Supporting Information

Bi- and tri-metallic Rh and Ir complexes containing click derived (pyrazolyl-*1,2,3*-triazolyl) N-N' donor ligands and their application as alkyne dihydroalkoxylation catalysts

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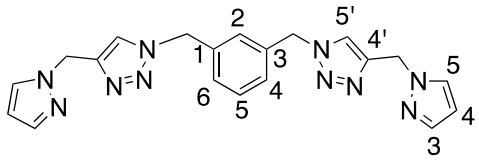
S1. Synthesis of Ligands

S1.1 Synthesis of m-C_6H_4(PyT)$_2$ (1b)



m-C_6H_4(PyT)$_2$ **1b**

Dimethylsulfoxide (30 mL) was added to a flask containing sodium azide (1.27 g, 21.0 mmol) under an atmosphere of nitrogen and the reaction mixture was stirred at room temperature for 1 hour. 1,3-*Bis*(bromomethyl)benzene (2.64 g, 20.0 mmol) was added and the yellow solution was stirred overnight. 1-Propargylpyrazole (2.13 g, 20.0 mmol) was then added to the reaction mixture and the reaction mixture was deoxygenated by briefly putting the reaction flask under vacuum and refilling with nitrogen (house vacuum *ca.* 20 mmHg, x3)Sodium L-ascorbate (0.800 g, 4.0 mmol, 40 mol%) and $CuSO_4.5H_2O$ (0.250 g, 5.0 mmol, 10 mol%) were added to the reaction mixture and the reaction mixture was stirred overnight at room temperature.

The reaction mixture was poured into a saturated aqueous Na_2EDTA solution (100 mL), extracted with dichloromethane (3 x 150 mL), washed with saturated aqueous Na_2EDTA (5 x 30 mL, until the Na_2EDTA layer became colourless) and water (2 x 30 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent was removed *in vacuo* to afford a very pale yellow solid. The crude product was purified by recrystallization from hot methanol to afford the ligand *m*-C_6H_4(PyT)$_2$ (**1b**) as white needle-like crystals. Yield: 3.53 g, 88%; m.p. 159-161 °C.

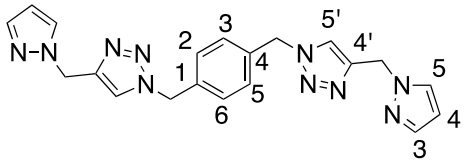
Elemental analysis, found: C, 59.50; H, 4.99 and N, 35.23; calculated for $C_{10}H_{20}N_{10}$: C, 59.99; H, 5.03 and N, 34.98%.

ESI-MS (ESI$^+$, acetonitrile): *m/z* (%, assignment): 423.15 (100, $[M+Na]^+$) amu.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, ^3J = 2.2 Hz, 2H, Pz-**H**3), 7.50 (d, ^3J = 1.9 Hz, 2H, Pz-**H**5), 7.43 (s, 2H, Tz-**H**5'), 7.35 (t, ^3J = 7.6 Hz, 1H, C_6H_4-**H**5), 7.20 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 2H, *m*-C_6H_4-**H**4 and **H**6), 7.13 (s, 1H, C_6H_4-**H**2), 6.26 (apparent t, ^3J = 2.0 Hz, 2H, Pz-**H**4), 5.45 (s, 4H, Tz-NC**H**$_2$), 5.42 (s, 4H, Pz-N**C**H$_2$) ppm.

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 144.20 (Tz-**C**4'), 139.89 (Pz-**C**3), 135.51 (C_6H_4-**C**1 and **C**3), 130.04 (C_6H_4-**C**5), 129.50 (Pz-**C**5), 128.41 (C_6H_4-**C**4 and **C**6), 127.54 (C_6H_4-**C**2), 122.57 (Tz-**C**5'), 106.12 (Pz-**C**4), 53.80 (TzN-**C**H_2), 47.38 (Pz-N**C**H_2) ppm.

S1.2 Synthesis of p-C_6H_4(PyT)$_2$ (1c)



p-C_6H_4(PyT)$_2$ **1c**

Dimethylsulfoxide (40 mL) was added to a flask containing sodium azide (1.37 g, 21. 0 mmol) and the mixture was stirred at room temperature for one hour. 1,4-*Bis*(bromomethyl)benzene (2.64 g, 10.0 mmol) was then added and the reaction mixture was stirred at room temperature under nitrogen for one day. 1-Propargylpyrazole (2.13 g, 20.0 mmol) was added. The reaction mixture was deoxygenated by briefly putting the reaction flask under vacuum and refilling with nitrogen (house vacuum *ca.* 20 mmHg, x3). Sodium L-ascorbate (0.800 g, 4.00 mmol) and $CuSO_4.5H_2O$ (0.250 g, 1.00 mmol) were added to the reaction mixture and the reaction mixture was stirred at room temperature for 48 hours.

The reaction mixture was poured into an aqueous saturated Na_2EDTA solution with rigorous stirring. A white precipitate formed together with a yellow green solution. The precipitate was collected by filtration, washed with saturated aqueous Na_2EDTA until the filtrate become colourless (15 x 15 mL) and water (5 x 20 mL). The precipitate was air dried and then dried in a vacuum desiccator for two days. Yield: 3.29 g, 82%; m.p. 221-223 °C.

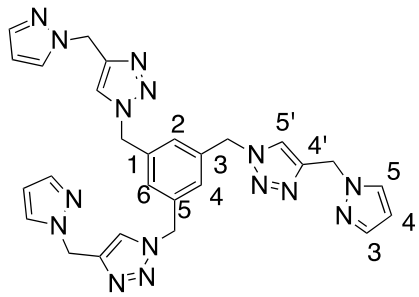
Elemental analysis, found: C, 59.31; H, 4.95; N, 34.59; calculated for $C_{10}H_{20}N_{10}.0.25H_2O$: C, 59.32; H, 5.10; N, 34.59 %.

HR-MS (ESI^+, MeOH): *m/z* (%, assignment): 423.2500 (100, $[M+Na]^+$), 401.3333 (10, $[M+H]^+$) amu.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.51 (d, ^{3}J = 2.1 Hz, 2H, Pz-**H**5), 7.50 (d, ^{3}J = 1.7 Hz, 2H, Pz-**H**3), 7.43 (s, 2H, Tz-**H**5'), 7.24 (s, 4H, C_6H_4-**H**), 6.25 (apparent t, ^{3}J = 1.9 Hz, 2H, Pz-**H**4), 5.47 (s, 4H, Tz-N**C**H_2), 5.42 (s, 4H, Pz-N**C**H_2) ppm.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 144.35 (Tz-**C**4'), 140.03 (Pz-**C**3), 135.28 (*ipso*-**C** of C_6H_4), 129.63 (C_6H_4-**C**H), 128.96 (Pz-**C**5), 122.66 (Tz-**C**5'), 106.26 (Pz-**C**4), 53.86 (Tz-N**C**H_2), 47.54 (Pz-N**C**H_2) ppm.

S1.3 Synthesis of 1,3,5-C_6H_3(PyT)$_3$ (1d)



1,3,5-C_6H_3(PyT)$_3$ **1d**

Dimethylsulfoxide (30 mL) was added to a flask containing sodium azide (1.07 g, 16.5 mmol) under an atmosphere of nitrogen. The reaction mixture was stirred under nitrogen for 1 hour and 1,3,5-*tris*(bromomethyl)benzene (1.78 g, 5.0 mmol) was added, the brownish yellow solution obtained was stirred at room temperature for three days. 1-Propargylpyrazole (1.59 g, 15.0 mmol) was added and the reaction mixture was deoxygenated by placing it under vacuum and refilling with nitrogen (x3). Sodium L-ascorbate (0.60 g, 3.0 mmol) and $CuSO_4.5H_2O$ (0.187 g, 0.75 mmol) were added to the reaction mixture and the reaction mixture was stirred for one week at room temperature. The reaction mixture was poured into saturated aqueous Na_2EDTA (150 mL) and stirred vigorously for 30 minutes at room temperature. A white solid precipitate formed, together with some brown solid and a yellowish green solution. The mixture was extracted with dichloromethane (5 x 120 mL). The combined organic layer was washed with aqueous saturated Na_2EDTA (5 x 30 mL), water (2 x 30 mL) and dried over anhydrous magnesium sulfate before it was filtered through a pad of Celite. The solvent was removed *in vacuo* to afford an off-white solid.

Yield: 1.59 g, 57%; m.p. 147-149 °C.

Elemental analysis, found: C, 57.47; H, 4.84 and N, 37.48; calculated for $C_{27}H_{27}N_{15}$: C, 57.41; H, 4.85 and N, 37.41%.

MS (ESI, MeOH): *m/z* (%, assignment): 584.20 ($[M+Na]^+$, 100) amu.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, ^3J = 2.1 Hz, 3H, Pz-**H**5), 7.50 (d, ^3J = 1.7 Hz, 3H, Pz-**H**3), 7.45 (s, 3H, Tz-**H**5'), 7.06 (s, 3H, C_6H_3C**H**), 6.25 (apparent t, ^3J = 1.9 Hz, 3H, Pz-**H**4), 5.42 (s, 6H, Tz-N**C**H_2), 5.39 (s, 6H, Pz-N**C**H_2) ppm.

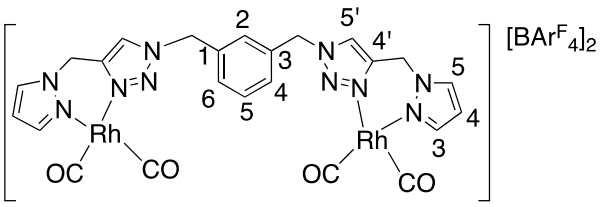
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.35 (Tz-**C**4'), 139.98 (Pz-**C**3), 136.77 (*ipso*-**C** of C_6H_3), 129.74 (Pz-**C**5), 127.78 (C_6H_3**C**H), 122.90 (Tz-**C**5'), 106.26 (Pz-**C**4), 53.43 (Pz-N**C**H_2), 47.39 (Tz-N**C**H_2) ppm.

^{1}H NMR (600 MHz, dmso-d_6): δ 8.05 (s, 3H), 7.77 (s, 3H), 7.45 (s, 3H), 7.25 (s, 3H), 6.26 (s, 3H), 5.55 (s, 6H), 5.40 (s, 6H) ppm.

^{13}C{^{1}H} NMR (150MHz, dmso-d_6): δ 138.94, 137.11, 129.88, 127.55, 123.88, 105.48, 52.29 and 46.37 ppm.

S2. Synthesis of $Rh(CO)_2$ Complexes

S2.1 Synthesis of m-C_6H_4[(PyT)Rh(CO)$_2$]$_2$[BAr$^F{}_4$]$_2$ (2b)



Dichloromethane (25 mL) was added to a flask containing $[Rh(Cl)(CO)_2]_2$ (0.039 g, 0.10 mmol) and *m*-$C_6H_4(PyT)_2$ (**1b**, 0.040 g, 0.10 mmol) under an atmosphere of argon. The pale yellow solution was stirred at room temperature for 45 minutes. $NaBAr^F{}_4$ (0.177 g, 0.20 mmol) was added and the reaction mixture was stirred at room temperature for one hour. The reaction mixture was filtered through a pad of Celite, rinsed with dichloromethane (2 x 15 mL) and the solvent was reduced *in vacuo* until about 3 mL of solvent left. Pentane (30 mL) was added to the reaction mixture with rigorous stirring. The solid and oil mixture obtained was collected by filtration, washed with pentane (2 x 5 mL) and dried *in vacuo* to afford complex **2b** as a bright yellow solid. Yield: 0.225 g, 92%; m.p. 65-70 °C.

MS (MeOH): *m/z* (%, assignment): 661.25 (8, $[M - 2CO + H]^+$), 633.01 (12, $[M-3CO+H]^+$), 503.20 (100, $[M-Rh(CO)_4]^+$) amu.

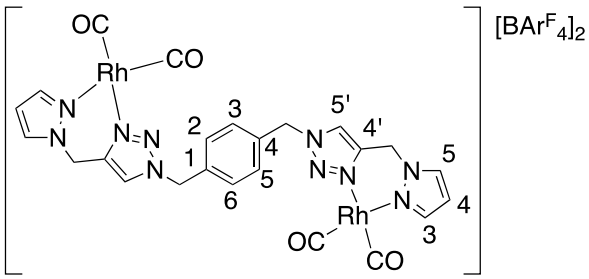
Elemental Analysis, found: C, 43.24; H, 1.83 and N, 5.82; calculated for $C_{88}H_{44}B_2F_{48}N_{10}O_4Rh_2$: C, 43.23; H, 1.81; N, 5.73 %.

FT-IR (DCM): ν 2109 (s, νCO), 2051 (s, νCO) cm^{-1}.

^{1}H NMR (DCM-d_2, 400 MHz): δ 7.80 (d, ^3J = 2.2 Hz, 2H, Pz-**H**3), 7.73 (s, 2H, Tz-**H**5'), 7.71 (br m, 16H, *o*-C**H** of BAr^F_4), 7.65 (d, ^3J = 2.5 Hz, 2H, Pz-**H**5), 7.53 (br s, 8H, *p*-C**H** of BAr^F_4), 7.37 (t, ^3J = 7.5 Hz, 1H, C_6H_4-**H**5), 7.35 (s, 1H, C_6H_4-**H**2), 7.28 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 2H, C_6H_4-**H**4 and **H**6), 6.51 (apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 5.54 (s, 4H, Tz-NC**H**$_2$), 5.34 (s, 4H, Pz-NC**H**$_2$) ppm.

^{13}C{^{1}H} NMR (DCM-d_2, 100 MHz): δ 182.46 (d, $^1J_{Rh\text{-}C}$ = 69.3 Hz, **C**O), 181.90 (d, $^1J_{Rh\text{-}C}$ = 69.9 Hz, **C**O), 162.13 (q, $^1J_{B\text{-}C}$ = 49.5 Hz), 147.24 (Pz-**C**3), 140.39 (Tz-**C**4'), 135.18 (*o*-**C**H of BAr^F_4), ~135.15 (Pz-**C**5) (last two resonances overlap), 133.52 (C_6H_4-**C**5), 131.35 (C_6H_4-**C**1 and **C**3), 130.31 (C_6H_4-**C**4 and **C**6), 129.29 (C_6H_4-**C**2), 129.24 (q, $^2J_{F\text{-}C}$ = 31.0 Hz, **C**CH_3), 124.96 (q, ^1J = 271. 2 Hz, **C**F_3), 123.93 (Tz-**C**5'), 117.90 (*p*-**C**H of BAr^F_4), 109.07 (Pz-**C**4), 56.21 (Tz-N**C**H_2), 45.67 (Pz-N**C**H_2) ppm.

S2.2 Synthesis of p-C_6H_4[(PyT)Rh(CO)$_2$]$_2$[BAr^F_4]$_2$ (2c)



Dichloromethane (25 mL) was added to a flask containing $[Rh(Cl)(CO)_2]_2$ (0.039 g, 0.10 mmol) and *p*-$C_6H_4(PyT)_2$ (**1c**, 0.040 g, 0.10 mmol) under an atmosphere of argon. The pale yellow solution was stirred at room temperature for 30 minutes. $NaBAr^F_4$ (0.177 g, 0.20 mmol) was added and the reaction mixture was stirred at room temperature for one hour. The reaction mixture was filtered through a pad of Celite, rinsed with dichloromethane (2 x 15 mL) and the solvent was reduced to approximately 3 mL. Pentane (30 mL) was added to the reaction mixture with rigorous stirring. The solid and oil mixture obtained was collected by filtration, washed with pentane (2 x 5 mL) and dried *in vacuo* to afford complex **2c** as a pale creamy yellow solid. Yield: 0.193 g, 79%.

m.p. 177-181 °C (melted then decomposed).

Elemental analysis, found: C, 43.51; H, 2.03 and N, 5.40; calculated for $C_{88}H_{44}B_2F_{48}N_{10}O_4Rh_2$: C, 43.23; H, 1.81; N, 5.73 %.

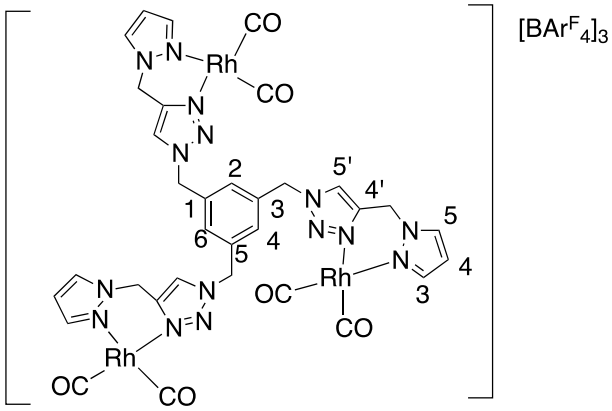
HR-MS (MeOH): *m/z* (%, assignment): 1581.2500 (2, $[M+BAr^F{}_4]^+$), 559.2500 (8, $[M\text{-}Rh(CO)_2]^+$), 531.2500 (12, $[M - Rh - 3\ xCO]^+$), 503.1667 (32, $[M - Rh - 4\ x\ CO]^+$) amu.

IR (dcm): *v* 2109 (s, νCO), 2051 (s, νCO) cm^{-1}.

^1H NMR (DCM-d_2, 600 MHz): δ 7.79 (d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.72 (br s, 18H, *o*-C**H** of $BAr^F{}_4$ and Tz-**H**5'), 7.63 (d, ^3J = 2.5 Hz, 2H, Pz-**H**5), 7.54 (br s, 8H, *p*-C**H** of $BAr^F{}_4$), 7.31 (s, 4H, C_6H_4-**H**), 6.50 (apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 5.52 (s, 4H, Tz-NC$\mathbf{H}_2$), 5.32 (s, 4H, Pz-NC$\mathbf{H}_2$) ppm.

$^{13}C\{^1H\}$ NMR (DCM-d_2, 150 MHz): δ 182.49 (d, $^1J_{Rh\text{-}C}$ = 69.8 Hz, **C**O), 181.82 (d, $^1J_{Rh\text{-}C}$ = 70.6 Hz, **C**O), 162.16 (q, $^1J_{B\text{-}C}$ = 49.7 Hz), 147.25 (Pz-**C**3), 140.395 (Tz-**C**4'), 135.21 (*o*-**C**H of $BAr^F{}_4$), 135.14 (Pz-**C**5), 133.86 (C_6H_4-**C**5), 130.06 (C_6H_4-**C**H), 129.28 (q, $^2J_{F\text{-}C}$ = 31.0 Hz, **C**CF_3), 124.99 (q, ^1J = 271. 2 Hz, **C**F_3), 123.94 (Tz-**C**5'), 117.92 (*p*-**C**H of $BAr^F{}_4$), 109.07 (Pz-**C**4), 56.21 (Tz-N**C**H_2), 45.67 (Pz-N**C**H_2) ppm.

S2.3 Synthesis of 1,3,5-C_6H_3[(PyT)Rh(CO)$_2$]$_3$[BAr$^F{}_4$]$_3$ (2d)



Dichloromethane (25 mL) was added to a flask containing a mixture of $[RhCl(CO)_2]_2$ (0.042 g, 0.11 mmol) and *1,3,5*-$C_6H_3(PyT)_3$ (**1d**, 0.039 g, 0.70 mmol) under argon. The yellow reaction was stirred at room temperature for one hour. $NaBAr^F{}_4$ (0.188 g, 2.10 mmol) was added and the reaction mixture went cloudy. The reaction mixture was stirred at room temperature for two hours, filtered through a pad of Celite, rinsed with dichloromethane (3 x 15 mL) and the filtrate was reduced *in vacuo* to approximately 3 mL. Pentane (25 mL) was added to the reaction mixture with rigorous stirring. The oil and solid mixture was collected by filtration and washed with pentane

(3 x 5mL) and dried *in vacuo* to afford complex **2d** as a yellow solid. Yield: 0.219 g, 86%; m.p. 74-77 °C (melted then decomposed).

Elemental analysis, found: C, 42.98; H, 1.96 and N, 5.78; calculated for $C_{129}H_{63}B_3F_{72}N_{15}O_6Rh_3$: C, 42.71; H, 1.75 and N, 5.79 %.

HRMS (ESI, MeOH): *m/*z (%, assignment): 2764.0719 (3, $[M + 2\ BAr^F{}_4]^+$), 1714.1176 (17, $[M - Rh(CO)_3 + 2\ BAr^F{}_4]^+$), 950.5026 (100, $[M+BAr^F{}_4]^{2+}$) amu.

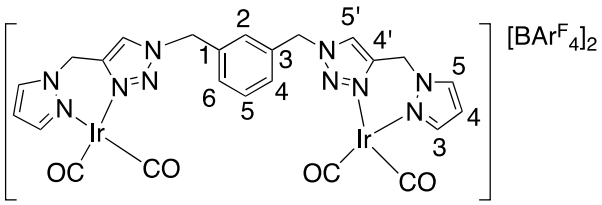
FTIR (dcm): *v* 2110 (s, *v*CO), 2052 (s, *v*CO) ppm.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.72 (s, 3H, Tz-**H**5'), 8.27 (m (two overlapping doublets), ^3J = 2.5 Hz, 6H, Pz-**H**3 & **H**5), 7.80 (s, 3H, C_6H_3-**H**), 7.79 (m, 24H, *o*-C**H** of $BAr^F{}_4$), 7.67 (s, 12H, *p*-C**H** of $BAr^F{}_4$), 6.72 (apparent t, ^3J = 2.5 Hz, 3H, Pz-**H**4), 5.97 (s, 6H, Tz-NC**H**$_2$), 5.95 (s, 6H, Pz-NC**H**$_2$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 183.8 (d, $^1J_{Rh\text{-}C}$ = 69.3 Hz, two **C**Os overlapping), 162.52 (q, $^1J_{B\text{-}C}$ = 50.81 Hz, *ipso*-**C**B of $BAr^F{}_4$), 147.78 (Pz-**C**3), 142.00 (Tz-**C**4'), 136.86 (Pz-**C**5), 136.75 (*ipso***C** of C_6H_3), 135.54 (*o*-**C**H of $BAr^F{}_4$), 130.75 (C_6H_3-**C**H), 130.02 (q, $^2J_{F\text{-}C}$ = 30.2 Hz, **C**CF_3), 126.66 (Tz-**C**5'), 125.41 (q, ^1J = 271. 5 Hz, **C**F_3), 118.50 (*p*-**C**H of $BAr^F{}_4$), 108.99 (Pz-**C**4), 55.81 (Tz-N**C**H_2), 46.09 (Pz-N**C**H_2) ppm.

S3. Synthesis of $Ir(CO)_2$ Complexes

S3.1 Synthesis of m-C_6H_4[(PyT)Ir(CO)$_2$]$_2$[BAr$^F{}_4$]$_2$ (3b)



Dichloromethane (25 mL) was added to a mixture of *m*-$C_6H_4(PyT)_2$ (**1b**, 0.040 g, 0.10 mmol) and $[IrCl(COD)]_2$ (0.067 g, 0.10 mmol) under argon. The bright yellow solution was stirred at RT for 30 minutes and $NaBAr^F{}_4$ (0.178 g, 0.10 mmol) was added. The cloudy yellow solution was stirred at RT at 1 hour, filtered through a pad of Celite and rinsed with dichloromethane (2 x 20 mL). The combined organic layer was deoxygenated *via* freeze-pump-thaw (x2) and

was placed under at atmosphere of carbon monoxide and stirred overnight. The solvent was reduced to approximately 3 mL and pentane (35 mL) was added to the reaction mixture with vigorous stirring. The yellow solid and thick oil residue obtained was collected by filtration, washed with pentane (3 x 7 mL) and dried *in vacuo* to afford **3b** as an orangish yellow solid. Yield: 0.203 g, 81%; m.p. 70-80 °C (slowly decomposed).

HR-MS (MeOH): *m/z* (%, assignment): 1761.1578 (5, $[M+BAr^F_4]^+$), 649.1384 (100, $[M - Ir(CO)_2]^+$) amu.

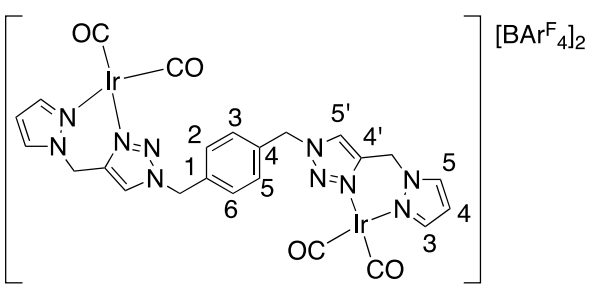
Elemental analysis, found: C, 40.80; H, 1.75 and N, 5.60; calculated for $C_{88}H_{44}B_2F_{48}Ir_2N_{10}O_4$: C, 40.29; H, 1.69; N, 5.34 %.

FT-IR (DCM): ν 2098 (s, νCO), 2034 (s, νCO) cm^{-1}.

^{1}H NMR (DCM-d_2, 600 MHz): δ 7.96 (d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.80 (s, 2H, Tz-**H**5'), 7.71 (br m, 18H, *o*-C**H** of BAr^F_4 and Pz-**H**5), 7.54 (br s, 8H, *p*-C**H** of BAr^F_4), 7.40 (t, ^3J = 7.5 Hz, 1H, C_6H_4-**H**5), 7.39 (s, 1H, C_6H_4-**H**2), 7.32 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 2H, C_6H_4-**H**4 and **H**6), 6.60 (apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 5.57 (s, 4H, Tz-NC**H**$_2$), 5.34 (s, 4H, Pz-NC**H**$_2$) ppm.

^{13}C{^{1}H} NMR (DCM-d_2, 150 MHz): δ 170.31 (**C**O), 169.18 (**C**O), 162.16 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** of BAr^F_4), 147.24 (Pz-**C**3), 140.06 (Tz-**C**4'), 135.79 (Pz-**C**5), 135.20 (*o*-**C**H of BAr^F_4), 133.23 (C_6H_4-**C**1 and **C**3), 131.49 (C_6H_4-**C**5), 130.61 (C_6H_4-**C**4 and **C**6), 129.50 (C_6H_4-**C**2), 129.25 (q, $^2J_{F\text{-}C}$ = 30.9 Hz, **C**CH_3), 124.97 (q, ^1J = 271. 2 Hz, **C**F_3), 124.24 (Tz-**C**5'), 117.93 (*p*-**C**H of BAr^F_4), 109.78 (Pz-**C**4), 56.56 (Tz-N**C**H_2), 45.85 (Pz-N**C**H_2) ppm.

S3.2 Synthesis of p-C_6H_3[(PyT)Ir(CO)$_2$]$_2$[BAr$^F_4$]$_2$ (3c)



Dichloromethane (25 mL) was added to a mixture of *p*-$C_6H_4(PyT)_2$ (**1c**, 0.040 g, 0.10 mmol) and $[IrCl(COD)]_2$ (0.067 g, 0.10 mmol) under argon. The bright yellow solution was stirred at RT for 30 minutes and $NaBAr^F_4$ (0.180 g, 0.10 mmol) was

added. The cloudy yellow solution was stirred at RT at 1 hour, filtered through a pad of Celite and rinsed with dichloromethane (2 x 25 mL). The combined organic layer was deoxygenated *via* freeze-pump-thaw (x2) and was placed under at atmosphere of carbon monoxide and stirred overnight. The solvent was reduced to approximately 3 mL and pentane (35 mL) was added to the reaction mixture with vigorous stirring. The pale yellow solid and thick oil residue obtained was collected by filtration, washed with pentane (3 x 7 mL) and dried *in vacuo* to afford **3c** as an orange solid. Yield: 0.209 g, 83%; m.p. 69-72 °C (melted and turned red).

Elemental analysis, found: C, 40.59; H, 1.82 and N, 5.28; calculated for $C_{88}H_{44}B_2F_{48}Ir_2N_{10}O_4$: C, 40.29; H, 1.82; N, 5.28 %.

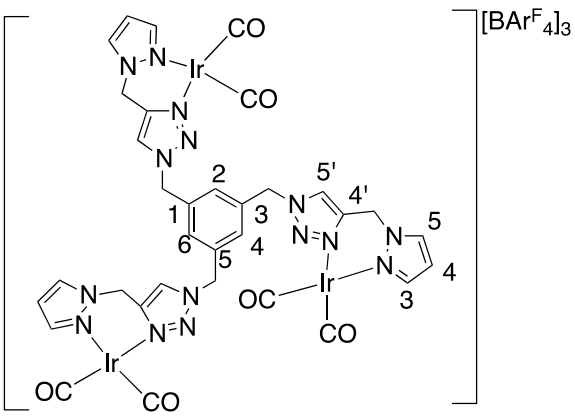
HR-MS (MeOH): *m/z* (%, assignment): 1759.1558 (67, $[M+BAr^F{}_4]^+$), 649.1382 (100, $[M-Ir(CO)_2]^+$), amu.

FT-IR (DCM): ν 2099 (s, νCO), 2034 (s, νCO) cm^{-1}.

^1H NMR (acetone-d_6, 600 MHz): δ 8.80 (s, 2H, Pz-**H**5'), 8.40 (s, 2H, Pz-**H**3), 8.36 (s, 2H, Pz-**H**5), 7.78 (br m, 16H, *o*-C**H** of $BAr^F{}_4$), 7.67 (br s, 8H, *p*C**H** of $BAr^F{}_4$), 7.60 (s, 4H, C_6H_4-**H**), 6.79 (s, 2H, Pz-**H**4), 6.04 (s, 4H, Tz-NC$\mathbf{H}_2$), 6.00 (s, 4H, Pz-NC$\mathbf{H}_2$) ppm.

$^{13}C\{^1H\}$ NMR (acetone-d_6, 150 MHz): δ 172.15 (**C**O), 171.40 (**C**O), 162.58 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-**C**-B of $BAr^F{}_4$), 148.57 (Pz-**C**3), 141.84 (Tz-**C**4'), 135.52 (*o*-**C**H of $BAr^F{}_4$, **C**1 & **C**4), 130.36 (C_6H_4-**C**H), 130.00 (q, $^2J_{F\text{-}C}$ = 31.0 Hz, **C**CF_3), 126.87 (Tz-**C**5'), 125.53 (q, ^1J = 271.4 Hz, **C**F_3), 118.46 (*p*-**C**H of $BAr^F{}_4$), 109.45 (Pz-**C**4), 56.18 (Tz-N**C**H_2), 46.35 (Pz-N**C**H_2) ppm.

S3.3 Synthesis of 1,3,5-C_6H_3-[(PyT)Ir(CO)$_2$]$_3$[BAr$^F{}_4$]$_3$ (3d)



Dichloromethane (25 mL) was added to a mixture of *1,3,5*-$C_6H_3(PyT)_3$ (**1d**, 0.393 g, 0.70 mmol) and $[IrCl(COD)]_2$ (0.071 g, 1.05 mmol) in a flask under an atmosphere of argon. The bright orange yellow solution obtained was stirred at room

temperature for 30 minutes. $NaBAr^F_4$ (0.187 g, 2.10 mmol) was added and the cloudy yellow reaction mixture was stirred for one hour at room temperature. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 20 mL). The combined filtrate was reduced until about 25 mL of solvent was left. The solution was then degassed *via* three cycles of freeze-pump-thaw and placed under an atmosphere of carbon monoxide overnight. The reaction mixture was degassed again and placed under carbon monoxide for 3 hours. The solvent was reduced to approximately 3 ml and pentane (30 mL) was added to the reaction mixture with vigorous stirring. The yellow orange solid and thick oil residue obtained was collected by filtration, washed with pentane (3 x 10 mL) and dried *in vacuo* to afford the product as an orange solid. Yield: 0.249 g, 91%; m.p. 77-80 °C.

Elemental analysis, found: C, 40.26; H, 1.49 and N, 5.10; calculated for: $C_{129}H_{63}B_3Ir\ F_{72}N_{15}O_6$: C, 39.77; H, 1.63 and N, 5.39 %.

MS (ESI, MeOH): *m/*z (%, assignment): 1695.49 (40, $[M\text{-}2Ir(CO)_2 + NaBAr^F_4]^+$), 810.26 (100, $[M\text{-}2Ir(CO)_2]^+$ amu.

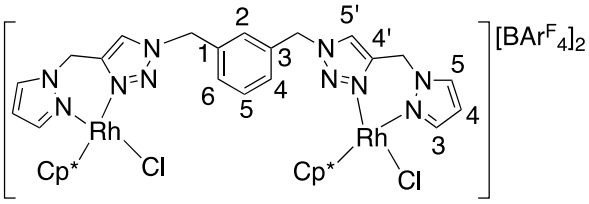
FT-IR (DCM): ν 2099 (s, νCO), 2035 (s, νCO) cm^{-1}.

^{1}H NMR (DCM-d_2, 400 MHz): δ 7.91 (d, ^3J = 2.5 Hz, 3H, Pz-**H**3), 7.80 (s, 3H, Tz-**H**5'), 7.71 (br m, 24H, *o*-C**H** of BAr^F_4), 7.67 (d, ^3J = 2.6 Hz, 3H, Pz-**H**3), 7.53 (br s, 12H, *p*-C**H** of BAr^F_4), 7.37 (s, 3H, C_6H_3-**H**), 6.56 (apparent t, ^3J = 2.5 Hz, 3H, Pz-**H**4), 5.43 (s, 6H, Tz-NC$\mathbf{H}_2$), 5.34 (s, 6H, Pz-NC$\mathbf{H}_2$) ppm.

^{13}C{^{1}H} NMR (DCM-d_2, 150 MHz): δ 169.86 (**C**O), 169.41 (**C**O), 162.11 (q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**B of BAr^F_4), 148.30 (Pz-**C**3), 140.26 (Tz-**C**4'), 135.74 (Pz-**C**5), 135.16 (*o*-**C**H of BAr^F_4), 134.74 (*ipso*-**C** of C_6H_3), 130.80 (C_6H_3-**C**H), 129.20 (q, $^2J_{F\text{-}C}$ = 30.6 Hz, **C**CF_3), 126.27 (Tz-**C**5'), 124.91 (q, $^1J_{F\text{-}C}$ = 272. 5 Hz, **C**F_3), 117.91 (*p*-**C**H of BAr^F_4), 109.82 (Pz-**C**4), 55.73 (Tz-N**C**H_2), 45.59 (Pz-N**C**H_2) ppm.

S4. Synthesis of RhCp* Complexes

S4.1 Synthesis of m-C_6H_4-[(PyT)Rh(Cp*)Cl]$_2$[$BAr^F{}_4$]$_2$ (4b)



Dichloromethane (25 mL) was added to a flask containing a solid mixture of *m*-$C_6H_4(PyT)_2$ (**1b**, 0.040 g, 0.10 mmol), $[Rh(Cp^*)Cl_2]_2$ (0.062 g 0.10 mmol) and $NaBAr^F{}_4$ (0.178 g, 0.20 mmol) under argon. The slightly cloudy orange solution obtained was stirred at RT for 3 hours. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined filtrate was reduced to approximately 3 mL and pentane (30 mL) was added to the reaction mixture with rigorous stirring. The bright yellow precipitate formed was collected by filtration, washed with pentane (2 x 5 mL) and dried *in vacuo*. Yield: 0.232 g, 87%; m.p. 98-103 °C. The product is a mixture of two diastereoisomers, **I1** and **I2** (**I1** : **I2** = 1.37 : 1.00).

Elemental analysis, found: C, 47.16; H, 2.93; and N, 5.18; calculated for: $C_{104}H_{74}B_2Cl_2F_{48}N_{10}Rh_2$: C, 46.71, H, 2.93 and N, 5.24 %.

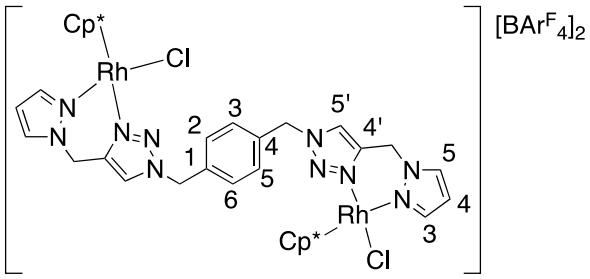
HR-MS (MeOH): *m/z* (%, assignment): 1809.3334 (3, $[M + BAr^F{}_4]^+$), 673.3334 (33, $[M\text{-}RhCp^*Cl]^+$), 637.4167 (23, $[M\text{-}RhCp^*Cl_2]^+$, 473.2500 (16, $[M]^{2+}$) amu.

^{1}H NMR (DCM-d_2, 400 MHz): δ 7.82 (**I1**, s, 2H, Tz-**H**5'), 7.81 (**I2**, s, 2H, Tz-**H**5'), 7.73-7.70 (**I1** + **I2**, m, 18H + 18H, *o*-C**H** of $BAr^F{}_4$ (16H) and Pz-**H5**), 7.64 (**I1**, d, ^3J = 2.5 Hz, Pz-**H**3), 7.56-7.54 (br s and d (overlapped), 8H + 8H + 2H, *p*-C**H** of $BAr^F{}_4$ (**I1** + **I2**) and Pz-**H**3 (**I2**)), 7.42-7.40 (**I1** + **I2**, m, 2H + 2H, C_6H_4-**H**4 and **H**6), 7.38-7.33 (**I1** + **I2**, m, 1H + 1H, C_6H_4-**H5**), 7.28 (**I2**, s, 1H, C_6H_4-**H**2), 7.21 (**I1**, s, 1H, C_6H_4-**H**2), 6.49 (**I2**, t, ^3J = 2. 5Hz, 2H, Pz-**H**4), 6.45 (**I1**, t, ^3J = 2. 5Hz, 2H, Pz-**H**4), 5.73-5.67 (**I1** + **I2**, m, 2H + 2H, C**H**$_2$), 5.56-5.42 (**I1** + **I2**, m, 4H + 4H, C**H**$_2$), 5.0 (**I2**, d, ^3J = 16.2 Hz, Pz-NC**H**$_2$), 4.94 (**I1**, d, ^3J = 15.7 Hz, Pz-NC**H**$_2$) ppm.

^{13}C{^{1}H} NMR (DCM-d_2, 100 MHz): δ 162.13 (**I1** + **I2**, q, $^1J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C**-B of $BAr^F{}_4$), 145.44 (**I1**, Pz-**C**3), 145.30 (**I2**, Pz-**C**3), 140.13 (**I1** + **I2**, Tz-**C**4'), 135.19 (**I1** + **I2**, *o*-**C**H of $BAr^F{}_4$),

134.84, 134.74, 134.46, 134.29, 130.99, 130.91, 130.19, 130.06, 129.25 (q, $^2J_{B\text{-}C}$ = 31.0 Hz, **C**CF_3), 124.97 (q, $^1J_{B\text{-}C}$ = 272.1 Hz, **C**F_3), 124.62 (**I1**, Tz-C5'), 124.50 (**I2**, Tz-C5'), 117.88 (br s, *p*-**C**H $BAr^F{}_4$) ppm.

S4.2 Synthesis of p-C_6H_4[(PyT)Rh(Cp*)Cl][$BAr^F{}_4$]$_2$ (4c)



Dichloromethane (20 mL) was added to a mixture of *p*-$C_6H_4(PyT)_2$ (**1c**, 0.040 g, 0.10 mmol) and $[RhCp^*Cl_2]_2$ (0.062 g, 0.10 mmol) in a flask under argon. The bright orange solution obtained was stirred at RT for 30 minutes. $NaBAr^F{}_4$ (0.177 g, 0.20 mmol) was added and the reaction mixture was stirred at RT for 3 hours. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15mL). The combined dichloromethane solution was reduced to approximately 3 mL and pentane (30 mL) was added with stirring. The solid obtained was collected by filtration and was washed with pentane (3 x 5mL) and dried *in vacuo*. *p*-C_6H_4[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4c**) was obtained as a bright orangish yellow solid. Yield: 0.237 g, 89%; m.p. 102-106 °C. The product is a mixture of two diastereoisomers, **I1** and **I2** (**I1** : **I2** = 1.00 : 1.00).

Elemental analysis; found: C, 47.00; H, 2.75 and N, 5.19; calculated for: $C_{104}H_{74}B_2Cl_2F_{48}N_{10}Rh_2$: C, 46.71, H, 2.93 and N, 5.24 %.

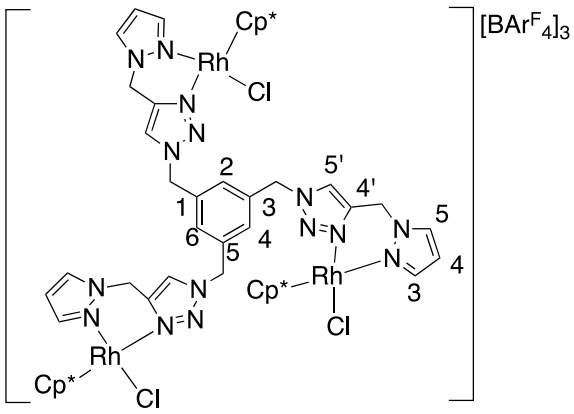
HR-MS (MeOH): *m/z* (%, assignment): 1809.4167 (20, [M + $BAr^F{}_4$]$^+$), 673.3333 (72, [M-RhCp*Cl]$^+$), 637.4167 (100, [M-RhCp*Cl_2]$^+$, 473.2500 (43, [M]$^{2+}$) amu.

^{1}H NMR (DCM-d_2, 600 MHz): δ 7.76 (**I1**, d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.75 (**I2**, d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.65 (**I1** + **I2**, s, 2H + 2H, Tz-**H**5'), 7.61 (**I1**, d, ^3J = 2.5 Hz, 2H, Pz-**H**5), 7.59 (**I2**, d, ^3J = 2.5 Hz, Pz-**H**5), 7.58 (br s, 8H, *p*-C**H** of $BAr^F{}_4$), 7.312 (**I1**, s, 4H, C_6H_4-C**H**), 7.310 (**I2**, s, 4H, C_6H_4-C**H**), 5.69 (**I1** + **I2**, d, ^2J = 15.0 Hz, 1H + 1H, Tz-NC**H**H), 5.55 (**I1** + **I2**, d, ^2J = 15.0 Hz, 1H + 1H, Tz-NC**H**), 5.46 (**I1**, d, ^2J = 15.8 Hz, 1H, Pz-NC**H**), 5.45 (**I2**, d, ^2J = 15.8 Hz, 1H, Pz-NC**H**),

5.00 (**I1**, d, ^{2}J = 15.8 Hz, 1H, Pz-NC**H**$_b$), 4.99 (**I1**, d, ^{2}J = 15.8 Hz, 1H, Pz-NC**H**$_b$), 1.641 (**I1**, s, 15H, C**H**$_3$), 1.637 (**I2**, s, 15H, C**H**$_3$) ppm.

$^{13}C\{^{1}H\}$ NMR (DCM-d_2, 150 MHz): δ 162.16 (**I1** + **I2**, q, $^{1}J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C**B of BAr^{F}_4), 145.49 (**I1** + **I2**, Pz-**C**3), 140.18 (**I1** + **I2**, Tz-C4'), 135.22 (*o*-**C**H of BAr^{F}_4), 134.70 (Pz-**C**5), 134.39 (**I1**, *ipso*-**C** of C_6H_4), 134.36 (**I2**, *ipso*-**C** of C_6H_4), 129.80 (**I1** + **I2**, **C**H of C_6H_4), 129.29 (**I1** + **I2**, q, $^{2}J_{F\text{-}C}$ = 31.7 Hz, **C**CF_3), 125.00 (**I1** + **I2**, q, $^{1}J_{F\text{-}C}$ = 271.7 Hz, **C**F_3), 124.10 (**I1** + **I2**, Tz-**C**5' (overlapped with the **C**F_3 quartet), 117.91 (*p*-**C**H of BAr^{F}_4), 109.21 (**I1**, Pz-**C**4), 109.20 (**I2**, Pz-**C**4), 97.65 (**I1** + **I2**, d, $^{1}J_{Rh\text{-}C}$ = 8.7 Hz, **C**CH_3), 55.91 (**I1** + **I2**, Tz-N**C**H_2), 45.28 (**I1** + **I2**, Pz-N**C**H_2), 9.46 (**C**H_3) ppm.

S4.3 Synthesis of 1,3,5-C_6H_3[(PyT)Rh(Cp*)Cl]$_3$[BAr^{F}_4]$_3$ (4d)



Dichloromethane (20 mL) was added to a mixture of *1,3,5*-C_6H_3[$(PyT)_3$ (**1d**, 0.0.28 g, 0.050 mmol) and $[RhCp^{*}Cl_2]_2$ (0.0464 g, 0.750 mmol) in a flask and the resulting orange solution was stirred at RT for 30 minutes. $NaBAr^{F}_4$ (0.133 g, 1.50 mmol) was added to the reaction mixture and the mixture was stirred at RT for 1.5 hours. The mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The yellow solution obtained was reduced to approximately 2 mL and pentane (30 mL) was added with rigorous stirring. The yellow solid and thick solid residue was collected by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo*. *1,3,5*-C_6H_3[(PyT)Rh(Cp*)Cl]$_3$ $[BAr^{F}_4]_3$ (**4d**) was obtained as an yellow orange solid. Yield: 0.199 g, 85%. m.p. 103-106 °C. The product is a mixture of three diastereoisomers in ratio: **I1** : **I2** : **I3** = 1.00 : 1.79 :1.26.

Elemental analysis; found: C, 46.78; H, 2.68; N, 5.58; calculated for $C_{153}H_{108}B_3Cl_3F_{72}N_{15}Rh_3$: 46.27; H, 2.74 and N, 5.58 %.

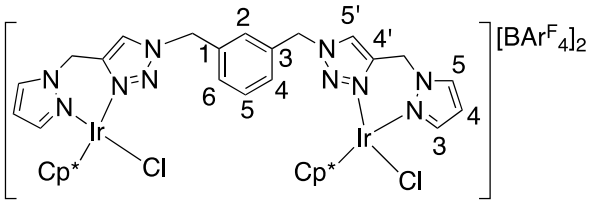
HR-MS (MeOH): *m/z* (%, assignment): 3108.3592 (3, $[M+2BAr^F{}_4]^+$), 1970.3040 (4, [M-RhCp*Cl+$BAr^F{}_4]^+$), 1122.6465 (100, $[M+BAr^F{}_4]^{2+}$), 460.0782 (6, $[M]^{3+}$) amu.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.50 (**I1**, s, 3H), 8.48 (**I2**, s, 3H), 8.33 (**I3**, s, 3H), 8.13 (**I1**, d, ^3J = 2.3 Hz, 3H, Pz-**H**5), 8.08 (**I2**, d, ^3J = 2.3 Hz, 3H, Pz-**H**5), 8.01 (**I3**, d, ^3J = 2.3 Hz, 3H, Pz-**H**5), 7.95-7.94 (**I1** + **I2** + **I3**, m, 3H + 3H + 3H, Pz-**H**3), 7.79 (**I1** + **I2** + **I3**, br m, 24H + 24H + 24H, *o*-C**H** of $BAr^F{}_4$), 7.70 (**I1**, s, 3H, C_6H_3-C**H**), 7.67 (br s, *p*-C**H** of $BAr^F{}_4$), 7.66 (**I**2, s, 3H, C_6H_3-C**H**), 7.55 (**I**3, s, 3H, C_6H_3-C**H**), 6.62-6.60 (m, 3H + 3H + 3H, Pz-**H**4), 6.10-5.88 (**I1** + **I2** + **I3**, m, 18H + 9H, Tz-NC$\mathbf{H}_2$ and Pz-NC$\mathbf{H}_a$), 5.39 (**I1**, d, ^2J = 16.2 Hz, 3H, Pz-NC$\mathbf{H}_b$), 5.37 (**I1**, d, ^2J = 16.2 Hz, 3H, Pz-NC$\mathbf{H}_b$), 5.34 (**I3**, d, ^2J = 16.2 Hz, 3H, Pz-NC$\mathbf{H}_b$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 162.60 (q, $^1J_{B\text{-}C}$ = 162.6 Hz, *ipso*-**C** of $BAr^F{}_4$), 145.96, 145.93, 145.86 (last three resonances **I1**/**I2**/**I3**, Pz-**C**3), 141.45, 141.41, 141.39 (last three resonances **I1**/**I2**/**I3**, Tz-**C**4'), 137.33, 137.26 (*ipso*-**C** of C_6H_3), 136.06, 135.97, 135.91 ((last three resonances **I1**/**I2**/**I3**, C_6H_3-**C**H), 135.55 (br s, *o*-**C**H of $BAr^F{}_4$), 130.40 (**I1** + **I2** + **I3**, s, *ipso*-**C** of C_6H_3), 130.02 (**I1** + **I2** + **I3**, q, $^2J_{F\text{-}C}$ = 29.7 Hz, **C**CF_3), 126.27 (**I1**, Tz-**C**5'), 126.18 (**I2**, Tz-**C**5'), 126.03 (**I3**, Tz-**C**5'), 125.39 (q, $^1J_{F\text{-}C}$ = 271.3 Hz, **C**F_3), 118.45 (**I1** + **I2** + **I3**, *p*-**C**H of $BAr^F{}_4$), 108.91 (**I1**/**I3**, Pz-**C**4), 108.86 (**I2**, Pz-**C**4), 108.73 (**I3**/**I1**, Pz-**C**4), 98.06, 98.02 (three resonances for **I1** + **I2** + **I3**, **C**CH_3), 55.46, 55.43, 55.37 (last three resonances, Tz-N**C**H_2), 45.77 (br, **I1** + **I2** + **I3**, Pz-N**C**H_2), 9.39, 9.34 (last two resonances **I1**/**I2** and **I3**, **C**H_3) ppm.

S5. Synthesis of IrCp* Complexes

S5.1 Synthesis of m-C_6H_4[(PyT)Ir(Cp)Cl]$_2$[$BAr^F{}_4$]$_2$ (5b)*



Dichloromethane (25 mL) was added to a mixture of *m*-$C_6H_4(PyT)_2$ (**1b**, 0.040 g, 0.10 mmol) and $[IrCp^*Cl_2]_2$ (0.080 g, 0.10 mmol) in a flask. The yellow reaction mixture was stirred for 45 minutes at room temperature. $NaBAr^F{}_4$ (0.178 g, 0.20 mmol) was added and the cloudy yellow solution was stirred at RT under argon overnight.

The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined organic layer was reduced to approximately 3mL and pentane (30 mL) was added to the dichloromethane solution with rigorous stirring. The yellow thick oil and solid residue was collected by filtration, washed with pentane (2 x 5mL) and dried *in vacuo*. *m*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5b**) was collected as a bright yellow solid. Yield: 0.159 g, 91%; m.p. 99-102 °C. The product is a mixture of two diastereoisomers **I1** and **I2** (**I1** : **I2** = 1.00 : 1.08).

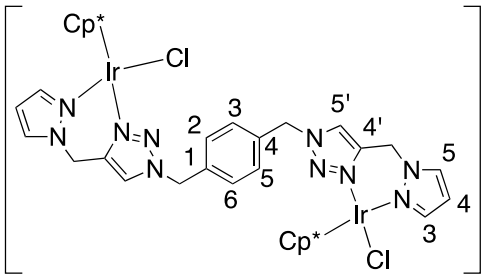
Elemental analysis; found: C, 43.91; H, 2.62 and N, 4.90; calculated for $C_{104}H_{74}B_2Cl_2F_{48}Ir_2N_{10}$: C, 43.79, H, 2.61 and N, 4.91 %.

HR-MS (ESI$^+$, MeOH): *m/z* (%, assignment): 1990.3334 (1, [M + BAr^F_4]$^+$), 763.3334 (12, [M-IrCp*Cl]$^+$), 747.2500 (17, [M-IrCp*Cl_2 + H_2O]$^+$), 657.4167 (100, [M-IrCl-2xCp* + OMe]$^+$) amu.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.54 (**I1**, s, 2H, Tz-**H**5'), 8.49 (**I2**, s, 2H, Tz-**H**5'), 8.12 (**I1**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 8.08 (**I2**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 7.89 (**I1** + **I2**, br s, 2H + 2H, Pz-**H**3), 7.80 (**I1** + **I2**, br m, 16H + 16H, *o*-C**H** of BAr^F_4), 7.68 (**I1** + **I2**, br s, 8H + 8H, *p*-C**H** of BAr^F_4), 7.64 (**I1**/**I2**, s, 1H, C_6H_4-**H**2), 7.60 (**I1**/**I2**, s, 1H, C_6H_4-**H**2), 7.51-7.49 (**I1** + **I2**, m, 3H + 3H, **H**4, **H**5 and **H**6 of C_6H_4), 6.64-6.63 (**I1** + **I2**, apparent t, ^3J = 2.4 Hz, 2H + 2H, Pz-**H**4), 6.13-5.88 (**I1** + **I2**, m, 6H + 6H, NC**H**$_2$ (AB systems)), 5.262 (**I1**, d, ^2J = 16.1 Hz, 2H, Pz-NC**H**b), 5.255 (**I2**, d, ^2J = 16.1 Hz, 2H, Pz-NC**H**), 1.72 (**I1**, s, 15H, CH_3), 1.69 (**I2**, s, 15H, CH_3) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 162.62 (**I1** + **I2**, q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**B of BAr^F_4), 145.80 (**I2**, Pz-**C**3), 145.75 (**I1**, Pz-**C**3), 140.57 (**I2**, Tz-**C**4'), 140.56 (**I1**, Tz-**C**4'), 136.38 (**I1**/**I2**, Tz-**C**5'), 136.30 (**I1**/**I2**, Tz-**C**5'), 135.63 (**I1** and/or **I2**, Pz-**C**5), 135.57 (**I1** + **I2**, *o*-**C**H of BAr^F_4), 130.81 (**I1**/**I2**, *ipso*-**C**H of C_6H_4), 130.06 (q, $^2J_{F\text{-}C}$ = 31.9 Hz, **C**CF_3), 129.96 ((**I1**/**I2**, **C**H of C_6H_4 (overlapped with C**C**F_3 resonances)), 129.59 (**I1** + **I2***ipso*-**C** of C_6H_4), 129.44 (*ipso*-**C** of C_6H_4), 126.05 (**I1**/**I2**, Tz-C5'), 126.04 (**I1**/**I2**, Tz-C5'), 125.40 (**I1** + **I2**, q, $^1J_{F\text{-}C}$ = 271.2 Hz, **C**F_3), 118.47 (*p*-**C**H of BAr^F_4), 89.80 (**I2**, **C**CH_3), 89.78 (**I1**, **C**CH_3), 55.88 (**I1** + **I2**, Tz-N**C**H_2), 46.18 (**I1** + **I2**, Pz-N**C**H_2), 9.10 (**I1**/**I2**, **C**H_3), 9.07 (**I2**/**I1**, **C**H_3) ppm.

S5.2 Synthesis of p-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[$BAr^F{}_4$]$_2$ (5c)



Dichloromethane (20 mL) was added to a mixture of *p*-$C_6H_4(PyT)_2$ (**1c**, 0.040 g, 0.10 mmol) and $[IrCp^*Cl_2]_2$ (0.080 g, 0.10 mmol) in a flask and the yellow reaction mixture was stirred for 30 minutes at RT. $NaBAr^F{}_4$ (0.178 g, 0.20 mmol) was added and the cloudy yellow solution was stirred at RT under argon for 1hr. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined organic layer was reduced to approximately 3mL and pentane (30 mL) was added to the dichloromethane solution with rigorous stirring. The yellow precipitate formed was collected by filtration, washed with pentane (2 x 5mL) and dried *in vacuo*. *p*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[$BAr^F{}_4$]$_2$ (**5c**) was collected as a light yellow solid. Yield: 0.285g, 95%; m.p. 103-108 °C. The product is a mixture of two diastereomers **I1** and **I2** (**I1** : **I2** = 1.00 : 1.00).

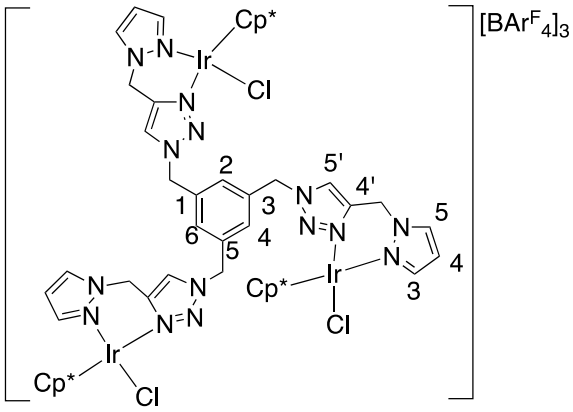
Elemental analysis; found: C, 44.00; H, 2.62 and N, 4.90; calculated for $C_{104}H_{74}B_2Cl_2F_{48}Ir_2N_{10}$: C, 43.79, H, 2.61 and N, 4.91 %.

HR-MS (ESI^+, MeOH): *m/z* (%, assignment): 1989.3509 (32, $[M + BAr^F{}_4]^+$), 763.2343 (7, [M-IrCp*Cl]), 563.1402 (100, $[M]^{2+}$) amu.

^{1}H NMR (DCM-d_2, 600 MHz): δ 7.73-7.72 (**I1** + **I2**, br m, 16H + 16H, *o*-C**H** of $BAr^F{}_4$), 7.70 (**I1** + **I2**, apparent t, ^3J = 2.5 Hz, 2H + 2H, Pz-**H**5), 7.66 (**I1** + **I2**, s, 2H + 2H, Tz-**H**5'), 7.61 (**I1**, d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.59 (**I2**, d, ^3J = 2.5 Hz, 2H, Pz-**H**3), 7.56 (br s, 8H + 8H, *p*-C**H** of $BAr^F{}_4$), 7.31 (**I1** + **I2**, s, 4H + 4H, C**H** of C_6H_4), 6.53 (**I1**, apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 6.52 (**I2**, apparent t, ^3J = 2.5 Hz, Pz-**H**4), 5.70 (**I1** + **I2**, d, ^2J = 15.2 Hz, 2H + 2H, Tz-NC$\mathbf{H}_a$), 5.57 (**I1** + **I2**, d, ^2J = 15.2 Hz, 2H + 2H, Tz-NC$\mathbf{H}_b$), 5.425 (**I1**, d, ^2J = 15.8 Hz, 2H, Tz-NC$\mathbf{H}_a$), 5.419 (**I2**, d, ^2J = 15.8 Hz, 2H, Tz-NC$\mathbf{H}_a$), 4.86 (**I1** + **I2**, d, ^2J = 15.8 Hz, 2H + 2H, Tz-NC$\mathbf{H}_b$), 1.61 (**I1**, s, 15H, CCH_3), 1.60 (**I1**, s, 15H, CCH_3) ppm.

$^{13}C\{^1H\}$ NMR (DCM-d_2, 150 MHz): δ 162.15 (**I1** + **I2**, q, $^1J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C**B of BAr^F_4), 145.49 (**I1** + **I2**, Pz-**C**3), 139.26 (Tz-**C4**'), 135.21 (br s, *o*-C**H** of BAr^F_4), 134.34 (**I1** + **I2**, Pz-**C**5), 129.77 (**I1** + **I2**, *ipso*-**C** of C_6H_4), 129.28 (**I1** + **I2**, d, $^2J_{F\text{-}C}$ = 31.7 Hz, **C**CF_3), 125.00 (**I1** + **I2**, q, $^1J_{F\text{-}C}$ = 272.5 Hz, **C**F_3), 123.98 (**I1** + **I2**, Tz-**C**5'), 117.91 (**I1** + **I2**, s, *p*-**C**H of BAr^F_4), 89.63 (**I1** + **I2**, **C**CH_3), 56.04 (**I1** + **I2**, Tz-N**C**H_2), 45.59 (**I1** + **I2**, Pz-N**C**H_2), 9.20 (**I1** + **I2**, **C**H_3) ppm.

S5.3 Synthesis of 1,3,5-C_6H_3[(PyT)Ir(Cp*)Cl]$_3$[BAr^F_4]$_3$ (5d)



Dichloromethane (25 mL) was added to a mixture of *1,35*-$C_6H_3(PyT)_3$ (**1d**, 0.039 g, 0.070 mmol) and $[IrCp^*Cl_2]_2$ (0.084 g, 0.105 mmol) in a flask and the yellow reaction mixture was stirred for 30 minutes at room temperature. $NaBAr^F_4$ (0.187 g, 0.210 mmol) was added and the cloudy yellow solution was stirred at RT under argon for 1 hour. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined organic layer was reduced to approximately 3mL and pentane (30 mL) was added to with rigorous stirring. The yellow precipitate formed was collected by filtration, washed with pentane (2 x 5mL) and dried *in vacuo*. *1,35*-C_6H_3[(PyT)Ir(Cp*)Cl]$_3$[BAr^F_4]$_3$ (**5d**) was collected as a light yellow solid. Yield: 0.235 g, 93%; m.p. 126-132 °C. The product is a mixture of three diastereoisomers, **I1**, **I2** and **I3** (**I1** : **I2** : **I3** = 1.00 : 1.92 : 1.29).

Elemental analysis; found: C, 43.38; H, 2.56; and N, 5.09. Calculated for $C_{153}H_{108}B_3Cl_3F_{72}Ir_3N_{15}$: C, 43.34, H, 2.57 and N, 4.98 %.

HR-MS (MeOH): *m/z* (%, assignment): 3376.5320 (4, $[M + 2BAr^F_4]^+$), 2150.4193 (3, $[M\text{-}IrCp^*Cl + BAr^F_4]^+$), 1256.7327 (100, $[M+BAr^F_4]^{2+}$), 550.1322 (8, $[M]^{3+}$) amu.

^1H NMR (aceton-d_6, 600 MHz): δ 8.56 (**I1**, s, 3H, Tz-**H**5'), 8.52 (**I2**, s, 3H, Tz-**H**5'), 8.42 (**I3**, s, 3H, Tz-**H**5'), 8.15 (**I1**, d, ^3J = 2.5 Hz, 3H, Pz-**H**5), 8.11 (**I2**, d, ^3J = 2.5 Hz, 3H, Pz-**H**5), 8.06 (**I3**, d,

^{3}J = 2.5 Hz, 3H, Pz-**H**5), 7.91-7.89 (**I1** + **I2** + **I3**, m, 3H + 3H + 3H, Pz-**H**3), 7.79 (**I1** + **I2** + **I3**, br m, 16H + 16H + 16H, *o*-C**H** of BAr^{F}_{4}), 7.69 (**I1**, s, **3H**, C_6H_3-**H**), 7.68 (**I2**, s, **3H**, C_6H_3-**H**), 7.67 (br s, 4H + 4H + 4H, *p*-C**H** of BAr^{F}_{4}), 7.60 (**I3**, s, **3H**, C_6H_3-**H**), 6.66-6.64 (**I1** + **I2** + **I3**, m, 3H + 3H +3H, Pz-**H**4), 6.16-5.84 (**I1** + **I2** + **I3**, m, 18H + 9H, Tz-NCH_2 and Pz-NCH_a), 5.25-5.19 (**I1** + **I2** + **I3**, three doublets, 3H + 3H + 3H, Pz-NC**H**$_b$), 1.74 (**I3**, 15H, C**H**$_3$), 1.71 (**I2**, 15H, C**H**$_3$), 1.64 (**I1**, 15H, C**H**$_3$) ppm.

$^{13}C\{^{1}H\}$ NMR (acetone-d_6, 150 MHz): δ 162.61 (**I1** + **I2** + **I3**, $^{1}J_{B\text{-}C}$ = 50.0 Hz, *ipso*-**C**B of BAr^{F}_{4}), 145.80 (**I1**, Pz-**C**3), 145.75 (**I2**, Pz-**C**3), 145.69 (**I3**, Pz-**C**3), 140.57 (**I1**, Tz-**C**4'), 140.54 (**I2**, Tz-**C**4'), 140.50 (**I3**, Tz-**C**4'), 137.32 (**I1/I2/I3**, *ipso*-**C** of C_3H_6), 137.29 (**I1/I2/I3**, *ipso*-**C** of C_3H_6), 137.23 (**I1/I2/I3**, *ipso*-**C** of C_3H_6), 135.78 (**I1**, Pz-C5), 135.70 (**I2**, Pz-C5), 135.64 (**I2**, Pz-C5), 135.55 (*p*-**C**H of BAr^{F}_{4}), 130.46 (**I1**, **C**H of C_6H_3), 130.34 (**I2**, **C**H of C_6H_3), 130.05 (**I3**, **C**H of C_6H_3), 130.02 (**I1** + **I2** + **I3**, q, $^{2}J_{F\text{-}C}$ = 31.4 Hz, **C**CF_3), 126.27 (**I1**, Tz-**C**5'), 126.19 (**I2**, Tz-**C**5'), 126.04 (**I3**, Tz-**C**5'), 125.39 (**I1** + **I2** + **I3**, q, $^{1}J_{F\text{-}C}$ = 271.8 Hz, **C**F_3), 118.46 (**I1** + **I2** + **I3**, *p*-**C**H of BAr^{F}_{4}), 109.19 (**I1**, Pz-**C**4), 109.14 (**I2**, Pz-**C**4), 109.03 (**I3**, Pz-**C**4), 89.90 (**I1**, **C**CH_3), 89.88 (**I2**, **C**CH_3), 89.81 (**I3**, **C**CH_3), 55.58, 55.51 (last two Tz-N**C**H_2, two resonances overlap), 46.21, 46.17 (last two Pz-N**C**H_2, two resonances overlap), 9.15, 9.10 (last two **C**H_3, two resonances overlap) ppm.

Table S1: νCO (cm^{-1})[a] and δ (ppm) of the carbonyls co-ligands in complexes **2a-d** and **3a-d**.

Complex	νCO (cm^{-1})	^{13}CO δ (ppm)
$[Rh(PyT)(CO)_2][BAr^F{}_4]$[d]	2108, 2050	182.8 (J = 68.9 Hz), 182.0 (J = 71.5 Hz)[b]
o-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2a**)	2109, 2051	183.76 (J = 70)[c]
m-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2b**)	2109, 2051	182.46 (J = 69.3), 181.90 (J = 69.9)[b]
p-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2c**)	2109, 2051	182.49 (J = 69.0), 181.82 (J = 70.6)[b]
1,3,5-$C_6H_3[Rh(PyT)(CO)_2]_3[BAr^F{}_4]_3$ (**2d**)	2110, 2052	183.8 (J = 69.7)[c]
$[Ir(PyT)(CO)_2][BAr^F{}_4]$[d]	2097, 2034	170.7, 169.2 [b]
o-$C_6H_4[Ir(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3a**)	2099, 2034	171.88, 171.20[c]
o-$C_6H_4[Ir(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3b**)	2098, 2034	170.31, 169.18[b]
o-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3c**)	2099, 2034	172.14, 171.40[c]
1,3,5-$C_6H_3[Rh(PyT)(CO)_2]_3[BAr^F{}_4]_3$ (**3d**)	2099, 2035	169.86, 169.41[b]

[a] Spectra were acquired in dcm solution. [b] Spectra were acquired in dcm-d_2. [c] Spectra were acquired in acetone-d_6. [d] From reference 1

Table S2: Molar ratios of different diastereoisomers in solution of complexes **4a-d** and **5a-d** as determined by ^{1}H NMR spectroscopy.

Complexes	**Solvent**	**Diastereoisomeric Ratios**
o-C_6H_4[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4a**)	acetone-d_6	1.16 : 1.00
m-C_6H_4[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4b**)	dcm-d_2	1.37 : 1.00
p-C_6H_4[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4c**)	dcm-d_2	1.00 : 1.00
1,3,5-C_6H_3[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4d**)	acetone-*d*6	1.00 : 1.79 : 1.26
o-C_6H_4[(PyT)IrCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**5a**)	acetone-d_6	1.00 : 1.00
m-C_6H_4[(PyT)IrCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**5b**)	acetone-d_6	0.93 : 1.00
p-C_6H_4[(PyT)IrCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**5c**)	dcm-d_2	1.00 : 1.00
1,3,5-C_6H_4[(PyT)IrCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**5d**)	acetone-d_6	1.00 : 1.92 : 1.29

S6. Experimental for X-ray Crystallography

***Bruker Diffractometer*:** Suitable single crystals of **1c**, **2b**, **4a**, **6** and **7** selected under the polarizing microscope (Leica M165Z), were picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K by using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). The single crystals, mounted on the goniometer using cryo loops for intensity measurements, were coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS[2] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software.[3] All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL.[4] The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using Mercury.[5] Key crystallographic data and refinement details are presented in the Tables S3 and S4.

Synchrotron: The X-ray diffraction measurement for **1b** and **1c** was carried out at MX1 and MX2 beamlines at the Australian Synchrotron Facility, Melbourne. The procedure for diffraction intensity measurements on both the beam lines was similar. The crystal was mounted on the goniometer using cryo loop for diffraction measurements, was coated with paraffin oil and then quickly transferred to the cold stream using Cryo stream attachment. Data was collected using Si<111> monochromated synchrotron X-ray radiation (λ = 0.71073 Å) at 100(2) K and was corrected for Lorentz and polarization effects using the XDS software.[6] The structure was solved by Direct methods and the full-matrix least-squares refinements was carried out using SHELXL.[4]

Table S3: Crystallographic data *m*-$C_6H_4(PyT)_2$ (**1b**), *p*-$C_6H_4(PyT)_2$ (**1c**), [Cp*Rh(μ-Cl)$_3$Cp*][$BAr^F{}_4$] (**6**) and [Cp*Ir(μ-Cl)$_3$Cp*][$BAr^F{}_4$] (**7**)

	1b[a]	**1c**	**6**	**7**
Chemical formula	$C_{20}H_{20}N_{10}$	$C_{20}H_{20}N_{10}$	$C_{52}H_{42}BCl_3F_{24}Rh_2$	$C_{52}H_{42}BCl_3F_{24}Ir_2$
M (g mol^{-1})	400.46	400.46	1445.83	3248.83
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	*Pnma*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal habit	Colourless needles	Colourless needles	Yellow orange plates	Yellow cubic
Temperature (K)	100	181	150	150
a (Å)	10.140(2)	21.252(4)	10.8624(7)	10.9964(3)
b (Å)	41.977(8)	4.4589(9)	12.9587(10)	13.0959(4)
c (Å)	4.4970(9)	10.309(2)	19.9534(15)	20.2446(6)
α (°)	90	90	89.701(4)	84.849(1)
β (°)	90	100.184(9)	82.578(4)	82.289(1)
γ (°)	90	90	82.676(4)	82.375(1)
V (Å^3)	1914.1(7)	961.5(3)	2762.3(3)	2863.13(14)
Z	4	2	2	1
Radiation type	Synchrotron, l = 0.71073 Å	MoK_α	Mo$K\alpha$	Mo$K\alpha$
μ (mm^{-1})	0.09	0.09	0.86	4.90
Crystal size (mm)	0.04 x 0.02 x 0.01	0.30 × 0.12 × 0.05	0.30 × 0.16 × 0.07	0.33 × 0.28 × 0.18
T_{min}, T_{max}	-	0.973, 0.996		0.299, 0.479
Refl. measured	20945	6785	58653	40446
Unique reflections	1695	1696	9711	9927
Obsd. Reflections [I > 2σ(I)]	1630	1398	7917	8868
R_{int}	0.042	0.027	0.039	0.028
R[$F^2 > 2\sigma(F^2)$]	0.076	0.036	0.039	0.035
wR(F^2)	0.179	0.122	0.129	0.076
S	1.21	0.80	0.88	1.05
Reflections used	1695	1696	9711	9927
Parameters	140	137	839	851
Restraints	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, -0.33	0.18 -0.15	0.93,-0.69	1.49, -0.83

[a] Diffractometer: 3BM1 Australian Synchrotron diffractometer.

Table S4: Crystallographic data for *m*-C_6H_4[(PyT)Rh(CO)$_2$] [$BAr^F{}_4$]$_2$ (**2b**), *p*-C_6H_4 [(PyT)Rh(CO)$_2$]$_2$ [$BAr^F{}_4$]$_2$ (**2c**) and *o*-C_6H_4[(PyT)RhCp*Cl]$_2$[$BAr^F{}_4$]$_2$ (**4a**).

	2b	**2c**[a]	**4a**
Chemical formula	$C_{24}H_{20}N_{10}O_4Rh_2$ $C_{64}H_{24}F_{48}B_2$ $2CH_2Cl_2$	$C_{24}H_{20}N_{10}O_4Rh_2$ $C_{64}H_{24}F_{48}B_2$	$C_{40}H_{50}Cl_2N_{10}Rh_2$ $C_{64}H_{24}F_{48}B_2$
M (g mol^{-1})	2614.62	2444.77	2674.07
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Crystal habit	Yellow blocks	Yellow thin plates	Yellow orange plates
Temperature (K)	170	100	150
a (Å)	12.5978(9)	13.054(3)	19.4592(9)
b (Å)	13.8067(10)	13.837(3)	26.2685(12)
c (Å)	15.8805(11)	15.174(3)	22.0969(10)
α (°)	91.334(3)	69.18(3)	90
β (°)	106.014(3)	73.80(3)	94.742(2)
γ (°)	108.407(3)	64.55(3)	90
V (Å^3)	2500.6(3)	2287.3(8)	11256.5(9)
Z	1	1	4
Radiation type	Mo*K*α	Synchrotron, l = 0.71073 Å	Mo*K*α
μ (mm^{-1})	0.58	0.52	0.47
Crystal size (mm)	0.30 × 0.29 × 0.10	0.03 × 0.02 × 0.02	0.37 × 0.26 × 0.14
T_{min}, T_{max}	0.845, 0.946	-	0.844, 0.936
Refl. measured	33733	28387	123686
Unique reflections	8771	7450	19804
Obsd. Reflections [I > 2σ(I)]	7768	7042	16411
R_{int}	0.36	0.022	0.040
R[$F^2 > 2\sigma(F^2)$]	0.045	0.037	0.056
wR(F^2)	0.128	0.094	0.185
S	1.02	1.05	1.27
Reflections used	8771	7450	19804
Parameters	1105	733	1600
Restraints	991	174	12
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, -0.74	0.76, -0.89	1.49, -1.01

[a]Diffractometer: 3BM1 Australian Synchrotron diffractometer.

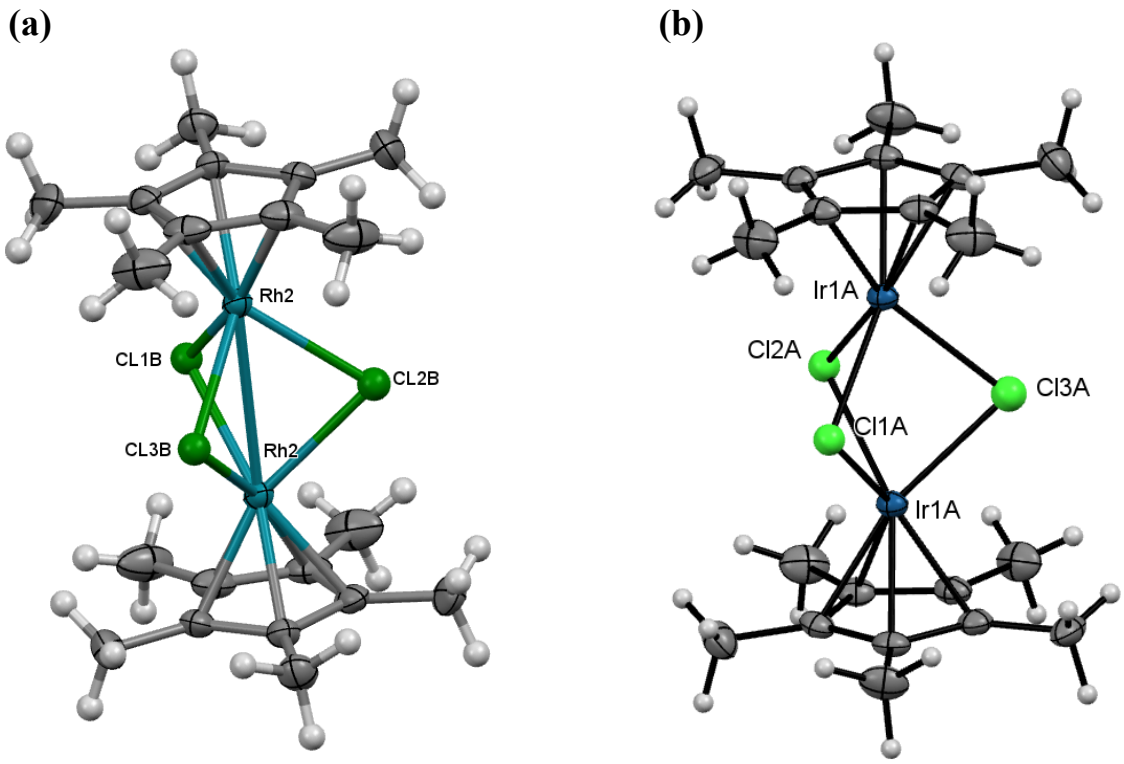


Figure S1: ORTEP depictions of the cationic fragment of the single crystal solid state structures of [Cp*Rh(μ-Cl)$_3$RhCp*][BAr$^F{}_4$] (**6**) and [Cp*Ir(μ-Cl)$_3$IrCp*][BAr$^F{}_4$] (**7**) at 40% thermal ellipsoid for the non-hydrogen atoms.

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