	C32—C33—C26—Ir1	37.6 (2)
C7—C12—C11—C10	−0.1 (4)	C32—C33—C26—C27	−42.9 (3)
C30—C29—C28—C27	−32.8 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···F2	0.95	2.36	3.285 (3)	165
C20—H20···F1^{i}	0.95	2.47	3.329 (3)	150
C25—H25*B*···F4^{ii}	0.98	2.37	3.245 (3)	149

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