Supplementary and Supporting Information for Group 9 Metallocorroles

Characterization data:

Figure 1: 300 MHz $^1$H NMR of 1-Ir(py)$_2$. 
Figure 2: 300 MHz $^{19}$F NMR of 1-Ir(py)$_2$.

Figure 3: ESI-MS of 1-Ir(py)$_2$. 
Figure 4: 300 MHz $^1$H NMR of 1-Ir(PPh$_3$).

Figure 5: 300 MHz $^{19}$F NMR of 1-Ir(PPh$_3$).
**Notes on synthesis:**

A number of corroles with different substituted pyridines could be synthesized using the same technique as was utilized for the creation of complex 1-Ir(py)₂. The ligands attached to iridium corroles in this manner include 4-cyanopyridine, 4-methoxypyridine, 3,5-dichloropyridine, and 3,5-bis(trifluoromethyl)pyridine. In all cases, the primary product was the six-coordinate bis-pyridine complex.

**Synthetic summary for substituted bis-pyridine iridium(III) corroles:**

**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis-4-cyanopyridine.**

H₃tpfc (40 mg), [Ir(cod)Cl]₂ (170 mg), and K₂CO₃ (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Cyanopyridine (105 mg) was added, and the solution was allowed to slowly cool to room temperature.
temperature while open to the laboratory atmosphere. Column chromatography of the red-green mixture (silica, 4:1 hexanes:CH₂Cl₂ followed by 2:3 hexanes:CH₂Cl₂) provided a bright red solution which upon evaporation provided (tpfc)Ir(III)(4-CNpy)₂ (36 mg, 66% yield) as a purple solid. ¹H NMR (CDCl₃): δ 8.91 (d, 2H, J = 4.5), 8.60 (d, 2H, J = 5.1), 8.39 (d, 2H, J = 4.8), 8.26 (d, 2H, J = 4.5), 5.43 (d/d, 4H, 3J = 6.9, 4J = -4.2), 1.75 (d/d, 4H, 3J = 6.9, 4J = -3.9). ¹⁹F NMR (CDCl₃): δ -138.38 (d/d, 2F, 3J = 34.8, 4J = 17.4), -138.95 (d/d, 4F, 3J = 34.8, 4J = 17.4), -153.75 (t, 2F, J = 22.5), -154.11 (t, 1F, J = 22.2), -162.48 (m, 4F). MS (ESI): 1089.0 ([M⁺-4-CNpy]), 986.1 ([M⁺-2(4-CNpy)]) UV-vis (CH₂Cl₂, nm, ε x 10⁻³ M⁻¹cm⁻¹): 388 (8.8), 406 (14), 580 (4.2), 608 (2.8).

5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis-4-methoxypyridine.  
H₃tpfc (40 mg), [Ir(cod)Cl]₂ (170 mg), and K₂CO₃ (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 4-Methoxypyridine (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the dark green mixture (silica, 4:1 hexanes:CH₂Cl₂ followed by 2:3 hexanes:CH₂Cl₂) provided an olive solution which upon evaporation provided (tpfc)Ir(III)(4-MeOpy)₂ (28 mg, 50% yield) as a dark green solid. ¹H NMR (CDCl₃): δ 8.81 (d, 2H, J = 4.2), 8.49 (d, 2H, J = 4.5), 8.31 (d, 2H, J = 4.5), 8.12 (d, 2H, J = 3.9), 4.69 (d/d, 4H, 3J = 7.2, 4J = -4.5), 2.93 (s, 6H), 1.56 (m, 4H). ¹⁹F NMR (CDCl₃): δ -138.40 (d/d, 2F, 3J = 35.7, 4J = 17.4), -138.64 (d/d, 4F, 3J = 35.7, 4J = 17.4), -154.98 (t, 2F, J = 22.5), -155.35 (t, 1F, J = 22.4), -163.33 (m, 4F). -163.69 (m, 2F). UV-vis (CH₂Cl₂, nm, ε x 10⁻³ M⁻¹cm⁻¹): 394 (42), 412 (57), 394 (42), 412 (57).
**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis[3,5-bis(trifluoromethyl)pyridine].** H₃tpfc (40 mg), [Ir(cod)Cl]₂ (170 mg), and K₂CO₃ (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-bis-trifluoromethylpyridine (215 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the deep green mixture (silica, 4:1 hexanes:CH₂Cl₂ followed by 100% CH₂Cl₂) provided a red-green solution, which upon evaporation yielded (tpfc)Ir[3,5-(CF₃)₂py]₂ (13 mg, 20% yield) as a filmy red-purple solid. ¹H NMR (CDCl₃): δ 9.00 (d, 2H, J = 4.2), 8.70 (d, 2H, J = 4.8), 8.44 (d, 2H, J = 4.8), 8.38 (d, 2H, J = 4.2), 6.65 (s, 2H), 1.97 (s, 4H). ¹⁹F NMR (CDCl₃): δ = -64.29 (t, 12F, J = 7.5), -138.47 (m, 6F), -153.52 (t, 2F, J = 22.2), -153.82 (m, 1F), -162.35 (m, 6F). UV-vis (CH₂Cl₂, nm, ε x 10⁻³ M⁻¹cm⁻¹): 384 (9.7), 406 (15), 580 (4.5), 602 (2.8).

**5,10,15-tris-pentafluorophenylcorrolato-iridium(III) bis[3,5-dichloropyridine].** H₃tpfc (40 mg), [Ir(cod)Cl]₂ (170 mg), and K₂CO₃ (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. 3,5-dichloropyridine (150 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the bright green mixture (silica, 4:1 hexanes:CH₂Cl₂ followed by 100% CH₂Cl₂) provided a vivid green solution, from which dark green crystals of (tpfc)Ir(3,5-Cl₂py)₂ (27 mg, 47% yield) could be grown by addition of toluene followed by slow evaporation. ¹H NMR (CDCl₃): δ 8.91 (d, 2H, J = 4.2), 8.64 (d, 2H, J = 4.5), 8.40 (d, 2H, J = 4.5), 8.30 (d, 2H, J = 4.2), 6.16 (t, 2H, J = 1.8), 1.52 (d, 4H, J = 1.8). ¹⁹F NMR (CDCl₃): δ -137.49 (d/d, 2F, ³J = 34.8, ⁴J = 17.7), -137.71 (d/d, 4F, ³J = 34.8, ⁴J =
17.1), -153.87 (t, 2F, J = 22.5), -154.28 (t, 1F, J = 22.2), -162.39 (m, 4F), -162.82 (m, 2F). UV-vis (CH₂Cl₂, nm, ε x 10⁻³ M⁻¹cm⁻¹): 390 (26), 406 (38), 580 (12), 608 (7.3).

Titrations not included in the main body of the article:

Figure 7: Changes to the electronic absorption spectrum of 1-Co(PPh₃) in CH₂Cl₂ upon addition of excess PPh₃.
Figure 8: Reaction of 1-Co(PPh₃) with iodine in CH₂Cl₂.

Figure 9: Reaction of 1-Rh(PPh₃) with iodine in CH₂Cl₂.
Figure 10: Reaction of 1-Ir(PPh₃) with iodine in CH₂Cl₂.

Figure 11: Electronic absorption spectrum of 1-Co(py)₂ in 5% pyridine/CH₂Cl₂.
Figure 12: Electronic absorption spectrum of 1-Ir(PPh₃) in 5% pyridine/CH₂Cl₂, showing that 1-Ir(PPh₃) is not converted to 1-Ir(py)₂ under these conditions.
Figure 13: EPR spectrum, taken at 20K in frozen toluene, of singly oxidized corrole 1-Co(PPh$_3$).
Figure 14: EPR spectrum, taken at 20K in frozen toluene, of singly oxidized corrole 1-Rh(PPh₃).