Supporting Information

Synthesis and Structural Characterization of a Binuclear Iridium Complex with Bridging Bidentate N-Heterocycle Carbene Coordination of 2,2′:6′,2′′-Terpyridine

General Experimental:

All common reagents were obtained from commercial suppliers and were used without further purification. Tetrahydrofuran and Et_2O were distilled from sodium benzophenone ketyl. All other solvents used for preparation of products, chromatography and crystallization were reagent grade. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ was obtained by the published procedure[1]. Infrared spectra were recorded on a Bruker Vector 22 spectrometer. UV-Vis spectra were obtained with a Varian Cary-100-Conc. NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetrametylsilane and are referenced to the carbon and the residual protio resonances of the deuterated solvent. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate.

[1] O. Boutry, M. L. Poveda and E. Carmona, *J. Organomet. Chem.*, 1997, **528**, 143.

X-Ray crystal structure analyses of 2_M, 2_T (2_M is the monoclinic form of the compound 2 and 2_T is the triclinic form) and 3:

A suitable single crystal of each representative compound was mounted on a glass fibre using perfluoropolyether oil (FOMBLIN® 140/13, Aldrich) under the cold N_2 stream of the low-temperature device attachment. Intensity data for complexes **2** and **3** were collected on a Bruker-AXS X8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Mo $K_{\alpha1}$ (λ = 0.71073 Å) and a Bruker Cryo-Flex low-temperature device. The data collection strategy used in all instances was phi and omega scans with narrow frames. Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times and no decay was observed. The data were reduced (SAINT)[2] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (SADABS)[3] . The structures were solved by direct methods (SIR-2002)[4] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.14)[5] minimizing $w[Fo^2\text{-}Fc^2]^2$. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bonded to the nitrogen atoms were located from the difference Fourier synthesis and refined isotropically with geometric restraints. The other hydrogen atoms were placed in calculated positions and refined with isotropic displacement parameters by using a riding model.

[2] SAINT+, Bruker-APEX 2 package. Version 2.1. Bruker Analytical X-ray Solutions, Madison, Wisconsin, USA (2006).

[3] SADABS, Bruker-APEX 2 package. Version 2.1. Bruker Analytical X-ray Solutions, Madison, Wisconsin, USA (2006).

[4] M.C.Burla, M. Camalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna SIR2002: the program; J. Appl. Cryst, (2003). 36, 1103

[5] SHELXTL 6.14, Bruker AXS, Inc., Madison, Wisconsin, USA, 2000–2003.

Crystal data for **2_M**. $C_{36}H_{43}BIrN_9$, Mw = 804.80, plate red crystal, size: 0.27 x 0.18 x 0.15 mm^3, monoclinic, space group $P2_1/n$, a = 12.0676(3) Å, b = 22.2040(7) Å, c = 13.7392(4) Å, β = 108.8360(10)º, V = 3484.25(17) Å^3, T = 173(2) K, , Z = 4, D = 1.534 Mg/m^3, ρ = 3.872 mm^{-1}, F(000) = 1616; 91260 reflections measured, of which 10431 were unique (R_{int} = 0.0388). The asymmetric unit of the structure is formed by one mononuclear Ir(III) complex **2**. In this monoclinic polymorph of **2** the polypyridine moiety occupies a region of the space opposite to that of the Tp^{Me2} ligand and features a "*trans-trans*" conformation of the pyridine rings. 435 Refined parameters, final R_1 = 0.0226 for reflections with I > 2σ(I), wR_2 = 0.0533 (all data), GOF = 1.041. Final largest diffraction peak and hole: 1.193 and -0.801 e. Å^{-3}. CCDC 731545.

Crystal data for **2_T**. $C_{74}H_{91}B_2Ir_2N_{18}O$, $[2(C_{36}H_{43}BIrN_9), 0.5(C_4H_{10}O)]$, Mw = 1654.71, plate red crystal, size: 0.28 x 0.14 x 0.10 mm^3, triclinic, space group $P\bar{1}$, a = 10.2938(15) Å, b = 11.8722(17) Å, c = 16.064(2) Å, α = 100.103(4)º, β = 102.473(3)º, γ = 95.845(3)º, V = 1867.1(5) Å^3, T = 223(2) K, , Z = 1, D = 1.472 Mg/m^3, ρ = 3.616 mm^{-1}, F(000) = 833; 44999 reflections measured, of which 7919 were unique (R_{int} = 0.0695). The asymmetric unit of the structure is formed by one mononuclear Ir(III) complex **2** and a half solvation diethyl ether molecule. In the triclinic crystal form of **2**, the polypyridine moiety occupies an adjacent region of the space to that of the Tp^{Me2} ligand and features a "*cis-trans*" conformation of the pyridine rings. The solvent diethyl ether molecule was observed close a crystallographic inversion centre. In this way, there are no atoms on the special position, but nevertheless the diethyl ether molecule is disordered around the inversion centre in a 1:1 ratio. Therefore in the refinement the disordered atoms have been flanked by PART -1 and PART 0 and the site occupation factors fixed to 0.5, taking into account the multiplicity of this special position. Several geometric restraints (DFIX commands) were needed to maintain a reasonable molecular geometry and other restraints (SIMU, DELU) have been used to make the ADP values of the disordered atoms more reasonable. 480 Refined parameters, final R_1 = 0.0499 for reflections with I > 2σ(I), wR_2 = 0.1364 (all data), GOF = 1.115. Final largest diffraction peak and hole: 2.631 and -2.369 e. Å^{-3}. CCDC 731546.

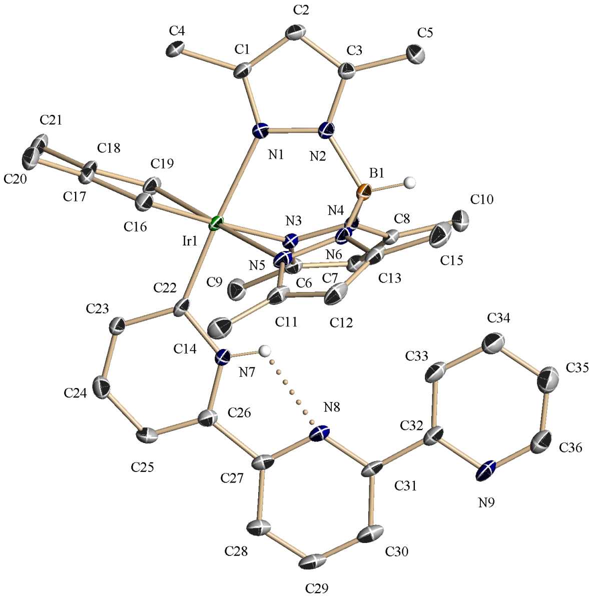


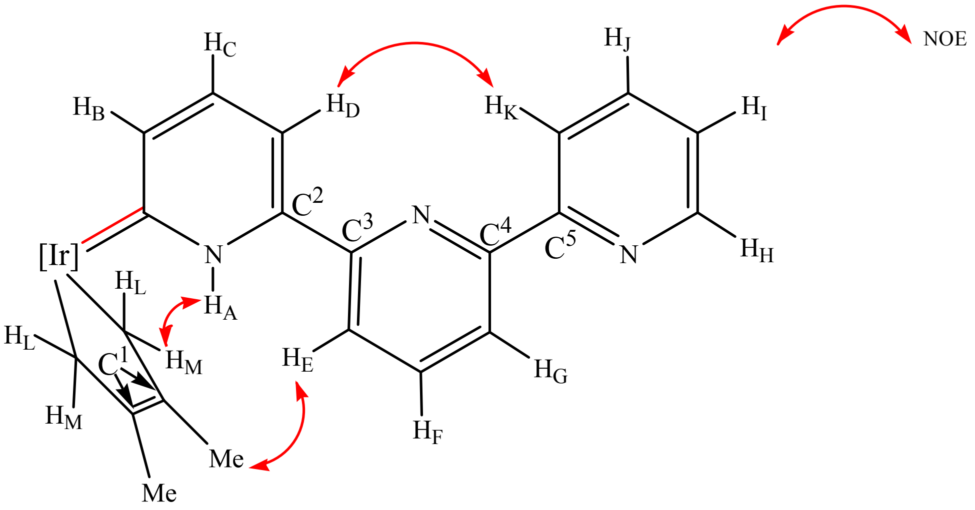
Fig. S1 Perspective view of **2_T**, the triclinic polymorph of compound **2**.

Crystal data for **3**. $C_{61}H_{83}B_2Ir_2N_{15}O$, [$C_{57}H_{75}B_2Ir_2N_{15}$, C_4H_8O], Mw = 1448.44, plate red crystal, size: 0.11 x 0.05 x 0.03 mm^3, triclinic, space group P$\bar{1}$, a = 10.9949(9) Å, b = 17.1764(14) Å, c = 17.3819(14) Å, α = 104.057(2)º, β = 102.473(3)º, γ = 93.350(2)º, V = 3093.4(4) Å^3, T = 173(2) K, , Z = 2, D = 1.555 Mg/m^3, ρ = 4.351 mm^{-1}, F(000) = 1452; 40562 reflections measured, of which 12549 were unique (R_{int} = 0.0967). The asymmetric unit of the structure is formed by one binuclear Ir(III) complex **3** and one solvation THF molecule. The solvent THF molecule was observed disordered in two positions. The occupancy factors for these two disordered moieties were first refined and the latest stages of refinement, due to the convergence, were both fixed to 0.5. All the non-hydrogen atoms were refined with anisotropic displacement parameters. 797 Refined parameters, final R_1 = 0.0498 for reflections with I > 2σ(I), wR_2 = 0.1021 (all data), GOF = 1.001. Final largest diffraction peak and hole: 1.437 and -1.205 e. Å^{-3}. CCDC 731547.

Synthesis of compounds 2 and 3:

The compound Tp^{Me2}Ir(η^4-CH_2=C(Me)C(Me)=CH_2) (**1**) (0.1 g, 0.175 mmol) and 2,2′:6′,2′′-terpyrydine (0.086 g, 0.35 mmol) were heated, with stirring, in 4 mL of C_6H_{12} at 90 ºC for 20 hours. The solvent was evaporated under vacuum and the solid residue dissolved in CH_2Cl_2 and subjected to column chromatography on silica gel, using first a mixture of n-hexane:diethyl ether (19:1) to elute complex **3** as a dark red solid. A second fraction (complex **2**) was obtained using a mixture of hexane:diethyl ether (9:1) as the eluent. This compound is a bright red solid that was recrystallized from a mixture of dichloromethane:dietyl ether (**2_T**) or dichloromethane:pentane (**2_M**). Yield 37%.

Spectroscopic and analytical data for 2:



IR (KBr): ν(N-H) 3225, ν(B-H) 2520 cm^{-1}.

^{1}H NMR ($CDCl_3$, 25 ºC): δ = 11.80 (br, 1 H, NH_A), 8.72 (d, 1 H, H_H), 8.56 (d, 1 H, H_K), 8.54 (d, 1 H, H_G), 8.01 (t, 1 H, H_F), 7.92 (t, 1 H, H_J), 7.71 (d, 1 H, H_E), 7.59 (d, 1 H, H_D), 7.38 (dd, 1 H, H_I), 7.04 (d, 1 H, H_B), 6.95, (t, 1 H, H_C), 5.69, 5.67 (s, 1:2, 3 CH_{pz}), 3.14 (d, 2 H, $^2J_{HH}$ = 14.4 Hz, 2 IrC$\mathit{H}_L$$H_M$,), 2.42 (d, 2 H, 2 IrC$H_L$$\mathit{H}_M$), 2.39, 2.37, 2.05, 1.62 (s, 2:1:1:2, 6 Me_{pz}), 1.83 (s, 6 H, 2 Me). All $^3J_{HH}$ aromatics ≈ 7.5 Hz except $^3J_{HI}$ = 4.5 Hz.

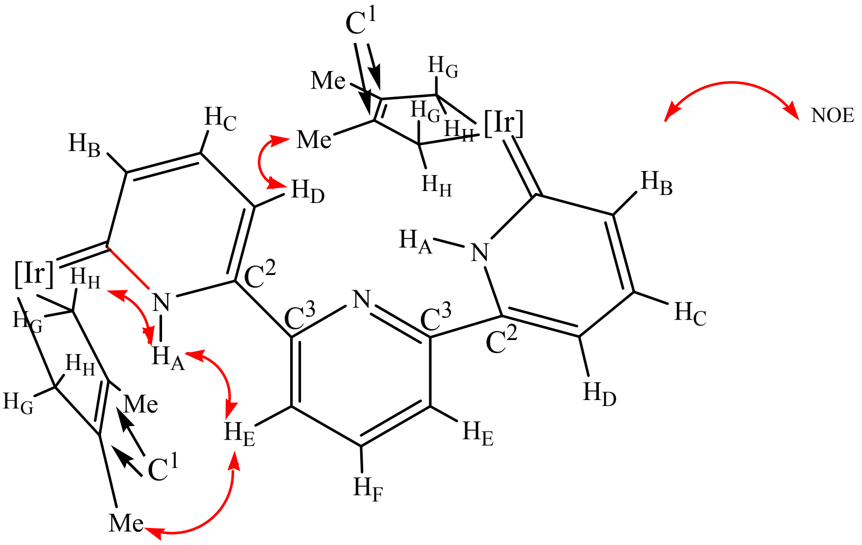
^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC): δ = 185.7 (Ir=C), 156.0 (C^4), 155.1 (C^5), 150.9, 149.3 (1:2, C$_{qpz}$), 149.8 (C^3), 148.9 (CH$_H$), 146.9 (C^2), 143.9 (CH$_B$), 143.1, 142.2 (1:2, C$_{qpz}$), 142.5 (2 C^1), 138.3 (CH$_F$), 137.5 (CH$_J$), 130.3 (CH$_C$), 124.3 (CH$_I$), 121.8, 121.8 (CH$_K$, CH$_G$), 119.2 (CH$_E$), 111.8 (CH$_D$), 107.6, 106.4 (1:2, CH$_{pz}$), 19.9 (2 Me), 14.1, 13.1, 12.8, 11.2 (2:1:2:1, Me$_{pz}$), 12.0 (2 IrCH$_2$, $^1J_{CH}$ = 121 Hz).

Elemental analysis: Found: C, 53.9; H, 5.6; N, 15.2. Calc. for $C_{36}H_{43}BIrN_9$: C, 53.7; H, 5.4; N, 15.6.

HRMS *m/z* calcd. for $C_{36}H_{43}BIrN_9$ (epxt.): 804.3286 (804.3281).

As discussed in the text, using a **1**:terpy ratio of 2, complex **3** becomes the major product. Following chromatography it can be recrystallized from a mixture of tetrahydrofuran:pentane. Starting with 0.1 g of **1** the yield of **3** was 64%.

Spectroscopic and analytical data for 3:



IR (KBr): ν(N-H) 3175, ν(B-H) 2520 cm^{-1}.

^{1}H NMR (CDCl$_3$, 25 ºC): δ = 11.76 (br, 2 H, 2 NH$_A$), 8.04 (t, 1 H, H$_F$), 7.72 (d, 2 H, 2 H$_E$), 7.53 (d, 2 H, 2 H$_D$), 7.07 (d, 2 H, 2 H$_B$), 6.98 (t, 2 H, 2 H$_C$), 5.69, 5.66 (s, 1:2, 6 CH$_{pz}$), 3.15 (d, 4 H, $^2J_{HH}$ = 14.6 Hz, 2 IrCH_GH$_H$,), 2.38 (d, 4 H, 2 IrCH$_G$$H_H$), 2.38, 2.36, 2.03, 1.61 (s, 2:1:1:2, 12 Me$_{pz}$), 1.81 (s, 12 H, 4 Me). All $^3J_{HH}$ aromatics ≈ 7.5 Hz.

^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC): δ = 186.0 (2 Ir=C), 151.1, 149.1 (1:2, 6 C$_{qpz}$), 150.8 (2 C^3), 146.1 (2 C^2), 144.2 (2 CH$_B$), 143.1, 142.1 (1:2, 6 C$_{qpz}$), 142.4 (4 C^1), 138.6 (CH$_F$), 130.1 (2 CH$_C$), 119.3 (2 CH$_E$), 112,3 (2 CH$_D$), 107.5, 106.2 (1:2, 6 CH$_{pz}$), 19.7 (4 Me), 13.8, 12.9, 12.6, 11.1 (2:1:2:1, 12 Me$_{pz}$), 12 (4 IrCH$_2$).

Elemental analysis: Found: C, 50.6; H, 5.7; N, 14.5. Calc. for $C_{57}H_{75}B_2Ir_2N_{15}$: C, 49.7; H, 5.5; N, 15.2.

UV-Vis spectra of compounds 2 and 3

UV-Vis absorptions are given below and have been graphically represented in Fig. S2. Acetonitrile solutions of **2** and **3** are characterized by peaks in the range 240 to 310 nm, with extinction coefficients of the order 10^4-10^5 M^{-1} cm^{-1} that may be assigned to ligand-centred π-π* transitions. A somewhat weaker absorption (ε ≈ 10^4 M-1) centred around 370 nm is probably due predominantly to metal-ligand-charge-transfer.

UV absorptions: λ_{max}(MeCN)/nm (ε/dm^3 mol^{-1} cm^{-1}). Compound **2**: 193 (10^5), 279 ($2.5x10^4$), 305 ($2.1x10^4$), 370 ($7.2x10^3$). Compound **3**: 193 ($1.4x10^5$), 308 ($2.7x10^4$), 370 ($1.3x10^4$).

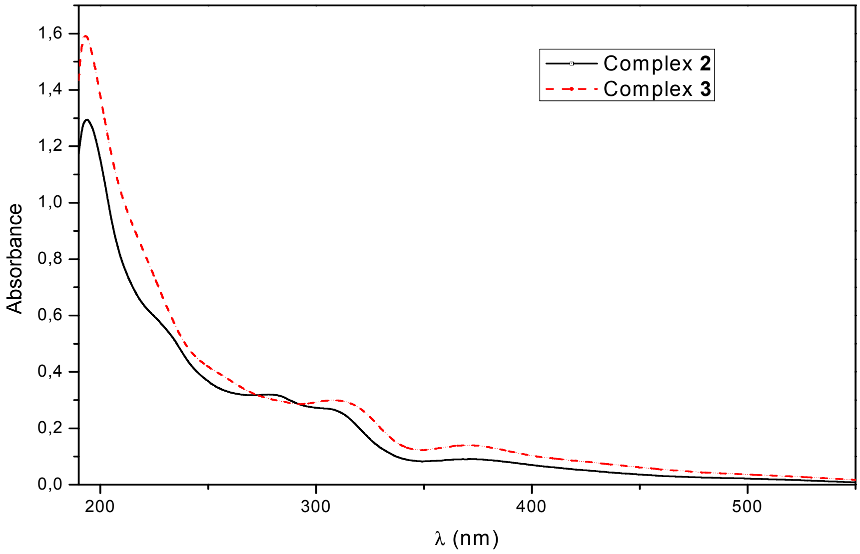


Fig. S2 UV-Vis absorption spectra of **2** (—) and **3** (---) in acetonitrile solutions.