

Supporting Information

Aromatic Alkyne Insertion into Six-membered Cyclometalated Pyridine Complexes of Iridium: Different Insertion Modes and Structurally Novel Products

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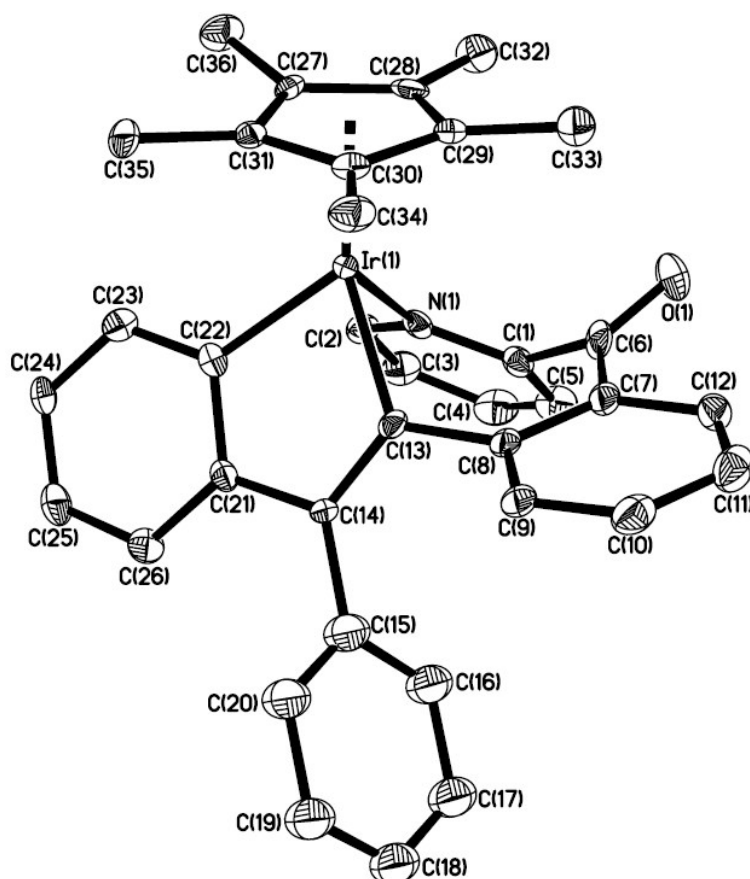


Figure 1. Thermal ellipsoid drawing of **5a** showing the labeling scheme and 30% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ir(1)–N(1) 2.088(6), Ir(1)–C(13) 2.055(7), Ir(1)–C(22) 2.048(6), C(13)–C(14) 1.361(10), C(8)–C(13) 1.466(10), Ir(1)–Cp(centroid) 1.864, $\angle$ N(1)–Ir(1)–C(13) 80.7(2), $\angle$ N(1)–Ir(1)–C(22) 86.5(3), $\angle$ C(13)–Ir(1)–C(22) 78.2(3), $\angle$ Ir(1)–C(13)–C(14) 117.9(5), $\angle$ Ir(1)–C(13)–C(8) 119.9(5).

Table S1. Crystal Data and Summary of X-ray Data Collection for **3**, **4c**, **5a**, and **6c**

	3	4c	5a	6c
formula	C ₂₃ H ₂₅ Cl ₃ NORh	C ₃₀ H ₂₇ FIrNO	C ₃₆ H ₃₂ IrNO	C ₅₂ H ₄₃ Br ₄ Cl ₅ IrNO
fw	540. 70	628. 72	686.82	1386. 96
<i>T</i> (K)	104. 66 (14)	157. 39 (15)	99.99(10)	134. 5 (7)
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic
space group	Pca2 ₁	P-1	Pca2 ₁	C2/c
<i>a</i> (Å)	26. 166 (5)	13. 1460 (4)	17.5282(5)	23. 3666 (4)
<i>b</i> (Å)	10. 162 (2)	14. 8634 (4)	11.5480(3)	18. 5319 (4)
<i>c</i> (Å)	8. 6509 (17)	27. 0887 (9)	13.7850(4)	23. 8394 (4)
α (deg)	90	82. 995 (2)	90	90
β (deg)	90	79. 253 (3)	90	101. 9383 (18)
γ (deg)	90	89. 665 (2)	90	90
<i>V</i> (Å ³)	2300. 3 (8)	5160. 5 (3)	2790.31(12)	10099. 8 (3)
<i>Z</i>	4	8	4	8
<i>D</i> _{calc} (g·cm ⁻³)	1.561	1.618	1.635	1.824
μ (mm ⁻¹)	1.105	10. 245	4.815	11. 563
<i>F</i> (000)	1096.0	2464.0	1360.0	5376.0
cryst size (mm)	0.20 × 0.17 × 0.15	0.25 × 0.22 × 0.2	0.25 × 0.22 × 0.2	0.22 × 0.21 × 0.2
max. 2 θ (deg)	50. 014	134. 154	50.018	134. 156
no. of reflns collected	15348	54956	23163	19852
no. of indep reflns/ <i>R</i> _{int}	3372/0.0567	18399/0.0912	4480/0.0523	9000/0.0349
no. of params	268	1245	357	582
goodness-of-fit on <i>F</i> ²	1.078	1.031	1.051	1.015
<i>R</i> _{<i>I</i>} , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0310, 0.0757	0.0830, 0.1989	0.0233, 0.0469	0.0410, 0.0983
<i>R</i> _{<i>I</i>} , w <i>R</i> ₂ (all data)	0.0323, 0.0765	0.1048, 0.2110	0.0276, 0.0490	0.0499, 0.1035
largest diff peak and hole (e Å ⁻³)	1.19, -0.51	7.08, -2.60	0.79, -0.57	2.13, -1.06

Table S2. Crystal Data and Summary of X-ray Data Collection for **7**, **8b**, and **9**

	7	8b	9
formula	C ₃₇ H ₃₅ ClIrNO ₃	C ₃₈ H ₃₈ IrNO ₂	C ₆₉ H ₄₇ BF ₂₄ IrNO
fw	769.31	732.89	1565.08
<i>T</i> (K)	151.0 (3)	143.2 (3)	296(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	P2 ₁ /n	P2 ₁ /c	P-1
<i>a</i> (Å)	8.2945 (2)	10.6814 (5)	14.5879(15)
<i>b</i> (Å)	24.4790 (7)	15.2053 (7)	15.7035(16)
<i>c</i> (Å)	15.6644 (4)	18.9380 (8)	17.2298(17)
α (deg)	90	90	107.147(2)
β (deg)	101.702 (3)	101.078 (4)	105.890(2)
γ (deg)	90	90	109.408(2)
<i>V</i> (Å ³)	3114.40 (16)	3018.5 (2)	3240.5(6)
<i>Z</i>	4	4	2
<i>D</i> _{calc} (g·cm ⁻³)	1.641	1.613	1.604
μ (mm ⁻¹)	9.385	4.459	2.174
<i>F</i> (000)	1528.0	1464.0	1548
cryst size (mm)	0.25 × 0.22 × 0.2	0.25 × 0.22 × 0.2	0.22 × 0.21 × 0.2
max. 2 θ (deg)	134.156	50.02	53.00
no. of reflns collected	15453	13794	19099
no. of indep reflns/ <i>R</i> _{int}	5547/0.0487	5309/0.0390	13261/0.0175
no. of params	396	386	884
goodness-of-fit on <i>F</i> ²	1.057	1.020	1.041
<i>R</i> _I , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0311, 0.0667	0.0306, 0.0576	0.0372, 0.0899
<i>R</i> _I , w <i>R</i> ₂ (all data)	0.0420, 0.0723	0.0411, 0.0616	0.0473, 0.0935
largest diff peak and hole (e Å ⁻³)	1.18, -0.71	1.46, -0.86	0.755, -0.599