# metal-organic compounds

# Azido($\eta^5$-pentamethylcyclopentadienyl)-[2-(pyridin-2-yl)phenyl]iridium(III)

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In the title compound, [Ir(C₁₀H₁₅)(C₁₁H₈N)(N₃)], the Ir$^{III}$ ion is coordinated by three anionic ligands, namely, pentamethyl-cyclopentadienyl (Cp*$^-$), 2-(pyridin-2-yl)phenyl (ppy$^-$) and azide (N₃$^-$), and adopts a three-legged piano-stool geometry The coordination mode of N₃$^-$ is typical for Cp*Ir$^{III}$–N₃ complexes, with an Ir—N(N₃) bond length of 2.125 (2) Å and an Ir—N=N bond angle of 116.5 (2)°. The N₃$^-$ ligand is almost linear [N=N=N = 176.0 (3)°], and the N=N bond length between the central and coordinating N atom and that between the central and non-coordinating terminal N atom are 1.194 (3) and 1.157 (3) Å, respectively. For the ppy$^-$ ligand, the Ir—C and Ir—N bond lengths are 2.066 (3) and 2.079 (3) Å, respectively, which are rather close to each other, compared to the related Ir$^{III}$– or Rh$^{III}$–ppy complexes. The Ir—C(Cp*) bond lengths vary in the range 2.163 (2)–2.232 (2) Å, indicating a strong *trans* influence of the cyclo-metallated C-donor atom of the ppy$^-$ ligand.

## Related literature

For crystallographic analyses of [Cp*Ir$^{III}$(N₃)(L–L')] (L–L' = bidentate chelate ligands; *e.g.*, bpy, 2-Spy, *etc.*) complexes, see: Suzuki *et al.* (2009); Suzuki (2005). For crystallographic analyses of mononuclear [Cp*Ir(ppy)X] complexes (X = Cl, I, MeCN₄, *etc.*), see: Boutadla *et al.* (2009); Park-Gehrke *et al.* (2009); Takayama *et al.* (2013). For photochemistry of [Cp*Ir$^{III}$(N₃)(L–L')] complexes, see: Sekioka *et al.* (2005); Kotera *et al.* (2008).



## Experimental

### Crystal data

| | |
|---|---|
| [Ir(C₁₀H₁₅)(C₁₁H₈N)(N₃)] | $V$ = 1798.2 (4) Å³ |
| $M_r$ = 523.63 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a$ = 15.4821 (18) Å | $\mu$ = 7.44 mm$^{-1}$ |
| $b$ = 7.3938 (9) Å | $T$ = 193 K |
| $c$ = 15.7137 (18) Å | 0.30 × 0.30 × 0.20 mm |
| $\beta$ = 91.477 (4)° | |

### Data collection

| | |
|---|---|
| Rigaku R-AXIS RAPIDII diffractometer | 27640 measured reflections |
| Absorption correction: numerical (*NUMABS*; Rigaku, 1999) | 4115 independent reflections |
| $T_{min}$ = 0.103, $T_{max}$ = 0.225 | 4022 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.045 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.017 | 240 parameters |
| $wR(F^2)$ = 0.042 | H-atom parameters constrained |
| $S$ = 1.13 | $\Delta\rho_{max}$ = 1.61 e Å$^{-3}$ |
| 4115 reflections | $\Delta\rho_{min}$ = −0.65 e Å$^{-3}$ |

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *DIRDIF99-PATTY* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2013*.

## References

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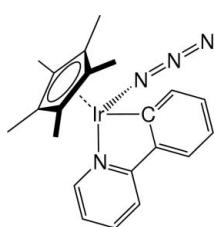
# supporting information

# Azido($\eta^5$-pentamethylcyclopentadienyl)[2-(pyridin-2-yl)phenyl]iridium(III)

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### S1. Comment

In previous studies we have prepared a number of iridium(III) azido complexes, [Cp*Ir$^{III}$(N$_3$)(L–L′)] (Cp* = pentamethyl-cyclopentadienyl, L–L′ = various kinds of bidentate chelate ligands), and investigated their structures and photochemical reactivities. Among them, complexes of [Cp*Ir(N$_3$)(Me$_2$dtc)] (Me$_2$dtc$^-$ = *N,N*-dimethyldithiocarbamate) and [Cp*Ir(N$_3$)(2-Spy)] (2-Spy$^-$ = 2-pyridinethiolate) afforded interesting photolysis products with two-legged piano-stool structures, [Cp*Ir{SC(NMe$_2$)SN}] and [Cp*Ir(1-N-2Spy)], respectively, by insertion of a N-atom originating from the coordinated azido ligand, into the Ir–S and Ir–N(py) bonds, respectively (Sekioka *et al.*, 2005). In contrast, photolysis of the related complexes with an N—N, N—P or P—P type four-membered chelate ligand (*i.e.*, 1,8-naphthyridine, 2-diphenyl-phosphinopyridine or bis(dimethylphosphino)methane) gave a complicated mixture of uncharacterized products, due probably to reductive elimination of the coordinated azide (Suzuki *et al.*, 2009). In the case of [Cp*Ir(N$_3$)(bpy)]PF$_6$ (bpy = 2,2′-bipyridine), photolysis in acetonitrile produced a 5-methyltetrazolato complex, [Cp*Ir(N$_3$)(MeCN$_4$)]$^+$, which was confirmed by $^1$H NMR spectroscopy (Kotera *et al.*, 2008). In addition, the X-ray structural analysis of the bpy complex, [Cp*Ir$^{III}$(N$_3$)(bpy)]PF$_6$, revealed some structural characteristics different from those of the other [Cp*Ir(N$_3$)(L–L′)] complexes (Suzuki, 2005; Suzuki *et al.*, 2009). For instance, the Ir—N(N$_3$) bond in the bpy complex [2.230 (6) Å] was longer by *ca* 0.1 Å than the typical Ir—N(N$_3$) bond lengths in the other [Cp*Ir(N$_3$)(L–L′)] complexes. Triatomic unit of N$_3^-$ was almost linear as usual, but the N—N bond length between the central and coordinated N atoms was unusually longer by *ca* 0.25 Å than that between the central and non-coordinated terminal N atoms. In this study, we have prepared and characterized the analogous Cp*Ir$^{III}$(N$_3$) complex with a structurally similar but an anionic 2-(pyridin-2-yl)phenyl (ppy$^-$) ligand, [Cp*Ir(N$_3$)(ppy)].

The title compound crystallized in a monoclinic space group *P*2$_1$/*n* with *Z* = 4. The Ir$^{III}$ ion was coordinated by three anionic ligands, Cp*$^-$, ppy$^-$ and N$_3^-$, and it took a three-legged piano-stool structure. The ppy$^-$ ligand formed a planar chelate, having the Ir1—C11 bond of 2.066 (2) Å and the Ir1—N22 bond of 2.079 (2) Å. It is noted that the difference between the Ir—C and Ir—N bond lengths is not so large (0.013 Å), compared to the typical Ir$^{III}$ or Rh$^{III}$ (*M*$^{III}$)–ppy complexes, where the M—C bond is significantly shorter than the M—N bond (Takayama *et al.*, 2013). In some cases of Ir$^{III}$–ppy complexes with a simple halide, similarly small differences in the Ir—C and Ir—N bonds were also reported; for example, 0.016 Å in [Cp*IrCl(ppy)] (Boutadla *et al.*, 2009) and 0.029 Å in [Cp*IrI(ppy)] (Park-Gehrke *et al.*, 2009). These small differences may be due to a partial configurational disorder of the ppy coordination.

The Ir1—N1 coordination bond length is 2.125 (2) Å and the Ir1—N1—N2 bond angle is 116.5 (2)°, while the triatomic azide moiety is almost linear: N1—N2—N3 176.0 (3)°. The N1—N2 and N2—N3 bond lengths are 1.194 (3) and 1.157 (3) Å, respectively. These structural parameters are typical for [Cp*Ir$^{III}$(N$_3$)(L–L′)] complexes (Suzuki *et al.*, 2009), except for [Cp*Ir(N$_3$)(bpy)]PF$_6$ (Suzuki, 2005).

The five Ir1—Cn(Cp*) bond lengths are 2.175 (2), 2.163 (2), 2.201 (2), 2.230 (2) and 2.232 (2) Å for n = 1–5, respectively (Table 1). Two relatively long (to C4 and C5) bonds are approximately *trans* to the C-donor atom of ppy⁻ ligand. A similar elongation of the Ir—C bonds are also observed in the other mononuclear [Cp*Ir$^{III}$(ppy)*X*] complexes (Park-Gehrke *et al.*, 2009; Takayama *et al.*, 2013), indicating a strong *trans* influence of the cyclometalated C-donor. The Ir1—C3 bond, which is *trans* to the N-donor of ppy⁻, is a little longer than the other two; this may indicate a partial configurational disorder of the N– and C-donor of ppy⁻ ligand in the Cp*Ir$^{III}$(ppy) complexes.

In the crystal structure there are no solvent molecules of crystallization. Further, any characteristic intermolecular interaction is not observed in this crystal.

When UV light was irradiated to an acetonitrile solution of this complex, a tetrazolato complex, [Cp*Ir(ppy)(MeCN$_4$)] (Takayama *et al.*, 2013) was formed, which was confirmed by ¹H NMR spectroscopy.

### S2. Experimental

A methanol solution (20 cm³) of NaN$_3$ (377 mg, 5.18 mmol) was added with stirring to an orange solution of [Cp*IrCl(ppy)] (260 mg, 0.503 mmol) in a 1:1 mixture of methanol and dichloromethane (15 cm³). The color of mixture turned to yellow immediately, and yellow precipitate was formed. After stirring at room temperature for 5 h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (50 cm³), and the filtered extract was concentrated under reduced pressure. Diethyl ether vapor was diffused into the concentrate in a closed vessel, affording orange needle crystals. Yield: 208 mg (79%). Anal. Found: C 48.01, H 4.16, N 10.56%. Calcd for C$_{23}$H$_{23}$IrN$_4$: C 48.16, H 4.43, N 10.70%. ¹H NMR (400 MHz, 21 °C, CD$_3$CN): $\delta$ 1.68 (s, Cp*, 15H), 7.09 (t, $J$ = 7.3 Hz, ppy, 1H), 7.18–7.26 (m, ppy, 2H), 7.77–7.87 (m, ppy, 3H), 7.98 (d, $J$ = 8.1 Hz, ppy, 1H) and 8.71 (d, $J$ = 5.4 Hz, ppy, 1H). IR (KBr disc): $\nu$(N$_3$) = 2027 cm⁻¹.

### S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95 (for aromatic) or 0.98 Å (for methyl) and with $U_{iso}$(H) = 1.2 (for aromatic) or 1.5 (for methyl) $U_{eq}$(C).
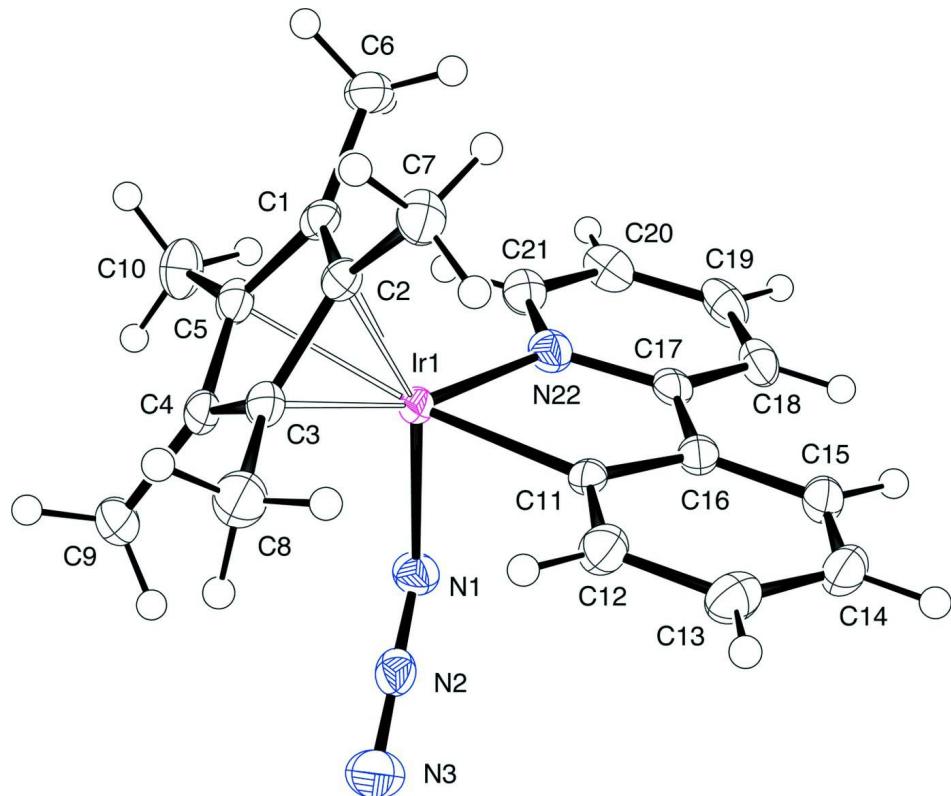
**Figure 1**

The molecular structure of the title compound with atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level.

**Azido($\eta^5$-pentamethylcyclopentadienyl)[2-(pyridin-2-yl)phenyl]iridium(III)**

*Crystal data*

| | |
|---|---|
| [Ir($C_{10}H_{15}$)($C_{11}H_8N$)($N_3$)] | $F(000) = 1016$ |
| $M_r = 523.63$ | $D_x = 1.934$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å |
| $a = 15.4821$ (18) Å | Cell parameters from 17777 reflections |
| $b = 7.3938$ (9) Å | $\theta = 3.0–27.5°$ |
| $c = 15.7137$ (18) Å | $\mu = 7.44$ mm$^{-1}$ |
| $\beta = 91.477$ (4)° | $T = 193$ K |
| $V = 1798.2$ (4) Å$^3$ | Needle, orange |
| $Z = 4$ | $0.30 \times 0.30 \times 0.20$ mm |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPIDII diffractometer | 4115 independent reflections |
| Detector resolution: 10.000 pixels mm$^{-1}$ | 4022 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.045$ |
| Absorption correction: numerical (*NUMABS*; Rigaku, 1999) | $\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$ |
| $T_{min} = 0.103$, $T_{max} = 0.225$ | $h = -20 \rightarrow 20$ |
| 27640 measured reflections | $k = -9 \rightarrow 9$ |
| | $l = -20 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.017$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.042$ | |
| $S = 1.13$ | H-atom parameters constrained |
| 4115 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0078P)^2 + 2.039P]$ |
| 240 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} = 0.002$ |
| Primary atom site location: heavy-atom method | $\Delta\rho_{max} = 1.61$ e Å⁻³ |
| | $\Delta\rho_{min} = -0.65$ e Å⁻³ |

*Special details*

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

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

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Ir1 | 0.50470 (2) | 0.26864 (2) | 0.74054 (2) | 0.01605 (4) |
| N22 | 0.42229 (13) | 0.3666 (3) | 0.64468 (14) | 0.0241 (4) |
| N1 | 0.55974 (13) | 0.5315 (3) | 0.73529 (14) | 0.0252 (4) |
| N2 | 0.58798 (13) | 0.5919 (3) | 0.80076 (14) | 0.0247 (4) |
| N3 | 0.61722 (17) | 0.6587 (3) | 0.86156 (16) | 0.0384 (6) |
| C1 | 0.51540 (15) | −0.0120 (3) | 0.70066 (15) | 0.0194 (5) |
| C2 | 0.50048 (15) | −0.0035 (3) | 0.79079 (15) | 0.0189 (5) |
| C3 | 0.57313 (15) | 0.0883 (3) | 0.83098 (15) | 0.0217 (5) |
| C4 | 0.63164 (15) | 0.1339 (3) | 0.76593 (16) | 0.0229 (5) |
| C5 | 0.59759 (15) | 0.0731 (3) | 0.68515 (16) | 0.0218 (5) |
| C6 | 0.46049 (17) | −0.1057 (3) | 0.63532 (16) | 0.0261 (5) |
| H6A | 0.4003 | −0.1058 | 0.6532 | 0.039* |
| H6B | 0.4805 | −0.2306 | 0.6289 | 0.039* |
| H6C | 0.4645 | −0.0424 | 0.5808 | 0.039* |
| C7 | 0.42773 (16) | −0.0905 (3) | 0.83631 (17) | 0.0262 (5) |
| H7A | 0.4470 | −0.2067 | 0.8600 | 0.039* |
| H7B | 0.3791 | −0.1104 | 0.7963 | 0.039* |
| H7C | 0.4094 | −0.0113 | 0.8825 | 0.039* |
| C8 | 0.59008 (19) | 0.1038 (4) | 0.92487 (17) | 0.0331 (6) |
| H8A | 0.6274 | 0.2084 | 0.9366 | 0.050* |
| H8B | 0.6187 | −0.0064 | 0.9458 | 0.050* |
| H8C | 0.5352 | 0.1195 | 0.9537 | 0.050* |
| C9 | 0.71557 (18) | 0.2319 (4) | 0.7806 (2) | 0.0329 (7) |
| H9A | 0.7603 | 0.1457 | 0.7992 | 0.049* |
| H9B | 0.7085 | 0.3242 | 0.8246 | 0.049* |
| H9C | 0.7327 | 0.2899 | 0.7275 | 0.049* |
| C10 | 0.64306 (17) | 0.0740 (4) | 0.60188 (17) | 0.0314 (6) |
| H10A | 0.6575 | −0.0504 | 0.5859 | 0.047* |

| | | | |
|---|---|---|---|
| H10B | 0.6962 | 0.1454 | 0.6076 | 0.047* |
| H10C | 0.6052 | 0.1274 | 0.5577 | 0.047* |
| C11 | 0.40789 (14) | 0.3875 (3) | 0.80932 (14) | 0.0169 (4) |
| C12 | 0.40386 (17) | 0.3927 (3) | 0.89675 (16) | 0.0266 (5) |
| H12 | 0.4490 | 0.3388 | 0.9300 | 0.032* |
| C13 | 0.33557 (18) | 0.4749 (4) | 0.93770 (17) | 0.0294 (6) |
| H13 | 0.3340 | 0.4748 | 0.9981 | 0.035* |
| C14 | 0.27000 (17) | 0.5567 (3) | 0.89033 (18) | 0.0296 (6) |
| H14 | 0.2231 | 0.6130 | 0.9179 | 0.036* |
| C15 | 0.27330 (16) | 0.5559 (3) | 0.80278 (18) | 0.0267 (5) |
| H15 | 0.2288 | 0.6129 | 0.7698 | 0.032* |
| C16 | 0.34190 (15) | 0.4715 (3) | 0.76237 (16) | 0.0208 (5) |
| C17 | 0.35097 (15) | 0.4629 (3) | 0.67030 (16) | 0.0210 (5) |
| C18 | 0.29488 (16) | 0.5441 (3) | 0.61069 (17) | 0.0265 (5) |
| H18 | 0.2469 | 0.6122 | 0.6293 | 0.032* |
| C19 | 0.30904 (16) | 0.5255 (4) | 0.52521 (18) | 0.0298 (6) |
| H19 | 0.2706 | 0.5792 | 0.4845 | 0.036* |
| C20 | 0.38019 (17) | 0.4273 (4) | 0.49885 (17) | 0.0295 (6) |
| H20 | 0.3907 | 0.4128 | 0.4399 | 0.035* |
| C21 | 0.43519 (16) | 0.3516 (3) | 0.55904 (16) | 0.0251 (5) |
| H21 | 0.4841 | 0.2862 | 0.5405 | 0.030* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ir1 | 0.01507 (6) | 0.01433 (6) | 0.01873 (6) | 0.00073 (3) | −0.00018 (4) | 0.00032 (3) |
| N22 | 0.0226 (10) | 0.0210 (10) | 0.0287 (11) | −0.0024 (8) | −0.0007 (8) | 0.0020 (8) |
| N1 | 0.0248 (10) | 0.0208 (11) | 0.0298 (12) | −0.0029 (8) | −0.0020 (9) | 0.0012 (8) |
| N2 | 0.0207 (10) | 0.0181 (10) | 0.0353 (12) | 0.0013 (8) | 0.0010 (9) | 0.0027 (9) |
| N3 | 0.0418 (14) | 0.0316 (13) | 0.0412 (14) | 0.0002 (11) | −0.0107 (11) | −0.0059 (11) |
| C1 | 0.0219 (11) | 0.0142 (11) | 0.0220 (12) | 0.0027 (9) | 0.0001 (9) | 0.0005 (8) |
| C2 | 0.0198 (11) | 0.0151 (11) | 0.0218 (12) | 0.0022 (9) | −0.0003 (9) | 0.0014 (8) |
| C3 | 0.0207 (11) | 0.0203 (12) | 0.0239 (12) | 0.0051 (9) | −0.0037 (9) | −0.0010 (9) |
| C4 | 0.0175 (11) | 0.0162 (11) | 0.0348 (14) | 0.0037 (9) | −0.0022 (10) | 0.0007 (9) |
| C5 | 0.0201 (11) | 0.0186 (11) | 0.0267 (12) | 0.0041 (9) | 0.0011 (9) | 0.0027 (9) |
| C6 | 0.0292 (13) | 0.0216 (12) | 0.0273 (13) | −0.0001 (10) | −0.0050 (10) | −0.0043 (9) |
| C7 | 0.0234 (12) | 0.0239 (13) | 0.0317 (14) | −0.0005 (10) | 0.0049 (10) | 0.0051 (10) |
| C8 | 0.0354 (15) | 0.0388 (16) | 0.0247 (13) | 0.0093 (12) | −0.0077 (11) | −0.0064 (11) |
| C9 | 0.0187 (13) | 0.0269 (14) | 0.053 (2) | −0.0019 (10) | −0.0026 (13) | −0.0053 (11) |
| C10 | 0.0271 (13) | 0.0379 (15) | 0.0295 (14) | 0.0073 (11) | 0.0077 (11) | 0.0069 (11) |
| C11 | 0.0166 (10) | 0.0131 (10) | 0.0210 (11) | −0.0014 (8) | 0.0018 (9) | −0.0014 (8) |
| C12 | 0.0279 (13) | 0.0241 (13) | 0.0278 (13) | 0.0031 (10) | 0.0006 (10) | −0.0011 (10) |
| C13 | 0.0338 (14) | 0.0270 (13) | 0.0279 (13) | −0.0006 (11) | 0.0070 (11) | −0.0043 (10) |
| C14 | 0.0253 (12) | 0.0240 (13) | 0.0400 (15) | 0.0005 (10) | 0.0103 (11) | −0.0068 (11) |
| C15 | 0.0192 (11) | 0.0205 (12) | 0.0403 (15) | 0.0014 (10) | 0.0011 (10) | −0.0028 (10) |
| C16 | 0.0184 (11) | 0.0144 (11) | 0.0296 (13) | −0.0015 (8) | 0.0006 (9) | 0.0003 (9) |
| C17 | 0.0172 (10) | 0.0148 (11) | 0.0309 (13) | −0.0041 (9) | −0.0014 (9) | 0.0014 (9) |
| C18 | 0.0178 (11) | 0.0219 (12) | 0.0395 (15) | −0.0014 (9) | −0.0021 (10) | 0.0074 (10) |

| C19 | 0.0233 (12) | 0.0302 (14) | 0.0354 (15) | −0.0058 (10) | −0.0096 (11) | 0.0134 (11) |
|-----|-------------|-------------|-------------|--------------|--------------|-------------|
| C20 | 0.0307 (13) | 0.0323 (14) | 0.0253 (13) | −0.0062 (11) | −0.0036 (11) | 0.0071 (10) |
| C21 | 0.0241 (12) | 0.0248 (13) | 0.0266 (13) | −0.0013 (10) | 0.0022 (10) | 0.0034 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ir1—N1 | 2.125 (2) | C8—H8A | 0.9800 |
| Ir1—C11 | 2.066 (2) | C8—H8B | 0.9800 |
| Ir1—N22 | 2.079 (2) | C8—H8C | 0.9800 |
| Ir1—C1 | 2.175 (2) | C9—H9A | 0.9800 |
| Ir1—C2 | 2.163 (2) | C9—H9B | 0.9800 |
| Ir1—C3 | 2.201 (2) | C9—H9C | 0.9800 |
| Ir1—C4 | 2.230 (2) | C10—H10A | 0.9800 |
| Ir1—C5 | 2.232 (2) | C10—H10B | 0.9800 |
| N1—N2 | 1.194 (3) | C10—H10C | 0.9800 |
| N2—N3 | 1.157 (3) | C11—C12 | 1.377 (3) |
| N22—C17 | 1.383 (3) | C11—C16 | 1.391 (3) |
| N22—C21 | 1.370 (3) | C12—C13 | 1.391 (4) |
| C1—C2 | 1.442 (3) | C12—H12 | 0.9500 |
| C1—C5 | 1.446 (3) | C13—C14 | 1.383 (4) |
| C1—C6 | 1.487 (3) | C13—H13 | 0.9500 |
| C2—C3 | 1.445 (3) | C14—C15 | 1.378 (4) |
| C2—C7 | 1.495 (3) | C14—H14 | 0.9500 |
| C3—C4 | 1.424 (3) | C15—C16 | 1.398 (3) |
| C3—C8 | 1.496 (3) | C15—H15 | 0.9500 |
| C4—C5 | 1.434 (3) | C16—C17 | 1.459 (3) |
| C4—C9 | 1.500 (3) | C17—C18 | 1.396 (3) |
| C5—C10 | 1.502 (3) | C18—C19 | 1.373 (4) |
| C6—H6A | 0.9800 | C18—H18 | 0.9500 |
| C6—H6B | 0.9800 | C19—C20 | 1.391 (4) |
| C6—H6C | 0.9800 | C19—H19 | 0.9500 |
| C7—H7A | 0.9800 | C20—C21 | 1.376 (4) |
| C7—H7B | 0.9800 | C20—H20 | 0.9500 |
| C7—H7C | 0.9800 | C21—H21 | 0.9500 |
| | | | |
| C11—Ir1—N22 | 77.94 (9) | C1—C6—H6A | 109.5 |
| C11—Ir1—N1 | 85.90 (8) | C1—C6—H6B | 109.5 |
| N22—Ir1—N1 | 83.83 (8) | H6A—C6—H6B | 109.5 |
| C11—Ir1—C1 | 128.17 (9) | C1—C6—H6C | 109.5 |
| N22—Ir1—C1 | 99.98 (9) | H6A—C6—H6C | 109.5 |
| N1—Ir1—C1 | 145.88 (9) | H6B—C6—H6C | 109.5 |
| C11—Ir1—C2 | 100.10 (9) | C2—C7—H7A | 109.5 |
| N22—Ir1—C2 | 124.38 (8) | C2—C7—H7B | 109.5 |
| N1—Ir1—C2 | 151.76 (9) | H7A—C7—H7B | 109.5 |
| C11—Ir1—C3 | 105.28 (9) | C2—C7—H7C | 109.5 |
| N22—Ir1—C3 | 162.78 (8) | H7A—C7—H7C | 109.5 |
| N1—Ir1—C3 | 113.11 (9) | H7B—C7—H7C | 109.5 |
| C11—Ir1—C4 | 138.08 (9) | C3—C8—H8A | 109.5 |

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| N22—Ir1—C4 | 143.78 (9) | C3—C8—H8B | 109.5 |
| N1—Ir1—C4 | 93.62 (8) | H8A—C8—H8B | 109.5 |
| C11—Ir1—C5 | 164.32 (8) | C3—C8—H8C | 109.5 |
| N22—Ir1—C5 | 109.43 (9) | H8A—C8—H8C | 109.5 |
| N1—Ir1—C5 | 108.32 (9) | H8B—C8—H8C | 109.5 |
| C1—Ir1—C2 | 38.84 (9) | C4—C9—H9A | 109.5 |
| C1—Ir1—C3 | 64.47 (9) | C4—C9—H9B | 109.5 |
| C1—Ir1—C4 | 63.39 (9) | H9A—C9—H9B | 109.5 |
| C1—Ir1—C5 | 38.27 (9) | C4—C9—H9C | 109.5 |
| C2—Ir1—C3 | 38.66 (9) | H9A—C9—H9C | 109.5 |
| C2—Ir1—C4 | 63.51 (9) | H9B—C9—H9C | 109.5 |
| C2—Ir1—C5 | 64.25 (9) | C5—C10—H10A | 109.5 |
| C3—Ir1—C4 | 37.47 (9) | C5—C10—H10B | 109.5 |
| C3—Ir1—C5 | 63.57 (9) | H10A—C10—H10B | 109.5 |
| C4—Ir1—C5 | 37.50 (9) | C5—C10—H10C | 109.5 |
| N2—N1—Ir1 | 116.55 (17) | H10A—C10—H10C | 109.5 |
| N1—N2—N3 | 176.0 (3) | H10B—C10—H10C | 109.5 |
| C21—N22—Ir1 | 125.55 (17) | C12—C11—C16 | 117.7 (2) |
| C17—N22—Ir1 | 116.63 (16) | C12—C11—Ir1 | 125.87 (18) |
| C21—N22—C17 | 117.7 (2) | C16—C11—Ir1 | 116.43 (17) |
| C2—C1—C5 | 108.1 (2) | C11—C12—C13 | 121.9 (2) |
| C2—C1—C6 | 126.5 (2) | C11—C12—H12 | 119.1 |
| C5—C1—C6 | 125.2 (2) | C13—C12—H12 | 119.1 |
| C2—C1—Ir1 | 70.14 (12) | C14—C13—C12 | 119.9 (2) |
| C5—C1—Ir1 | 73.00 (13) | C14—C13—H13 | 120.1 |
| C6—C1—Ir1 | 126.65 (17) | C12—C13—H13 | 120.1 |
| C1—C2—C3 | 107.9 (2) | C15—C14—C13 | 119.3 (2) |
| C1—C2—C7 | 126.4 (2) | C15—C14—H14 | 120.3 |
| C3—C2—C7 | 125.5 (2) | C13—C14—H14 | 120.3 |
| C1—C2—Ir1 | 71.03 (12) | C14—C15—C16 | 120.2 (2) |
| C3—C2—Ir1 | 72.09 (13) | C14—C15—H15 | 119.9 |
| C7—C2—Ir1 | 127.23 (16) | C16—C15—H15 | 119.9 |
| C4—C3—C2 | 107.5 (2) | C11—C16—C15 | 121.0 (2) |
| C4—C3—C8 | 126.2 (2) | C11—C16—C17 | 114.7 (2) |
| C2—C3—C8 | 125.6 (2) | C15—C16—C17 | 124.3 (2) |
| C4—C3—Ir1 | 72.38 (14) | N22—C17—C18 | 120.9 (2) |
| C2—C3—Ir1 | 69.26 (13) | N22—C17—C16 | 114.1 (2) |
| C8—C3—Ir1 | 131.27 (18) | C18—C17—C16 | 125.0 (2) |
| C3—C4—C5 | 109.6 (2) | C19—C18—C17 | 120.1 (2) |
| C3—C4—C9 | 124.7 (2) | C19—C18—H18 | 120.0 |
| C5—C4—C9 | 125.8 (2) | C17—C18—H18 | 120.0 |
| C3—C4—Ir1 | 70.14 (13) | C18—C19—C20 | 119.4 (2) |
| C5—C4—Ir1 | 71.31 (13) | C18—C19—H19 | 120.3 |
| C9—C4—Ir1 | 124.56 (17) | C20—C19—H19 | 120.3 |
| C4—C5—C1 | 107.0 (2) | C21—C20—C19 | 119.2 (3) |
| C4—C5—C10 | 126.9 (2) | C21—C20—H20 | 120.4 |
| C1—C5—C10 | 125.7 (2) | C19—C20—H20 | 120.4 |
| C4—C5—Ir1 | 71.19 (13) | N22—C21—C20 | 122.6 (2) |

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| C1—C5—Ir1 | 68.73 (13) | N22—C21—H21 | 118.7 |
| C10—C5—Ir1 | 131.16 (17) | C20—C21—H21 | 118.7 |
| | | | |
| C5—C1—C2—C3 | 0.5 (2) | C6—C1—C5—C4 | −175.5 (2) |
| C6—C1—C2—C3 | 175.4 (2) | Ir1—C1—C5—C4 | 61.27 (16) |
| Ir1—C1—C2—C3 | −63.08 (16) | C2—C1—C5—C10 | 172.1 (2) |
| C5—C1—C2—C7 | −173.7 (2) | C6—C1—C5—C10 | −2.9 (4) |
| C6—C1—C2—C7 | 1.3 (4) | Ir1—C1—C5—C10 | −126.2 (2) |
| Ir1—C1—C2—C7 | 122.8 (2) | C2—C1—C5—Ir1 | −61.72 (15) |
| C5—C1—C2—Ir1 | 63.57 (15) | C6—C1—C5—Ir1 | 123.2 (2) |
| C6—C1—C2—Ir1 | −121.5 (2) | C16—C11—C12—C13 | 1.5 (4) |
| C1—C2—C3—C4 | −0.3 (3) | Ir1—C11—C12—C13 | −179.50 (19) |
| C7—C2—C3—C4 | 173.9 (2) | C11—C12—C13—C14 | −1.0 (4) |
| Ir1—C2—C3—C4 | −62.72 (16) | C12—C13—C14—C15 | −0.1 (4) |
| C1—C2—C3—C8 | −171.0 (2) | C13—C14—C15—C16 | 0.6 (4) |
| C7—C2—C3—C8 | 3.2 (4) | C12—C11—C16—C15 | −0.9 (3) |
| Ir1—C2—C3—C8 | 126.6 (2) | Ir1—C11—C16—C15 | 179.99 (18) |
| C1—C2—C3—Ir1 | 62.40 (15) | C12—C11—C16—C17 | 179.1 (2) |
| C7—C2—C3—Ir1 | −123.4 (2) | Ir1—C11—C16—C17 | 0.0 (3) |
| C2—C3—C4—C5 | 0.0 (3) | C14—C15—C16—C11 | −0.1 (4) |
| C8—C3—C4—C5 | 170.6 (2) | C14—C15—C16—C17 | 179.8 (2) |
| Ir1—C3—C4—C5 | −60.66 (16) | C21—N22—C17—C18 | −0.9 (3) |
| C2—C3—C4—C9 | 179.6 (2) | Ir1—N22—C17—C18 | 175.84 (17) |
| C8—C3—C4—C9 | −9.8 (4) | C21—N22—C17—C16 | 179.7 (2) |
| Ir1—C3—C4—C9 | 118.9 (2) | Ir1—N22—C17—C16 | −3.6 (3) |
| C2—C3—C4—Ir1 | 60.70 (16) | C11—C16—C17—N22 | 2.3 (3) |
| C8—C3—C4—Ir1 | −128.7 (3) | C15—C16—C17—N22 | −177.7 (2) |
| C3—C4—C5—C1 | 0.3 (3) | C11—C16—C17—C18 | −177.1 (2) |
| C9—C4—C5—C1 | −179.3 (2) | C15—C16—C17—C18 | 3.0 (4) |
| Ir1—C4—C5—C1 | −59.68 (15) | N22—C17—C18—C19 | 1.4 (4) |
| C3—C4—C5—C10 | −172.2 (2) | C16—C17—C18—C19 | −179.2 (2) |
| C9—C4—C5—C10 | 8.2 (4) | C17—C18—C19—C20 | −0.8 (4) |
| Ir1—C4—C5—C10 | 127.9 (2) | C18—C19—C20—C21 | −0.3 (4) |
| C3—C4—C5—Ir1 | 59.94 (16) | C17—N22—C21—C20 | −0.3 (4) |
| C9—C4—C5—Ir1 | −119.6 (2) | Ir1—N22—C21—C20 | −176.68 (19) |
| C2—C1—C5—C4 | −0.5 (2) | C19—C20—C21—N22 | 0.9 (4) |