

Supporting Information:

## **Stereoselective Synthesis of Cyclometalated Iridium (III) Complexes: Characterization and Photophysical Properties**

Liangru Yang,<sup>a,b</sup> Alex von Zelewsky,<sup>\*,b</sup> Huong P. Nguyen,<sup>c</sup> Gilles Muller,<sup>c</sup> Gaël Labat,<sup>d</sup> and Helen Stoeckli-Evans<sup>d</sup>

School of Chemistry and Chemical Engineering, He'nan University of Technology, 450001 He'nan, P. R. China; Department of Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland; Department of Chemistry, San José State University, One Washington Square, San José, CA 95192-0101, United States and Institute of Microtechnology, University of Neuchâtel, 2002 Neuchâtel, Switzerland.

### **Experimental Section**

Iridium trichloride hydrate (0.8 mmol) was combined with (8*R*, 10*R*)-2-(2'-phenyl)-5,6-pinenopyridine (HL<sup>II</sup>) (2.4 mmol), dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and heated at 110 °C for 24 h. After removal of the solvent, the residue was purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>). Complex **1**, [Ir(L<sup>II</sup>)<sub>2</sub>(μ-Cl)]<sub>2</sub> (190 mg, 33%) was obtained as a red powder. Yellow-orange crystals obtained from **1**, which was obtained by slow diffusion of hexane into a dichloromethane solution of complex **1** containing small amounts (1 drop) of acetonitrile, turned out to be

$\text{Ir(L}^{\text{II}}\text{)}_2(\text{CH}_3\text{CN})\text{Cl}\cdot(\text{CH}_2\text{Cl}_2)_{0.25}$ . Complex **1** 80 mg (0.055 mmol), 2,4-pentanedione 17 mg (0.17 mmol), and sodium carbonate 58 mg (0.55 mmol) were refluxed under argon in 2-ethoxyethanol (10 mL) for 12 h. After removal of the solvent, the residue was purified by column chromatography (silica,  $\text{CH}_2\text{Cl}_2$ ). Pure complex **2**,  $\Delta\text{-Ir(L}^{\text{II}}\text{)}_2(\text{acac})$  (20 mg, 23 %) as a light yellow solid was obtained. Crystals of **2** were obtained as yellow plates by slow diffusion of hexane into a dichloromethane solution.

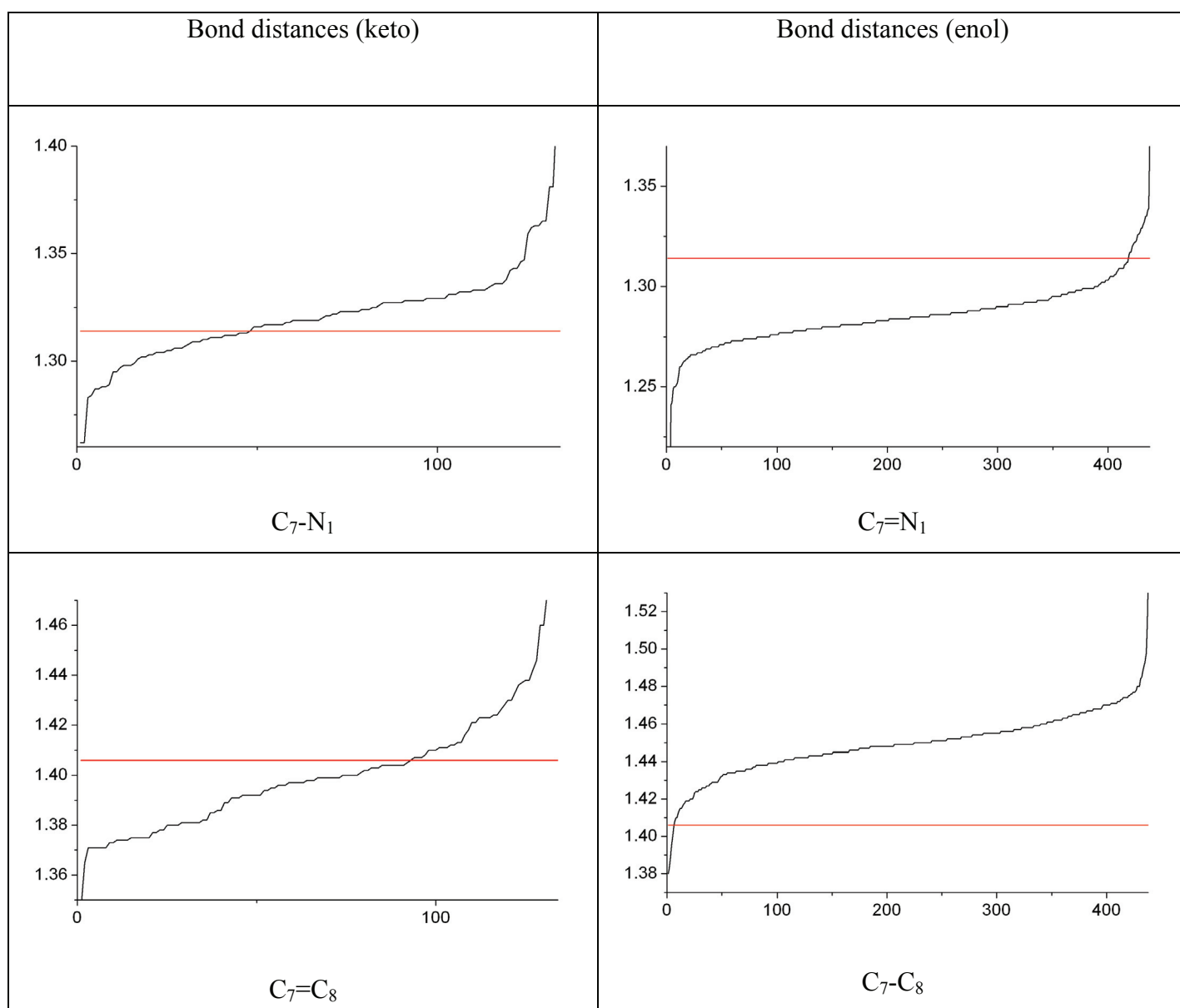
Complex **1**:  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.67 (m, 4H; H-3); 7.55 (m, 4H; H-6'); 7.44 (m, 4H; H-4); 6.89 (m, 4H; H-5'); 6.63 (m, 4H; H-4'); 6.03 (m, 4H; H-3'); 4.70 (m, 4H; H-7a); 2.91 (m, 4H; H-7b); 2.75 (m, 4H; H-9<sub>exo</sub>); 2.65 (m, 4H; H-10); 2.28 (m, 4H; H-8); 1.47 (d,  $J = 9.7$ , 2H; H-9<sub>endo-a</sub>); 1.42 (s, 6H; H-13a); 1.39 (s, 6H; H-13b); 1.22 (d,  $J = 9.6$ , 2H; H-9<sub>endo-b</sub>); 0.92 (s, 6H; H-12a); 0.69 (s, 6H; H-12b).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  163.8; 163.4; 160.5; 160.3; 144.84; 144.80; 142.1; 141.8; 134.8; 134.7; 134.6; 134.2; 133.4; 132.8; 127.9; 127.6; 123.10; 123.08; 122.05; 122.0; 114.8; 46.9; 46.8; 40.3; 39.8; 38.8; 37.1; 36.5; 32.0; 31.6; 31.2; 25.9; 25.7; 22.1; 21.5. Anal. Calcd. for  $\text{C}_{72}\text{H}_{72}\text{Cl}_2\text{Ir}_2\text{N}_4$ : C, 59.69; H, 5.01; N, 3.87. Found: C, 59.72; H, 5.11; N, 3.89%. UV-vis ( $\lambda$  in nm ( $\epsilon$ ,  $\text{M}^{-1}\text{ cm}^{-1}$ );  $\text{CH}_2\text{Cl}_2$ ,  $1.0 \times 10^{-5}$  M): 262 (132 900); 278 (123 500); 319 (49 100); 339 (36 000); 382 (15 200); 499 (5 900).

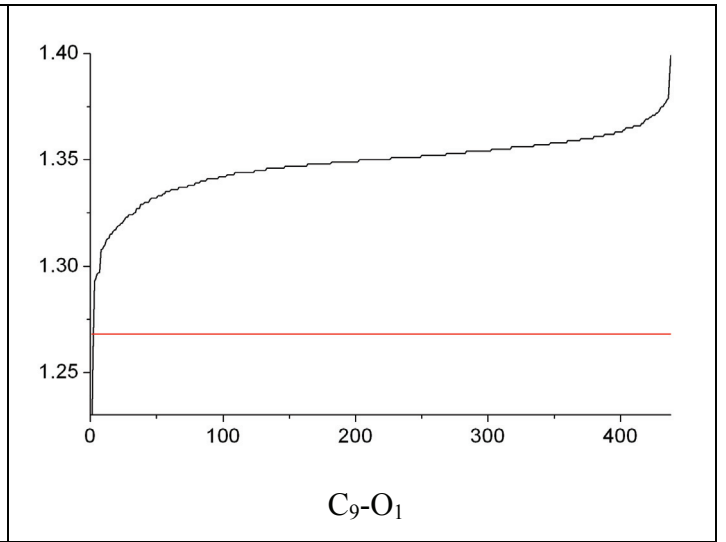
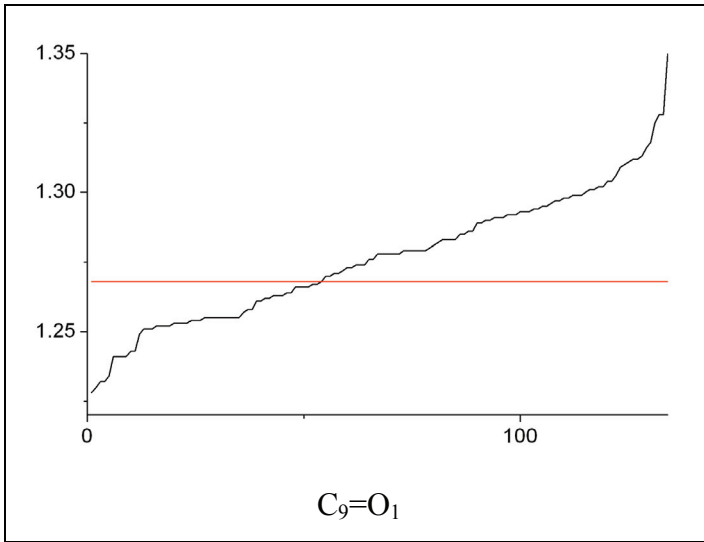
Complex **2**:  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.60 (d,  $J = 8.1$ , 2H; H-3); 7.50 (dd,  $J = 1.3$ ,  $J = 7.8$ , 2H; H-6'); 7.33 (d,  $J = 8.1$ , 2H; H-4); 6.82 (dt,  $J = 1.3$ ,  $J = 6.5$ , 2H; H-5'); 6.63 (dd,  $J = 1.3$ ,  $J = 6.5$ , 2H; H-4'); 6.33 (dd,  $J = 1.3$ ,  $J = 7.8$ , 2H; H-3'); 5.33 (s, 1H; COCHCO); 3.34 (dd,  $J = 2.7$ ,  $J = 18.6$ , 2H; H-7a); 3.14 (dd,  $J = 3.3$ ,  $J = 18.6$ , 2H; H-7b); 2.84 (t,  $J = 5.5$ , 2H;

H-9<sub>exo</sub>); 2.65 (m, 2H; H-10); 2.22 (m, 2H; H-8); 1.61 (s, 6H; COCH<sub>3</sub>); 1.39 (s, 6H; H-13); 1.27 (d,  $J = 9.45$ , 2H; H-9<sub>endo</sub>); 0.70 (s, 6H; H-12). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  185.8; 166.5; 161.2; 147.5; 144.3; 141.5; 135.2; 134.3; 128.0; 123.4; 121.2; 115.0; 101.7; 47.4; 40.6; 39.1; 36.1; 31.5; 28.1; 25.7; 21.0. Anal. Calcd. for C<sub>41</sub>H<sub>44</sub>IrN<sub>2</sub>O<sub>2</sub>: C, 62.41; H, 5.62; N, 3.55. Found: C, 62.21; H, 5.49; N, 3.32%. UV-vis ( $\lambda$  in nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>); CH<sub>2</sub>Cl<sub>2</sub>, 1.0  $\times$  10<sup>-5</sup> M): 273 (43 100); 311 (26 200); 368 (5 700). CD ( $\lambda$  in nm ( $\Delta\epsilon$ ); CH<sub>2</sub>Cl<sub>2</sub>, 1.0  $\times$  10<sup>-5</sup> M): 264 (-18); 286 (-15); 311 (3); 331 (-12); 357 (3); 377 (-2).

Supplementary information:

Figure S1: Search performed in the CSD, the y-axis unit is Å while the x-axis is the number of hits obtained in the database. Bond distances for each hit is ordered ascending and are represented with the black line, the red flat one being for the distance of the corresponding bond.





# checkCIF/PLATON report

No syntax errors found.    CIF dictionary    Interpreting this report

## Datablock: cpd2

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Bond precision:    C-C = 0.0095 A                      Wavelength=0.71073

Cell:    a=13.5401(8)    b=13.5401(8)    c=18.8928(12)  
          alpha=90            beta=90            gamma=120

	Calculated	Reported
Volume	2999.7(3)	2999.6(3)
Space group	P 31 2 1	P 31 2 1
Hall group	P 31 2"	P 31 2"
Moiety formula	C41 H44 Ir N2 O2	C36 H36 IR N2, (C5 H8 O2), (H2 O)
Sum formula	C41 H44 Ir N2 O2	C41 H46 IR N2 O3
Mr	789.00	807.00
Dx,g cm-3	1.310	1.340
Z	3	3
Mu (mm-1)	3.371	3.374
F000	1191.0	1221.0
F000'	1187.14	
h,k,lmax	16,16,23	16,16,23
Nref	2215( 3915)	3844
Tmin,Tmax	0.378,0.430	0.346,0.422
Tmin'	0.378	

Correction method= 'MULTI-SCAN'

Data completeness= 1.74(0.98)                      Theta(max)= 25.940

R(reflections)= 0.0301( 3009)                      wR2(reflections)= 0.0614( 3844)

S = 0.874

Npar= 212

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The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

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### Alert level A

PLAT035\_ALERT\_1\_A No \_chemical\_absolute\_configuration info given .                      ?

PLAT601\_ALERT\_2\_A Structure Contains Solvent Accessible VOIDS of .                      546.00 A\*\*3

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### Alert level C

CHEMW03\_ALERT\_2\_C The ratio of given/expected molecular weight as

calculated from the \_atom\_site\* data lies outside  
the range 0.99 <> 1.01

From the CIF: \_cell\_formula\_units\_Z 3  
From the CIF: \_chemical\_formula\_weight 807.00  
TEST: Calculate formula weight from \_atom\_site\*

atom	mass	num	sum
C	12.01	41.00	492.45
H	1.01	44.00	44.35
N	14.01	2.00	28.01
O	16.00	2.00	32.00
Ir	192.22	1.00	192.22

Calculated formula weight 789.03

PLAT041\_ALERT\_1\_C Calc. and Rep. SumFormula Strings Differ .... ?  
PLAT042\_ALERT\_1\_C Calc. and Rep. MoietyFormula Strings Differ .... ?  
PLAT043\_ALERT\_1\_C Check Reported Molecular Weight ..... 807.00  
PLAT068\_ALERT\_1\_C Reported F000 Differs from Calcd (or Missing)... ?  
PLAT220\_ALERT\_2\_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 2.76 Ratio  
PLAT222\_ALERT\_3\_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.03 Ratio  
PLAT342\_ALERT\_3\_C Low Bond Precision on C-C bonds (x 1000) Ang ... 10  
PLAT366\_ALERT\_2\_C Short? C(sp?)-C(sp?) Bond C19 - C20 ... 1.39 Ang.  
PLAT710\_ALERT\_4\_C Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 65  
C2 -C1 -IR1 -O1 -29.00 2.00 1.555 1.555 1.555 1.555  
PLAT710\_ALERT\_4\_C Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 66  
C6 -C1 -IR1 -O1 145.50 1.90 1.555 1.555 1.555 1.555  
PLAT710\_ALERT\_4\_C Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 71  
C11 -N1 -IR1 -N1 -124.30 0.50 1.555 1.555 1.555 6.556  
PLAT710\_ALERT\_4\_C Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 72  
C7 -N1 -IR1 -N1 51.50 0.40 1.555 1.555 1.555 6.556  
PLAT710\_ALERT\_4\_C Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 77  
C19 -O1 -IR1 -C1 -67.00 2.00 1.555 1.555 1.555 1.555

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### Alert level G

FORMU01\_ALERT\_2\_G There is a discrepancy between the atom counts in the  
\_chemical\_formula\_sum and the formula from the \_atom\_site\* data.  
Atom count from \_chemical\_formula\_sum: C41 H46 Ir1 N2 O3  
Atom count from the \_atom\_site data: C41 H44 Ir1 N2 O2

CELLZ01\_ALERT\_1\_G Difference between formula and atom\_site contents detected.

CELLZ01\_ALERT\_1\_G ALERT: Large difference may be due to a  
symmetry error - see SYMMG tests

From the CIF: \_cell\_formula\_units\_Z 3  
From the CIF: \_chemical\_formula\_sum C41 H46 Ir N2 O3  
TEST: Compare cell contents of formula and atom\_site data

atom	Z*formula	cif sites	diff
C	123.00	123.00	0.00
H	138.00	132.00	6.00
Ir	3.00	3.00	0.00
N	6.00	6.00	0.00
O	9.00	6.00	3.00

REFLT03\_ALERT\_4\_G Please check that the estimate of the number of Friedel pairs is  
correct. If it is not, please give the correct count in the  
\_publ\_section\_exptl\_refinement section of the submitted CIF.

From the CIF: \_diffn\_refl\_theta\_max 25.94  
From the CIF: \_reflns\_number\_total 3844  
Count of symmetry unique reflns 2215  
Completeness (\_total/calc) 173.54%  
TEST3: Check Friedels for noncentro structure  
Estimate of Friedel pairs measured 1629  
Fraction of Friedel pairs measured 0.735  
Are heavy atom types Z>Si present yes

PLAT199_ALERT_1_G	Check the Reported _cell_measurement_temperature	293 K
PLAT200_ALERT_1_G	Check the Reported _diffrn_ambient_temperature .	293 K
PLAT791_ALERT_1_G	Confirm the Absolute Configuration of C12 = .	R
PLAT791_ALERT_1_G	Confirm the Absolute Configuration of C14 = .	R

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2 **ALERT level A** = In general: serious problem  
0 **ALERT level B** = Potentially serious problem  
14 **ALERT level C** = Check and explain  
8 **ALERT level G** = General alerts; check

11 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
5 ALERT type 2 Indicator that the structure model may be wrong or deficient  
2 ALERT type 3 Indicator that the structure quality may be low  
6 ALERT type 4 Improvement, methodology, query or suggestion  
0 ALERT type 5 Informative message, check

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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C or E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 14/11/2006; check.def file version of 13/11/2006

Datablock cpd2 - ellipsoid plot

