Supporting Information:

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

Liangru Yang,[a,b] Alex von Zelewsky,*[,b] Huong P. Nguyen,[c] Gilles Muller,[c] Gaël Labat,[d] and Helen Stoeckli-Evans[d]

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^{II}) (2.4 mmol), dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and heated at 110 ^{o}C for 24 h. After removal of the solvent, the residue was purified by column chromatography (silica, CH_2Cl_2). Complex **1**, $[Ir(L^{II})_2(\mu\text{–}Cl)]_2$ (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

$Ir(L^{II})_2(CH_3CN)Cl\cdot(CH_2Cl_2)_{0.25}$. 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, CH_2Cl_2). Pure complex **2**, Δ-$Ir(L^{II})_2$(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.

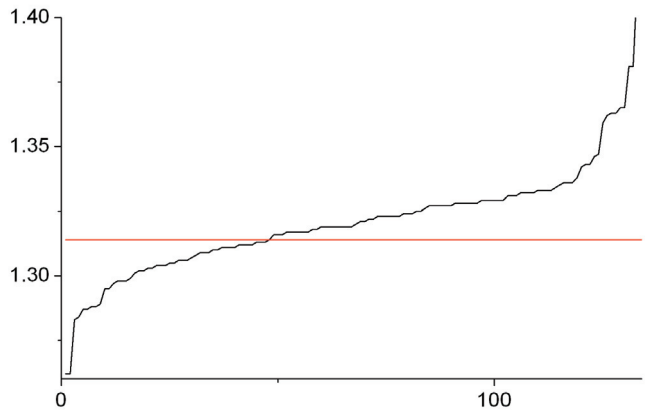
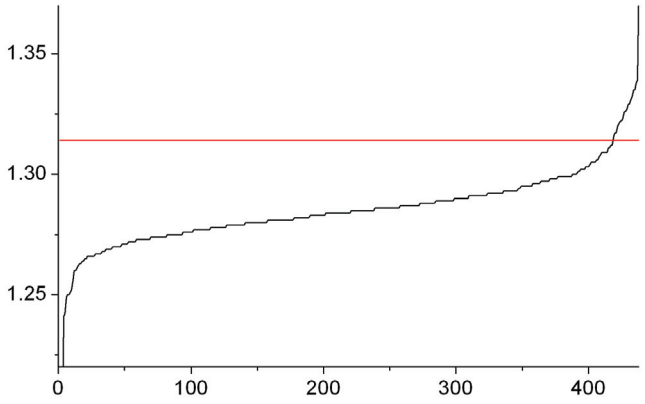
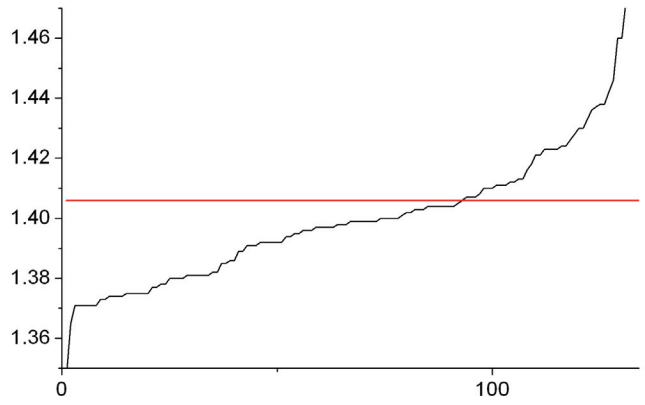
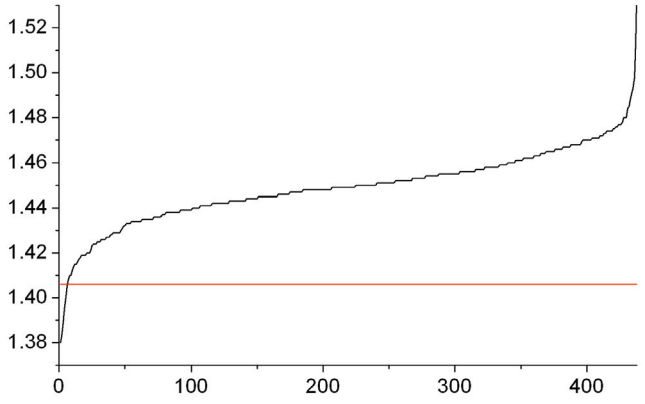
Complex **1**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.67 (m, 4H; H-3); 7.55 (m, 4H; H-6'); 7.44 (m, 4H; H-4); 6.89 (m, 4H; H-5'); 6.63 (m, 4H; H-4'); 6.03 (m, 4H; H-3'); 4.70 (m, 4H; H-7a); 2.91 (m, 4H; H-7b); 2.75(m, 4H; H-9exo); 2.65 (m, 4H; H-10); 2.28 (m, 4H; H-8); 1.47 (d, *J* = 9.7, 2H; H-9endo-a); 1.42 (s, 6H; H-13a); 1.39 (s, 6H; H-13b); 1.22 (d, *J* = 9.6, 2H; H-9endo-b); 0.92 (s, 6H; H-12a); 0.69 (s, 6H; H-12b). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 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 $C_{72}H_{72}Cl_2Ir_2N_4$: C, 59.69; H, 5.01; N, 3.87. Found: C, 59.72; H, 5.11; N, 3.89%. UV-vis (λ in nm (ε, M^{-1} cm^{-1}); CH_2Cl_2, 1.0×10^{-5} M): 262 (132 900); 278 (123 500); 319 (49 100); 339 (36 000); 382 (15 200); 499 (5 900).

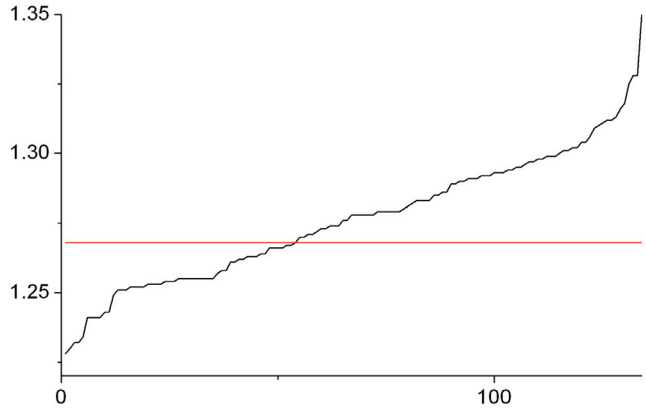
Complex **2**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.60 (d, *J* = 8.1, 2H; H-3); 7.50 (dd, *J* = 1.3, *J* = 7.8, 2H; H-6'); 7.33 (d, *J* = 8.1, 2H; H-4); 6.82 (dt, *J* = 1.3, *J* = 6.5, 2H; H-5'); 6.63 (dd, *J* = 1.3, *J* = 6.5, 2H; H-4'); 6.33 (dd, *J* = 1.3, *J* =7.8, 2H; H-3'); 5.33 (s, 1H; CO*CH*CO); 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-9exo); 2.65 (m, 2H; H-10); 2.22 (m, 2H; H-8); 1.61 (s, 6H; CO*CH*$_3$); 1.39 (s, 6H; H-13); 1.27 (d, *J* = 9.45, 2H; H-9endo); 0.70 (s, 6H; H-12). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 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 $C_{41}H_{44}IrN_2O_2$: C, 62.41; H, 5.62; N, 3.55. Found: C, 62.21; H, 5.49; N, 3.32%. UV-vis (λ in nm (ε, M^{-1} cm^{-1}); CH_2Cl_2, 1.0 × 10^{-5} M): 273 (43 100); 311 (26 200); 368 (5 700). CD (λ in nm (Δε); CH_2Cl_2, 1.0 × 10^{-5} M): 264 (-18); 286 (-15); 311 (3); 331 (-12); 357 (3); 377 (-2).

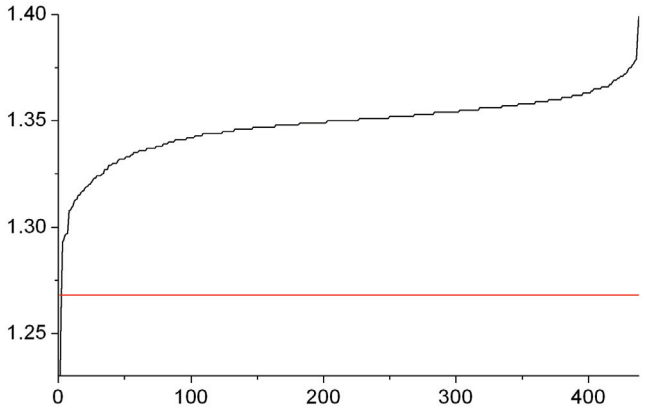
Supplementary information:

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.

Bond distances (keto)	Bond distances (enol)
 C_7-N_1	 C_7=N_1
 C_7=C_8	 C_7-C_8



C_9=O_1



C_9-O_1

checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: cpd2

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

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.

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

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
```

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: _diffrn_reflns_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
```

```
   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
```

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