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Kinetics and Mechanism of Indene C-H Bond Activation by [(COD)Ir(μ -OH)]₂

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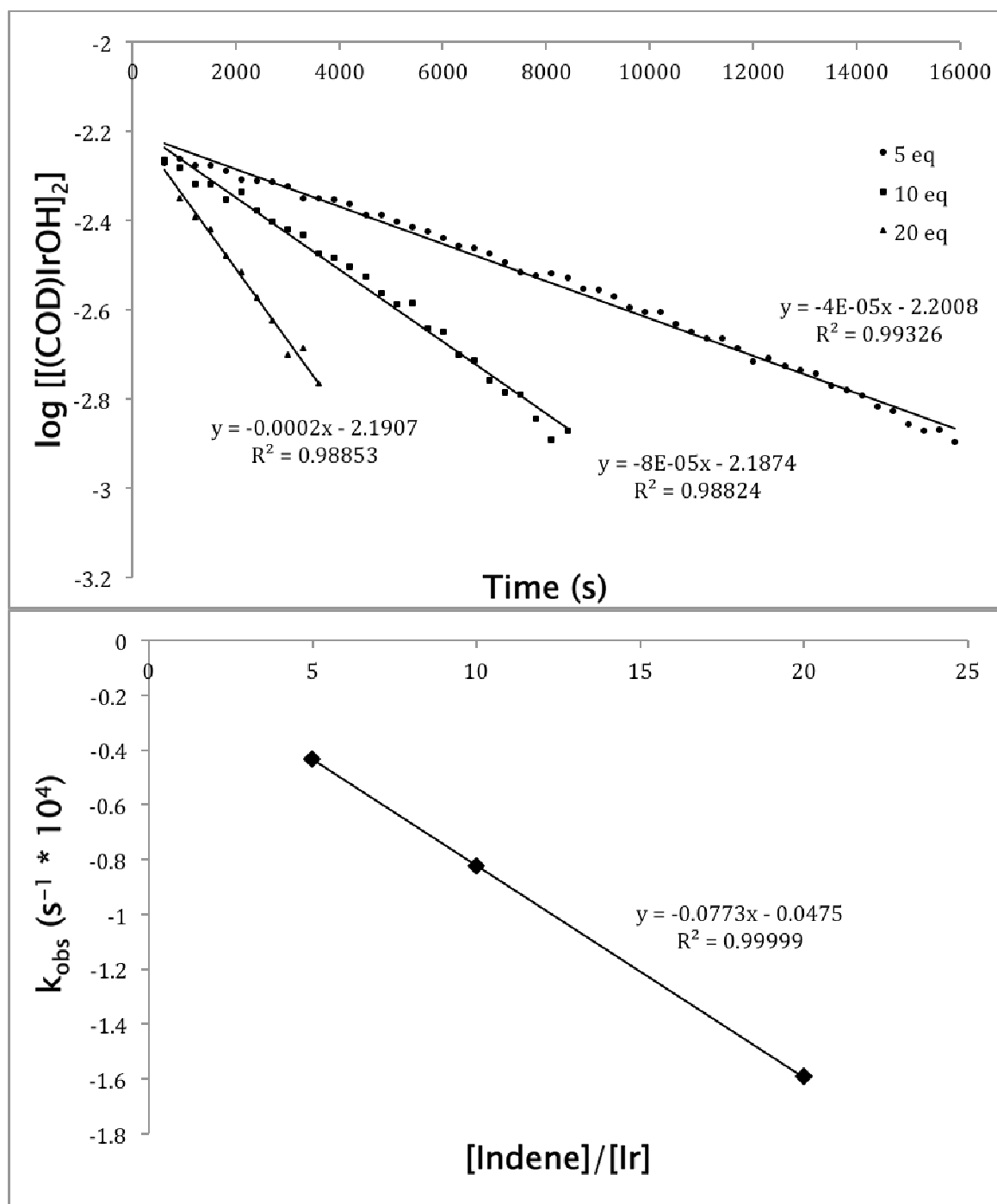


Figure S1. Log plot analysis of the reaction of $[(\text{COD})\text{Ir}(\mu_2\text{-OH})]_2$ with varying concentrations of indene. Log plots remain linear up to about 3 half lives of the reaction, confirming 1st order with respect to $[(\text{COD})\text{Ir}(\mu_2\text{-OH})]_2$.

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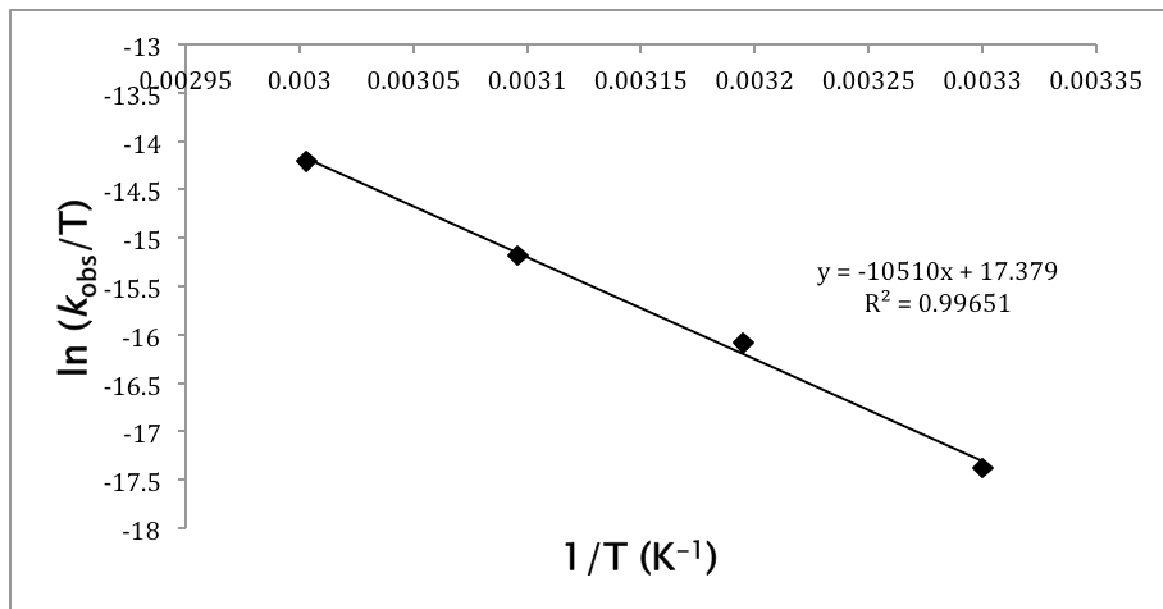


Figure S2. Eyring analysis of the reaction of $[(\text{COD})\text{Ir}(\mu_2\text{-OH})_2]$ with indene.

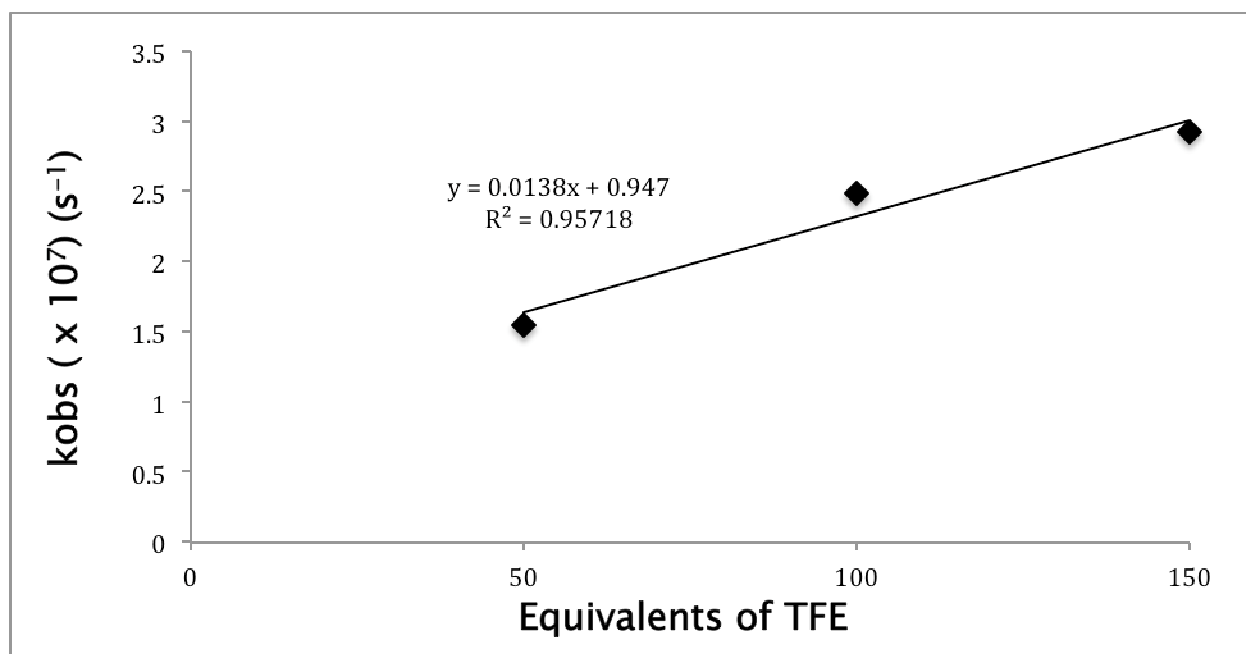


Figure S3. Plot of initial rates of reactions carried out with varying $[\text{TFE}]$ and 10 eq indene. While the reaction has some dependence on $[\text{TFE}]$, doubling $[\text{TFE}]$ does not double the initial rate and the large, nonzero intercept indicates potential competing pathways (see Scheme 1).

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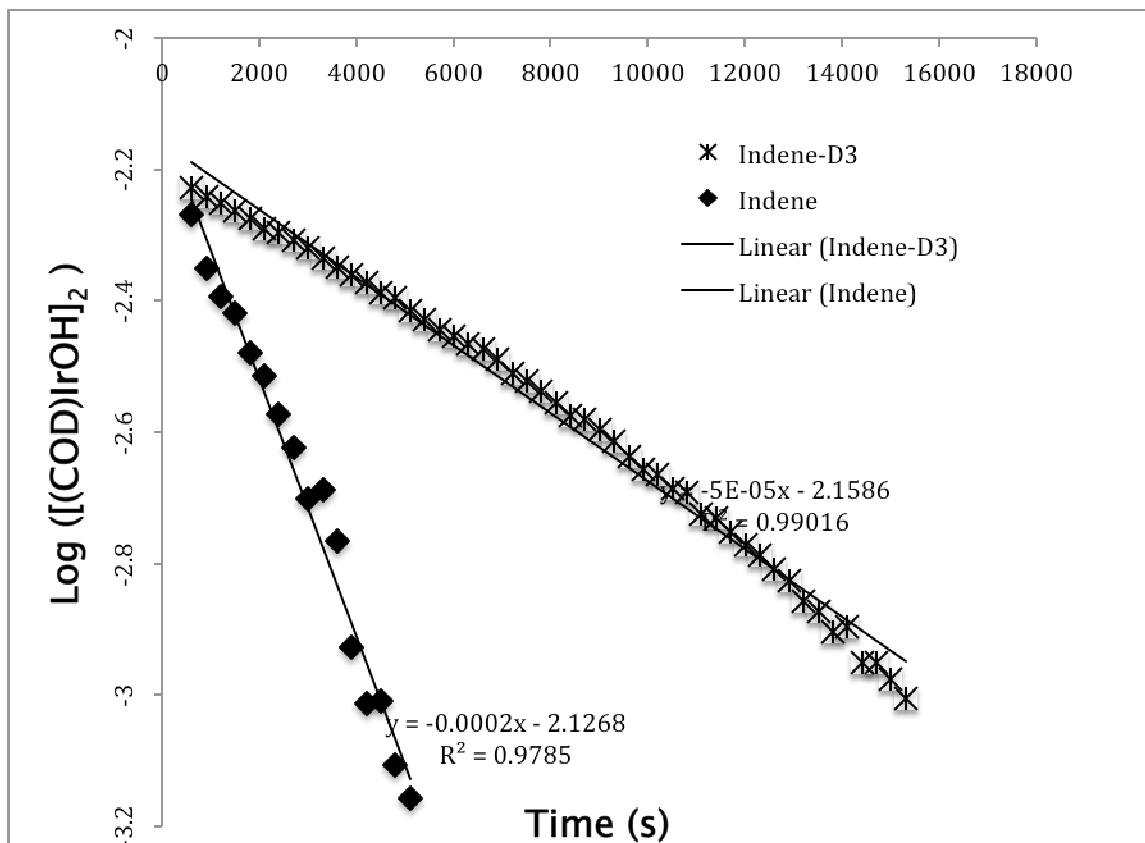


Figure S4. KIE experiments with 20 eq indene and indene-*d*₃ under standard conditions.

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Crystal Structure Analysis of:

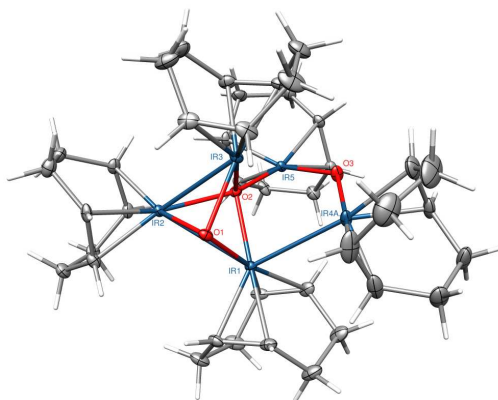
Complex 4 (IAT93)

(shown below)

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IAT93

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 855854.

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Table 1. Crystal data and structure refinement for IAT93 (CCDC 885854).

Empirical formula	$C_{40}H_{60}O_3Ir_5 \cdot CH_2Cl_2$
Formula weight	1634.81
Crystallization Solvent	Dichloromethane
Crystal Habit	Blade
Crystal size	0.28 x 0.11 x 0.04 mm ³
Crystal color	Dark-red



Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoK α	
Data Collection Temperature	100(2) K	
θ range for 9980 reflections used in lattice determination	2.17 to 32.54°	
Unit cell dimensions	a = 10.3282(4) Å b = 22.4057(9) Å c = 17.2239(7) Å	$\alpha = 90^\circ$ $\beta = 92.280(2)^\circ$ $\gamma = 90^\circ$
Volume	3982.6(3) Å ³	
Z	4	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Density (calculated)	2.726 Mg/m ³	
F(000)	3004	
θ range for data collection	2.17 to 32.63°	
Completeness to $\theta = 32.63^\circ$	99.8 %	
Index ranges	$-15 \leq h \leq 15, -33 \leq k \leq 33, -25 \leq l \leq 26$	
Data collection scan type	ω scans; 12 settings	
Reflections collected	130812	
Independent reflections	14536 [$R_{int} = 0.0556$]	
Absorption coefficient	16.819 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6518 and 0.1483	

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Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F ²
Data / restraints / parameters	14536 / 0 / 470
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F ²	1.436
Final R indices [I>2σ(I), 12336 reflections]	R1 = 0.0236, wR2 = 0.0381
R indices (all data)	R1 = 0.0341, wR2 = 0.0393
Type of weighting scheme used	Sigma
Weighting scheme used	w=1/σ ² (Fo ²)
Max shift/error	0.018
Average shift/error	0.001
Largest diff. peak and hole	1.619 and -1.772 e.Å ⁻³

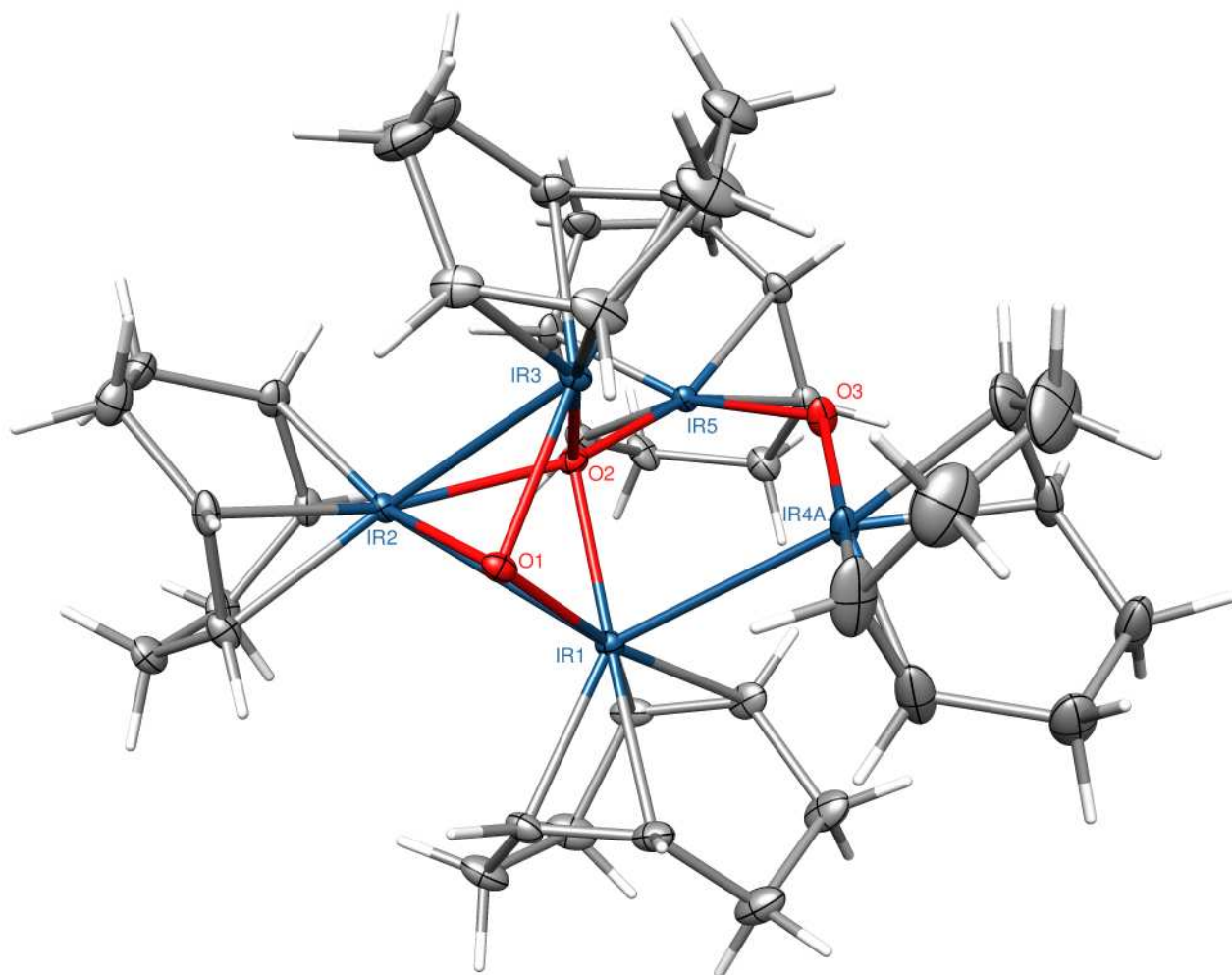
Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F² against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F², conventional R-factors (R) are based on F, with F set to zero for negative F². The threshold expression of F² > 2σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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.

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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for IAT93 (CCDC 885854). $U(\text{eq})$ is defined as the trace of the orthogonalized U^i tensor.

	x	y	z	U_{eq}	Occ
Ir(1)	3351(1)	1092(1)	1568(1)	10(1)	1
Ir(2)	5623(1)	587(1)	2156(1)	9(1)	1
Ir(3)	5518(1)	1789(1)	2406(1)	10(1)	1
Ir(4A)	2834(2)	2314(1)	1898(1)	13(1)	0.892(11)
Ir(4B)	3115(15)	2416(5)	2017(6)	15(1)	0.108(11)
Ir(5)	2932(1)	1235(1)	3597(1)	9(1)	1
O(1)	5244(2)	1291(1)	1410(1)	11(1)	1
O(2)	4193(2)	1117(1)	2693(1)	11(1)	1
O(3)	2568(2)	2029(1)	3034(1)	14(1)	1
C(1)	1803(3)	507(2)	1830(2)	16(1)	1
C(2)	1553(4)	23(2)	1217(2)	23(1)	1
C(3)	2643(3)	9(2)	638(2)	20(1)	1
C(4)	3271(3)	606(2)	526(2)	14(1)	1
C(5)	2617(3)	1151(2)	392(2)	16(1)	1
C(6)	1132(3)	1182(2)	291(2)	24(1)	1
C(7)	490(3)	1304(2)	1067(2)	23(1)	1
C(8)	1307(3)	1088(2)	1765(2)	16(1)	1
C(9)	5396(3)	-225(2)	2749(2)	14(1)	1
C(10)	5443(3)	-761(2)	2213(2)	18(1)	1
C(11)	6324(3)	-648(2)	1525(2)	18(1)	1
C(12)	6373(3)	11(2)	1325(2)	15(1)	1
C(13)	7369(3)	399(2)	1629(2)	14(1)	1
C(14)	8435(3)	212(2)	2210(2)	20(1)	1
C(15)	7886(3)	-126(2)	2902(2)	17(1)	1
C(16)	6512(3)	74(2)	3055(2)	15(1)	1
C(17)	6614(3)	2496(2)	1948(2)	19(1)	1
C(18)	6572(4)	3069(2)	2409(2)	31(1)	1
C(19)	6229(4)	2970(2)	3255(2)	26(1)	1
C(20)	5555(3)	2376(2)	3383(2)	16(1)	1
C(21)	6252(3)	1851(2)	3554(2)	17(1)	1
C(22)	7715(3)	1795(2)	3600(2)	26(1)	1
C(23)	8338(4)	2029(2)	2880(2)	28(1)	1
C(24)	7434(3)	2011(2)	2158(2)	19(1)	1
C(25)	2328(4)	2550(2)	746(2)	29(1)	1
C(26)	1259(4)	3007(2)	656(2)	29(1)	1
C(27)	622(4)	3139(2)	1431(2)	33(1)	1
C(28)	1499(4)	2986(2)	2125(2)	21(1)	1
C(29)	2775(4)	3216(2)	2257(3)	30(1)	1
C(30)	3377(5)	3656(2)	1666(3)	48(1)	1
C(31)	4032(5)	3336(2)	998(3)	44(1)	1
C(32)	3612(4)	2702(2)	916(2)	34(1)	1
C(33)	2718(3)	343(2)	3933(2)	14(1)	1
C(34)	1466(3)	210(2)	4347(2)	18(1)	1
C(35)	510(3)	725(2)	4246(2)	19(1)	1
C(36)	1192(3)	1320(2)	4171(2)	14(1)	1
C(37)	2241(3)	1522(2)	4664(2)	14(1)	1
C(38)	2761(3)	1174(2)	5364(2)	17(1)	1

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C(39)	3913(3)	780(2)	5154(2)	18(1)	1
C(40)	3836(3)	596(2)	4310(2)	14(1)	1
C(51)	1295(4)	3440(2)	4770(2)	28(1)	1
Cl(1)	2955(1)	3288(1)	4722(1)	41(1)	1
Cl(2)	332(1)	2928(1)	4231(1)	23(1)	1

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Table 3. Selected bond lengths [Å] and angles [°] for IAT93 (CCDC 885854).

Ir(1)-O(1)	2.035(2)	C(1)-Ir(1)-C(5)	89.90(13)
Ir(1)-O(2)	2.093(2)	O(1)-Ir(1)-C(8)	167.54(12)
Ir(1)-C(4)	2.098(3)	O(2)-Ir(1)-C(8)	103.23(11)
Ir(1)-C(1)	2.130(3)	C(4)-Ir(1)-C(8)	97.29(13)
Ir(1)-C(5)	2.138(3)	C(1)-Ir(1)-C(8)	38.22(13)
Ir(1)-C(8)	2.151(3)	C(5)-Ir(1)-C(8)	80.58(12)
Ir(1)-Ir(2)	2.76162(19)	O(1)-Ir(1)-Ir(2)	48.05(6)
Ir(1)-Ir(4A)	2.8508(14)	O(2)-Ir(1)-Ir(2)	49.87(6)
Ir(1)-Ir(3)	3.04491(19)	C(4)-Ir(1)-Ir(2)	96.02(9)
Ir(1)-Ir(4B)	3.077(12)	C(1)-Ir(1)-Ir(2)	107.71(10)
Ir(2)-O(1)	2.063(2)	C(5)-Ir(1)-Ir(2)	129.53(9)
Ir(2)-C(13)	2.093(3)	C(8)-Ir(1)-Ir(2)	139.96(9)
Ir(2)-C(12)	2.098(3)	O(1)-Ir(1)-Ir(4A)	90.28(7)
Ir(2)-C(9)	2.104(3)	O(2)-Ir(1)-Ir(4A)	82.20(7)
Ir(2)-C(16)	2.109(3)	C(4)-Ir(1)-Ir(4A)	131.87(10)
Ir(2)-O(2)	2.135(2)	C(1)-Ir(1)-Ir(4A)	113.62(10)
Ir(2)-Ir(3)	2.7305(2)	C(5)-Ir(1)-Ir(4A)	93.87(10)
Ir(3)-O(1)	2.056(2)	C(8)-Ir(1)-Ir(4A)	77.30(11)
Ir(3)-C(21)	2.094(3)	Ir(2)-Ir(1)-Ir(4A)	118.93(4)
Ir(3)-C(24)	2.101(3)	O(1)-Ir(1)-Ir(3)	42.18(6)
Ir(3)-O(2)	2.106(2)	O(2)-Ir(1)-Ir(3)	43.70(6)
Ir(3)-C(17)	2.117(3)	C(4)-Ir(1)-Ir(3)	132.42(9)
Ir(3)-C(20)	2.136(3)	C(1)-Ir(1)-Ir(3)	139.36(9)
Ir(3)-Ir(4B)	2.906(11)	C(5)-Ir(1)-Ir(3)	130.04(9)
Ir(3)-Ir(4A)	3.1046(12)	C(8)-Ir(1)-Ir(3)	129.42(10)
Ir(4A)-O(3)	2.088(2)	Ir(2)-Ir(1)-Ir(3)	55.843(5)
Ir(4A)-C(32)	2.091(4)	Ir(4A)-Ir(1)-Ir(3)	63.45(4)
Ir(4A)-C(28)	2.090(3)	O(1)-Ir(1)-Ir(4B)	84.8(3)
Ir(4A)-C(25)	2.099(4)	O(2)-Ir(1)-Ir(4B)	77.0(3)
Ir(4A)-C(29)	2.115(4)	C(4)-Ir(1)-Ir(4B)	135.6(2)
Ir(4B)-C(29)	1.877(11)	C(1)-Ir(1)-Ir(4B)	118.2(2)
Ir(4B)-O(3)	2.054(5)	C(5)-Ir(1)-Ir(4B)	98.6(3)
Ir(4B)-C(32)	2.086(6)	C(8)-Ir(1)-Ir(4B)	82.9(3)
Ir(4B)-C(28)	2.117(7)	Ir(2)-Ir(1)-Ir(4B)	112.2(3)
Ir(4B)-C(25)	2.324(14)	Ir(4A)-Ir(1)-Ir(4B)	6.8(3)
Ir(5)-O(3)	2.053(2)	Ir(3)-Ir(1)-Ir(4B)	56.7(3)
Ir(5)-C(40)	2.083(3)	O(1)-Ir(2)-C(13)	91.67(11)
Ir(5)-O(2)	2.087(2)	O(1)-Ir(2)-C(12)	96.41(11)
Ir(5)-C(36)	2.093(3)	C(13)-Ir(2)-C(12)	39.92(13)
Ir(5)-C(33)	2.095(3)	O(1)-Ir(2)-C(9)	160.37(11)
Ir(5)-C(37)	2.098(3)	C(13)-Ir(2)-C(9)	98.72(13)
		C(12)-Ir(2)-C(9)	81.43(13)
O(1)-Ir(1)-O(2)	75.63(8)	O(1)-Ir(2)-C(16)	160.13(11)
O(1)-Ir(1)-C(4)	90.24(11)	C(13)-Ir(2)-C(16)	81.48(13)
O(2)-Ir(1)-C(4)	143.76(11)	C(12)-Ir(2)-C(16)	90.26(13)
O(1)-Ir(1)-C(1)	153.75(12)	C(9)-Ir(2)-C(16)	39.29(13)
O(2)-Ir(1)-C(1)	96.19(11)	O(1)-Ir(2)-O(2)	74.16(8)
C(4)-Ir(1)-C(1)	81.83(13)	C(13)-Ir(2)-O(2)	157.27(11)
O(1)-Ir(1)-C(5)	99.54(11)	C(12)-Ir(2)-O(2)	156.71(11)
O(2)-Ir(1)-C(5)	173.69(11)	C(9)-Ir(2)-O(2)	100.25(11)
C(4)-Ir(1)-C(5)	38.84(13)	C(16)-Ir(2)-O(2)	105.83(11)

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O(1)-Ir(2)-Ir(3)	48.38(6)	C(20)-Ir(3)-Ir(4A)	88.65(10)
C(13)-Ir(2)-Ir(3)	107.87(10)	Ir(2)-Ir(3)-Ir(4A)	111.73(4)
C(12)-Ir(2)-Ir(3)	137.09(9)	Ir(4B)-Ir(3)-Ir(4A)	7.0(3)
C(9)-Ir(2)-Ir(3)	140.37(9)	Ir(1)-Ir(3)-Ir(4A)	55.23(4)
C(16)-Ir(2)-Ir(3)	116.12(10)	O(3)-Ir(4A)-C(32)	162.79(19)
O(2)-Ir(2)-Ir(3)	49.47(6)	O(3)-Ir(4A)-C(28)	86.10(12)
O(1)-Ir(2)-Ir(1)	47.20(6)	C(32)-Ir(4A)-C(28)	97.43(16)
C(13)-Ir(2)-Ir(1)	131.14(9)	O(3)-Ir(4A)-C(25)	157.81(16)
C(12)-Ir(2)-Ir(1)	109.49(9)	C(32)-Ir(4A)-C(25)	38.71(16)
C(9)-Ir(2)-Ir(1)	115.02(9)	C(28)-Ir(4A)-C(25)	81.58(14)
C(16)-Ir(2)-Ir(1)	146.21(9)	O(3)-Ir(4A)-C(29)	90.63(15)
O(2)-Ir(2)-Ir(1)	48.56(6)	C(32)-Ir(4A)-C(29)	81.73(18)
Ir(3)-Ir(2)-Ir(1)	67.338(5)	C(28)-Ir(4A)-C(29)	39.60(15)
O(1)-Ir(3)-C(21)	148.94(12)	C(25)-Ir(4A)-C(29)	91.53(17)
O(1)-Ir(3)-C(24)	93.36(12)	O(3)-Ir(4A)-Ir(1)	85.76(7)
C(21)-Ir(3)-C(24)	82.38(13)	C(32)-Ir(4A)-Ir(1)	99.05(13)
O(1)-Ir(3)-O(2)	74.89(8)	C(28)-Ir(4A)-Ir(1)	149.26(15)
C(21)-Ir(3)-O(2)	92.29(11)	C(25)-Ir(4A)-Ir(1)	95.48(13)
C(24)-Ir(3)-O(2)	147.47(12)	C(29)-Ir(4A)-Ir(1)	169.65(14)
O(1)-Ir(3)-C(17)	98.80(12)	O(3)-Ir(4A)-Ir(3)	76.68(7)
C(21)-Ir(3)-C(17)	97.04(14)	C(32)-Ir(4A)-Ir(3)	91.06(12)
C(24)-Ir(3)-C(17)	39.17(14)	C(28)-Ir(4A)-Ir(3)	143.99(14)
O(2)-Ir(3)-C(17)	169.77(12)	C(25)-Ir(4A)-Ir(3)	123.23(11)
O(1)-Ir(3)-C(20)	171.62(11)	C(29)-Ir(4A)-Ir(3)	108.41(14)
C(21)-Ir(3)-C(20)	38.74(13)	Ir(1)-Ir(4A)-Ir(3)	61.324(12)
C(24)-Ir(3)-C(20)	91.50(14)	C(29)-Ir(4B)-O(3)	98.9(4)
O(2)-Ir(3)-C(20)	104.29(11)	C(29)-Ir(4B)-C(32)	87.8(3)
C(17)-Ir(3)-C(20)	80.76(14)	O(3)-Ir(4B)-C(32)	172.5(9)
O(1)-Ir(3)-Ir(2)	48.58(6)	C(29)-Ir(4B)-C(28)	41.25(19)
C(21)-Ir(3)-Ir(2)	101.51(10)	O(3)-Ir(4B)-C(28)	86.3(2)
C(24)-Ir(3)-Ir(2)	99.11(11)	C(32)-Ir(4B)-C(28)	96.7(3)
O(2)-Ir(3)-Ir(2)	50.38(6)	C(29)-Ir(4B)-C(25)	91.3(3)
C(17)-Ir(3)-Ir(2)	130.83(10)	O(3)-Ir(4B)-C(25)	139.5(10)
C(20)-Ir(3)-Ir(2)	137.09(9)	C(32)-Ir(4B)-C(25)	36.2(2)
O(1)-Ir(3)-Ir(4B)	89.0(3)	C(28)-Ir(4B)-C(25)	75.9(4)
C(21)-Ir(3)-Ir(4B)	117.3(3)	C(29)-Ir(4B)-Ir(3)	125.2(9)
C(24)-Ir(3)-Ir(4B)	129.9(2)	O(3)-Ir(4B)-Ir(3)	82.0(3)
O(2)-Ir(3)-Ir(4B)	81.0(3)	C(32)-Ir(4B)-Ir(3)	96.9(3)
C(17)-Ir(3)-Ir(4B)	91.0(3)	C(28)-Ir(4B)-Ir(3)	160.2(7)
C(20)-Ir(3)-Ir(4B)	82.7(3)	C(25)-Ir(4B)-Ir(3)	122.9(2)
Ir(2)-Ir(3)-Ir(4B)	118.6(4)	C(29)-Ir(4B)-Ir(1)	173.6(9)
O(1)-Ir(3)-Ir(1)	41.63(6)	O(3)-Ir(4B)-Ir(1)	80.5(3)
C(21)-Ir(3)-Ir(1)	135.50(10)	C(32)-Ir(4B)-Ir(1)	92.5(4)
C(24)-Ir(3)-Ir(1)	134.92(10)	C(28)-Ir(4B)-Ir(1)	132.4(8)
O(2)-Ir(3)-Ir(1)	43.35(6)	C(25)-Ir(4B)-Ir(1)	85.2(5)
C(17)-Ir(3)-Ir(1)	126.96(10)	Ir(3)-Ir(4B)-Ir(1)	61.11(9)
C(20)-Ir(3)-Ir(1)	132.79(9)	O(3)-Ir(5)-C(40)	160.59(11)
Ir(2)-Ir(3)-Ir(1)	56.818(4)	O(3)-Ir(5)-O(2)	82.30(9)
Ir(4B)-Ir(3)-Ir(1)	62.2(4)	C(40)-Ir(5)-O(2)	94.24(11)
O(1)-Ir(3)-Ir(4A)	83.05(7)	O(3)-Ir(5)-C(36)	90.01(11)
C(21)-Ir(3)-Ir(4A)	121.75(10)	C(40)-Ir(5)-C(36)	99.02(13)
C(24)-Ir(3)-Ir(4A)	133.66(11)	O(2)-Ir(5)-C(36)	159.56(11)
O(2)-Ir(3)-Ir(4A)	75.89(7)	O(3)-Ir(5)-C(33)	159.67(11)
C(17)-Ir(3)-Ir(4A)	95.54(11)	C(40)-Ir(5)-C(33)	39.72(13)

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O(2)-Ir(5)-C(33)	99.24(11)	O(2)-Ir(5)-C(37)	159.50(11)
C(36)-Ir(5)-C(33)	81.61(13)	C(36)-Ir(5)-C(37)	39.69(12)
O(3)-Ir(5)-C(37)	94.95(11)	C(33)-Ir(5)-C(37)	90.37(13)
C(40)-Ir(5)-C(37)	81.60(13)		

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Table 4. Bond lengths [Å] and angles [°] for IAT93 (CCDC 885854).

Ir(1)-O(1)	2.035(2)	C(10)-C(11)	1.544(5)
Ir(1)-O(2)	2.093(2)	C(11)-C(12)	1.518(5)
Ir(1)-C(4)	2.098(3)	C(12)-C(13)	1.431(5)
Ir(1)-C(1)	2.130(3)	C(13)-C(14)	1.516(5)
Ir(1)-C(5)	2.138(3)	C(14)-C(15)	1.539(5)
Ir(1)-C(8)	2.151(3)	C(15)-C(16)	1.522(4)
Ir(1)-Ir(2)	2.76162(19)	C(17)-C(24)	1.414(5)
Ir(1)-Ir(4A)	2.8508(14)	C(17)-C(18)	1.512(5)
Ir(1)-Ir(3)	3.04491(19)	C(18)-C(19)	1.529(5)
Ir(1)-Ir(4B)	3.077(12)	C(19)-C(20)	1.521(5)
Ir(2)-O(1)	2.063(2)	C(20)-C(21)	1.404(5)
Ir(2)-C(13)	2.093(3)	C(21)-C(22)	1.515(5)
Ir(2)-C(12)	2.098(3)	C(22)-C(23)	1.513(5)
Ir(2)-C(9)	2.104(3)	C(23)-C(24)	1.525(5)
Ir(2)-C(16)	2.109(3)	C(25)-C(32)	1.389(6)
Ir(2)-O(2)	2.135(2)	C(25)-C(26)	1.508(5)
Ir(2)-Ir(3)	2.7305(2)	C(26)-C(27)	1.540(5)
Ir(3)-O(1)	2.056(2)	C(27)-C(28)	1.510(5)
Ir(3)-C(21)	2.094(3)	C(28)-C(29)	1.425(6)
Ir(3)-C(24)	2.101(3)	C(29)-C(30)	1.563(6)
Ir(3)-O(2)	2.106(2)	C(30)-C(31)	1.535(7)
Ir(3)-C(17)	2.117(3)	C(31)-C(32)	1.491(7)
Ir(3)-C(20)	2.136(3)	C(33)-C(40)	1.420(5)
Ir(3)-Ir(4B)	2.906(11)	C(33)-C(34)	1.531(4)
Ir(3)-Ir(4A)	3.1046(12)	C(34)-C(35)	1.525(5)
Ir(4A)-O(3)	2.088(2)	C(35)-C(36)	1.514(5)
Ir(4A)-C(32)	2.091(4)	C(36)-C(37)	1.423(5)
Ir(4A)-C(28)	2.090(3)	C(37)-C(38)	1.516(5)
Ir(4A)-C(25)	2.099(4)	C(38)-C(39)	1.537(5)
Ir(4A)-C(29)	2.115(4)	C(39)-C(40)	1.509(5)
Ir(4B)-C(29)	1.877(11)	C(51)-Cl(1)	1.754(4)
Ir(4B)-O(3)	2.054(5)	C(51)-Cl(2)	1.759(4)
Ir(4B)-C(32)	2.086(6)		
Ir(4B)-C(28)	2.117(7)	O(1)-Ir(1)-O(2)	75.63(8)
Ir(4B)-C(25)	2.324(14)	O(1)-Ir(1)-C(4)	90.24(11)
Ir(5)-O(3)	2.053(2)	O(2)-Ir(1)-C(4)	143.76(11)
Ir(5)-C(40)	2.083(3)	O(1)-Ir(1)-C(1)	153.75(12)
Ir(5)-O(2)	2.087(2)	O(2)-Ir(1)-C(1)	96.19(11)
Ir(5)-C(36)	2.093(3)	C(4)-Ir(1)-C(1)	81.83(13)
Ir(5)-C(33)	2.095(3)	O(1)-Ir(1)-C(5)	99.54(11)
Ir(5)-C(37)	2.098(3)	O(2)-Ir(1)-C(5)	173.69(11)
C(1)-C(8)	1.402(5)	C(4)-Ir(1)-C(5)	38.84(13)
C(1)-C(2)	1.529(5)	C(1)-Ir(1)-C(5)	89.90(13)
C(2)-C(3)	1.535(5)	O(1)-Ir(1)-C(8)	167.54(12)
C(3)-C(4)	1.503(5)	O(2)-Ir(1)-C(8)	103.23(11)
C(4)-C(5)	1.409(5)	C(4)-Ir(1)-C(8)	97.29(13)
C(5)-C(6)	1.538(5)	C(1)-Ir(1)-C(8)	38.22(13)
C(6)-C(7)	1.541(5)	C(5)-Ir(1)-C(8)	80.58(12)
C(7)-C(8)	1.518(5)	O(1)-Ir(1)-Ir(2)	48.05(6)
C(9)-C(16)	1.417(5)	O(2)-Ir(1)-Ir(2)	49.87(6)
C(9)-C(10)	1.517(5)	C(4)-Ir(1)-Ir(2)	96.02(9)

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C(1)-Ir(1)-Ir(2)	107.71(10)	Ir(3)-Ir(2)-Ir(1)	67.338(5)
C(5)-Ir(1)-Ir(2)	129.53(9)	O(1)-Ir(3)-C(21)	148.94(12)
C(8)-Ir(1)-Ir(2)	139.96(9)	O(1)-Ir(3)-C(24)	93.36(12)
O(1)-Ir(1)-Ir(4A)	90.28(7)	C(21)-Ir(3)-C(24)	82.38(13)
O(2)-Ir(1)-Ir(4A)	82.20(7)	O(1)-Ir(3)-O(2)	74.89(8)
C(4)-Ir(1)-Ir(4A)	131.87(10)	C(21)-Ir(3)-O(2)	92.29(11)
C(1)-Ir(1)-Ir(4A)	113.62(10)	C(24)-Ir(3)-O(2)	147.47(12)
C(5)-Ir(1)-Ir(4A)	93.87(10)	O(1)-Ir(3)-C(17)	98.80(12)
C(8)-Ir(1)-Ir(4A)	77.30(11)	C(21)-Ir(3)-C(17)	97.04(14)
Ir(2)-Ir(1)-Ir(4A)	118.93(4)	C(24)-Ir(3)-C(17)	39.17(14)
O(1)-Ir(1)-Ir(3)	42.18(6)	O(2)-Ir(3)-C(17)	169.77(12)
O(2)-Ir(1)-Ir(3)	43.70(6)	O(1)-Ir(3)-C(20)	171.62(11)
C(4)-Ir(1)-Ir(3)	132.42(9)	C(21)-Ir(3)-C(20)	38.74(13)
C(1)-Ir(1)-Ir(3)	139.36(9)	C(24)-Ir(3)-C(20)	91.50(14)
C(5)-Ir(1)-Ir(3)	130.04(9)	O(2)-Ir(3)-C(20)	104.29(11)
C(8)-Ir(1)-Ir(3)	129.42(10)	C(17)-Ir(3)-C(20)	80.76(14)
Ir(2)-Ir(1)-Ir(3)	55.843(5)	O(1)-Ir(3)-Ir(2)	48.58(6)
Ir(4A)-Ir(1)-Ir(3)	63.45(4)	C(21)-Ir(3)-Ir(2)	101.51(10)
O(1)-Ir(1)-Ir(4B)	84.8(3)	C(24)-Ir(3)-Ir(2)	99.11(11)
O(2)-Ir(1)-Ir(4B)	77.0(3)	O(2)-Ir(3)-Ir(2)	50.38(6)
C(4)-Ir(1)-Ir(4B)	135.6(2)	C(17)-Ir(3)-Ir(2)	130.83(10)
C(1)-Ir(1)-Ir(4B)	118.2(2)	C(20)-Ir(3)-Ir(2)	137.09(9)
C(5)-Ir(1)-Ir(4B)	98.6(3)	O(1)-Ir(3)-Ir(4B)	89.0(3)
C(8)-Ir(1)-Ir(4B)	82.9(3)	C(21)-Ir(3)-Ir(4B)	117.3(3)
Ir(2)-Ir(1)-Ir(4B)	112.2(3)	C(24)-Ir(3)-Ir(4B)	129.9(2)
Ir(4A)-Ir(1)-Ir(4B)	6.8(3)	O(2)-Ir(3)-Ir(4B)	81.0(3)
Ir(3)-Ir(1)-Ir(4B)	56.7(3)	C(17)-Ir(3)-Ir(4B)	91.0(3)
O(1)-Ir(2)-C(13)	91.67(11)	C(20)-Ir(3)-Ir(4B)	82.7(3)
O(1)-Ir(2)-C(12)	96.41(11)	Ir(2)-Ir(3)-Ir(4B)	118.6(4)
C(13)-Ir(2)-C(12)	39.92(13)	O(1)-Ir(3)-Ir(1)	41.63(6)
O(1)-Ir(2)-C(9)	160.37(11)	C(21)-Ir(3)-Ir(1)	135.50(10)
C(13)-Ir(2)-C(9)	98.72(13)	C(24)-Ir(3)-Ir(1)	134.92(10)
C(12)-Ir(2)-C(9)	81.43(13)	O(2)-Ir(3)-Ir(1)	43.35(6)
O(1)-Ir(2)-C(16)	160.13(11)	C(17)-Ir(3)-Ir(1)	126.96(10)
C(13)-Ir(2)-C(16)	81.48(13)	C(20)-Ir(3)-Ir(1)	132.79(9)
C(12)-Ir(2)-C(16)	90.26(13)	Ir(2)-Ir(3)-Ir(1)	56.818(4)
C(9)-Ir(2)-C(16)	39.29(13)	Ir(4B)-Ir(3)-Ir(1)	62.2(4)
O(1)-Ir(2)-O(2)	74.16(8)	O(1)-Ir(3)-Ir(4A)	83.05(7)
C(13)-Ir(2)-O(2)	157.27(11)	C(21)-Ir(3)-Ir(4A)	121.75(10)
C(12)-Ir(2)-O(2)	156.71(11)	C(24)-Ir(3)-Ir(4A)	133.66(11)
C(9)-Ir(2)-O(2)	100.25(11)	O(2)-Ir(3)-Ir(4A)	75.89(7)
C(16)-Ir(2)-O(2)	105.83(11)	C(17)-Ir(3)-Ir(4A)	95.54(11)
O(1)-Ir(2)-Ir(3)	48.38(6)	C(20)-Ir(3)-Ir(4A)	88.65(10)
C(13)-Ir(2)-Ir(3)	107.87(10)	Ir(2)-Ir(3)-Ir(4A)	111.73(4)
C(12)-Ir(2)-Ir(3)	137.09(9)	Ir(4B)-Ir(3)-Ir(4A)	7.0(3)
C(9)-Ir(2)-Ir(3)	140.37(9)	Ir(1)-Ir(3)-Ir(4A)	55.23(4)
C(16)-Ir(2)-Ir(3)	116.12(10)	O(3)-Ir(4A)-C(32)	162.79(19)
O(2)-Ir(2)-Ir(3)	49.47(6)	O(3)-Ir(4A)-C(28)	86.10(12)
O(1)-Ir(2)-Ir(1)	47.20(6)	C(32)-Ir(4A)-C(28)	97.43(16)
C(13)-Ir(2)-Ir(1)	131.14(9)	O(3)-Ir(4A)-C(25)	157.81(16)
C(12)-Ir(2)-Ir(1)	109.49(9)	C(32)-Ir(4A)-C(25)	38.71(16)
C(9)-Ir(2)-Ir(1)	115.02(9)	C(28)-Ir(4A)-C(25)	81.58(14)
C(16)-Ir(2)-Ir(1)	146.21(9)	O(3)-Ir(4A)-C(29)	90.63(15)
O(2)-Ir(2)-Ir(1)	48.56(6)	C(32)-Ir(4A)-C(29)	81.73(18)

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C(28)-Ir(4A)-C(29)	39.60(15)	Ir(1)-O(2)-Ir(3)	92.95(9)
C(25)-Ir(4A)-C(29)	91.53(17)	Ir(5)-O(2)-Ir(2)	149.03(12)
O(3)-Ir(4A)-Ir(1)	85.76(7)	Ir(1)-O(2)-Ir(2)	81.57(8)
C(32)-Ir(4A)-Ir(1)	99.05(13)	Ir(3)-O(2)-Ir(2)	80.15(7)
C(28)-Ir(4A)-Ir(1)	149.26(15)	Ir(4B)-O(3)-Ir(5)	135.75(18)
C(25)-Ir(4A)-Ir(1)	95.48(13)	Ir(4B)-O(3)-Ir(4A)	11.5(5)
C(29)-Ir(4A)-Ir(1)	169.65(14)	Ir(5)-O(3)-Ir(4A)	132.75(12)
O(3)-Ir(4A)-Ir(3)	76.68(7)	C(8)-C(1)-C(2)	123.5(3)
C(32)-Ir(4A)-Ir(3)	91.06(12)	C(8)-C(1)-Ir(1)	71.71(19)
C(28)-Ir(4A)-Ir(3)	143.99(14)	C(2)-C(1)-Ir(1)	113.4(2)
C(25)-Ir(4A)-Ir(3)	123.23(11)	C(1)-C(2)-C(3)	110.9(3)
C(29)-Ir(4A)-Ir(3)	108.41(14)	C(4)-C(3)-C(2)	113.3(3)
Ir(1)-Ir(4A)-Ir(3)	61.324(12)	C(5)-C(4)-C(3)	125.9(3)
C(29)-Ir(4B)-O(3)	98.9(4)	C(5)-C(4)-Ir(1)	72.09(19)
C(29)-Ir(4B)-C(32)	87.8(3)	C(3)-C(4)-Ir(1)	110.8(2)
O(3)-Ir(4B)-C(32)	172.5(9)	C(4)-C(5)-C(6)	121.8(3)
C(29)-Ir(4B)-C(28)	41.25(19)	C(4)-C(5)-Ir(1)	69.07(18)
O(3)-Ir(4B)-C(28)	86.3(2)	C(6)-C(5)-Ir(1)	115.1(2)
C(32)-Ir(4B)-C(28)	96.7(3)	C(5)-C(6)-C(7)	111.8(3)
C(29)-Ir(4B)-C(25)	91.3(3)	C(8)-C(7)-C(6)	112.7(3)
O(3)-Ir(4B)-C(25)	139.5(10)	C(1)-C(8)-C(7)	123.3(3)
C(32)-Ir(4B)-C(25)	36.2(2)	C(1)-C(8)-Ir(1)	70.07(18)
C(28)-Ir(4B)-C(25)	75.9(4)	C(7)-C(8)-Ir(1)	113.1(2)
C(29)-Ir(4B)-Ir(3)	125.2(9)	C(16)-C(9)-C(10)	123.8(3)
O(3)-Ir(4B)-Ir(3)	82.0(3)	C(16)-C(9)-Ir(2)	70.56(19)
C(32)-Ir(4B)-Ir(3)	96.9(3)	C(10)-C(9)-Ir(2)	112.4(2)
C(28)-Ir(4B)-Ir(3)	160.2(7)	C(9)-C(10)-C(11)	111.8(3)
C(25)-Ir(4B)-Ir(3)	122.9(2)	C(12)-C(11)-C(10)	111.0(3)
C(29)-Ir(4B)-Ir(1)	173.6(9)	C(13)-C(12)-C(11)	122.6(3)
O(3)-Ir(4B)-Ir(1)	80.5(3)	C(13)-C(12)-Ir(2)	69.86(18)
C(32)-Ir(4B)-Ir(1)	92.5(4)	C(11)-C(12)-Ir(2)	115.3(2)
C(28)-Ir(4B)-Ir(1)	132.4(8)	C(12)-C(13)-C(14)	124.4(3)
C(25)-Ir(4B)-Ir(1)	85.2(5)	C(12)-C(13)-Ir(2)	70.22(18)
Ir(3)-Ir(4B)-Ir(1)	61.11(9)	C(14)-C(13)-Ir(2)	112.7(2)
O(3)-Ir(5)-C(40)	160.59(11)	C(13)-C(14)-C(15)	111.5(3)
O(3)-Ir(5)-O(2)	82.30(9)	C(16)-C(15)-C(14)	111.4(3)
C(40)-Ir(5)-O(2)	94.24(11)	C(9)-C(16)-C(15)	123.1(3)
O(3)-Ir(5)-C(36)	90.01(11)	C(9)-C(16)-Ir(2)	70.15(18)
C(40)-Ir(5)-C(36)	99.02(13)	C(15)-C(16)-Ir(2)	114.5(2)
O(2)-Ir(5)-C(36)	159.56(11)	C(24)-C(17)-C(18)	123.2(3)
O(3)-Ir(5)-C(33)	159.67(11)	C(24)-C(17)-Ir(3)	69.82(19)
C(40)-Ir(5)-C(33)	39.72(13)	C(18)-C(17)-Ir(3)	114.4(2)
O(2)-Ir(5)-C(33)	99.24(11)	C(17)-C(18)-C(19)	113.0(3)
C(36)-Ir(5)-C(33)	81.61(13)	C(20)-C(19)-C(18)	112.9(3)
O(3)-Ir(5)-C(37)	94.95(11)	C(21)-C(20)-C(19)	122.0(3)
C(40)-Ir(5)-C(37)	81.60(13)	C(21)-C(20)-Ir(3)	69.03(19)
O(2)-Ir(5)-C(37)	159.50(11)	C(19)-C(20)-Ir(3)	114.8(2)
C(36)-Ir(5)-C(37)	39.69(12)	C(20)-C(21)-C(22)	125.6(3)
C(33)-Ir(5)-C(37)	90.37(13)	C(20)-C(21)-Ir(3)	72.23(19)
Ir(1)-O(1)-Ir(3)	96.19(9)	C(22)-C(21)-Ir(3)	111.5(2)
Ir(1)-O(1)-Ir(2)	84.75(8)	C(23)-C(22)-C(21)	112.6(3)
Ir(3)-O(1)-Ir(2)	83.04(8)	C(22)-C(23)-C(24)	113.1(3)
Ir(5)-O(2)-Ir(1)	116.44(10)	C(17)-C(24)-C(23)	122.0(3)
Ir(5)-O(2)-Ir(3)	121.00(11)	C(17)-C(24)-Ir(3)	71.02(19)

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C(23)-C(24)-Ir(3)	113.1(2)
C(32)-C(25)-C(26)	123.0(4)
C(32)-C(25)-Ir(4A)	70.3(2)
C(26)-C(25)-Ir(4A)	115.0(2)
C(32)-C(25)-Ir(4B)	62.5(4)
C(26)-C(25)-Ir(4B)	114.3(3)
Ir(4A)-C(25)-Ir(4B)	9.1(3)
C(25)-C(26)-C(27)	112.2(3)
C(28)-C(27)-C(26)	112.3(3)
C(29)-C(28)-C(27)	124.5(4)
C(29)-C(28)-Ir(4A)	71.2(2)
C(27)-C(28)-Ir(4A)	113.3(3)
C(29)-C(28)-Ir(4B)	60.3(6)
C(27)-C(28)-Ir(4B)	121.2(5)
Ir(4A)-C(28)-Ir(4B)	11.3(5)
C(28)-C(29)-C(30)	120.9(4)
C(28)-C(29)-Ir(4B)	78.5(6)
C(30)-C(29)-Ir(4B)	112.1(4)
C(28)-C(29)-Ir(4A)	69.2(2)
C(30)-C(29)-Ir(4A)	113.2(3)
Ir(4B)-C(29)-Ir(4A)	9.8(5)
C(31)-C(30)-C(29)	113.2(4)
C(32)-C(31)-C(30)	112.3(4)
C(25)-C(32)-C(31)	121.7(4)
C(25)-C(32)-Ir(4B)	81.3(6)
C(31)-C(32)-Ir(4B)	106.7(5)
C(25)-C(32)-Ir(4A)	71.0(2)
C(31)-C(32)-Ir(4A)	116.1(3)
Ir(4B)-C(32)-Ir(4A)	11.4(5)
C(40)-C(33)-C(34)	123.5(3)
C(40)-C(33)-Ir(5)	69.68(18)
C(34)-C(33)-Ir(5)	114.5(2)
C(35)-C(34)-C(33)	110.7(3)
C(36)-C(35)-C(34)	112.0(3)
C(37)-C(36)-C(35)	125.0(3)
C(37)-C(36)-Ir(5)	70.34(18)
C(35)-C(36)-Ir(5)	111.8(2)
C(36)-C(37)-C(38)	123.3(3)
C(36)-C(37)-Ir(5)	69.97(18)
C(38)-C(37)-Ir(5)	114.7(2)
C(37)-C(38)-C(39)	111.1(3)
C(40)-C(39)-C(38)	111.9(3)
C(33)-C(40)-C(39)	124.0(3)
C(33)-C(40)-Ir(5)	70.59(18)
C(39)-C(40)-Ir(5)	112.7(2)
Cl(1)-C(51)-Cl(2)	112.5(2)

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Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for IAT93 (CCDC 885854). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ir(1)	97(1)	112(1)	83(1)	-2(1)	12(1)	-6(1)
Ir(2)	100(1)	87(1)	97(1)	2(1)	21(1)	-3(1)
Ir(3)	113(1)	88(1)	95(1)	-1(1)	11(1)	-19(1)
Ir(4A)	172(2)	127(2)	105(2)	37(2)	42(2)	51(2)
Ir(4B)	200(20)	111(15)	126(14)	21(12)	50(16)	48(15)
Ir(5)	104(1)	90(1)	80(1)	7(1)	18(1)	0(1)
O(1)	141(11)	105(11)	93(10)	-4(9)	14(8)	-18(9)
O(2)	88(10)	123(12)	111(11)	-3(9)	1(8)	-11(8)
O(3)	196(12)	121(12)	113(11)	52(9)	45(9)	33(9)
C(1)	129(15)	241(19)	96(14)	-3(13)	33(12)	-88(13)
C(2)	260(20)	250(20)	179(17)	-32(15)	57(15)	-123(16)
C(3)	267(19)	184(19)	149(16)	-52(14)	50(14)	-77(15)
C(4)	142(16)	178(17)	109(15)	-44(13)	34(12)	-24(13)
C(5)	128(16)	240(20)	111(15)	-23(13)	-5(12)	-21(13)
C(6)	142(17)	410(30)	150(17)	33(16)	-7(13)	-7(16)
C(7)	104(16)	400(30)	191(18)	23(17)	19(13)	10(15)
C(8)	101(15)	270(20)	127(15)	11(14)	50(12)	-2(13)
C(9)	139(16)	130(16)	152(16)	38(12)	46(12)	26(12)
C(10)	194(17)	115(16)	230(18)	23(14)	54(14)	-2(13)
C(11)	203(17)	149(18)	177(17)	-27(14)	25(14)	6(14)
C(12)	178(16)	139(17)	134(15)	-9(13)	48(13)	4(13)
C(13)	124(15)	150(17)	163(16)	24(13)	83(12)	34(12)
C(14)	149(17)	250(20)	211(18)	55(15)	37(14)	27(14)
C(15)	116(16)	198(19)	208(17)	6(14)	-9(13)	9(13)
C(16)	158(16)	160(17)	122(15)	45(13)	19(12)	35(13)
C(17)	276(19)	135(17)	169(17)	18(13)	59(14)	-92(14)
C(18)	460(30)	150(20)	320(20)	0(17)	51(19)	-128(18)
C(19)	350(20)	164(19)	250(20)	-62(15)	22(17)	-60(16)
C(20)	183(17)	153(17)	149(16)	-30(13)	-9(13)	-32(13)
C(21)	163(16)	224(19)	115(15)	-3(13)	11(12)	-28(14)
C(22)	198(19)	400(30)	173(18)	-8(17)	-38(14)	16(17)
C(23)	159(18)	440(30)	230(20)	-11(18)	-35(15)	-61(17)
C(24)	142(16)	260(20)	171(17)	-2(14)	57(13)	-91(14)
C(25)	470(30)	260(20)	134(17)	54(15)	93(17)	182(19)
C(26)	420(20)	320(20)	133(17)	51(16)	10(16)	139(19)
C(27)	420(20)	370(30)	192(19)	44(18)	-15(17)	240(20)
C(28)	290(20)	201(19)	134(16)	36(14)	74(14)	135(15)
C(29)	420(20)	135(19)	330(20)	27(17)	-10(19)	89(17)
C(30)	500(30)	190(20)	730(40)	180(20)	-40(30)	10(20)
C(31)	410(30)	440(30)	470(30)	210(20)	60(20)	10(20)
C(32)	430(30)	340(30)	280(20)	215(19)	183(19)	170(20)
C(33)	176(16)	117(16)	120(15)	0(12)	47(12)	-17(13)
C(34)	215(18)	100(16)	230(18)	-13(14)	79(14)	-40(13)
C(35)	182(17)	177(18)	216(18)	-10(14)	50(14)	-25(14)
C(36)	152(16)	140(17)	120(15)	15(12)	34(12)	7(12)
C(37)	163(16)	143(17)	118(15)	-10(12)	43(12)	7(13)
C(38)	201(17)	202(19)	111(15)	-15(13)	14(13)	26(14)

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C(39)	247(19)	194(19)	109(15)	10(13)	-30(14)	4(15)
C(40)	164(16)	117(16)	138(15)	44(12)	27(12)	32(13)
C(51)	280(20)	300(20)	250(20)	-108(17)	68(16)	-57(17)
Cl(1)	217(5)	450(7)	571(8)	-169(6)	-43(5)	-25(5)
Cl(2)	216(4)	240(5)	240(5)	-61(4)	-8(3)	0(4)
