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Supporting information for article:

Conformational and structural diversity of iridium dimethyl sulfoxide complexes

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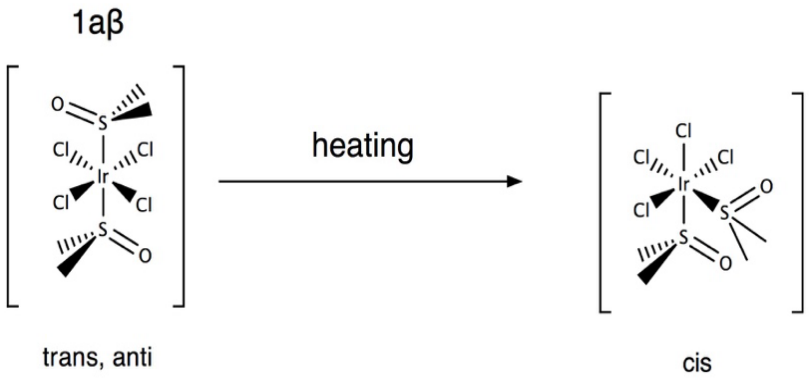
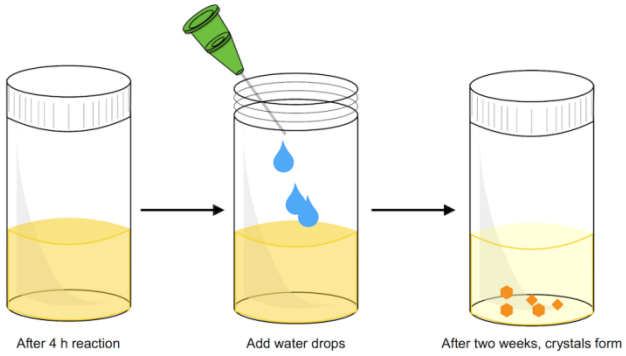
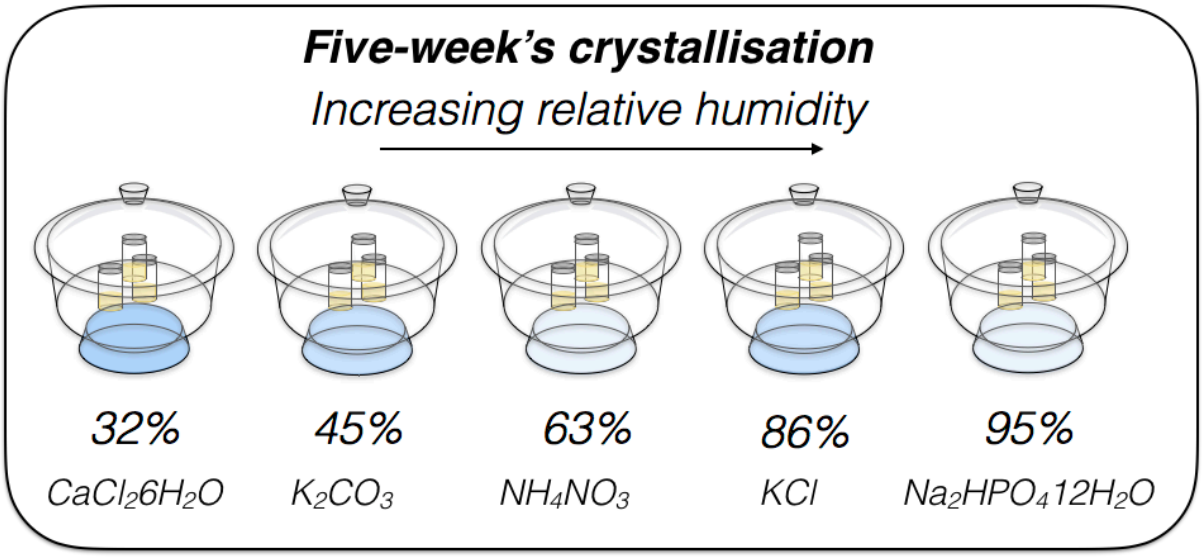
S1. Supplementary Figures and Schemes



Scheme S 1 Heating the trans-containing crystal **1aβ** yields a *cis* complex.



Scheme A. Crystals obtained after slow evaporation of the reaction solvent.



Scheme B. Controlled humidity experiments, showing the general setup of samples in desiccators. Each desiccator was equipped with a vial containing DMSO, the iridium complex, and the various humidity-controlling agents, from left to right, calcium chloride heptahydrate, potassium carbonate, ammonium nitrate, potassium chloride, and sodium hydrogen phosphate dodecahydrate, which yield relative humidities of 32, 45, 63, 86, and 95%, relatively.

Figure S1 Crystallization procedures

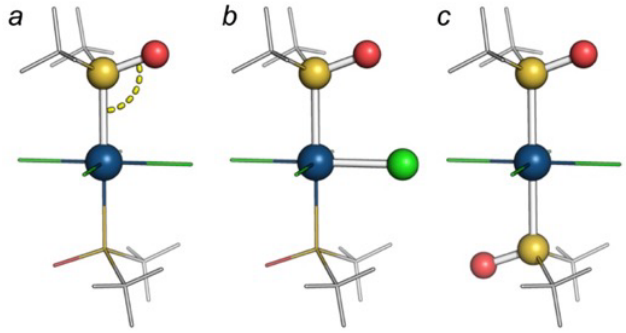


Figure S2 (a) The OSIr angle, (b) OSIrCl dihedral, and (c) OSSO dihedrals.

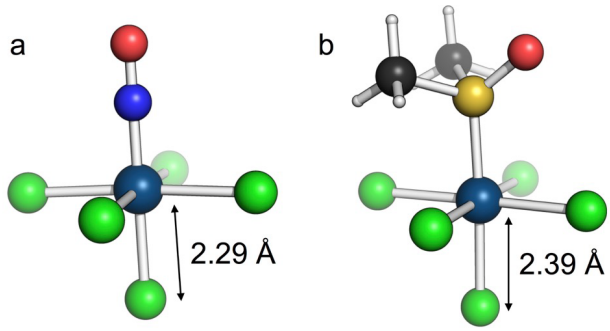


Figure S3 DFT (B3LYP/def2-SVP/def2-TZVP(Ir)) calculated structures of (a) IrCl5NO and (b) trans-IrCl5(DMSO) the bond lengths between Ir and the Cl trans to NO or DMSO. The bond lengths are (a) 2.29 and (b) 2.39 Å.

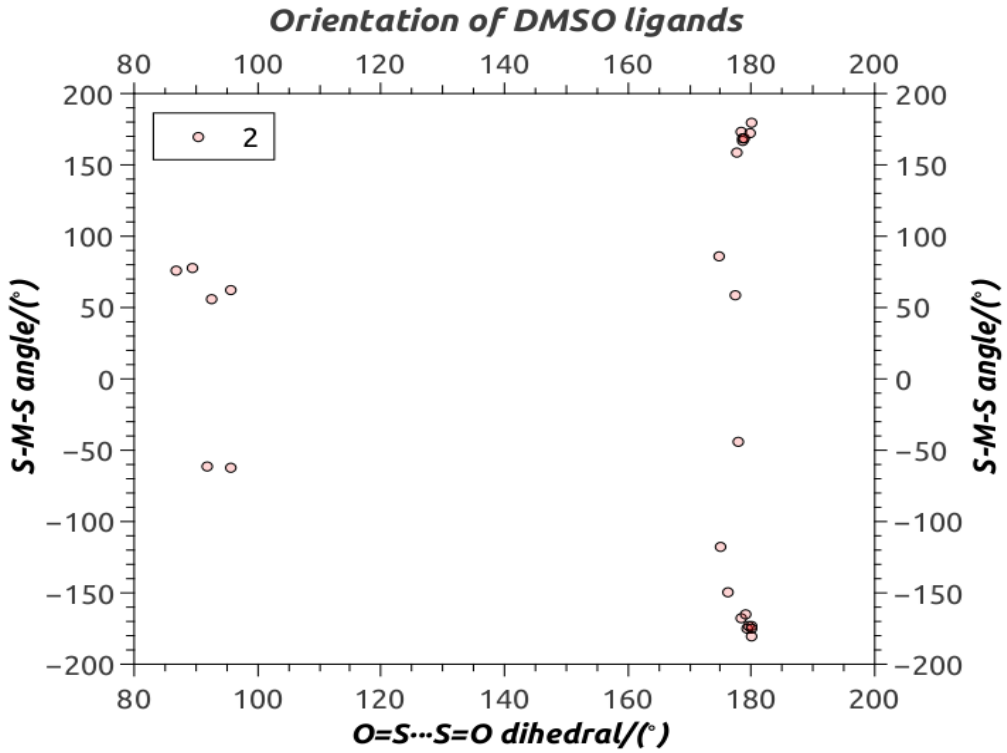


Figure S4 Scatter plot of the orientation of the S=O dihedrals versus the S-M-S angle (180° for *trans* structures and 90° for *cis* structures) extracted from the CSD (23 hits). As shown, no *syn*-rotamers are present in the CSD.

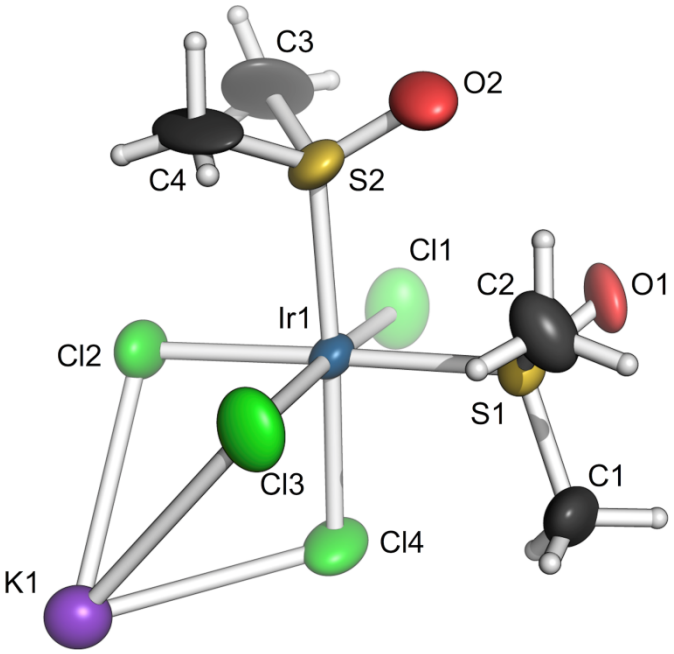


Figure S5 Ellipsoid plots at 50% probability for **2**, *cis*-K[$IrCl_4(DMSO)_2$], K^+ and water molecules are not shown for clarity.

Figure S6 Hydrogen bonding around the ammonium group in **1b**.

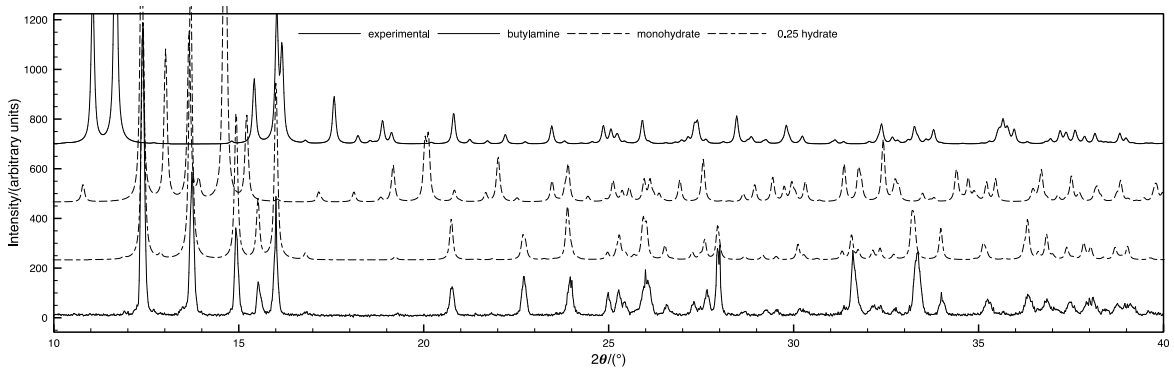


Figure S7 Predicted PXRD data for the three crystal structures and the experimentally obtained powder diffraction data.

S2. Supplementary Tables

Table S1 Kitaigorodskii packing indices for **1aα, 1aβ**, and **1b**, as calculated by PLATON.

	1a α	**1a β**	**1b**
Solvent water	77.3	81.2	68.6
No solvent water	74.2	77.5	66.9

Table S2 Geometric parameters for **1b** (Å, º)

Ir1—S1	2.3063 (16)	C1—H1A	0.96
Ir1—Cl1	2.3514 (14)	C1—H1B	0.96
Ir1—Cl2	2.3627 (13)	C1—H1C	0.96
Ir2—S2	2.3099 (17)	C2—H2A	0.96
Ir2—Cl4	2.3572 (15)	C2—H2B	0.96
Ir2—Cl3	2.3593 (17)	C2—H2C	0.96
Cl1—K1	3.185 (2)	C4—H4A	0.96
Cl4—K1	3.271 (3)	C4—H4B	0.96
S1—O1	1.474 (5)	C4—H4C	0.96
S1—C2	1.766 (7)	O2—K1	2.850 (5)
S1—C1	1.771 (6)	O1W—K1	3.071 (19)
Cl3—K1	3.217 (2)	O1W—H1W	0.82
S2—O2	1.471 (5)	C3—H3A	0.96
S2—C4	1.767 (7)	C3—H3B	0.96
S2—C3	1.774 (8)	C3—H3C	0.96
S1^{i}—Ir1—S1	180	S1—C2—H2B	109.5
S1—Ir1—Cl1	88.62 (6)	H2A—C2—H2B	109.5
S1^{i}—Ir1—Cl2	91.61 (6)	S1—C2—H2C	109.5
S1—Ir1—Cl2	88.39 (5)	H2A—C2—H2C	109.5
Cl1—Ir1—Cl2	90.12 (5)	H2B—C2—H2C	109.5
Cl2^{i}—Ir1—Cl2	180	S2—C4—H4A	109.5
S2^{ii}—Ir2—S2	180	S2—C4—H4B	109.5
S2—Ir2—Cl4	85.72 (6)	H4A—C4—H4B	109.5
S2—Ir2—Cl3	89.27 (7)	S2—C4—H4C	109.5
Cl4—Ir2—Cl3	89.46 (7)	H4A—C4—H4C	109.5
Ir1—Cl1—K1	101.27 (6)	H4B—C4—H4C	109.5

Ir2—Cl4—K1	97.03 (6)	S2—O2—K1	123.0 (3)
O1—S1—C2	108.4 (4)	K1—O1W—H1W	109.6
O1—S1—C1	107.5 (3)	K1—O1W—H2W	119.4
C2—S1—C1	100.8 (4)	H1W—O1W—H2W	97.7
O1—S1—Ir1	116.0 (2)	S2—C3—H3A	109.5
C2—S1—Ir1	111.7 (3)	S2—C3—H3B	109.5
C1—S1—Ir1	111.3 (2)	H3A—C3—H3B	109.5
Ir2—Cl3—K1	98.44 (6)	S2—C3—H3C	109.5
O2—S2—C4	107.4 (4)	H3A—C3—H3C	109.5
O2—S2—C3	106.8 (4)	H3B—C3—H3C	109.5
C4—S2—C3	101.7 (4)	O2—K1—O1W	48.8 (3)
O2—S2—Ir2	115.7 (2)	O2—K1—Cl1	73.44 (12)
C4—S2—Ir2	111.9 (3)	O1W—K1—Cl1	76.3 (4)
C3—S2—Ir2	112.3 (3)	O2—K1—Cl3	62.55 (11)
S1—C1—H1A	109.5	O1W—K1—Cl3	94.5 (4)
S1—C1—H1B	109.5	Cl1—K1—Cl3	126.65 (6)
H1A—C1—H1B	109.5	O2—K1—Cl4	70.60 (12)
S1—C1—H1C	109.5	O1W—K1—Cl4	118.3 (3)
H1A—C1—H1C	109.5	Cl1—K1—Cl4	76.91 (6)
H1B—C1—H1C	109.5	Cl3—K1—Cl4	61.54 (5)
S1—C2—H2A	109.5		

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

Table S3 Geometric parameters for **1aα** (Å, º)

C2—S1	1.776 (5)	C4—H4C	0.96
C2—H2A	0.96	O1—S1	1.472 (3)

C2—H2B	0.96	O1—K1	2.995 (4)
C2—H2C	0.96	O2—S2	1.468 (4)
C1—S1	1.773 (5)	O1W—K1	2.765 (5)
C1—H1A	0.96	O1W—H1W	0.85
C1—H1B	0.96	O1W—H2W	0.85
C1—H1C	0.96	S1—Ir1	2.3058 (11)
C3—S2	1.774 (6)	S2—Ir1	2.3167 (11)
C3—H3A	0.96	Cl1—Ir1	2.3621 (11)
C3—H3B	0.96	Cl1—K1	3.2658 (18)
C3—H3C	0.96	Cl2—Ir1	2.3666 (11)
C4—S2	1.767 (5)	Cl2—K1	3.1986 (17)
C4—H4A	0.96	Cl3—Ir1	2.3470 (12)
C4—H4B	0.96	Cl4—Ir1	2.3498 (12)
S1—C2—H2A	109.5	C1—S1—Ir1	111.14 (19)
S1—C2—H2B	109.5	C2—S1—Ir1	111.7 (2)
H2A—C2—H2B	109.5	O2—S2—C4	107.8 (3)
S1—C2—H2C	109.5	O2—S2—C3	107.3 (3)
H2A—C2—H2C	109.5	C4—S2—C3	101.1 (3)
H2B—C2—H2C	109.5	O2—S2—Ir1	115.70 (16)
S1—C1—H1A	109.5	C4—S2—Ir1	111.73 (19)
S1—C1—H1B	109.5	C3—S2—Ir1	112.1 (2)
H1A—C1—H1B	109.5	Ir1—Cl1—K1	96.00 (4)
S1—C1—H1C	109.5	Ir1—Cl2—K1	97.69 (4)
H1A—C1—H1C	109.5	S1—Ir1—S2	178.49 (4)
H1B—C1—H1C	109.5	S1—Ir1—Cl3	89.38 (4)
S2—C3—H3A	109.5	S2—Ir1—Cl3	91.87 (4)
S2—C3—H3B	109.5	S1—Ir1—Cl4	93.01 (4)

H3A—C3—H3B	109.5	S2—Ir1—Cl4	87.83 (4)
S2—C3—H3C	109.5	Cl3—Ir1—Cl4	89.79 (5)
H3A—C3—H3C	109.5	S1—Ir1—Cl1	90.45 (4)
H3B—C3—H3C	109.5	S2—Ir1—Cl1	88.29 (4)
S2—C4—H4A	109.5	Cl3—Ir1—Cl1	179.48 (5)
S2—C4—H4B	109.5	Cl4—Ir1—Cl1	90.72 (5)
H4A—C4—H4B	109.5	S1—Ir1—Cl2	86.98 (4)
S2—C4—H4C	109.5	S2—Ir1—Cl2	92.18 (4)
H4A—C4—H4C	109.5	Cl3—Ir1—Cl2	90.05 (5)
H4B—C4—H4C	109.5	Cl4—Ir1—Cl2	179.84 (4)
K1—O1W—H1W	110.5	Cl1—Ir1—Cl2	89.45 (5)
K1—O1W—H2W	140.9	O1W—K1—O1	75.91 (13)
H1W—O1W—H2W	107.7	O1W—K1—Cl2	83.46 (11)
O1—S1—C1	107.9 (3)	O1—K1—Cl2	73.78 (7)
O1—S1—C2	108.3 (2)	O1W—K1—Cl1	129.75 (11)
C1—S1—C2	100.7 (3)	O1—K1—Cl1	60.72 (8)
O1—S1—Ir1	116.05 (15)	Cl2—K1—Cl1	61.95 (4)

Table S4 Bond angles and distances for **1aβ** (Å, º)

Ir1—S1^{i}	2.309 (2)	C1—H1A	0.96
Ir1—S1	2.309 (2)	C1—H1B	0.96
Ir1—Cl2^{i}	2.358 (2)	C1—H1C	0.96
Ir1—Cl2	2.358 (2)	C2—H2A	0.96
Ir1—Cl1	2.367 (2)	C2—H2B	0.96
Ir1—Cl1^{i}	2.367 (2)	C2—H2C	0.96

Ir2—S2^{ii}	2.317 (2)	N1—C5	1.465 (12)
Ir2—S2	2.317 (2)	N1—H1D	0.89
Ir2—Cl3	2.3576 (19)	N1—H1E	0.89
Ir2—Cl3^{ii}	2.3576 (19)	N1—H1F	0.89
Ir2—Cl4^{ii}	2.360 (2)	C5—C6	1.496 (17)
Ir2—Cl4	2.360 (2)	C5—H5A	0.97
S2—O2	1.459 (7)	C5—H5B	0.97
S2—C3	1.762 (10)	C6—C7	1.34 (2)
S2—C4	1.780 (10)	C6—H6A	0.97
S1—O1	1.475 (6)	C6—H6B	0.97
S1—C1	1.765 (9)	C7—C8	1.525 (19)
S1—C2	1.777 (8)	C7—H7A	0.97
C4—H4A	0.96	C7—H7B	0.97
C4—H4B	0.96	C8—H8A	0.96
C4—H4C	0.96	C8—H8B	0.96
C3—H3A	0.96	C8—H8C	0.96
C3—H3B	0.96	O1W—H1W	0.8197
C3—H3C	0.96		
S1^{i}—Ir1—S1	179.68 (10)	O2—S2—C3	107.8 (6)
S1^{i}—Ir1—Cl2^{i}	93.10 (7)	O2—S2—C4	108.0 (5)
S1—Ir1—Cl2^{i}	87.13 (7)	C3—S2—C4	99.1 (5)
S1^{i}—Ir1—Cl2	87.13 (7)	O2—S2—Ir2	117.1 (3)
S1—Ir1—Cl2	93.10 (7)	C3—S2—Ir2	112.0 (4)
Cl2^{i}—Ir1—Cl2	87.47 (11)	C4—S2—Ir2	111.3 (4)
S1^{i}—Ir1—Cl1	88.29 (7)	O1—S1—C1	108.2 (4)
S1—Ir1—Cl1	91.49 (7)	O1—S1—C2	109.3 (4)
Cl2^{i}—Ir1—Cl1	177.31 (7)	C1—S1—C2	99.6 (5)

Cl2—Ir1—Cl1	90.30 (8)	O1—S1—Ir1	114.6 (3)
S1^{i}—Ir1—Cl1^{i}	91.49 (7)	C1—S1—Ir1	112.1 (3)
S1—Ir1—Cl1^{i}	88.29 (7)	C2—S1—Ir1	111.9 (3)
Cl2^{i}—Ir1—Cl1^{i}	90.30 (8)	N1—C5—C6	111.0 (9)
Cl2—Ir1—Cl1^{i}	177.31 (8)	N1—C5—H5A	109.4
Cl1—Ir1—Cl1^{i}	91.96 (11)	C6—C5—H5A	109.4
S2^{ii}—Ir2—S2	180.00 (14)	N1—C5—H5B	109.4
S2^{ii}—Ir2—Cl3	87.74 (8)	C6—C5—H5B	109.4
S2—Ir2—Cl3	92.26 (8)	H5A—C5—H5B	108
S2^{ii}—Ir2—Cl3^{ii}	92.26 (8)	C7—C6—C5	121.6 (16)
S2—Ir2—Cl3^{ii}	87.74 (8)	C7—C6—H6A	106.9
Cl3—Ir2—Cl3^{ii}	180.00 (13)	C5—C6—H6A	106.9
S2^{ii}—Ir2—Cl4^{ii}	91.37 (8)	C7—C6—H6B	106.9
S2—Ir2—Cl4^{ii}	88.63 (8)	C5—C6—H6B	106.9
Cl3—Ir2—Cl4^{ii}	89.29 (8)	H6A—C6—H6B	106.7
Cl3^{ii}—Ir2—Cl4^{ii}	90.71 (8)	C6—C7—C8	121.1 (19)
S2^{ii}—Ir2—Cl4	88.63 (8)	C6—C7—H7A	107
S2—Ir2—Cl4	91.37 (8)	C8—C7—H7A	107
Cl3—Ir2—Cl4	90.71 (8)	C6—C7—H7B	107
Cl3^{ii}—Ir2—Cl4	89.29 (8)	C8—C7—H7B	107
Cl4^{ii}—Ir2—Cl4	180.00 (9)	H7A—C7—H7B	106.8

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

Table S5 Hydrogen bonds in **1b**

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length-VdW
1	Cl2	H1E	*-x,y,1/2-z*	*x,y,z*	2.848	-0.102

2	O1	H1E	*-x,y,1/2-z*	*x,y,z*	2.081	-0.639
3	Cl1	H1W	*x,y,z*	*-x,-1+y,1/2-z*	2.589	-0.361
4	Cl3	H1F	*1/2-x,1/2-y,-z*	*1/2+x,-1/2+y,z*	2.707	-0.243
5	Cl4	H1F	*1/2-x,1/2-y,-z*	*1/2+x,-1/2+y,z*	2.574	-0.376
6	Cl3	H1W	*1/2-x,1/2-y,-z*	*1/2-x,-1/2+y,1/2-z*	2.911	-0.039
7	H1D	O1W	*x,y,z*	*x,y,z*	2.035	-0.685

Table S6 Hydrogen bonds in **1aα**

		Length/(Å)		Angle/(°)	Symmetry code
D-H···A	D-H	H···A	D···A	D-H···A	
O1w–H2W···O2	0.85	2.14	2.99	176.5	*x,1.5-y, -1/2+z*

Table S7 Short contacts in **1aα**, excluding hydrogen bonds

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length
C1	Cl3	*x,y,z*	*-x,-1/2+y,1/2-z*	3.54
K1	Cl1	*x,y,z*	*1-x,-1/2+y,1/2-z*	4.251
K1	S2	*x,y,z*	*1-x,-1/2+y,1/2-z*	3.91
K1	Ir1	*x,y,z*	*1-x,-1/2+y,1/2-z*	4.56
K1	C2	*x,y,z*	*1-x,1/2+y,1/2-z*	4.28
K1	S1	*x,y,z*	*1-x,1/2+y,1/2-z*	3.966
O1	C2	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	2.639
O1	C1	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	2.63
O1	S1	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	1.472
O1	Ir1	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.235
O2	C3	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	2.619

O2	C4	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	2.619
O2	S2	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	1.468
O2	Ir1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.236
Cl1	Cl2	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.327
Cl1	C3	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.34
Cl1	S1	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.314
Cl1	S2	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.259
Cl1	Cl4	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	3.353
Cl1	Ir1	*1-x,1/2+y,1/2-z*	*1-x,1/2+y,1/2-z*	2.362
Cl2	C1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.315
Cl2	S1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.216
Cl2	S2	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.374
Cl2	Cl3	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.334
Cl2	Ir1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	2.367
K1	O2	*1-x,-1/2+y,1/2-z*	*x,-1+y,z*	2.724
K1	Cl2	*1-x,-1/2+y,1/2-z*	*x,-1+y,z*	3.17
K1	O1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	2.994
K1	C1	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	4.365
K1	H1C	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.835
K1	O1W	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	2.765
K1	H1W	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.164
K1	H2W	*1-x,-1/2+y,1/2-z*	*1-x,-1/2+y,1/2-z*	3.467
O2	O1W	*x,y,z*	*x,1.5-y,-1/2+z*	2.989
O2	H2W	*x,y,z*	*x,1.5-y,-1/2+z*	2.14
Cl1	H1W	*x,y,z*	*x,1/2-y,-1/2+z*	3.031
Cl4	H1A	*x,y,z*	*x,1/2-y,-1/2+z*	2.865

Cl4	H1W	*x,y,z*	*x,1/2-y,-1/2+z*	2.98
O1W	O1W	*x,y,z*	*1-x,1-y,1-z*	2.963

Table S8 Short contacts in **1b**, excluding hydrogen bonds

Atom1	Atom2	*Symm. op. 1*	*Symm. op. 2*	Length
Cl2	H4A	*-x,y,1/2-z*	*x,y,z*	2.949
C1	O2	*-x,y,1/2-z*	*-x,-y,-z*	3.183
H1B	O2	*-x,y,1/2-z*	*-x,-y,-z*	2.489
H1C	Cl3	*-x,y,1/2-z*	*-x,-y,-z*	2.978
O1	N1	*-x,y,1/2-z*	*x,y,z*	2.865
Cl1	O1W	*x,y,z*	*x,-1+y,z*	3.243
Cl1	H1W	*x,y,z*	*-x,-1+y,1/2-z*	2.589
Cl3	N1	*1/2-x,1/2-y,-z*	*1/2+x,-1/2+y,z*	3.348
Cl4	N1	*1/2-x,1/2-y,-z*	*1/2+x,-1/2+y,z*	3.332
Cl3	H1W	*1/2-x,1/2-y,-z*	*1/2-x,-1/2+y,1/2-z*	2.911
N1	O1W	*x,y,z*	*x,y,z*	2.901
H1D	O1W	*x,y,z*	*x,y,z*	2.035

Table S9 Short contacts in **1a β**, excluding hydrogen bonds

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length
Ir1	O1	*x,y,z*	*-x,1-y,1-z*	3.236
Ir2	K1	*x,y,z*	*1-x,-y,1-z*	4.259
Ir2	C4	*x,y,z*	*1-x,-y,1-z*	3.391
Ir2	O2	*x,y,z*	*1-x,-y,1-z*	3.231
Ir2	C3	*x,y,z*	*1-x,-y,1-z*	3.405
Cl1	C2	*x,y,z*	*-x,1-y,1-z*	3.225

Cl2	O1	*x,y,z*	*-x,1-y,1-z*	3.202
Cl4	C4	*x,y,z*	*1-x,-y,1-z*	3.246
Cl3	C3	*x,y,z*	*1-x,-y,1-z*	3.321
Cl1	S1	*-x,-y,1-z*	*x,-1+y,z*	3.333
Cl1	Cl2	*-x,-y,1-z*	*-x,-y,1-z*	3.337
Cl4	Cl3	*-x,-y,1-z*	*-1+x,y,z*	3.351
Cl4	S2	*-x,-y,1-z*	*-1+x,y,z*	3.421
S1	Cl2	*-x,-y,1-z*	*-x,-y,1-z*	3.255
Cl3	S2	*-x,-y,1-z*	*-1+x,y,z*	3.323
C1	Cl2	*-x,-y,1-z*	*-x,-y,1-z*	3.379
Ir1	K1	*x,-1+y,z*	*x,-1+y,z*	4.313
Ir1	Cl1	*x,-1+y,z*	*x,-1+y,z*	2.351
Ir1	S1	*x,-1+y,z*	*x,-1+y,z*	2.306
Ir1	Cl2	*x,-1+y,z*	*-x,-y,1-z*	2.363
Ir2	Cl4	*-1+x,y,z*	*-1+x,y,z*	2.357
Ir2	Cl3	*-1+x,y,z*	*-1+x,y,z*	2.359
Ir2	S2	*-1+x,y,z*	*-1+x,y,z*	2.31
Cl1	C1	*-x,1-y,1-z*	*-x,1-y,1-z*	3.293
Cl4	K1	*1-x,-y,1-z*	*1-x,-y,1-z*	3.271
Cl4	C3	*1-x,-y,1-z*	*1-x,-y,1-z*	3.417
S1	C1	-x,1-y,1-z	-x,1-y,1-z	1.771
S1	C2	-x,1-y,1-z	-x,1-y,1-z	1.766
S1	O1	-x,1-y,1-z	-x,1-y,1-z	1.474
Cl3	K1	1-x,-y,1-z	1-x,-y,1-z	3.216
Cl3	O2	1-x,-y,1-z	1-x,-y,1-z	3.165
S2	K1	1-x,-y,1-z	1-x,-y,1-z	3.854

S2	C4	1-x,-y,1-z	1-x,-y,1-z	1.767
S2	O2	1-x,-y,1-z	1-x,-y,1-z	1.471
S2	C3	1-x,-y,1-z	1-x,-y,1-z	1.775
K1	Cl1	x,1+y,z	x,1+y,z	3.185
K1	S1	x,1+y,z	x,1+y,z	4.228
K1	O2	x,1+y,z	x,1+y,z	2.85
K1	O1	x,1+y,z	x,1+y,z	3.558
K1	C2	x,1+y,z	-x,1-y,1-z	4.461
K1	Cl2	x,1+y,z	-x,2-y,1-z	3.282
Cl4	C1	x,y,z	x,1/2-y,-1/2+z	3.416
Cl4	H1C	x,y,z	x,1/2-y,-1/2+z	2.935
Cl4	O1W	x,y,z	x,1/2-y,-1/2+z	3.187
Cl4	H1W	x,y,z	x,1/2-y,-1/2+z	2.741
K1	C1	x,y,z	x,1/2-y,-1/2+z	4.437
K1	H1A	x,y,z	x,1/2-y,-1/2+z	3.773
Cl1	C4	-x,-y,1-z	-1+x,-1/2-y,-1/2+z	3.515
Cl1	H4C	-x,-y,1-z	-1+x,-1/2-y,-1/2+z	2.981
C2	O1W	-x,-y,1-z	x,-1/2-y,-1/2+z	3.031
C2	H2W	-x,-y,1-z	x,-1/2-y,-1/2+z	2.983
H2B	O1W	-x,-y,1-z	x,-1/2-y,-1/2+z	2.783
H2C	O1W	-x,-y,1-z	x,-1/2-y,-1/2+z	2.665
O2	H3C	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.793
O1W	C3	-x,-y,1-z	-1+x,1/2-y,-1/2+z	3.218
O1W	H3B	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.767
O1W	H3C	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.807
H2W	C3	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.45

H2W	H3B	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.007
H2W	H3C	-x,-y,1-z	-1+x,1/2-y,-1/2+z	2.142

Table S10 X-ray crystal structure data for structure **2** (Å, º)

	2
Empirical formula	$C_4H_{12}Cl_4IrKO_2S_2$
Formula weight	529.36
Temperature/K	298(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.9902(18)
b/Å	15.199(3)
c/Å	10.757(2)
α/°	90
β/°	91.42(3)
γ/°	90
Volume/Å^3	1469.4(5)
Z	4
ρ_{calc}g/cm^3	2.393
μ/mm^{-1}	10.357
F(000)	992.0
Crystal size/mm^3	0.143 × 0.051 × 0.051
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.022 to 49.42
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 16$, $-12 \le l \le 10$
Reflections collected	8725
Independent reflections	2502 [R_{int} = 0.1312, R_{sigma} = 0.1270]
Data/restraints/parameters	2502/0/132
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0712, wR_2 = 0.1538
Final R indexes [all data]	R_1 = 0.1103, wR_2 = 0.1767
Largest diff. peak/hole / e Å^{-3}	2.91/-2.28

Table S11 Bond lengths for **2** (Å)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	S2	2.237(6)	K1	Cl3	3.515(8)
Ir1	S1	2.266(5)	K1	K1[2]	4.316(10)
Ir1	Cl3	2.337(6)	Cl1	K1[2]	3.429(8)
Ir1	Cl1	2.344(6)	Cl2	K1[2]	3.246(9)
Ir1	Cl2	2.376(5)	S2	O2	1.462(16)
Ir1	Cl4	2.377(5)	S2	C4	1.76(3)
K1	O1[1]	2.703(16)	S2	C3	1.79(3)
K1	O2[1]	2.782(17)	Cl4	K1[2]	3.392(8)
K1	Cl4	3.161(8)	S1	O1	1.451(14)
K1	Cl2[2]	3.246(9)	S1	C1	1.77(2)
K1	Cl2	3.261(8)	S1	C2	1.78(2)
K1	Cl4[2]	3.392(8)	O1	K1[3]	2.703(16)
K1	Cl1[2]	3.429(8)	O2	K1[3]	2.782(17)
Ir1	S2	2.237(6)	K1	Cl3	3.515(8)
Ir1	S1	2.266(5)	K1	K1[2]	4.316(10)
Ir1	Cl3	2.337(6)	Cl1	K1[2]	3.429(8)
Ir1	Cl1	2.344(6)	Cl2	K1[2]	3.246(9)
Ir1	Cl2	2.376(5)	S2	O2	1.462(16)
Ir1	Cl4	2.377(5)	S2	C4	1.76(3)
K1	O1[1]	2.703(16)	S2	C3	1.79(3)
K1	O2[1]	2.782(17)	Cl4	K1[2]	3.392(8)
K1	Cl4	3.161(8)	S1	O1	1.451(14)
K1	Cl2[2]	3.246(9)	S1	C1	1.77(2)
K1	Cl2	3.261(8)	S1	C2	1.78(2)

[1]*1/2-X,-1/2+Y,1/2-Z;* [2]*-X,1-Y,-Z;* [3]*1/2-X,1/2+Y,1/2-Z*

Table S12 Bond angles for **2** (º)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S2	Ir1	S1	92.9(2)	O2[1]	K1	Cl3	99.8(4)
S2	Ir1	Cl3	95.6(3)	Cl4	K1	Cl3	58.80(16)
S1	Ir1	Cl3	92.0(2)	Cl2[2]	K1	Cl3	128.5(2)

S2	Ir1	Cl1	89.6(3)	Cl2	K1	Cl3	57.13(16)
S1	Ir1	Cl1	89.8(2)	Cl4^{2}	K1	Cl3	123.9(2)
Cl3	Ir1	Cl1	174.4(2)	Cl1^{2}	K1	Cl3	170.6(2)
S2	Ir1	Cl2	88.4(2)	O1^{1}	K1	K1^{2}	160.4(4)
S1	Ir1	Cl2	178.51(19)	O2^{1}	K1	K1^{2}	127.7(4)
Cl3	Ir1	Cl2	87.1(2)	Cl4	K1	K1^{2}	51.15(16)
Cl1	Ir1	Cl2	91.0(2)	Cl2^{2}	K1	K1^{2}	48.60(15)
S2	Ir1	Cl4	173.2(2)	Cl2	K1	K1^{2}	48.29(15)
S1	Ir1	Cl4	92.29(19)	Cl4^{2}	K1	K1^{2}	46.54(15)
Cl3	Ir1	Cl4	88.6(2)	Cl1^{2}	K1	K1^{2}	92.18(19)
Cl1	Ir1	Cl4	86.0(3)	Cl3	K1	K1^{2}	93.35(18)
Cl2	Ir1	Cl4	86.5(2)	Ir1	Cl1	K1^{2}	90.8(2)
O1^{1}	K1	O2^{1}	70.7(4)	Ir1	Cl2	K1^{2}	94.9(2)
O1^{1}	K1	Cl4	142.7(4)	Ir1	Cl2	K1	93.4(2)
O2^{1}	K1	Cl4	94.7(4)	K1^{2}	Cl2	K1	83.10(19)
O1^{1}	K1	Cl2^{2}	139.1(4)	O2	S2	C4	107.7(14)
O2^{1}	K1	Cl2^{2}	85.7(3)	O2	S2	C3	105.6(12)
Cl4	K1	Cl2^{2}	69.78(18)	C4	S2	C3	100.0(19)
O1^{1}	K1	Cl2	119.6(4)	O2	S2	Ir1	117.8(7)
O2^{1}	K1	Cl2	152.1(4)	C4	S2	Ir1	111.4(9)
Cl4	K1	Cl2	60.92(17)	C3	S2	Ir1	112.7(11)
Cl2^{2}	K1	Cl2	96.90(19)	Ir1	Cl3	K1	87.83(19)
O1^{1}	K1	Cl4^{2}	117.2(4)	Ir1	Cl4	K1	95.9(2)
O2^{1}	K1	Cl4^{2}	134.6(4)	Ir1	Cl4	K1^{2}	91.2(2)
Cl4	K1	Cl4^{2}	97.69(19)	K1	Cl4	K1^{2}	82.31(19)
Cl2^{2}	K1	Cl4^{2}	58.72(17)	O1	S1	C1	106.6(12)
Cl2	K1	Cl4^{2}	66.82(17)	O1	S1	C2	106.2(9)
O1^{1}	K1	Cl1^{2}	83.1(4)	C1	S1	C2	102.7(14)
O2^{1}	K1	Cl1^{2}	82.7(4)	O1	S1	Ir1	117.8(6)
Cl4	K1	Cl1^{2}	130.3(2)	C1	S1	Ir1	109.9(8)
Cl2^{2}	K1	Cl1^{2}	60.50(17)	C2	S1	Ir1	112.4(9)
Cl2	K1	Cl1^{2}	122.7(2)	S1	O1	K1^{3}	131.2(8)
Cl4^{2}	K1	Cl1^{2}	56.35(17)	S2	O2	K1^{3}	137.1(9)
O1^{1}	K1	Cl3	89.1(4)				

S2	Ir1	S1	92.9(2)	O2^{1}	K1	Cl3	99.8(4)
S2	Ir1	Cl3	95.6(3)	Cl4	K1	Cl3	58.80(16)
S1	Ir1	Cl3	92.0(2)	Cl2^{2}	K1	Cl3	128.5(2)
S2	Ir1	Cl1	89.6(3)	Cl2	K1	Cl3	57.13(16)
S1	Ir1	Cl1	89.8(2)	Cl4^{2}	K1	Cl3	123.9(2)
Cl3	Ir1	Cl1	174.4(2)	Cl1^{2}	K1	Cl3	170.6(2)
S2	Ir1	Cl2	88.4(2)	O1^{1}	K1	K1^{2}	160.4(4)
S1	Ir1	Cl2	178.51(19)	O2^{1}	K1	K1^{2}	127.7(4)
Cl3	Ir1	Cl2	87.1(2)	Cl4	K1	K1^{2}	51.15(16)
Cl1	Ir1	Cl2	91.0(2)	Cl2^{2}	K1	K1^{2}	48.60(15)
S2	Ir1	Cl4	173.2(2)	Cl2	K1	K1^{2}	48.29(15)
S1	Ir1	Cl4	92.29(19)	Cl4^{2}	K1	K1^{2}	46.54(15)
Cl3	Ir1	Cl4	88.6(2)	Cl1^{2}	K1	K1^{2}	92.18(19)
Cl1	Ir1	Cl4	86.0(3)	Cl3	K1	K1^{2}	93.35(18)
Cl2	Ir1	Cl4	86.5(2)	Ir1	Cl1	K1^{2}	90.8(2)
O1^{1}	K1	O2^{1}	70.7(4)	Ir1	Cl2	K1^{2}	94.9(2)
O1^{1}	K1	Cl4	142.7(4)	Ir1	Cl2	K1	93.4(2)
O2^{1}	K1	Cl4	94.7(4)	K1^{2}	Cl2	K1	83.10(19)
O1^{1}	K1	Cl2^{2}	139.1(4)	O2	S2	C4	107.7(14)
O2^{1}	K1	Cl2^{2}	85.7(3)	O2	S2	C3	105.6(12)
Cl4	K1	Cl2^{2}	69.78(18)	C4	S2	C3	100.0(19)
O1^{1}	K1	Cl2	119.6(4)	O2	S2	Ir1	117.8(7)
O2^{1}	K1	Cl2	152.1(4)	C4	S2	Ir1	111.4(9)
Cl4	K1	Cl2	60.92(17)	C3	S2	Ir1	112.7(11)
Cl2^{2}	K1	Cl2	96.90(19)	Ir1	Cl3	K1	87.83(19)
O1^{1}	K1	Cl4^{2}	117.2(4)	Ir1	Cl4	K1	95.9(2)
O2^{1}	K1	Cl4^{2}	134.6(4)	Ir1	Cl4	K1^{2}	91.2(2)
Cl4	K1	Cl4^{2}	97.69(19)	K1	Cl4	K1^{2}	82.31(19)
Cl2^{2}	K1	Cl4^{2}	58.72(17)	O1	S1	C1	106.6(12)
Cl2	K1	Cl4^{2}	66.82(17)	O1	S1	C2	106.2(9)
O1^{1}	K1	Cl1^{2}	83.1(4)	C1	S1	C2	102.7(14)
O2^{1}	K1	Cl1^{2}	82.7(4)	O1	S1	Ir1	117.8(6)
Cl4	K1	Cl1^{2}	130.3(2)	C1	S1	Ir1	109.9(8)
Cl2^{2}	K1	Cl1^{2}	60.50(17)	C2	S1	Ir1	112.4(9)

Cl2	K1	Cl1[2]	122.7(2)	S1	O1	K1[3]	131.2(8)
Cl4[2]	K1	Cl1[2]	56.35(17)	S2	O2	K1[3]	137.1(9)

[1]1/2-X,-1/2+Y,1/2-Z; [2]-X,1-Y,-Z; [3]1/2-X,1/2+Y,1/2-Z

Table S13 Torsion angles for **2** (º)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	S1	O1	K1[1]	-162.9(13)	C4	S2	O2	K1[1]	-175.1(17)
C2	S1	O1	K1[1]	-53.9(14)	C3	S2	O2	K1[1]	-69.0(19)
Ir1	S1	O1	K1[1]	73.1(11)	Ir1	S2	O2	K1[1]	58.0(17)

[1]1/2-X,1/2+Y,1/2-Z