Crystal structure of chloridobis[(1,2,5,6-η)-cyclo-octa-1,5-diene]iridium(I)

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The title complex, [IrCl(C_8H_{12})$_2$], was synthesized directly from the reaction of IrCl$_3\cdot$3H$_2$O with a large excess of cod (cod = cycloocta-1,5-diene) in alcoholic solvent. Large yellow needles were obtained by the slow cooling of a hot solution. Based on the positions of the chloride ligand and the mid-points of the four C=C bonds, the molecule adopts a five-coordinate geometry that is midway between square pyramidal and trigonal bipyramidal. The material crystallizes in the orthorhombic space group *Pbca* with one molecule per asymmetric unit in a general position and shows no significant intermolecular interactions. Individual molecules are aligned along [010], and these rows form a pseudo-hexagonal packing arrangement.

1. Chemical context

First reported in 1966 (Winkhaus & Singer, 1966) [Ir(cod)(μ-Cl)]$_2$ (cod = 1,5-cyclooctadiene, C_8H_{12}) is perhaps the most common organometallic precursor used in the synthesis of a variety of organoiridium compounds (Leigh & Richards, 1982). [Ir(cod)(μ-Cl)]$_2$ can be prepared using either Na$_2$IrCl$_6\cdot$6H$_2$O or IrCl$_3\cdot$3H$_2$O as the metal-containing precursor (Herde *et al.*, 1974). A few years later it was reported that a cyclooctene-ligated dimer [Ir(C_8H_{14})$_2$(μ-Cl)]$_2$
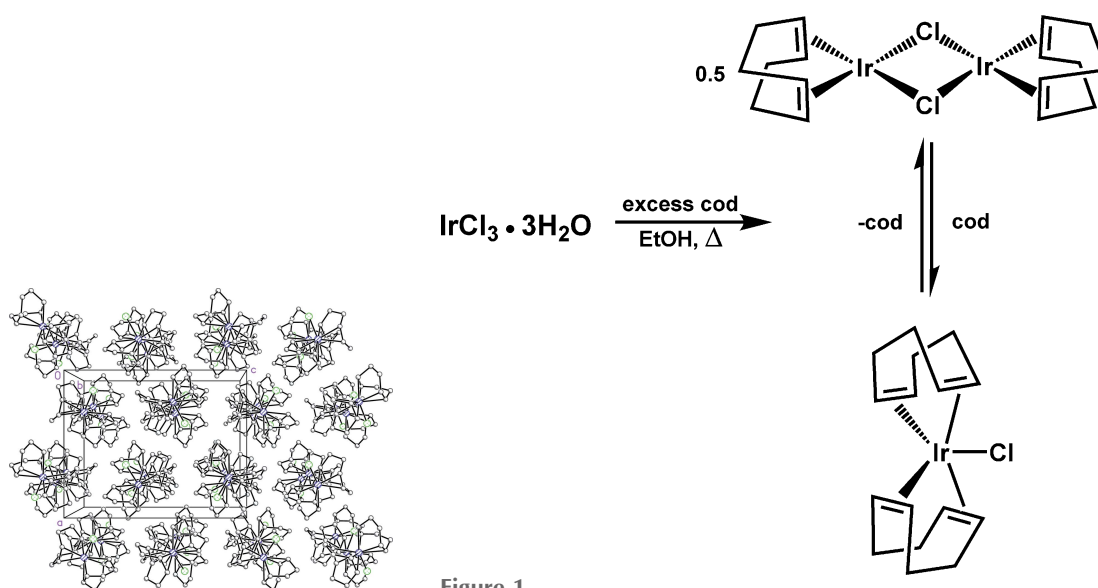
Figure 1
Reaction scheme showing the formation of the mixture of [Ir(cod)(μ-Cl)]$_2$ and IrCl(cod)$_2$. As the ethanol is removed under vacuum the solution becomes rich in cod, which drives the formation of IrCl(cod)$_2$. Loss of cod regenerates the dimer.

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had been synthesized from the reaction of ammonium hexachloridoiridiate(III) hydrate, $(NH_4)_3IrCl_6\cdot H_2O$, with cyclooctene in a mixture of 2-propanol and water (Onderdelinden & van der Ent, 1972). In all three cases, Ir^{IV} or Ir^{III} is reduced to Ir^I by oxidation of the alcoholic solvent. Upon suspension in pure cod, $[Ir(C_8H_{14})_2(\mu\text{-}Cl)]_2$ reacted to form mononuclear $IrCl(cod)_2$, which was then characterized by infra-red spectroscopy and elemental analysis (Onderdelinden & van der Ent, 1972). Analogous to thermally unstable $IrCl(C_2H_4)_4$, which releases ethylene to form the (slightly) more stable dimer $[Ir(C_2H_4)_2(\mu\text{-}Cl)]_2$ (Onderdelinden & van der Ent, 1972), $IrCl(cod)_2$ readily generates stable $[Ir(cod)(\mu\text{-}Cl)]_2$ with the loss of one equivalent of cod per iridium. We have found that if Herde's preparation using $IrCl_3\cdot 3H_2O$ is carried out with a large excess of cod (10 ×), the product isolated after removal of the alcoholic solvent is $IrCl(cod)_2$ (Fig. 1). This was apparent as the red–orange reaction mixture, which contained a mixture of red $[Ir(cod)(\mu\text{-}Cl)]_2$ and yellow $IrCl(cod)_2$, became pale yellow. Recrystallization from refluxing methanol/cod (7:1, v:v) followed by cooling produced yellow needles of $IrCl(cod)_2$ suitable for diffraction studies.

Herein we report the isolation and results of the single structure determination of mononuclear $IrCl(cod)_2$ and compare it to related $IrX(diene)_2$ (X = Cl, SnMe$_3$, SnCl$_3$) complexes.
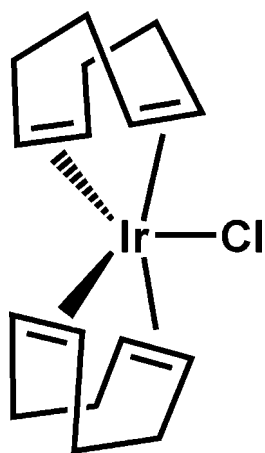
2. Structural commentary

Our single-crystal X-ray diffraction study confirmed the molecule to be mononuclear $IrCl(cod)_2$, in which the two cod ligands are bound in an η^2:η^2 fashion (Fig. 2). The material crystallizes in the orthorhombic space group *Pbca*, with one molecule per asymmetric unit in a general position. The five-coordinate complex adopts a geometry that is midway between square pyramidal (SP) and trigonal bipyramidal (TBP), with a τ_5 parameter of 0.52 (Addison *et al.*, 1984), calculated using the mid-points of the C=C double bonds and the axial chlorido ligand. The elongation of the cod double bonds (Table 1) compared to those of non-coordinating cod, 1.333 (4) and 1.334 (4) Å (Byrn *et al.*, 1990), or to that of free ethylene, 1.333 Å (Lide, 2002–2003), is consistent with back

Table 1
Selected bond lengths (Å).

Ir1—Cl1	2.5573 (8)	C9—C10	1.418 (5)
C1—C2	1.437 (5)	C13—C14	1.389 (4)
C5—C6	1.389 (4)		

donation to the π^* orbitals from a low-valent iridium atom, formally Ir^I. The elongations are asymmetric, with one double bond from each cod ligand being larger than the other by 0.048 (6) and 0.029 (6) Å, respectively, for cod ligands C1—C8 and C9—C16. Likewise the distances between Ir and the mid-points of the C=C bonds also show this asymmetry with two shorter distances, Ir—(C1/C2) = 2.047 (4) and Ir—(C9/C10) = 2.069 (4) Å, and two longer distances, Ir—(C5/C6) = 2.138 (4) and Ir—(C13/C14) = 2.141 (4) Å (Table 2). This is likely due to its intermediacy between the geometric extremes of SP and TBP. Ideal SP geometry (τ_5 = 0) would have very similar Ir–mid-point(C=C) distances as they would involve the same metal and ligand orbitals, while ideal TBP geometry (τ_5 = 1) would involve different orbitals, dependent upon on whether the ligand's C=C bond lay in an axial or an equatorial position. We see the former (SP) in Ir(SnCl$_3$)(nbd)$_2$ (nbd = norbornadiene; Malosh *et al.*, 2013), for which τ_5 = 0.06 and the Ir–mid-point(C=C) distances are similar, ranging from 2.067 (4) to 2.089 (4) Å. An example towards TBP is found in $[IrCl(cod)(CC^*)]^+$ (CC* = $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}(1,1\text{-di}(2\text{-propen-}$
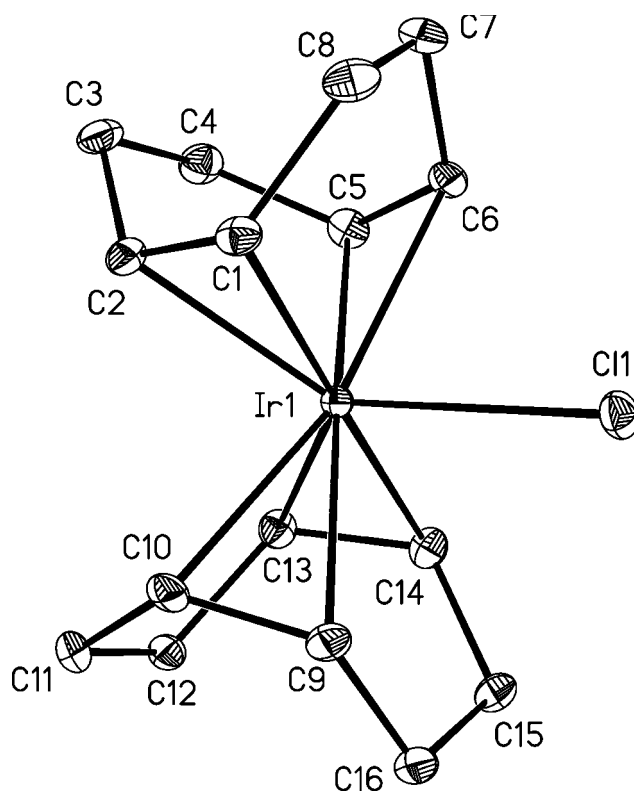

Figure 2
The molecular structure of $IrCl(cod)_2$, with displacement ellipsoids drawn at the 50% probability level.

Table 2
Comparison of bond lengths (Å) and τ_5 parameters for selected five-coordinate Ir complexes containing four substituted ethylene ligands and a terminal chlorido or stannato ligand, according to the labeling in Fig. 3.

Feature	IrCl(cod)₂	COIRSN[a]	DIVPAB[b]	DIVNUT[c]	DIVPIJ[d]	PUYCOB[e]
$M-X$[f]	2.5573 (8)	2.642 (2)	2.7090 (4)	2.6606 (4)	2.5850 (9)	2.3883 (15)
$M-[A]$	2.047 (4)	2.068 (31)	2.062 (4)	2.067 (4)	2.101 (5)	2.048 (8)
$M-[B]$	2.138 (4)	2.135 (26)	2.114 (4)	2.089 (4)	2.119 (5)	2.057 (8)
$M-[C]$	2.069 (4)	2.053 (34)	2.069 (4)	2.076 (4)	2.104 (5)	2.118 (8)
$M-[D]$	2.141 (4)	2.134 (24)	2.126 (4)	2.089 (4)	2.109 (5)	2.170 (8)
C═C[A]	1.437 (5)	1.320 (40)	1.425 (5)	1.408 (6)	1.415(8)	1.395 (9)
C═C[B]	1.389 (4)	1.450 (44)	1.416 (5)	1.415 (7)	1.389 (7)	1.372 (12)
C═C[C]	1.418 (5)	1.361 (44)	1.411 (5)	1.400 (7)	1.394 (7)	1.393 (8)
C═C[D]	1.389 (4)	1.375 (41)	1.407 (5)	1.423 (7)	1.404 (8)	1.386 (9)
τ_5[g]	0.52	0.53	0.55	0.10	0.06	0.76

Notes: (a) Ir(SnCl₃)(cod)₂ (Porta *et al.*, 1967); (b) Ir(SnMe₃)(cod)₂ (Malosh *et al.*, 2013); (c) Ir(SnMe₃)(nbd)₂ (Malosh *et al.*, 2013); (d) Ir(SnCl₃)(nbd)₂ (Malosh *et al.*, 2013); (e) [IrCl(cod)(CC*)]⁺ (Marcén *et al.*, 2002); (f) X = Sn or Cl; (g) Addison *et al.* (1984).

yl)-3-butenyl)benzene)]; Marcén *et al.*, 2002), for which $\tau_5 = 0.76$.

3. Supramolecular features

Although there are no significant intermolecular interactions, the packing has adopted a supramolecular arrangement. Individual molecules are aligned in columns parallel to [010], which are then arranged in an overall pseudo-hexagonal packing (Fig. 4).

4. Database survey

A survey of the Cambridge Structural Database (CSD, Version 5.38, update No. 1, November 2016, Groom *et al.*, 2016) revealed just a few related five-coordinate iridium complexes with four unconjugated substituted ethylene

Figure 3
Lettering scheme used for bonds in Table 2. Letters *A–D* are the midpoints of the C═C bonds. In cases of cyclodienes, consecutive letters *A*, *B* and/or *C*, *D* are on the same ligand; axial ligand *X* is SnR₃ or Cl.

ligands and a halido or stannato ligand in the fifth coordination site: Ir(SnCl₃)(cod)₂ (CSD refcode COIRSN; Porta *et al.*, 1967), Ir(SnMe₃)(cod)₂ (refcode DIVPAB), Ir(SnCl₃)(nbd)₂ (refcode DIVPIJ), Ir(SnMe₃)(nbd)₂ (refcode DIVNUT); Malosh *et al.*, 2013), and [IrCl(cod)(CC*)]⁺ (refcode PUYCOB; Marcén *et al.*, 2002). A report on the structure of IrCl(C₂H₄)₄ exists, but no positional parameters were given (van der Ent & van Soest, 1970), which is unfortunate because a comparison of this species with IrCl(cod)₂ would ostensibly show how the bite-angle restrictions imposed by the cod rings affect the overall geometry. The geometries of the two tin-containing compounds with cod are closely related to that of the title complex. Both Ir(SnCl₃)(cod)₂ and Ir(SnMe₃)(cod)₂ exhibit the same long–short variation of the Ir–midpoint(C═C) bond lengths within each cod ligand and have similar τ_5 parameters of 0.53 and 0.55, respectively (Table 2). Malosh and coworkers concluded that the bulk of the cod ligands relative to that of the nbd ligands was responsible for the geometric distortion from SP geometry, specifically due to CH₂···Me and CH₂···Cl repulsions (Malosh *et al.*, 2013). And indeed the two nbd complexes have near-perfect SP τ_5 values of 0.10 and 0.06. In complex [IrCl(cod)(CC*)]⁺, the non-cod diene is part of a 1,1-di(2-propenyl)-3-butenyl)benzene unit that is η^6-coordinating to an [Fe(C₅H₅)]⁺ cationic fragment. The pentacoordinated saturated (18 electron) iridium atom approaches a TBP geometry more than the other complexes mentioned ($\tau_5 = 0.76$), with the two apical positions being occupied by one C═C bond of the cod ligand and the chlorido ligand. The angles in the equatorial plane range between 109.73 (17) and 126.61 (16)°. The restriction of the cod ligand with its bite angle of 84.9 (2)° prevents the structure from ever achieving perfect TBP geometry, and this holds more so for structures with nbd ligands whose bite angles are even more acute. The Ir–mid-point(C═C) bond lengths differ, showing significantly longer bond lengths to the allylic C═C centroids [avg. 2.144 (11) Å] than to the cod C═C diolefin centroids [avg. 2.052 (11) Å]. The terminal Ir—Cl distance in IrCl(cod)₂ of 2.5573 (8) Å is longer than all of the 214 structures with five-coordinate iridium in the CSD containing an IrCl(η^2:η^2-
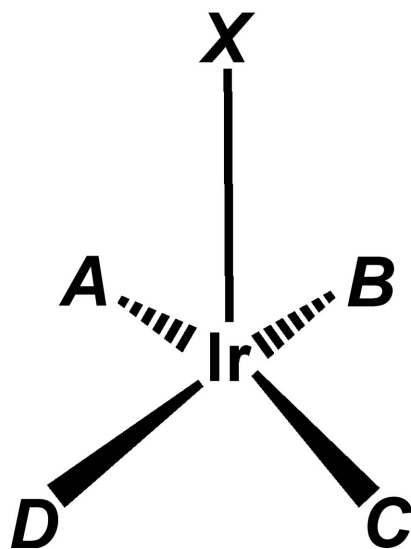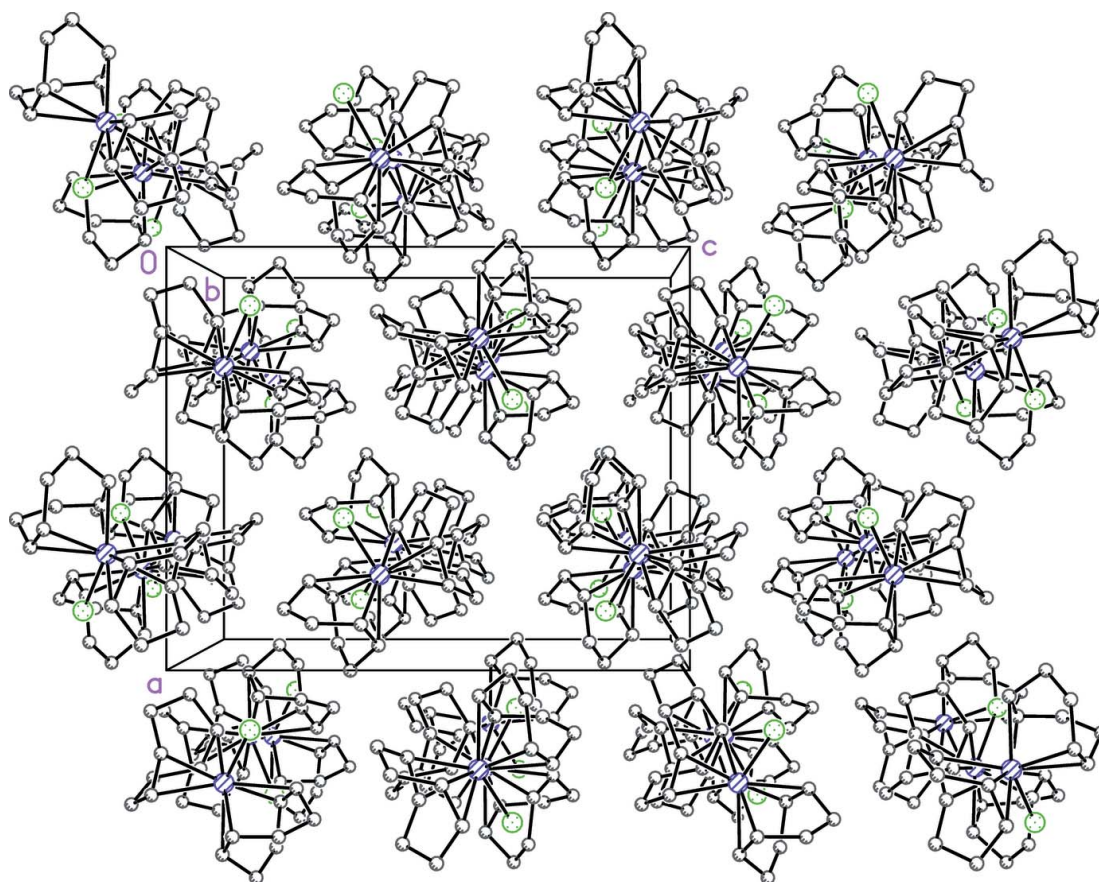
Figure 4
Pseudo-hexagonal arrangement of rows of molecules aligned along [010].

cod) fragment (avg. 2.368 Å), which may be attributable to its tendency to form the well-known stable cationic complex, $[Ir(cod)_2]^+$, whose structure (refcode TUQWOS) displays the anticipated d^8 square-planar geometry with $[BAr^F]^-$ {tetrakis[3,5-bis(trifluoromethyl)-

phenyl]borate} as the non-coordinating anion (Woodmansee *et al.*, 2010).

5. Synthesis and crystallization

All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Company Dri-Lab. A preparation of IrCl(cod)₂ *via* a cyclooctene-ligated dimer has been reported previously (Onderdelinden & van der Ent, 1972).

A two-necked round-bottom flask was charged with IrCl₃·3H₂O (6.0 g, 0.017 mol) and cod (20 g, 0.18 mol) in 80 ml of ethanol under nitrogen. The reaction mixture was refluxed for 24 h, followed by removal of the solvent under vacuum. As the ethanol evaporated, the red–orange solution became more yellow as the cod concentration increased, leading to the isolation of a yellow solid (5.32 g, 70.5%). The product was recrystallized by refluxing in a mixture 35 ml of methanol and 5 ml of cod, followed by cooling to obtain shiny yellow needles of IrCl(cod)₂ (5.06 g, 67.0%).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[IrCl(C_8H_{12})_2]$
M_r	444.00
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, b, c (Å)	12.8756 (8), 13.3719 (8), 15.9033 (10)
V (Å³)	2738.1 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	9.93
Crystal size (mm)	0.24 × 0.20 × 0.20
Data collection	
Diffractometer	Bruker SMART APEXII CCD platform
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.173, 0.278
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	83189, 7755, 5394
R_{int}	0.112
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.883
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.072, 1.01
No. of reflections	7755
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	1.34, −1.86

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were treated in the riding-model approximation, with C(methine)—H = 1.00 Å, C(methylene)—H = 0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The maximum and minimum electron densities are found 1.09 and 0.55 Å, respectively, from the iridium atom.

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supporting information

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Chloridobis[(1,2,5,6-*η*)-cycloocta-1,5-diene]iridium(I)

Crystal data

[IrCl(C$_8$H$_{12}$)$_2$]	$D_x = 2.154$ Mg m^{-3}
$M_r = 444.00$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 5121 reflections
$a = 12.8756$ (8) Å	$\theta = 2.5$–29.0°
$b = 13.3719$ (8) Å	$\mu = 9.93$ mm^{-1}
$c = 15.9033$ (10) Å	$T = 100$ K
$V = 2738.1$ (3) Å^3	Block, yellow
$Z = 8$	$0.24 \times 0.20 \times 0.20$ mm
$F(000) = 1712$	

Data collection

Bruker SMART APEXII CCD platform diffractometer	7755 independent reflections
	5394 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.112$
ω scans	$\theta_{max} = 38.9°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$h = -22\rightarrow22$
	$k = -23\rightarrow23$
$T_{min} = 0.173$, $T_{max} = 0.278$	$l = -27\rightarrow27$
83189 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.072$	
$S = 1.01$	H-atom parameters constrained
7755 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
163 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.34$ e Å^{-3}
	$\Delta\rho_{min} = -1.86$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir1	0.27908 (2)	0.39530 (2)	0.59862 (2)	0.00769 (3)
Cl1	0.13983 (6)	0.50996 (6)	0.66069 (5)	0.01377 (14)
C1	0.1656 (3)	0.2813 (2)	0.5723 (2)	0.0116 (5)
H1A	0.145496	0.241248	0.622824	0.014*
C2	0.2626 (2)	0.2509 (2)	0.5357 (2)	0.0123 (6)
H2A	0.296862	0.194607	0.566472	0.015*
C3	0.2855 (3)	0.2514 (3)	0.4419 (2)	0.0143 (6)
H3A	0.219685	0.241850	0.410691	0.017*
H3B	0.331572	0.194314	0.428387	0.017*
C4	0.3373 (3)	0.3486 (3)	0.4120 (2)	0.0157 (6)
H4A	0.413620	0.341604	0.416347	0.019*
H4B	0.319781	0.360032	0.352151	0.019*
C5	0.3028 (3)	0.4380 (2)	0.4632 (2)	0.0126 (6)
H5A	0.347039	0.498657	0.455193	0.015*
C6	0.2005 (2)	0.4593 (2)	0.4845 (2)	0.0114 (6)
H6A	0.186019	0.532519	0.489222	0.014*
C7	0.1063 (3)	0.3986 (2)	0.4565 (2)	0.0142 (6)
H7A	0.122928	0.363524	0.403371	0.017*
H7B	0.047558	0.444498	0.445506	0.017*
C8	0.0736 (3)	0.3211 (3)	0.5234 (2)	0.0157 (6)
H8A	0.023939	0.352582	0.562866	0.019*
H8B	0.037702	0.264779	0.495361	0.019*
C9	0.4463 (2)	0.4276 (2)	0.5992 (2)	0.0129 (5)
H9A	0.476894	0.435608	0.541763	0.015*
C10	0.3907 (2)	0.5127 (2)	0.6275 (2)	0.0127 (6)
H10A	0.390267	0.569889	0.587016	0.015*
C11	0.3863 (3)	0.5434 (2)	0.7186 (2)	0.0145 (6)
H11A	0.334721	0.597717	0.724955	0.017*
H11B	0.454933	0.570368	0.735239	0.017*
C12	0.3573 (3)	0.4571 (2)	0.7786 (2)	0.0143 (6)
H12A	0.421967	0.428574	0.802348	0.017*
H12B	0.316321	0.484671	0.825894	0.017*
C13	0.2957 (3)	0.3738 (2)	0.7378 (2)	0.0122 (6)
H13A	0.228508	0.359314	0.766834	0.015*
C14	0.3391 (3)	0.2906 (2)	0.6990 (2)	0.0121 (5)
H14A	0.296863	0.228253	0.705481	0.014*
C15	0.4533 (3)	0.2717 (2)	0.6889 (2)	0.0143 (6)
H15A	0.463587	0.216505	0.648278	0.017*
H15B	0.482493	0.250336	0.743567	0.017*

C16	0.5120 (2)	0.3639 (2)	0.6581 (2)	0.0132 (6)
H16A	0.533137	0.404768	0.707119	0.016*
H16B	0.575745	0.342441	0.628395	0.016*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.00792 (5)	0.00752 (5)	0.00763 (5)	−0.00044 (4)	−0.00014 (4)	0.00038 (4)
Cl1	0.0124 (3)	0.0145 (3)	0.0144 (4)	0.0035 (3)	0.0018 (3)	0.0005 (3)
C1	0.0128 (13)	0.0107 (13)	0.0111 (13)	−0.0039 (11)	−0.0013 (11)	0.0010 (10)
C2	0.0142 (14)	0.0104 (13)	0.0123 (14)	−0.0015 (11)	−0.0020 (11)	−0.0017 (11)
C3	0.0144 (14)	0.0176 (14)	0.0109 (14)	−0.0007 (12)	−0.0019 (12)	−0.0048 (11)
C4	0.0157 (14)	0.0192 (15)	0.0124 (15)	0.0007 (12)	0.0012 (12)	−0.0017 (12)
C5	0.0131 (13)	0.0136 (14)	0.0112 (14)	−0.0016 (11)	0.0016 (11)	0.0035 (11)
C6	0.0152 (14)	0.0103 (13)	0.0088 (13)	0.0003 (10)	−0.0017 (11)	0.0034 (10)
C7	0.0114 (13)	0.0173 (14)	0.0138 (14)	−0.0011 (12)	−0.0040 (11)	0.0007 (12)
C8	0.0131 (14)	0.0182 (15)	0.0157 (16)	−0.0057 (12)	−0.0012 (12)	−0.0014 (12)
C9	0.0117 (13)	0.0132 (13)	0.0137 (14)	0.0000 (10)	0.0007 (12)	−0.0007 (12)
C10	0.0136 (13)	0.0109 (13)	0.0137 (15)	−0.0019 (11)	0.0017 (12)	−0.0002 (11)
C11	0.0163 (14)	0.0125 (14)	0.0148 (16)	−0.0018 (11)	−0.0025 (12)	−0.0040 (11)
C12	0.0153 (14)	0.0170 (15)	0.0106 (14)	0.0025 (12)	−0.0018 (11)	−0.0025 (11)
C13	0.0145 (14)	0.0146 (14)	0.0076 (13)	0.0001 (11)	0.0011 (11)	−0.0005 (10)
C14	0.0159 (14)	0.0109 (13)	0.0094 (13)	−0.0004 (11)	−0.0012 (12)	0.0043 (10)
C15	0.0150 (14)	0.0121 (14)	0.0158 (16)	0.0046 (11)	−0.0035 (12)	−0.0004 (11)
C16	0.0106 (13)	0.0153 (14)	0.0137 (15)	0.0026 (11)	−0.0026 (11)	−0.0022 (12)

Geometric parameters (Å, º)

Ir1—C1	2.152 (3)	C7—H7A	0.9900
Ir1—C10	2.178 (3)	C7—H7B	0.9900
Ir1—C2	2.185 (3)	C8—H8A	0.9900
Ir1—C9	2.196 (3)	C8—H8B	0.9900
Ir1—C13	2.242 (3)	C9—C10	1.418 (5)
Ir1—C6	2.248 (3)	C9—C16	1.522 (5)
Ir1—C5	2.249 (3)	C9—H9A	1.0000
Ir1—C14	2.260 (3)	C10—C11	1.506 (5)
Ir1—Cl1	2.5573 (8)	C10—H10A	1.0000
C1—C2	1.437 (5)	C11—C12	1.543 (5)
C1—C8	1.514 (5)	C11—H11A	0.9900
C1—H1A	1.0000	C11—H11B	0.9900
C2—C3	1.521 (5)	C12—C13	1.514 (5)
C2—H2A	1.0000	C12—H12A	0.9900
C3—C4	1.537 (5)	C12—H12B	0.9900
C3—H3A	0.9900	C13—C14	1.389 (4)
C3—H3B	0.9900	C13—H13A	1.0000
C4—C5	1.512 (5)	C14—C15	1.500 (4)
C4—H4A	0.9900	C14—H14A	1.0000
C4—H4B	0.9900	C15—C16	1.527 (5)

C5—C6	1.389 (4)	C15—H15A	0.9900
C5—H5A	1.0000	C15—H15B	0.9900
C6—C7	1.525 (4)	C16—H16A	0.9900
C6—H6A	1.0000	C16—H16B	0.9900
C7—C8	1.543 (5)		
C1—Ir1—C10	178.38 (12)	C5—C6—C7	125.0 (3)
C1—Ir1—C2	38.68 (12)	C5—C6—Ir1	72.04 (18)
C10—Ir1—C2	142.92 (12)	C7—C6—Ir1	113.0 (2)
C1—Ir1—C9	143.67 (12)	C5—C6—H6A	113.3
C10—Ir1—C9	37.84 (12)	C7—C6—H6A	113.3
C2—Ir1—C9	105.71 (12)	Ir1—C6—H6A	113.3
C1—Ir1—C13	99.56 (12)	C6—C7—C8	111.9 (3)
C10—Ir1—C13	79.68 (12)	C6—C7—H7A	109.2
C2—Ir1—C13	110.35 (12)	C8—C7—H7A	109.2
C9—Ir1—C13	85.84 (12)	C6—C7—H7B	109.2
C1—Ir1—C6	78.85 (12)	C8—C7—H7B	109.2
C10—Ir1—C6	101.16 (12)	H7A—C7—H7B	107.9
C2—Ir1—C6	85.57 (12)	C1—C8—C7	112.1 (3)
C9—Ir1—C6	111.72 (12)	C1—C8—H8A	109.2
C13—Ir1—C6	152.77 (12)	C7—C8—H8A	109.2
C1—Ir1—C5	94.89 (12)	C1—C8—H8B	109.2
C10—Ir1—C5	85.98 (12)	C7—C8—H8B	109.2
C2—Ir1—C5	78.39 (12)	H8A—C8—H8B	107.9
C9—Ir1—C5	79.69 (12)	C10—C9—C16	122.2 (3)
C13—Ir1—C5	164.79 (12)	C10—C9—Ir1	70.37 (18)
C6—Ir1—C5	36.00 (11)	C16—C9—Ir1	115.9 (2)
C1—Ir1—C14	86.02 (12)	C10—C9—H9A	113.8
C10—Ir1—C14	94.13 (12)	C16—C9—H9A	113.8
C2—Ir1—C14	78.99 (12)	Ir1—C9—H9A	113.8
C9—Ir1—C14	77.53 (12)	C9—C10—C11	122.9 (3)
C13—Ir1—C14	35.94 (11)	C9—C10—Ir1	71.79 (18)
C6—Ir1—C14	163.81 (12)	C11—C10—Ir1	112.0 (2)
C5—Ir1—C14	141.95 (12)	C9—C10—H10A	114.3
C1—Ir1—Cl1	91.36 (9)	C11—C10—H10A	114.3
C10—Ir1—Cl1	87.07 (9)	Ir1—C10—H10A	114.3
C2—Ir1—Cl1	129.69 (8)	C10—C11—C12	113.6 (3)
C9—Ir1—Cl1	124.61 (9)	C10—C11—H11A	108.8
C13—Ir1—Cl1	76.29 (8)	C12—C11—H11A	108.8
C6—Ir1—Cl1	76.57 (9)	C10—C11—H11B	108.8
C5—Ir1—Cl1	108.22 (9)	C12—C11—H11B	108.8
C14—Ir1—Cl1	109.78 (9)	H11A—C11—H11B	107.7
C2—C1—C8	124.9 (3)	C13—C12—C11	114.3 (3)
C2—C1—Ir1	71.90 (18)	C13—C12—H12A	108.7
C8—C1—Ir1	112.5 (2)	C11—C12—H12A	108.7
C2—C1—H1A	113.5	C13—C12—H12B	108.7
C8—C1—H1A	113.5	C11—C12—H12B	108.7
Ir1—C1—H1A	113.5	H12A—C12—H12B	107.6

C1—C2—C3	124.4 (3)	C14—C13—C12	124.7 (3)
C1—C2—Ir1	69.42 (18)	C14—C13—Ir1	72.71 (18)
C3—C2—Ir1	115.3 (2)	C12—C13—Ir1	112.3 (2)
C1—C2—H2A	113.5	C14—C13—H13A	113.4
C3—C2—H2A	113.5	C12—C13—H13A	113.4
Ir1—C2—H2A	113.5	Ir1—C13—H13A	113.4
C2—C3—C4	113.0 (3)	C13—C14—C15	125.1 (3)
C2—C3—H3A	109.0	C13—C14—Ir1	71.35 (18)
C4—C3—H3A	109.0	C15—C14—Ir1	111.3 (2)
C2—C3—H3B	109.0	C13—C14—H14A	113.8
C4—C3—H3B	109.0	C15—C14—H14A	113.8
H3A—C3—H3B	107.8	Ir1—C14—H14A	113.8
C5—C4—C3	112.0 (3)	C14—C15—C16	112.6 (3)
C5—C4—H4A	109.2	C14—C15—H15A	109.1
C3—C4—H4A	109.2	C16—C15—H15A	109.1
C5—C4—H4B	109.2	C14—C15—H15B	109.1
C3—C4—H4B	109.2	C16—C15—H15B	109.1
H4A—C4—H4B	107.9	H15A—C15—H15B	107.8
C6—C5—C4	124.9 (3)	C9—C16—C15	112.0 (3)
C6—C5—Ir1	71.96 (18)	C9—C16—H16A	109.2
C4—C5—Ir1	110.8 (2)	C15—C16—H16A	109.2
C6—C5—H5A	113.9	C9—C16—H16B	109.2
C4—C5—H5A	113.9	C15—C16—H16B	109.2
Ir1—C5—H5A	113.9	H16A—C16—H16B	107.9
C8—C1—C2—C3	−2.0 (5)	C16—C9—C10—C11	−4.0 (5)
Ir1—C1—C2—C3	−107.2 (3)	Ir1—C9—C10—C11	104.9 (3)
C8—C1—C2—Ir1	105.2 (3)	C16—C9—C10—Ir1	−108.9 (3)
C1—C2—C3—C4	93.2 (4)	C9—C10—C11—C12	−49.6 (4)
Ir1—C2—C3—C4	11.7 (4)	Ir1—C10—C11—C12	32.3 (3)
C2—C3—C4—C5	−31.5 (4)	C10—C11—C12—C13	−24.8 (4)
C3—C4—C5—C6	−46.1 (4)	C11—C12—C13—C14	89.4 (4)
C3—C4—C5—Ir1	35.8 (3)	C11—C12—C13—Ir1	5.6 (3)
C4—C5—C6—C7	−2.8 (5)	C12—C13—C14—C15	−2.1 (5)
Ir1—C5—C6—C7	−106.0 (3)	Ir1—C13—C14—C15	103.4 (3)
C4—C5—C6—Ir1	103.2 (3)	C12—C13—C14—Ir1	−105.5 (3)
C5—C6—C7—C8	95.7 (4)	C13—C14—C15—C16	−45.8 (4)
Ir1—C6—C7—C8	12.1 (3)	Ir1—C14—C15—C16	35.9 (3)
C2—C1—C8—C7	−44.6 (4)	C10—C9—C16—C15	97.1 (4)
Ir1—C1—C8—C7	38.5 (3)	Ir1—C9—C16—C15	14.8 (4)
C6—C7—C8—C1	−32.5 (4)	C14—C15—C16—C9	−33.3 (4)