OM040128F

Supporting Information OM040128F

Metallaboratrane Formation – The Missing Link: The First Iridaboratranes

[IrH(CO)(PPh_3){κ^3-*B,S,S'*-B(mt)$_2$R}] (Ir→B; mt = methimazolyl, R = mt, H).

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(A) Synthetic Procedural Details

(B) Crystal Structure Determination report: [HIr($C_8H_{11}BN_4S_2$)(CO)($C_{18}H_{15}P$)].$CHCl_3$.

A full Crystallographic Information File has been deposited with the Cambridge Crystallographic Data Centre:

CCDC 252699

Summary of Data CCDC 252699

Authors: A.C.Willis,I.R.Crossley,A.F.Hill

Journal: Organometallics (0579)

Formula: C28 H28 B1 Cl3 Ir1 N4 O1 P1 S2

Unit cell parameters: a 9.3509(2) b 9.7847(2) c 19.1038(5)
alpha 92.7592(16) beta 99.6612(11) gamma 110.9262(14)
space group P-1

(A) Synthetic Procedural Details

Synthesis of [IrH(CO)(PPh$_3$){κ^3-*B*,*S*,*S*'-B(mt)$_3$}] (5). Under an atmosphere of N_2; to a solution of [IrCl(CO)(PPh$_3$)$_2$] (1.00 g, 1.28 mmol) in dichloromethane (30 cm^3) was added Na[HB(mt)$_3$][1a] (0.50 g, 1.34 mmol). The mixture was stirred for 3 h and then the resulting pale yellow solution filtered anaerobically to remove residual Na[HB(mt)$_3$] and resultant NaCl, and subsequently concentrated *in vacuo* until a solid began to form. The addition of diethyl ether (ca. 50 cm^3) resulted in precipitation of an off-white solid, which was collected by filtration, recrystallized from chloroform/hexane, then dried *in vacuo*. Yield 0.70 g, 66 %.

Synthesis of [IrH(CO)(PPh$_3$){κ^3-*B*,*S*,*S*'-B(mt)$_2$H}] (6). In an analogous procedure to **5**, a solution of [IrCl(CO)(PPh$_3$)$_2$] (2.00 g, 2.40 mmol) in dichloromethane (100 cm^3) was allowed to react with Na[H$_2$B(mt)$_2$].H$_2$O[7b] (0.70 g, 2.50 mmol) for 3 h. The crude product was isolated as for **5**, then recrystallized from chloroform/hexane to afford an off-white solid, which was dried *in vacuo*. Yield 1.40 g, 83 %.

16 Sep 2004

Crystal structure of $[HIr(C_8H_{11}BN_4S_2)(CO)(C_{18}H_{15}P)].CHCl_3$ –irc06

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Abstract

The crystal structure of $[HIr(C_8H_{11}BN_4S_2)(CO)(C_{18}H_{15}P)].CHCl_3$ is reported.

Comment

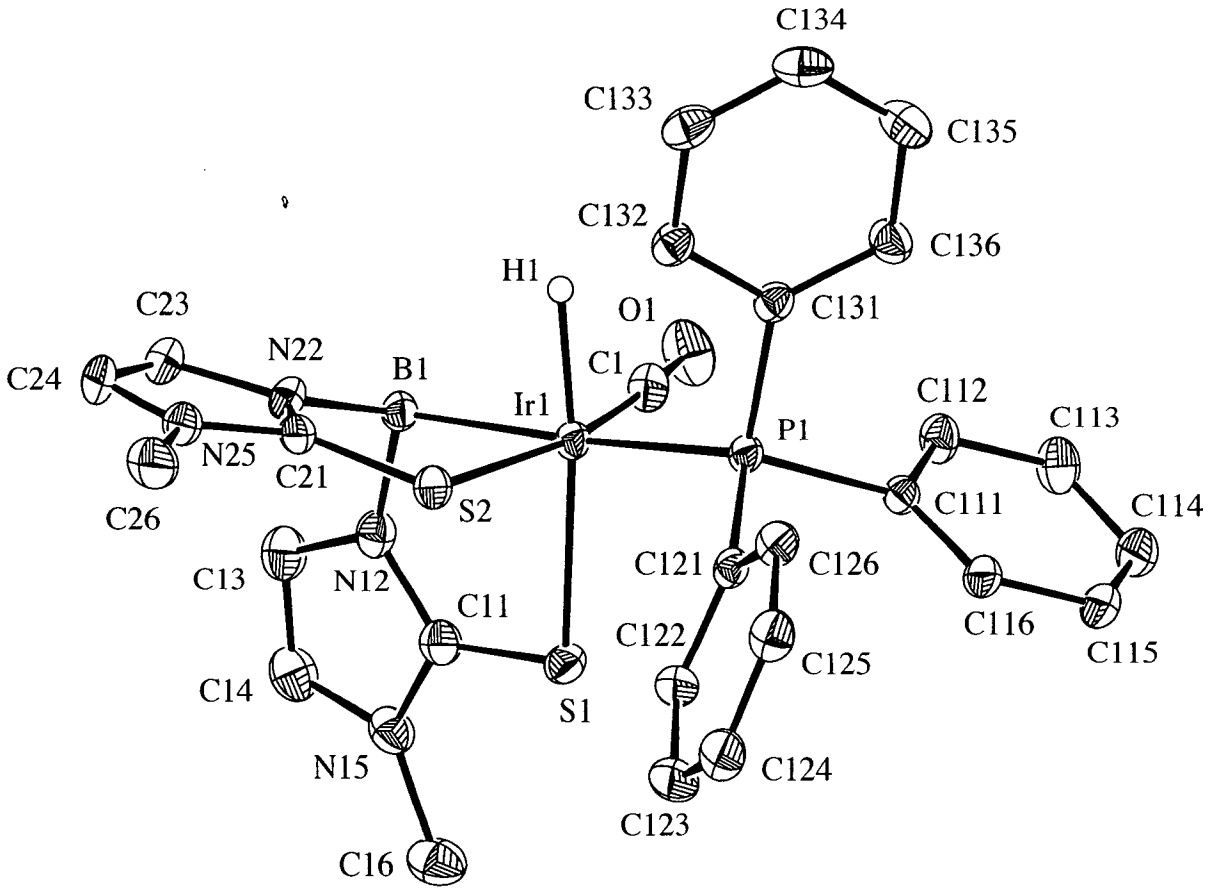
The crystallographic asymmetric unit consists of one $[HIr(C_8H_{11}BN_4S_2)(CO)(C_{18}H_{15}P)]$ molecule and one chloroform molecule of solvation.

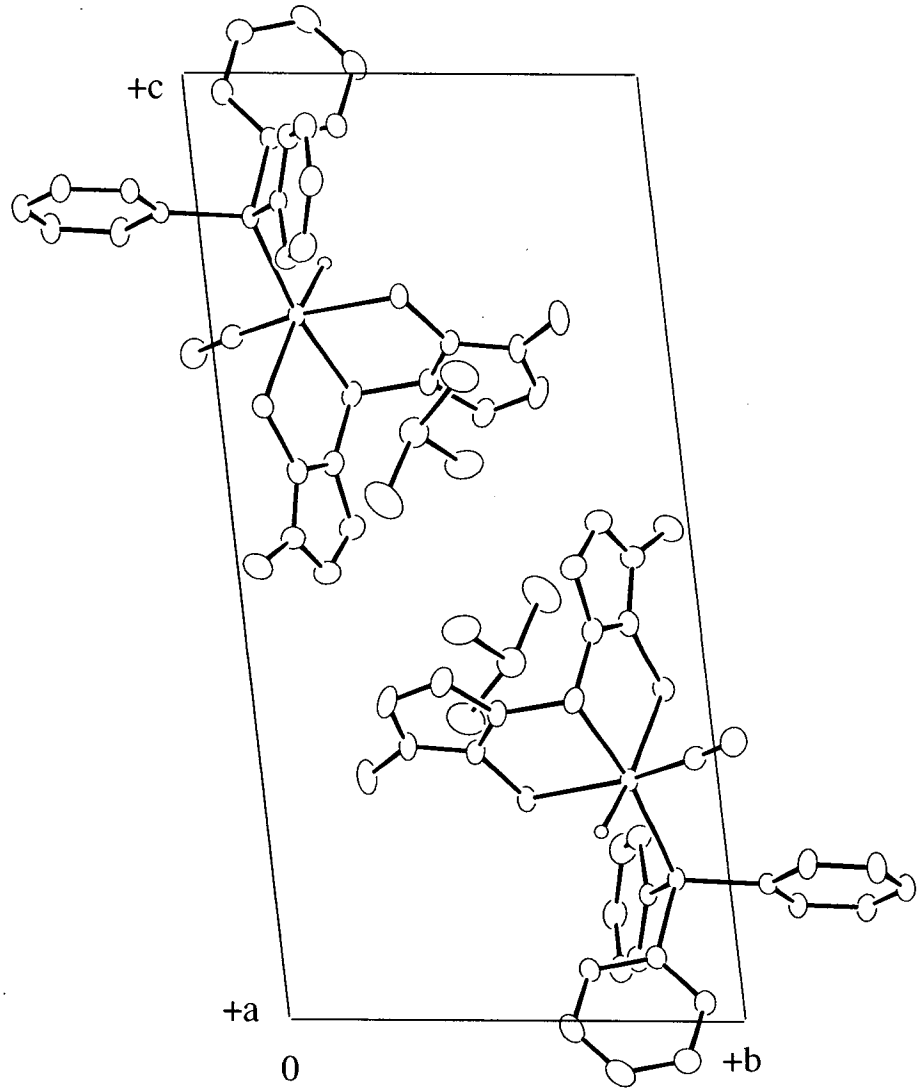
A peak attributable to the hydride was observed in a difference electron density map. It was included in the structure as a H atom and refined positionally with restraints that the H—Ir—(*cis*-atom) angles should be near equal and the Ir—H distance should tend to 1.65 Å (to match the bond length reported for Ir-hydrides in neutron studies). Distances and angles involving the hydride should not be regarded as being very reliable as it is in close proximity to a very heavy atom with its associated series-termination features.

The biggest peaks in the final difference electron density map are located near the Ir atom.

Experimental

The compound was prepared by IRC and recrystallized from chloroform/diethylether. The sample ID was irc-226.


C134
C133
C135
C132
C136
H1
C131
O1
C23
N22
C1
C24
B1
Ir1
C112
C113
P1
N25
C21
C111
C114
S2
C26
C13
N12
C121
C126
C11
C116
C122
C125
C115
C14
S1
N15
C124
C123
C16


+c
+a
0
+b

Crystal data

$C_{27}H_{27}BIrN_4OPS_2.CHCl_3$

$M_r = 841.05$

Triclinic

$P\bar{1}$

$a = 9.3509\,(2)$ Å

$b = 9.7847\,(2)$ Å

$c = 19.1038\,(5)$ Å

$\alpha = 92.7592\,(16)°$

$\beta = 99.6612\,(11)°$

$\gamma = 110.9262\,(14)°$

$V = 1598.35\,(7)$ Å^3

$Z = 2$

$D_x = 1.747$ Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 106915 reflections

$\theta = 3$–$27°$

$\mu = 4.638$ mm^{-1}

$T = 200$ K

Plate

Yellow

$0.30 \times 0.21 \times 0.10$ mm

Crystal source: ?

Data collection

Nonius Kappa CCD diffractometer

φ and ω scans with CCD

Absorption correction:

by integration *via* Gaussian method (Coppens, 1970) implemented in maXus (2000)

$T_{min} = 0.338$, $T_{max} = 0.656$

30196 measured reflections

7345 independent reflections

6032 reflections with

$I > 3.0u(I)$

$R_{int} = 0.07$

$\theta_{max} = 27.611°$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -24 \rightarrow 24$

every 0 reflections

frequency: 0 min

intensity decay: none

Refinement

Refinement on F

$R = 0.0300$

$wR = 0.0347$

$S = 1.0943$

6032 reflections

373 parameters

H atoms treated by a mixture of independent and constrained refinement

Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = $1.0/[A_0{*}T_0(x) + A_1{*}T_1(x) \ldots + A_{n-1}]{*}T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x= Fcalc/Fmax Method = Robust Weighting (Prince, 1982) W = [weight] * [1-(deltaF/6*sigmaF)^2]^2 A_i are: 1.55 −0.678 1.14 −0.205

$(\Delta/\sigma)_{max} = 0.0009$

$\Delta\rho_{max} = 1.33$ e Å^{-3}

$\Delta\rho_{min} = -1.92$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ir1—S1	2.4847 (11)	N25—C21	1.360 (5)
Ir1—S2	2.4173 (10)	N25—C24	1.388 (7)
Ir1—P1	2.4113 (10)	N25—C26	1.455 (7)
Ir1—C1	1.826 (5)	C13—C14	1.344 (8)
Ir1—B1	2.210 (5)	C23—C24	1.339 (8)
Cl1—C501	1.781 (6)	C111—C112	1.403 (6)
Cl2—C501	1.743 (6)	C111—C116	1.374 (6)
Cl3—C501	1.746 (6)	C112—C113	1.398 (6)
S1—C11	1.717 (5)	C113—C114	1.374 (7)
S2—C21	1.703 (5)	C114—C115	1.380 (7)
P1—C111	1.838 (4)	C115—C116	1.393 (6)
P1—C121	1.832 (4)	C121—C122	1.398 (6)
P1—C131	1.836 (4)	C121—C126	1.394 (6)
O1—C1	1.149 (6)	C122—C123	1.388 (6)
N12—C11	1.340 (6)	C123—C124	1.385 (8)
N12—C13	1.392 (6)	C124—C125	1.384 (7)
N12—B1	1.557 (6)	C125—C126	1.397 (6)
N15—C11	1.357 (6)	C131—C132	1.393 (6)
N15—C14	1.382 (7)	C131—C136	1.394 (6)
N15—C16	1.459 (7)	C132—C133	1.396 (7)
N22—C21	1.341 (6)	C133—C134	1.381 (8)
N22—C23	1.390 (6)	C134—C135	1.394 (8)
N22—B1	1.581 (6)	C135—C136	1.388 (7)

S1—Ir1—S2	91.69 (4)	S2—C21—N25	127.4 (4)
S1—Ir1—P1	100.14 (3)	S2—C21—N22	124.5 (3)
S2—Ir1—P1	88.46 (4)	N25—C21—N22	108.0 (4)
S1—Ir1—C1	92.19 (15)	N22—C23—C24	107.8 (5)
S2—Ir1—C1	167.76 (14)	N25—C24—C23	107.6 (4)
P1—Ir1—C1	102.27 (14)	P1—C111—C112	118.5 (3)
S1—Ir1—B1	85.90 (13)	P1—C111—C116	122.5 (3)
S2—Ir1—B1	86.01 (12)	C112—C111—C116	119.0 (4)
P1—Ir1—B1	171.94 (13)	C111—C112—C113	119.8 (4)
C1—Ir1—B1	82.69 (18)	C112—C113—C114	120.2 (4)
Ir1—S1—C11	96.27 (16)	C113—C114—C115	120.1 (4)
Ir1—S2—C21	97.18 (15)	C114—C115—C116	119.8 (4)
Ir1—P1—C111	118.04 (13)	C115—C116—C111	121.0 (4)
Ir1—P1—C121	116.75 (13)	P1—C121—C122	118.7 (3)
C111—P1—C121	101.81 (18)	P1—C121—C126	122.2 (3)
Ir1—P1—C131	111.90 (13)	C122—C121—C126	119.0 (4)
C111—P1—C131	102.96 (18)	C121—C122—C123	120.1 (4)
C121—P1—C131	103.46 (18)	C122—C123—C124	120.4 (5)
C11—N12—C13	107.6 (4)	C123—C124—C125	120.2 (4)
C11—N12—B1	124.9 (4)	C124—C125—C126	119.6 (5)
C13—N12—B1	127.4 (4)	C125—C126—C121	120.7 (4)
C11—N15—C14	108.3 (4)	P1—C131—C132	117.6 (3)
C11—N15—C16	125.2 (4)	P1—C131—C136	123.1 (3)
C14—N15—C16	126.5 (4)	C132—C131—C136	119.3 (4)
C21—N22—C23	108.4 (4)	C131—C132—C133	120.1 (4)
C21—N22—B1	122.6 (3)	C132—C133—C134	120.3 (5)
C23—N22—B1	128.7 (4)	C133—C134—C135	119.9 (4)
C21—N25—C24	108.1 (4)	C134—C135—C136	119.9 (5)
C21—N25—C26	124.5 (5)	C131—C136—C135	120.6 (4)
C24—N25—C26	127.3 (4)	Cl1—C501—Cl3	109.6 (3)
Ir1—C1—O1	175.6 (4)	Cl1—C501—Cl2	109.2 (3)
S1—C11—N15	127.0 (4)	Cl3—C501—Cl2	110.8 (4)
S1—C11—N12	124.4 (4)	N22—B1—Ir1	106.5 (3)
N15—C11—N12	108.6 (4)	N22—B1—N12	107.4 (3)
N12—C13—C14	108.4 (5)	Ir1—B1—N12	107.8 (3)
N15—C14—C13	107.1 (4)		

The hydride was refined positionally, with restraints, while other H atoms were included at idealized positions and ride on the atom to which they are attached.

Data collection: COLLECT (Nonius BV, 1997) . Cell refinement: Denzo/Scalepack (Otwinowski & Minor, 1996) . Data reduction: Denzo/Scalepack (Otwinowski & Minor, 1996) . Program(s) used to solve structure: PATTY in *DIRDIF* (Beurskens *et al.* 1996) implemented in maXus (2000) . Program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*2003) . Molecular graphics: *ORTEP*–II (Johnson 1976) in teXsan (MSC, 1992–1997) . Software used to prepare material for publication: *CRYSTALS* (Watkin *et al.*2003) .

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Supplementary data

Table S1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir1	**0.790196** (17)	**0.805640** (16)	**0.254344** (9)	0.0274
Cl1	0.3144 (2)	0.6606 (2)	0.45023 (12)	0.0841
Cl2	0.4759 (2)	0.4762 (2)	0.41227 (8)	0.0698
Cl3	0.19554 (18)	0.4637 (2)	0.31893 (9)	0.0755
S1	0.69247 (13)	0.90370 (12)	0.35082 (6)	0.0351
S2	0.56709 (12)	0.57615 (11)	0.23405 (6)	0.0334
P1	0.66453 (11)	0.88414 (10)	0.15196 (5)	0.0259
O1	1.1042 (4)	1.0438 (4)	0.2959 (2)	0.0584
N12	0.8748 (4)	0.7625 (4)	0.4118 (2)	0.0361
N15	0.7922 (5)	0.8697 (5)	0.4907 (2)	0.0417
N22	0.7973 (4)	0.5331 (4)	0.3249 (2)	0.0347
N25	0.5939 (5)	0.3297 (4)	0.2889 (2)	0.0438
C1	0.9813 (5)	0.9550 (5)	0.2778 (2)	0.0385
C11	0.7883 (5)	0.8435 (5)	0.4199 (3)	0.0366
C13	0.9346 (6)	0.7371 (6)	0.4795 (3)	0.0463
C14	0.8844 (6)	0.8034 (6)	0.5280 (3)	0.0494
C16	0.7131 (7)	0.9551 (7)	0.5214 (3)	0.0543
C21	0.6546 (5)	0.4764 (5)	0.2831 (2)	0.0347
C23	0.8291 (6)	0.4198 (5)	0.3569 (3)	0.0457
C24	0.7035 (7)	0.2955 (5)	0.3357 (3)	0.0508
C26	0.4359 (7)	0.2318 (5)	0.2558 (4)	0.0574
C111	0.7176 (5)	1.0830 (4)	0.1477 (2)	0.0288
C112	0.8755 (5)	1.1753 (5)	0.1679 (3)	0.0400
C113	0.9196 (6)	1.3268 (5)	0.1644 (3)	0.0455
C114	0.8082 (6)	1.3860 (5)	0.1439 (3)	0.0442
C115	0.6532 (6)	1.2951 (5)	0.1223 (3)	0.0421
C116	0.6090 (5)	1.1437 (5)	0.1245 (2)	0.0352
C121	0.4508 (4)	0.8183 (4)	0.1352 (2)	0.0291
C122	0.3769 (5)	0.8124 (5)	0.1935 (3)	0.0377
C123	0.2163 (6)	0.7752 (6)	0.1823 (3)	0.0480
C124	0.1277 (5)	0.7406 (5)	0.1135 (3)	0.0453
C125	0.1981 (5)	0.7403 (5)	0.0554 (3)	0.0433
C126	0.3601 (5)	0.7803 (5)	0.0663 (3)	0.0359
C131	0.7054 (4)	0.8208 (4)	0.0682 (2)	0.0294
C132	0.6754 (5)	0.6711 (5)	0.0542 (2)	0.0353
C133	0.7068 (6)	0.6172 (6)	−0.0081 (3)	0.0449
C134	0.7696 (6)	0.7120 (6)	−0.0558 (3)	0.0496
C135	0.8000 (6)	0.8620 (6)	−0.0422 (3)	0.0492
C136	0.7664 (5)	0.9155 (5)	0.0192 (2)	0.0388
C501	0.3651 (6)	0.5772 (7)	0.3783 (3)	0.0550
B1	0.8965 (5)	0.7042 (5)	0.3386 (3)	0.0321
H1	0.865 (3)	0.731 (3)	0.1993 (15)	0.0320
H11	1.0095 (5)	0.7267 (5)	0.3384 (3)	0.0396
H131	1.0033 (6)	0.6793 (6)	0.4903 (3)	0.0553
H141	0.9091 (6)	0.8046 (6)	0.5811 (3)	0.0567
H161	0.7343 (7)	0.9580 (7)	0.5747 (3)	0.0650
H162	0.7526 (7)	1.0578 (7)	0.5082 (3)	0.0650
H163	0.5980 (7)	0.9080 (7)	0.5025 (3)	0.0650
H231	0.9281 (6)	0.4293 (5)	0.3899 (3)	0.0596
H241	0.6910 (7)	0.1962 (5)	0.3508 (3)	0.0680
H261	0.4190 (7)	0.1296 (5)	0.2679 (4)	0.0667

H262	0.3591 (7)	0.2665 (5)	0.2741 (4)	0.0667
H263	0.4211 (7)	0.2319 (5)	0.2028 (4)	0.0667
H1121	0.9562 (5)	1.1330 (5)	0.1848 (3)	0.0456
H1131	1.0325 (6)	1.3923 (5)	0.1768 (3)	0.0495
H1141	0.8395 (6)	1.4951 (5)	0.1447 (3)	0.0533
H1151	0.5729 (6)	1.3377 (5)	0.1051 (3)	0.0533
H1161	0.4965 (5)	1.0783 (5)	0.1088 (2)	0.0422
H1221	0.4399 (5)	0.8350 (5)	0.2433 (3)	0.0471
H1231	0.1644 (6)	0.7734 (6)	0.2241 (3)	0.0597
H1241	0.0123 (5)	0.7156 (5)	0.1059 (3)	0.0527
H1251	0.1336 (5)	0.7117 (5)	0.0058 (3)	0.0492
H1261	0.4114 (5)	0.7817 (5)	0.0243 (3)	0.0419
H1321	0.6313 (5)	0.6021 (5)	0.0889 (2)	0.0413
H1331	0.6838 (6)	0.5095 (6)	−0.0182 (3)	0.0531
H1341	0.7931 (6)	0.6731 (6)	−0.1001 (3)	0.0584
H1351	0.8459 (6)	0.9310 (6)	−0.0765 (3)	0.0572
H1361	0.7861 (5)	1.0228 (5)	0.0283 (2)	0.0457
H5011	0.4285 (6)	0.6548 (7)	0.3518 (3)	0.0669

Table *S2. Anisotropic displacement parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir1	0.02616 (8)	0.02098 (8)	0.03369 (8)	0.00652 (5)	0.00687 (5)	0.00427 (5)
Cl1	0.0658 (10)	0.0923 (13)	0.0958 (13)	0.0387 (9)	0.0093 (9)	−0.0260 (11)
Cl2	0.0760 (10)	0.1035 (13)	0.0522 (8)	0.0550 (10)	0.0219 (7)	0.0158 (8)
Cl3	0.0485 (8)	0.0971 (13)	0.0661 (10)	0.0137 (8)	0.0065 (7)	−0.0063 (9)
S1	0.0400 (5)	0.0312 (5)	0.0365 (5)	0.0165 (4)	0.0072 (4)	0.0015 (4)
S2	0.0332 (5)	0.0226 (4)	0.0405 (5)	0.0051 (4)	0.0089 (4)	0.0034 (4)
P1	0.0245 (4)	0.0199 (4)	0.0324 (5)	0.0065 (3)	0.0070 (4)	0.0034 (4)
O1	0.0337 (17)	0.050 (2)	0.067 (3)	−0.0097 (15)	−0.0004 (16)	0.0107 (19)
N12	0.0342 (17)	0.0305 (18)	0.041 (2)	0.0098 (14)	0.0045 (14)	0.0067 (15)
N15	0.047 (2)	0.041 (2)	0.0339 (19)	0.0117 (17)	0.0103 (16)	0.0039 (16)
N22	0.0400 (19)	0.0249 (17)	0.044 (2)	0.0163 (14)	0.0110 (15)	0.0066 (15)
N25	0.054 (2)	0.0210 (17)	0.057 (3)	0.0092 (16)	0.0239 (19)	0.0065 (16)
C1	0.043 (2)	0.035 (2)	0.038 (2)	0.0156 (19)	0.0060 (18)	0.0077 (18)
C11	0.034 (2)	0.028 (2)	0.042 (2)	0.0051 (16)	0.0073 (17)	0.0022 (17)
C13	0.051 (3)	0.047 (3)	0.041 (3)	0.019 (2)	0.003 (2)	0.010 (2)
C14	0.053 (3)	0.052 (3)	0.037 (2)	0.014 (2)	0.004 (2)	0.007 (2)
C16	0.059 (3)	0.058 (3)	0.045 (3)	0.019 (3)	0.018 (2)	−0.006 (2)
C21	0.039 (2)	0.0245 (19)	0.043 (2)	0.0094 (16)	0.0172 (18)	0.0079 (17)
C23	0.053 (3)	0.037 (2)	0.059 (3)	0.026 (2)	0.019 (2)	0.017 (2)
C24	0.076 (4)	0.031 (2)	0.063 (3)	0.030 (2)	0.033 (3)	0.021 (2)
C26	0.060 (3)	0.026 (2)	0.081 (4)	0.001 (2)	0.035 (3)	0.002 (2)
C111	0.0336 (19)	0.0219 (18)	0.0297 (19)	0.0085 (15)	0.0077 (15)	0.0011 (14)
C112	0.036 (2)	0.027 (2)	0.051 (3)	0.0051 (17)	0.0065 (19)	0.0088 (18)
C113	0.043 (2)	0.026 (2)	0.055 (3)	−0.0008 (18)	0.006 (2)	0.004 (2)
C114	0.056 (3)	0.024 (2)	0.053 (3)	0.0119 (19)	0.019 (2)	0.0048 (19)
C115	0.050 (3)	0.028 (2)	0.055 (3)	0.0184 (19)	0.019 (2)	0.0090 (19)
C116	0.037 (2)	0.0236 (19)	0.045 (2)	0.0093 (16)	0.0118 (18)	0.0044 (17)
C121	0.0283 (18)	0.0209 (17)	0.037 (2)	0.0078 (14)	0.0060 (15)	0.0037 (15)
C122	0.036 (2)	0.041 (2)	0.041 (2)	0.0168 (18)	0.0133 (17)	0.0085 (18)
C123	0.035 (2)	0.055 (3)	0.059 (3)	0.017 (2)	0.022 (2)	0.015 (2)
C124	0.028 (2)	0.039 (2)	0.065 (3)	0.0070 (18)	0.008 (2)	0.011 (2)
C125	0.033 (2)	0.036 (2)	0.054 (3)	0.0078 (18)	0.0013 (19)	0.006 (2)
C126	0.0298 (19)	0.031 (2)	0.044 (2)	0.0087 (16)	0.0056 (17)	0.0027 (17)
C131	0.0251 (17)	0.0274 (19)	0.035 (2)	0.0100 (14)	0.0045 (14)	0.0015 (15)
C132	0.035 (2)	0.028 (2)	0.040 (2)	0.0103 (16)	0.0051 (17)	−0.0003 (17)
C133	0.043 (2)	0.038 (2)	0.051 (3)	0.017 (2)	0.006 (2)	−0.009 (2)
C134	0.042 (2)	0.056 (3)	0.047 (3)	0.016 (2)	0.013 (2)	−0.013 (2)
C135	0.049 (3)	0.050 (3)	0.044 (3)	0.008 (2)	0.020 (2)	0.004 (2)
C136	0.044 (2)	0.031 (2)	0.040 (2)	0.0079 (18)	0.0159 (18)	0.0035 (18)
C501	0.043 (3)	0.058 (3)	0.066 (4)	0.019 (2)	0.016 (2)	0.008 (3)
B1	0.029 (2)	0.029 (2)	0.041 (3)	0.0115 (17)	0.0102 (18)	0.0111 (19)

Table S3. *Geometric parameters (Å, °)*

Ir1—S1	2.4847 (11)	C26—H262	1.000
Ir1—S2	2.4173 (10)	C26—H263	1.000
Ir1—P1	2.4113 (10)	C111—C112	1.403 (6)
Ir1—C1	1.826 (5)	C111—C116	1.374 (6)
Ir1—B1	2.210 (5)	C112—C113	1.398 (6)
Ir1—H1	1.63 (3)	C112—H1121	1.000
Cl1—C501	1.781 (6)	C113—C114	1.374 (7)
Cl2—C501	1.743 (6)	C113—H1131	1.000
Cl3—C501	1.746 (6)	C114—C115	1.380 (7)
S1—C11	1.717 (5)	C114—H1141	1.000
S2—C21	1.703 (5)	C115—C116	1.393 (6)
P1—C111	1.838 (4)	C115—H1151	1.000
P1—C121	1.832 (4)	C116—H1161	1.000
P1—C131	1.836 (4)	C121—C122	1.398 (6)
O1—C1	1.149 (6)	C121—C126	1.394 (6)
N12—C11	1.340 (6)	C122—C123	1.388 (6)
N12—C13	1.392 (6)	C122—H1221	1.000
N12—B1	1.557 (6)	C123—C124	1.385 (8)
N15—C11	1.357 (6)	C123—H1231	1.000
N15—C14	1.382 (7)	C124—C125	1.384 (7)
N15—C16	1.459 (7)	C124—H1241	1.000
N22—C21	1.341 (6)	C125—C126	1.397 (6)
N22—C23	1.390 (6)	C125—H1251	1.000
N22—B1	1.581 (6)	C126—H1261	1.000
N25—C21	1.360 (5)	C131—C132	1.393 (6)
N25—C24	1.388 (7)	C131—C136	1.394 (6)
N25—C26	1.455 (7)	C132—C133	1.396 (7)
C13—C14	1.344 (8)	C132—H1321	1.000
C13—H131	1.000	C133—C134	1.381 (8)
C14—H141	1.000	C133—H1331	1.000
C16—H161	1.000	C134—C135	1.394 (8)
C16—H162	1.000	C134—H1341	1.000
C16—H163	1.000	C135—C136	1.388 (7)
C23—C24	1.339 (8)	C135—H1351	1.000
C23—H231	1.000	C136—H1361	1.000
C24—H241	1.000	C501—H5011	1.000
C26—H261	1.000	B1—H11	1.000
S1—Ir1—S2	91.69 (4)	C11—N12—B1	124.9 (4)
S1—Ir1—P1	100.14 (3)	C13—N12—B1	127.4 (4)
S2—Ir1—P1	88.46 (4)	C11—N15—C14	108.3 (4)
S1—Ir1—C1	92.19 (15)	C11—N15—C16	125.2 (4)
S2—Ir1—C1	167.76 (14)	C14—N15—C16	126.5 (4)
P1—Ir1—C1	102.27 (14)	C21—N22—C23	108.4 (4)
S1—Ir1—B1	85.90 (13)	C21—N22—B1	122.6 (3)
S2—Ir1—B1	86.01 (12)	C23—N22—B1	128.7 (4)
P1—Ir1—B1	171.94 (13)	C21—N25—C24	108.1 (4)
C1—Ir1—B1	82.69 (18)	C21—N25—C26	124.5 (5)
S1—Ir1—H1	172.3 (11)	C24—N25—C26	127.3 (4)
S2—Ir1—H1	87.7 (11)	Ir1—C1—O1	175.6 (4)
P1—Ir1—H1	87.6 (11)	S1—C11—N15	127.0 (4)
C1—Ir1—H1	86.9 (11)	S1—C11—N12	124.4 (4)
B1—Ir1—H1	86.4 (11)	N15—C11—N12	108.6 (4)
Ir1—S1—C11	96.27 (16)	N12—C13—C14	108.4 (5)
Ir1—S2—C21	97.18 (15)	N12—C13—H131	125.818
Ir1—P1—C111	118.04 (13)	C14—C13—H131	125.820
Ir1—P1—C121	116.75 (13)	N15—C14—C13	107.1 (4)
C111—P1—C121	101.81 (18)	N15—C14—H141	126.442
Ir1—P1—C131	111.90 (13)	C13—C14—H141	126.438
C111—P1—C131	102.96 (18)	N15—C16—H161	109.471
C121—P1—C131	103.46 (18)	N15—C16—H162	109.465
C11—N12—C13	107.6 (4)	H161—C16—H162	109.476

N15—C16—H163	109.464	C122—C123—C124	120.4 (5)
H161—C16—H163	109.476	C122—C123—H1231	119.803
H162—C16—H163	109.476	C124—C123—H1231	119.801
S2—C21—N25	127.4 (4)	C123—C124—C125	120.2 (4)
S2—C21—N22	124.5 (3)	C123—C124—H1241	119.889
N25—C21—N22	108.0 (4)	C125—C124—H1241	119.891
N22—C23—C24	107.8 (5)	C124—C125—C126	119.6 (5)
N22—C23—H231	126.078	C124—C125—H1251	120.223
C24—C23—H231	126.075	C126—C125—H1251	120.225
N25—C24—C23	107.6 (4)	C125—C126—C121	120.7 (4)
N25—C24—H241	126.192	C125—C126—H1261	119.670
C23—C24—H241	126.193	C121—C126—H1261	119.671
N25—C26—H261	109.462	P1—C131—C132	117.6 (3)
N25—C26—H262	109.469	P1—C131—C136	123.1 (3)
H261—C26—H262	109.476	C132—C131—C136	119.3 (4)
N25—C26—H263	109.468	C131—C132—C133	120.1 (4)
H261—C26—H263	109.476	C131—C132—H1321	119.964
H262—C26—H263	109.476	C133—C132—H1321	119.968
P1—C111—C112	118.5 (3)	C132—C133—C134	120.3 (5)
P1—C111—C116	122.5 (3)	C132—C133—H1331	119.832
C112—C111—C116	119.0 (4)	C134—C133—H1331	119.834
C111—C112—C113	119.8 (4)	C133—C134—C135	119.9 (4)
C111—C112—H1121	120.115	C133—C134—H1341	120.050
C113—C112—H1121	120.113	C135—C134—H1341	120.050
C112—C113—C114	120.2 (4)	C134—C135—C136	119.9 (5)
C112—C113—H1131	119.908	C134—C135—H1351	120.068
C114—C113—H1131	119.909	C136—C135—H1351	120.068
C113—C114—C115	120.1 (4)	C131—C136—C135	120.6 (4)
C113—C114—H1141	119.929	C131—C136—H1361	119.721
C115—C114—H1141	119.932	C135—C136—H1361	119.720
C114—C115—C116	119.8 (4)	Cl1—C501—Cl3	109.6 (3)
C114—C115—H1151	120.100	Cl1—C501—Cl2	109.2 (3)
C116—C115—H1151	120.098	Cl3—C501—Cl2	110.8 (4)
C115—C116—C111	121.0 (4)	Cl1—C501—H5011	109.977
C115—C116—H1161	119.524	Cl3—C501—H5011	108.387
C111—C116—H1161	119.523	Cl2—C501—H5011	108.788
P1—C121—C122	118.7 (3)	N22—B1—Ir1	106.5 (3)
P1—C121—C126	122.2 (3)	N22—B1—N12	107.4 (3)
C122—C121—C126	119.0 (4)	Ir1—B1—N12	107.8 (3)
C121—C122—C123	120.1 (4)	N22—B1—H11	112.125
C121—C122—H1221	119.937	Ir1—B1—H11	111.767
C123—C122—H1221	119.937	N12—B1—H11	110.968

Ir1—S1—C11—N12	−3.5 (3)	N22—C21—N25—C26	175.0 (5)
Ir1—S1—C11—N15	175.6 (4)	N22—C23—C24—N25	1.5 (7)
Ir1—S2—C21—N22	8.0 (4)	N22—B1—Ir1—C1	−159.5 (4)
Ir1—S2—C21—N25	−173.9 (4)	N22—B1—N12—C11	−106.3 (4)
Ir1—P1—C111—C112	42.1 (4)	N22—B1—N12—C13	71.2 (5)
Ir1—P1—C111—C116	−139.0 (3)	N25—C21—N22—C23	1.1 (6)
Ir1—P1—C121—C122	39.8 (4)	N25—C21—N22—B1	−173.1 (4)
Ir1—P1—C121—C126	−143.1 (3)	C1—Ir1—S1—C11	−76.8 (2)
Ir1—P1—C131—C132	52.9 (3)	C1—Ir1—P1—C111	−31.1 (2)
Ir1—P1—C131—C136	−126.2 (3)	C1—Ir1—P1—C121	−153.0 (2)
Ir1—B1—N12—C11	8.2 (4)	C1—Ir1—P1—C131	88.1 (2)
Ir1—B1—N12—C13	−174.3 (3)	C11—S1—Ir1—B1	5.7 (2)
Ir1—B1—N22—C21	−16.8 (5)	C11—N12—C13—C14	−0.3 (5)
Ir1—B1—N22—C23	170.4 (4)	C11—N15—C14—C13	−0.4 (5)
S1—Ir1—S2—C21	−98.3 (2)	C13—C14—N15—C16	−179.7 (4)
S1—Ir1—P1—C111	63.5 (2)	C14—C13—N12—B1	−178.1 (4)
S1—Ir1—P1—C121	−58.4 (2)	C21—S2—Ir1—B1	−12.6 (2)
S1—Ir1—P1—C131	−177.3 (1)	C21—N22—C23—C24	−1.6 (6)
S1—Ir1—B1—N12	−7.3 (2)	C21—N25—C24—C23	−0.8 (7)
S1—Ir1—B1—N22	107.7 (3)	C23—C24—N25—C26	−175.9 (6)
S1—C11—N12—C13	179.3 (3)	C24—C23—N22—B1	172.1 (5)
S1—C11—N12—B1	−2.8 (5)	C111—P1—C121—C122	−90.2 (4)
S1—C11—N15—C14	−179.0 (3)	C111—P1—C121—C126	86.8 (4)
S1—C11—N15—C16	0.3 (6)	C111—P1—C131—C132	−179.3 (3)
S2—Ir1—S1—C11	91.6 (1)	C111—P1—C131—C136	1.6 (4)
S2—Ir1—P1—C111	154.9 (2)	C111—C112—C113—C114	2.5 (9)
S2—Ir1—P1—C121	33.0 (2)	C111—C116—C115—C114	−0.2 (8)
S2—Ir1—P1—C131	−85.9 (1)	C112—C111—P1—C121	171.3 (4)
S2—Ir1—B1—N12	−99.3 (2)	C112—C111—P1—C131	−81.7 (4)
S2—Ir1—B1—N22	15.7 (3)	C112—C111—C116—C115	−1.4 (7)
S2—C21—N22—C23	179.5 (4)	C112—C113—C114—C115	−4.1 (9)
S2—C21—N22—B1	5.3 (7)	C113—C112—C111—C116	0.2 (7)
S2—C21—N25—C24	−178.5 (4)	C113—C114—C115—C116	3.0 (9)
S2—C21—N25—C26	−3.3 (8)	C116—C111—P1—C121	−9.7 (4)
P1—Ir1—S1—C11	−179.7 (1)	C116—C111—P1—C131	97.2 (4)
P1—Ir1—S2—C21	161.6 (2)	C121—P1—C131—C132	−73.6 (3)
P1—C111—C112—C113	179.2 (4)	C121—P1—C131—C136	107.3 (3)
P1—C111—C116—C115	179.7 (4)	C121—C122—C123—C124	1.4 (8)
P1—C121—C122—C123	174.5 (4)	C121—C126—C125—C124	1.0 (7)
P1—C121—C126—C125	−175.5 (4)	C122—C121—P1—C131	163.2 (4)
P1—C131—C132—C133	−178.9 (4)	C122—C121—C126—C125	1.5 (7)
P1—C131—C136—C135	177.8 (4)	C122—C123—C124—C125	1.1 (8)
N12—C11—N15—C14	0.2 (5)	C123—C122—C121—C126	−2.7 (7)
N12—C11—N15—C16	179.6 (4)	C123—C124—C125—C126	−2.3 (8)
N12—C13—C14—N15	0.4 (5)	C126—C121—P1—C131	−19.8 (4)
N12—B1—Ir1—C1	85.4 (3)	C131—C132—C133—C134	0.8 (7)
N12—B1—N22—C21	98.6 (5)	C131—C136—C135—C134	1.3 (7)
N12—B1—N22—C23	−74.3 (6)	C132—C131—C136—C135	−1.3 (6)
N15—C11—N12—C13	0.0 (4)	C132—C133—C134—C135	−0.8 (8)
N15—C11—N12—B1	177.9 (3)	C133—C132—C131—C136	0.2 (6)
N22—C21—N25—C24	−0.2 (6)	C133—C134—C135—C136	−0.3 (8)

Table *S4*. *Contact distances (Å)*

Cl2···C21	3.204 (5)	O1···C14^{v}	3.584 (7)
Cl2···N25	3.241 (5)	N25···C115^{vi}	3.343 (7)
Cl2···Cl2^{i}	3.294 (3)	C13···C16^{v}	3.586 (7)
Cl2···N22	3.565 (4)	C21···C114^{vi}	3.447 (8)
Cl3···C113^{ii}	3.429 (5)	C21···C115^{vi}	3.468 (7)
Cl3···C23^{iii}	3.502 (6)	C26···C116^{vi}	3.436 (9)
S2···C501	3.594 (6)	C26···C115^{vi}	3.47 (1)
O1···C26^{iv}	3.232 (7)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-1, y-1, z$; (iii) $x-1, y, z$; (iv) $1+x, 1+y, z$; (v) $2-x, 2-y, 1-z$; (vi) $x, y-1, z$.