Electronic Supporting Information for:

Cationic Rh and Ir complexes containing bidentate imidazolylidene-*1,2,3*-triazole donor ligands: synthesis, characterisation and preliminary catalytic studies

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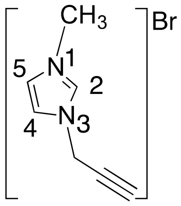
Part A: Synthesis of Ligands

A.1 Synthesis of 1-Methyl-3-propagylimidazolium bromide



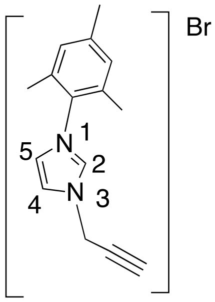
A solution of 1-methylimidazole (8.0 mL, 100 mmol) and propargyl bromide (80% (w/w), in toluene, 11.2 ml, 103 mmol) in acetonitrile (100 mL) was heated at reflux under an atmosphere of nitrogen overnight. During which time the colour of the solution changed from pale yellow to brown. The reaction mixture was cooled to room temperature and the solvent was completely removed *in vacuo* to afford a brown yellow solid, which was dried in a vacuum desiccator overnight. The crude product was used in subsequent reactions without further purification. Yield: 20.0 g, 99 %.

ESI-MS (ESI$^+$, CH$_3$CN) *m/z* (assignment, %): 121.05 (M$^+$, 100); calculated for $[C_7H_9N_2]^+$ 121.08 amu.

^{1}H (300 MHz, dmso-d_6): δ 9.34 (s, 1H, Im-**H**2), 7.83 (apparent t, ^4J = 1.72 Hz, 1H, Im-**H**4), 7.80 (apparent t, 1H, ^4J = 1.72 Hz, 1H, Im-**H**5), 5.27 (d, ^4J = 2.80 Hz, 2H, C**H**$_2$), 3.90 (s, 3H, C**H**$_3$), 3.85 (d, ^3J = 2.80 Hz, 1H, CC**H**) ppm.

^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 136.55 (Im-**C**2), 124.00 (Im-**C**5), 122.08 (Im-**C**4), 78.92 (C**C**H), 76.10 (**C**CH), 38.50 (**C**H$_2$), 35.99 (**C**H$_3$) ppm.

A.2 Synthesis of 1-Mesityl-3-propargylimidazolium bromide[1, 2]



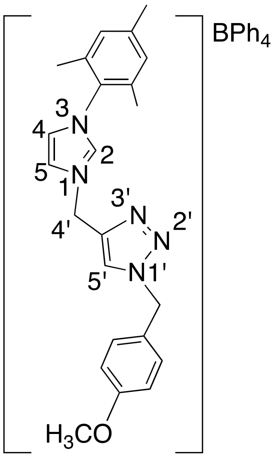
A solution of 1-mesitylimidazole (3.73 g, 20.0 mmol) and propargyl bromide (80% (w/w), in toluene, 3.0 ml, 20.0 mmol) in acetonitrile (100 mL) was heated at reflux under an atmosphere of nitrogen overnight. During which time, the colour of the solution changed from pale yellow to brown and a white precipitate formed. The reaction mixture was cooled to room temperature and the off white solid product was collected by filtration, washed with diethyl ether (4 x 20 mL) and dried in a vacuum desiccator overnight. Yield: 6.06 g, 99%.

ESI-MS (ESI$^+$, CH_3CN) *m/z* (assignment, %): 225.19 (M^+, 100); calculated for $[C_{15}H_{17}N_2]^+$ 225.14 amu.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (apparent t, ^4J = 1.7 Hz, 1H, Im-**H**2), 7.89 (t, ^4J = 1.7 Hz, 1H, Im-**H**5), 7.19 (t, ^4J = 1.7 Hz, 1H, Im-**H**5), 7.01 (s, 2H, *m*-C**H** of Mes), 5.81 (d, ^4J = 2.6 Hz, 2H, C**H**$_2$), 2.71 (t, ^4J = 2.6 Hz, 1H, CC**H**), 2.34 (s, 3H, *p*C**H**$_3$ of Mes), 2.10 (s, 6H, *o*-C**H**$_3$ of Mes) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.71 (*p*-**C** of Mes), 181.12 (Im-**C**2), 134.36 (*o*-**C** of Mes), 130.66 (N-**C** of Mes), 130.09 (*m*-**C**H of Mes), 123.15 (**C**5), 122.45 (**C**4), 77.96 (**C**CH), 74.47 (C**C**H), 40.88 (**C**H$_2$), 21.24 (*p*-**C**H$_3$), 17.90 (*o*-**C**H of Mes) ppm.

*A.3. Synthesis of [MesCaTBnOMe]BPh$_4$ (**1b**)*



1-Mesityl-3-propargylimidazolium bromide (0.916 g, 3.00 mmol), $CuSO_4.5H_2O$ (0.048 g, 0.19 mmol) and sodium *L*-ascorbate (0.178 g, 0.90 mmol) were dissolved in dry dimethyl sulfoxide (*ca.* 10 mL). 4-Methoxybenzyl azide (0.490 g, 3.00 mmol) was added to the solution. The reaction mixture was then deoxygenated briefly by two cycles of freeze-pump-thaw using an ice/salt mixture cooling bath and left stirring at room temperature overnight. The brownish yellow reaction mixture was poured into deionized water (100 mL). Sodium tetraphenylborate (1.03 g 3.01 mmol) was added and the reaction mixture was stirred at room temperature for 15 minutes. The solid precipitate was collected by filtration and washed with water (3 x 25 mL), saturated aqueous ammonium chloride (3 x 20 mL) and water (3 x 20 mL) and a small amount of cold methanol (3 x 2.0 mL). The crude product was then recrystallized from dichloromethane/hexane to afford [MesCaTBzOMe]BPh$_4$ (**1b**) as a white solid. Yield: 1.20 g, 57%.

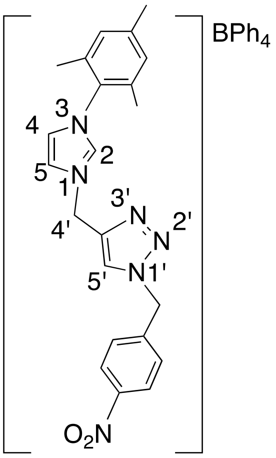
ESI-MS (ESI$^+$, CH_3CN) *m/z* (assignment, %): 388.05 (100, $[M]^+$); calculated for $C_{23}H_{26}N_5O$: 388.21 amu.

Elemental analysis: found C, 77.96; H, 6.47 and N, 9.87; calculated for $C_{47}H_{46}BN_5O.H_2O$: C, 77.78; H, 6.67 and N, 9.65 %.

^{1}H (500 MHz, dmso-d_6): δ 9.51 (s, 1H, Im-**H**2), 8.26 (s, 1H, Tz-**H**5'), 8.03 (s, 1H, Im-**H**5), 7.92 (s, 1H, Im-**H**4), 7.31 (d, ^3J = 7.5 Hz, 2H, *o*-C**H** of PhOMe), 7.16 (br s, 8H, *o*-C**H** of BPh_4), 7.14 (s, 2H, *m*-C**H** of Mes), 6.94 (t, ^3J = 7.5 Hz, 2H, *m*-C**H** of PhOMe), 6.92 (t, ^3J = 7.4 Hz, 8H, *m*-C**H** of BPh_4) (the last two resonances overlap), 6.79 (t, ^3J = 7.4 Hz, 4H, *p*-C**H** of BPh_4), 5.60 (s, 2H, ImN-C$\mathbf{H}_2$), 5.55 (s, 2H, TzN-C$\mathbf{H}_2$), 3.74 (s, 3H, OC$\mathbf{H}_3$), 2.33 (s, 3H, *p*-C$\mathbf{H}_3$ of Mes), 1.98 (s, 6H, *o*-C$\mathbf{H}_3$ of Mes) ppm.

^{13}C{^{1}H} (125 MHz, dmso-d_6): δ 163.34 (q, $^1J_{B-C}$ = 49.4 Hz, *ipso*-C of BPh_4), 159.20 (*p*-**C**OCH_3 of $PhOCH_3$), 140.57 (Tz-**C**4'), 140.25 (*p*-**C**H of Mes), 137.92 (Im**C**2), 135.49 (*o*-**C**H of BPh_4), 134.20 (*o*-**C** of Mes), 131.10 (N-**C** of Mes), 129.69 (*o*-**C**H of PhOMe), 129.19 (*m*-**C**H of Mes), 127.55 (*ipso*-**C**CH_2 of PhOMe), 125.25 (q, $^3J_{B-C}$ = 2.3 Hz, *m*-**C**H of BPh_4), 124.14 (**C**5'), 124.08 (Im-**C**4), 123.27 (Im-**C**5), 121.47 (*p*-**C**H of BPh_4), 114.11 (*m*-**C**H of PhOMe), 55.14 (O**C**H_3), 52.54 (TzN-**C**H_2), 44.27 (ImN-**C**H_2), 20.54 (*p*-**C**H_3 of Mes), 16.81 (*o*-**C**H_3 of Mes) ppm.

A.4. *Synthesis of [MesCaTBnNO$_2$]BPh$_4$ (**1c**)*



$CuSO_4.5H_2O$ (0.024 g, 0.10 mmol) and sodium L-ascorbate (0.180 g, 0.90 mmol) dissolved in dry and deoxygenated dimethyl sulfoxide (20 mL) in a Schlenk flask. 4-Nitrobenzyl azide (0.534 g, 3.00 mmol) and 1-mesityl-3-propargylimidazolium bromide (0.916 g, 3.00 mmol) were added to the reaction mixture. The colour of the solution changed from pale blue green to dark red. The reaction mixture was stirred at RT under nitrogen overnight. The mixture was poured in a conical flask containing water (150 mL) and the resulting mixture was stirred for 10 minutes. Sodium tetraphenylborate (1.15 g, 3.36 mmol) was added to this mixture with vigorous stirring. A pale yellow precipitate formed and was collected by filtration, washed with saturated aqueous ammonium chloride (3 x 15 mL), water (4 x 20 mL) and methanol (2 x 10 mL) and dried in a vacuum desiccator overnight. Yield: 1.72 g, 79%.

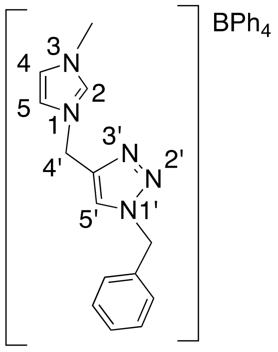
Elemental analysis: found: C, 76.44; H, 5.99; N, 11.86; calculated for $C_{46}H_{43}BN_6O_2$: C, 76.45; H, 6.00 and N, 11.63 %.

ESI-MS (ESI$^+$, CH_3CN) *m/z* (assignment, %): 403.07 ([M]$^+$, 100); calculated for $C_{22}H_{23}N_6O_2$: 403.19 amu.

^{1}H NMR (500 MHz, dmso-*d*$_6$): *δ* 9.52 (s, 1H, Im-**H**2), 8.40 (s, 1H, Tz-**H**5'), 8.24 (d, ^3J = 8.6 Hz, 2H, *m*-C**H** of PhNO$_2$), 8.04 (s, 1H, Im-**H**4), 7.93 (s, 1H, Im-**H**5), 7.55 (d, ^3J = 8.6, 2H, *o*-C**H** of PhNO$_2$), 7.17 (br s, 8H, *o*-C**H** of BPh$_4$), 7.14 (s, 2H, *m*-C**H** of Mes), 6.92 (t, ^3J = 7.2 Hz, 8H, *m*-**C**H of BPh$_4$), 6.78 (t, ^3J = 7.2 Hz, 4H, *p*-C**H** of BPh$_4$), 5.84 (s, 2H, C**H**$_2$-PhNO$_2$), 5.64 (s, 2H, Im-C**H**$_2$), 2.32 (s, 3H, *p*-C**H**$_3$ of Mes), 1.99 (s, 6H, *o*-C**H**$_3$ of Mes) ppm.

^{13}C{^{1}H} NMR (125 MHz, dmso-*d*$_6$): *δ* 163.39 (q, $^1J_{B\text{-}C}$ = 49.1 Hz, *ipso*-**C** of BPh$_4$), 147.34 (s, **C**$_q$-NO$_2$ of PhNO$_2$), 143.18 ((CH$_2$**C** of PhNO$_2$), 140.79 (Tz-**C**4'), 140.34 (*p*-**C** of Mes), 137.80 (Im-**C**2), 133.55 (*o*-**C**H of BPh$_4$), 134.27 (*o*-**C**(CH$_3$) of Mes), 131.15 (*ipso*-**C**-N of Mes), 129.26 (*m*-**C**H of Mes), 129.15 (*p*-**C** of PhNO$_2$), 125.32 (s, *m*-**C**H of BPh$_4$), 125.11 (Tz-**C**5), 124.16 (Im-**C**5'), 123.94 (m-**C**H of PhNO$_2$), 123.36 (Im-**C**4'), 121.54 (s, *p*-**C**H of BPh$_4$), 52.11 (TzN-**C**H$_2$), 44.29 (ImN-**C**H$_2$), 20.60 (*p*-C**C**H$_3$ of Mes), 16.87 (*o*-**C**H of Mes) ppm.

*A.5 Synthesis of [MeCaTBn]BPh$_4$ (**1e**)*



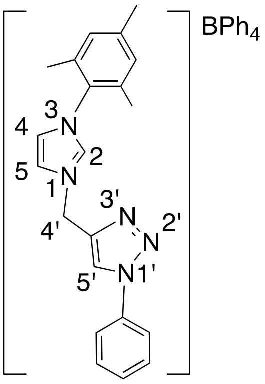
[CH_3CaTBz]BPh$_4$ (**1e**) was prepared following a modification of the literature procedure.[3, 4]

Benzyl azide (0.12 g, 0.90 mmol) was dissolved DMSO (4 ml). 3-(2-Propynyl)-1-methyl-1H-imidazolium bromide (0.11 g, 0.87 mmol), copper(II) sulphate pentahydrate (0.1 g, 0.4 mmol) and sodium L-ascorbate (0.15 g, 0.80 mmol) were added sequentially to the reaction mixture. The reaction mixture was deoxygenated and stirred for 48 h at room temperature. The reaction mixture was poured into a beaker containing water (100 ml) and NaBPh$_4$ (0.274 g, 0.80 mmol) was added. The mixture was stirred vigorously for 30 min to form a white precipitate which was then collected by vacuum filtration, washed saturated aqueous solution of Na_2EDTA (3 x 10 ml), methanol (10 ml) and dried under vacuum. Yield: 0.17 g (0.3 mmol), 34%.

ESI-MS (ESI^+, MeOH), *m/z* (%): 254.14 (100, M) amu; calculated for $[C_{14}H_{16}N_5]^+$ = 254.14 amu.

^{1}H NMR (500 MHz, dmso-d_6): δ 9.15 (br s, 1H, Im-**H**2), 8.27 (s, 1H, H5'), 7.74 (dd, 1H, H5), 7.63 (dd, 1H, H4), 7.35 (m, 5H, Hb, Hc, and Hd), 7.18 (br s, 8H, *o*-H of BPh_4), 6.92 (m, 8H, *m*-H of BPh_4), 6.79 (m, 4H, *p*-H of BPh_4), 5.62 (s, 2H, Ph-CH_2-triaz), 5.50 (s, 2H, triaz-CH_2-imid), 3.83 (s, 3H, CH_3) ppm.

*A.6. Synthesis of [MesCaTPh]BPh_4 (**1f**)*



Phenyl azide (0.301g, 2.52 mmol) and 1-mesityl-3-propargylimidazolium bromide (0.770g, 2.52 mmol) were added to a deoxygenated mixture of 2-propanol and water (12.0 mL, 1:1). Copper sulfate pentahydrate (0.031g, 0.13mmol) was added, followed by sodium L-ascorbate (0.099 g, 0.50 mmol). The solution was mixed for 18 hours at room temperature. The solvent was reduced by half under vacuum, and the aqueous mixture was extracted with dichloromethane (3 x 10mL). The organic layers were combined and washed with saturated aqueous Na_2EDTA solution until the aqueous phase was no longer blue (5 x 10mL). The organic layer was then dried over magnesium sulfate and the solvent reduced *in vacuo*. The crude product was recrystallised from dichloromethane and pentane. The white solid was then redissolved in dichloromethane and sodium tetraphenylborate (0.76 g, 2.22 mmol) was added. The mixture was stirred for 1 hour, then filtered through Celite. The solvent was removed in vacuo to yield the title product as a white solid. Yield: 1.44 g, 86%.

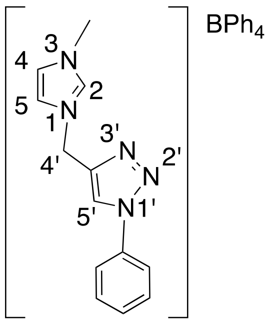
ESI-MS (ESI^+, MeOH), *m/z* (assignment, %): 344.17 (100, [M]); calculated for $[C_{21}H_{22}N_5]^+$: 344.19 amu.

^{1}H (600 MHz, dmso-d_6): δ 9.54 (apparent t, ^3J = 1.6 Hz, 1H, Im-**H**2), 9.00 (s, 1H, Tz-**H**5'), 8.12 (apparent t, ^3J = 1.6 Hz, 1H, Im-**H**4/**H**5), 7.97 (apparent t, ^3J = 1.6 Hz, 1H, Im-**H**5/**H**4), 7.91-7.90

(m (apparent d, ^3J = 8.0 Hz), 2H, *o*-C**H** of Ph), 7.64 (apparent t, ^3J = 8.0 Hz, 2H, *m*-C**H**), 7.54 (apparent t, ^3J = 8.0 Hz, 1H, *p*-C**H** of Ph), 7.18 (br m, 8H, *o*-C**H** of BPh_4), 7.15 (s, 2H, *m*-C**H** of Mes), 6.92 (t, ^3J = 7.4 Hz, 8H, *m*-C**H** of BPh_4), 6.79 (t, ^3J = 7.4 Hz, *p*-C**H** of BPh_4), 5.74 (s, 2H, Im-NC$\mathbf{H}_2$), 2.33 (s, 3H, *p*-CC$\mathbf{H}_3$ of Mes), 2.02 (s, 6H, *o*-CC$\mathbf{H}_3$ of Mes) ppm.

$^{13}C^1H$ (600 MHz, dmso-d_6): δ 163.36 (q, $^1J_{B\text{-}C}$ = 49.3 Hz, *ipso*-**C** of BPh_4), 141.14, 140.31, 137.71, 136.40, 135.53, 134.28, 131.15, 130.01, 129.23, 129.03, 125.30, 124.19, 123.44, 123.12, 121.50, 120.26, 44.27 (ImN-**C**H_2), 20.58 (*p*-C**C**H_3) and 16.90 (*o*-C**C**H_3) ppm.

*A.7. Synthesis of [MeCaTPh]BPh_4 (**1g**)*



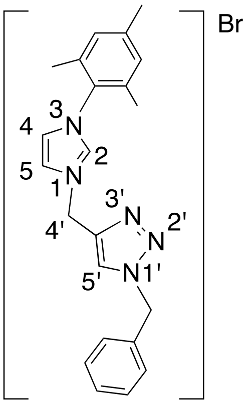
Phenyl azide (0.11 g, 0.90 mmol) was dissolved in a deoxygenated of H_2O/*i*-PrOH (1:1, 6 ml). 3-(2-Propynyl)-1-methyl-1H-imidazolium bromide (0.11 g, 0.87 mmol), copper(II) sulphate pentahydrate (0.10 g, 0.40 mmol) and sodium ascorbate (0.15 g, 0.80 mmol) were added sequentially to the reaction mixture. The reaction mixture was then deoxygenated and stirred for 72 h at room temperature. When starting materials were no longer detected by TLC, *i*-PrOH was removed in vacuum. $NaBPh_4$ (0.274 g, 0.80 mmol), DCM (10 ml) and saturated aqueous solution of Na_2EDTA (30 mL) were added to the reaction mixture. The resulting mixture was stirred for 1h. The organic and aqueous phases were separated and the organic fraction was washed with saturated aqueous Na_2EDTA solution (3×20ml*)*. The combined aqueous layer was continuously extracted with DCM (*2*×10ml*)* over the period of 3 h. The combined organic extract was washed with water, dried over anhydrous $MgSO_4$ and the solvent was removed in vacuum after the removal of the drying reagent by filtration to afford a white crystalline solid, which was recrystallised from DCM and pentane. Yield: 0.251 g (0.45 mmol), 56%; m.p. 181 °C.

Elemental analysis found: C, 77.08; H, 6.10; N, 12.20; calculated for: $C_{37}H_{34}BN_5 + H_2O$: C, 76.95; H, 6.28; N, 12.13%.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 9.21 (s, 1H, Im-**H**2), 8.90 (s, 1H, Tz-**H**5'), 7.88 (d, ^3J = 7.8 Hz, 2H, *o*-C**H** of Ph), 7.82 (s, 1H, Im-**H**5), 7.73 (s, 1H, Im-**H**4), 7.63 (t, ^3J = 7.6 Hz, 2H, *m*-C**H** of Ph), 7.53 (t, ^3J = 7.5 Hz, 1H, *p*-C**H** of Ph), 7.18 (br s, 8H, *o*-C**H** of BPh_4), 6.92 (m, 8H, *m*-C**H** of BPh_4), 6.79 (m, 4H, *p*-C**H** of BPh_4), 5.63 (s, 2H, ImN-C**H**$_2$), 3.86 (s, 3H, C**H**$_3$) ppm.

^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): *δ* 163.8 (q, *ipso*-**C** of BPh_4), 142.0 (**C**4'), 137.1 (d, **C**2), 136.8 (C_q-N of Mes), 135.9 (*o*-**C**H of BPh_4), 130.3 (*m*-**C**H of Ph), 129.5 (*p*-**C**H of Ph), 125.7 (*m*-**C**H of BPh_4), 124.3 (Im-**C**5), 123.4 (Tz-**C**5'), 122.9 (Im-**C**4), 121.9 (*p*-**C** of BPh_4), 120.7 (*m*-**C**H), 44.0 (ImN-**C**H$_2$), 36.3 (**C**H$_3$) ppm.

*A.8. Synthesis of [MesCaTBn]Br (**1h**)*



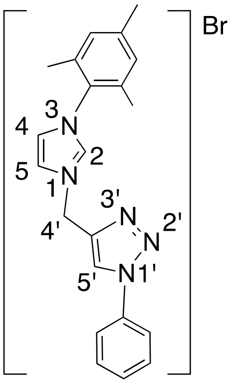
Copper(II) sulfate pentahydrate (0.062 g, 0.25 mmol), L-sodium ascorbate (0.198 g,1.00 mmol) were combined in a Schlenk flask. 2-Propanol (20 mL) and water (20 mL) were added and the reaction mixture was deoxygenated by briefly putting the reaction flask under vacuum and refilled with nitrogen. 1-Mesityl-3-propargylimidazolium bromide (1.53 g, 5.00 mmol) and benzyl azide (0.66 g, 5.0 mmol) were added. The reaction mixture was then stirred under nitrogen for 40 hours during which time a small amount of white solid formed. 2-Propanol was removed under vacuum, saturated aqueous Na_2EDTA solution (30 mL) was added to the reaction mixture, followed by dichloromethane (dcm, 80 mL). The mixture was stirred at RT for 15 minutes and the aqueous layer was extracted with dcm (3 x 50 mL). The combined dcm layer was washed with saturated aqueous Na_2EDTA solution (10 x 20 mL, the dcm-Na_2EDTA mixture was vigorously stirred in a round bottom flask for about 30 minutes and separated using a separating funnel) until the aqueous layer became colourless. The dcm layer was then washed with water (3 x 20 mL), dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to afford a pale yellow thick oil. The thick oil was then dried in a vacuum desiccator overnight to afford a fluffy off-white solid. Yield: 0.82 g, 37%.

ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 358.17 (100, [M]$^+$); calculated for $[C_2H_{24}N_5]^+$: 358.20 amu.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.34 (apparent t, ^3J = 1.7 Hz, 1H, Im-**H**2), 8.86 (s, 1H, Tz-**H**5'), 7.99 (apparent t, ^3J = 1.7 Hz, 1H, Im-**H**4/**H**5), 7.36-7.27 (m, 5H, Ph-**H**), 7.07 (apparent t, ^3J = 1.7 Hz, 1H, Im-**H**5/**H**4), 6.99 (s, 2H, *m*-**C**H of Mes), 6.25 (s, 2H, TzNC**H**$_2$), 5.51 (s, 2H, ImN-C**H**$_2$), 2.34 (s, 3H, *p*-CC**H**$_3$), 2.02 (s, 6H, *o*-CC**H**$_3$) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.68, 140.85, 137.80, 134.29, 130.67, 130.07, 129.28, 129.01, 128.30, 125.76, 123.36, 122.90 (expected thirteen ^{13}C resonances in the aromatic region, only observed twelve), 54.57 (Tz-N**C**H$_2$), 44.64 (Im-N**C**H$_2$), 21.23 (*p*-**C**CH$_3$), 17.17 (*o*-C**C**H$_3$) ppm.

*A.9. Synthesis of [MesCaTPh]Br (**1i**)*



Copper(II) sulfate pentahydrate (0.062 g, 0.25 mmol), L-sodium ascorbate (0.198 g,1.00 mmol) were combined in a Schlenk flask. 2-Propanol (20 mL) and water (20 mL) were added and the reaction mixture was deoxygenated by briefly putting it under vacuum and refilled with nitrogen. 1-Mesityl-3-propargylimidazolium bromide (1.53 g, 5.00 mmol) and phenyl azide (0.60 g, 5.0 mmol) were added. The reaction mixture was then stirred under nitrogen for 72 hours during which time a small amount of white solid formed. 2-Propanol was removed under vacuum, saturated aqueous Na_2EDTA solution (30 mL) was added to the reaction mixture, followed by dichloromethane (dcm, 100 mL). The mixture was stirred at RT for 15 minutes and the aqueous layer was extracted with dcm (3 x 50 mL). The combined dcm layer was washed with saturated aqueous Na_2EDTA solution (7 x 30 mL, the dcm-Na_2EDTA mixture was vigorously stirred in a RBF for about 30 minutes and separated using a separating funnel) until the aqueous layer became colourless. The dcm layer was then washed with water (3 x 20 mL), dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to afford a pale yellow thick oil. The thick oil was then dried in a vacuum desiccator overnight to afford a fluffy off white solid. Yield: 0.91 g,42%.

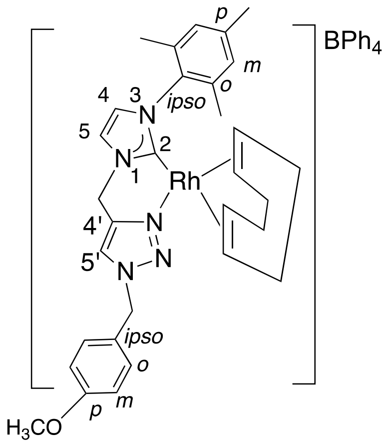
ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 344.16 (100, [M]$^+$); calculated for $[C_{21}H_{22}N_5]^+$: 344.19 amu.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.40 (apparent t, ^3J = 1.6 Hz, 1H, Im-**H**2), 9.19 (s, 1H, Tz-**H**5’), 8.06 (apparent t, ^3J = 1.7 Hz, 1H, Im-**H**4/**H**5), 7.81-7.77 (m, 2H, *o*-C**H** or *m*-C**H** of Ph), 7.54-7.41 (m, 3H, *o*-C**H** or *m*-C**H** and *p*-C**H** of Ph), 7.11 (apparent t, ^3J = 1.6 Hz, 1H, Im-**H**5/**H**4), 6.99 (s, 2H, *m*-**C**H of Mes), 6.26 (s, 2H, ImNC$\mathbf{H}_2$), 2.33 (s, 3H, *p*-CC$\mathbf{H}_3$), 2.05 (s, 6H, *o*-CC$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.86, 137.08, 136.21, 133.87, 130.32, 129.41, 128.65, 123.60, 123.54, 123.06, 120.08 (expected 13 ^{13}C resonances in the aromatic region, only observed 13 resonances due to overlapping of resonances), 44.20 (Im-N**C**H$_2$), 20.75 (*p*-C**C**H$_3$), 17.35 (*o*-C**C**H$_3$)ppm.

Part B: Synthesis of Cationic Rh(I) Complexes

B.1 Synthesis of [Rh(MesCaTBnOMe)(COD)]BPh$_4$ (**2b**)



Sodium ethoxide (0.050 g, 0.735 mmol) was added to a suspension of [Rh(*μ*-Cl)(COD)]$_2$ (0.099 g, 0.20 mmol) in ethanol (20 mL) and the suspension was stirred at RT for 15 minutes, during which time the color of the suspension changed from orange to pale yellow. The ligand, [MesCaTBnOMe]BPh$_4$ (**1b**, 0.283 g, 0.40 mmol) in tetrahydrofuran (15 mL) was added slowly over 15 minutes the metal precursor suspension above. The solvent was completely removed *in vacuo* and the residue was washed with methanol (4 x 2.5 mL) and dried *in vacuo*. The crude product was recrystallized from dichloromethane/pentane (10 mL/ 30 mL) to afford a yellow solid. Yield: 0.338 g, 92%.

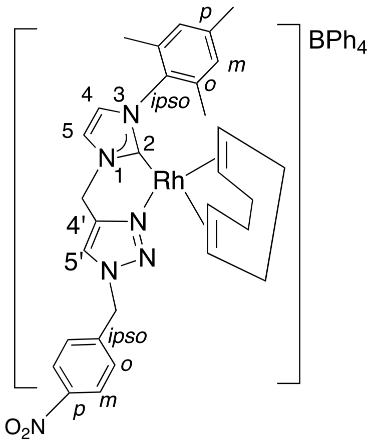
ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 597.92 ([M]$^+$, 100)]; calculated for $C_{31}H_{37}N_5ORh$: 598.21 amu.

Elemental analysis: found: C, 72.04, H, 6.34 and N, 7.73; calculated for $C_{55}H_{57}BN_5ORh$: C, 71.98; H, 6.26 and N, 7.63 %.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.41-7.39 (m, 8H, *o*-C**H** of BPh$_4$), 7.17 (m (apparent d, ^3J = 8.7 Hz), 2H, *o*-C**H** of PhOCH$_3$), 7.08 (s, 2H, *m*-C**H** of Mes), 7.04 (t, ^3J = 7.40 Hz, 8H, *m*-C**H** of BPh$_4$), 6.94 (m (apparent d, ^3J = 8.7 Hz), 2H, *m*-C**H** of PhOCH$_3$), 6.89 (t, ^3J = 7.40 Hz, 4H, *p*-C**H** of BPh$_4$), 6.88 (d, 1H, Im-**H**5, overlapped with the resonance at 6.89), 6.76 (d, ^3J = 1.82 Hz, 1H, Im-**H**4), 6.71 (s, 1H, Tz-**H**5'), 5.22 (s, 2H, Tz-NC**H**$_2$), 4.87 (br s, 2H, COD-C**H** *trans* N), 4.70 (s, 2H, Im-NC**H**$_2$), 3.84 (s, 3H, OC**H**$_3$), 3.65 (br s, 2H, COD-C**H** *trans* to NHC), 2.41 (s, 3H, *p*-CC**H**$_3$), 2.31-2.23 (m, 2H, COD-CH**H**), 2.11 (s, 6H, *o*-CC**H**$_3$), 2.09-1.98 (m, 4H, COD-CH**H**), 1.95-.191(m, 2H, COD-C**H**H) ppm.

$^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2): δ 176.16 (d, $^{1}J_{Rh\text{-}C2}$ = 52.3 Hz, Im-**C**2), 164.44 (q, $^{1}J_{B\text{-}C}$ 49.4 Hz, *ipso*-**C** of BPh_4), 160.81 (*p*-**C**OCH_3), 140.15 (*p*-**C** of Mes), 139.97 (Tz-**C**4'), 136.34 (*o*-**C**H of BPh_4), 135.89 (*ipso*-**C** of Mes), 135.52 (*o*-**C** of Mes), 130.34 (*o*-**C** of $PhOCH_3$), 129.54 (*m*-**C**H of Mes), 126.19 (*m*-**C**H of BPh_4), 125.30 (*ipso*-**C** of Mes), 123.25 (Im-**C**4), 123.13 (Tz-**C**5'), 122.60 (Im-**C**5), 121.31 (*p*-**C**H of BPh_4), 114.93 (*m*-**C**H of $PhOCH_3$), 96.60 (d, $^{1}J_{Rh\text{-}C}$ = 7.7 Hz, **C**H of COD *trans* N), 79.04 (d, $^{1}J_{Rh\text{-}C}$ = 12.1 Hz, COD-**C**H *trans* NHC), 55.80 (O**C**H_3), 55.33 (TzN**C**H_2), 45.12 (ImN-**C**H_2), 32.59 (COD-**C**H_2 *trans* N), 29.24 (COD-**C**H_2 *trans* NHC), 21.21 (*o*-C**C**H_3), 18.57 (*p*-C**C**H_3) ppm.

*B.2 Synthesis of [Rh(MesCaTBnNO$_2$)(COD)]BPh$_4$ (**2c**)*



A solution of [MesCaTBnNO$_2$]BPh$_4$ (**1c**, 0.292 g, 0.400 mmol) in tetrahydrofuran (20 mL) was added slowly over 15 minutes to a yellow suspension of [Rh(μ-Cl)(COD)]$_2$ (0.099 g, 0.200 mmol) and sodium ethoxide (0.055 g, 0.808 mmol) in ethanol 920 mL). The reaction mixture turned slight green and was stirred for 15 minutes at room temperature. The solvent was removed *in vacuo* to afford a yellow green solid, which was washed with methanol (4 x 3 mL) and dried *in vacuo*. The crude product was re-crystallised from dcm (10 mL)/pentane (35mL). The thick oil + solid product was collected by filtration and dried *in vacuo* to afford a greenish yellow solid. Yield: 0.325 g, 87%.

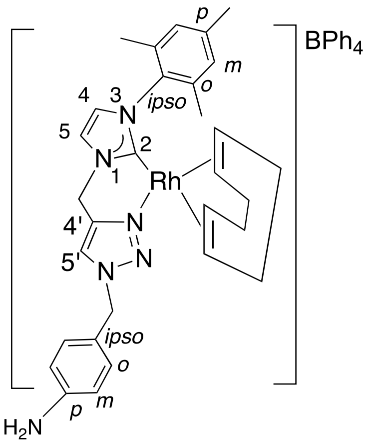
ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 612.90 ([M]$^+$, 100); calculated for $C_{30}H_{34}N_6O_2Rh$: 613.18 amu.

Elemental analysis, found: C, 69.72, H, 6.17 and N, 8.98; calculated for $C_{54}H_{54}BN_6O_2Rh$: C, 69.53; H, 5.84 and N, 9.01 %.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.17 (d, ^{3}J = 8.8 Hz, 2H, *m*-C**H** of $PhNO_2$), 7.39 (br s, 8H, *o*-C**H** of BPh_4), 7.17 (d, ^{3}J = 8.8 Hz, 2H, *o*-C**H** of $PhNO_2$), 7.04 (s, 2H, *m*-C**H** of Mes), 6.98 (t, *J* = 7.40 Hz, 8H, *m*-C**H** of BPh_4), 6.94 (d, ^3J = 1.70 Hz, 1H, Im-**H**5), 6.84 (t, ^3J = 7.40 Hz, 4H, *p*-C**H** of BPh_4), 6.74 (d, ^3J = 1.70 Hz, 1H, **H**4), 6.24 (s, 1H, Tz-**H**4'), 5.10 (s, 2H, TzNC$\mathbf{H}_2$), 4.77 (br m, 2H, COD-C**H** (*trans* to N)), 4.72 (s, 2H, Im-NC$\mathbf{H}_2$), 3.63 (br m, 2H, COD-C**H** (*trans* NHC)), 2.37 (s, 3H, *p*-CC$\mathbf{H}_3$), 2.26-2.19 (m, 2H, COD-C$\mathbf{H}_2$ (*trans* N)), 2.07 (s, 6H, *o*-CC$\mathbf{H}_3$), 2.06-2.19 (m, 2H, COD-C$\mathbf{H}_2$ (*trans* NHC)), 198-1.92 (m, 2H, COD-C$\mathbf{H}_2$ (*trans* N)), 1.92-1.85 (m, 2H, COD-C$\mathbf{H}_2$ (*trans* NHC)) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 176.19 (d, $^1J_{Rh\text{-}C}$ = 52.7 Hz, Im-**C**2), 164.42 (q, $^1J_{B\text{-}C}$ = 49.0 Hz, *ipso*-**C** of BPh_4), 148.61 (**C**-NO_2 of $PhNO_2$), 140.59 (**C**CH_2 of $PhNO_2$), 140.21 (*p*-**C** of Mes), 140.11 (Tz-**C**4'), 136.32 (*o*-**C**H of BPh_4), 135.84 (*ipso*-**C** of Mes), 135.47 (*o*-**C** of Mes), 129.57 (*m*-**C** of Mes), 129.20 (*o*-**C**H of $PhNO_2$), 126.27 (*m*-**C**H of BPh_4), 124.55 (*m*-**C**H of $PhNO_2$), 124.39 (Tz-**C**5'), 123.27 (Im-**C**4), 122.63 (Im-**C**5), 122.43 (*p*-**C**H of BPh_4), 96.65 (d, $^1J_{Rh\text{-}C}$ = 7.9 Hz, COD-C**H** (*trans* N)), 79.34 (d, $^1J_{Rh\text{-}C}$ = 11.3 Hz, COD-**C**H (*trans* NHC)), 54.25 (TzN**C**H_2), 45.12 (Im-N**C**H_2), 32.57 (COD-**C**H_2 (*trans* NHC)), 29.22 (COD-**C**H_2 (*trans* N)), 21.21 (*p*-C**C**H_3), 18.55 (*o*-C**C**H_3) ppm.

*B.3 Synthesis of [Rh(MesCaTBnNH$_2$)(COD)]BPh$_4$ (**2d**)*



Sodium ethoxide (0.060 g, 0.882 mmol) was added to a suspension of $[Rh(\mu\text{-}Cl)(COD)]_2$ (0.099 g, 0.20 mmol) in ethanol (20 mL) and the suspension was stirred for 10 minutes at room temperature, during which time the colour of the suspension changed from orange to pale yellow. A suspension of $[MesCaTBnNH_2]BPh_4$ (**1d**, 0.277 g, 0.40 mmol) in tetrahydrofuran (20 mL) was added slowly over 15 minutes to the metal precursor suspension. The reaction mixture was stirred for 15 minutes at RT and the solvent was removed under *vacuo* to afford a greenish yellow solid. The solid residue was washed with methanol (4 x 3 mL), dried under *vacuo*. The crude product was recrystallised from dcm (10 mL)/pentane (35 mL). The greenish yellow solid product was collected by filtration, and dried under vacuum overnight. Yield: 0.310 g, 86%.

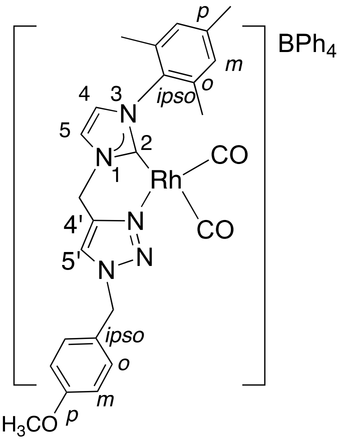
ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 583.26 ([M]$^+$, 100); calculated for $C_{30}H_{36}N_6Rh$: 583.21 amu.

Elemental analysis: found: C, 71.29, H, 6.54 and N, 9.19; calculated for $C_{54}H_{56}BN_6Rh$: C, 71.84; H, 6.25 and N, 9.31 %.

^{1}H NMR (500 MHz, CD_2Cl_2): 7.37 (br s, 8H, *o*-C**H** of BPh$_4$), 7.04 (s, 2H, *m*-C**H** of Mes), 7.00 (m, 10H, *m*-C**H** of BPh$_4$ (*J* = 7.40 Hz, 8H) and *m*-C**H** of PhNH$_2$ (2H, apparent t, ^3J = 8.4 Hz)), 6.86 (t, ^3J = 7.40 Hz, 4H, *p*-C**H** of BPh$_4$), 6.82 (d, ^3J = 1.70 Hz, 1H, Im-**H**4), 6.75 (s, 1H, Tz-**H**5'), 6.71 (d, ^3J = 1.70 Hz, 1H, **H**5), 6.63 (d, ^3J = 8.4 Hz, 2H, *o*-C**H** of PhNH$_2$), 5.15 (s, 2H, TzN-C**H**$_2$), 4.85 (br s, 2H, COD-C**H** (*trans* to N)), 4.63 (s, 2H, Im-NC**H**$_2$), 3.83 (br s, N**H**$_2$), 3.61 (br s, 2H, COD-C**H** (*trans* NHC)), 2.37 (s, 3H, *p*-CC**H**$_3$), 2.26-2.20 (m, 2H, COD-C**H**$_2$ (*trans* N)), 2.07 (s, 6H, *o*-CC**H**$_3$), 2.05-1.94 (m, 4H, COD-C**H**$_2$), 1.91-187 (m, 2H, COD-C**H**$_2$ (*trans* NHC)) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 176.18 (d, $^1J_{Rh\text{-}C}$ = 53.1 Hz, Im-**C**2), 164.41 (q, $^1J_{B\text{-}C}$ = 50.0.0 Hz, *ipso*-**C** of BPh$_4$), 148.35 (**C**-NH$_2$ of PhNH$_2$), 140.13 (*p*-**C** of Mes), 139.88 (Tz-**C**4'), 136.35 (*o*-**C**H of BPh$_4$), 135.91 (*ipso*-**C** of Mes), 135.53 (*o*-**C** of Mes), 130.37 (*o*-**C**H of PhNH$_2$), 129.53 (*m*-**C**H of Mes), 126.17 (*m*-**C**H of BPh$_4$), 123.09 (*ipso*-**C** of PhNH$_2$), 123.04 (Im-**C**5), 122.58 (Im-**C**4), 122.29 (*p*-**C**H of BPh$_4$), 122.20 (Tz-**C**5'), 115.47 (*m*-**C**H of PhNH$_2$), 96.57 (d, $^1J_{Rh\text{-}C}$ = 7.6 Hz, COD-C**H** (*trans* N)), 78.96 (d, $^1J_{Rh\text{-}C}$ = 12.1 Hz, COD-**C**H (*trans* NHC)), 55.68 (TzN-**C**H$_2$), 45.10 (Im-N**C**H$_2$), 32.59 (COD-**C**H$_2$ (*trans* NHC)), 29.24 (COD-**C**H$_2$ (*trans* N)), 21.20 (*p*-C**C**H$_3$), 18.59 (*o*-C**C**H$_3$) ppm.

*B.4 Synthesis of [Rh(MesCaTBnOMe)(CO)$_2$]BPh$_4$ (**3b**)*



A suspension of [Rh(MesCaTOCH$_3$)(COD)]BPh$_4$, (**2b**, 0.155 g, 0.169 mmol) in methanol (4 mL) and pentane (20 mL) was degassed *via* three cycles of freeze-pump-thaw. The reaction mixture was placed under an atmosphere of carbon monoxide using a balloon, the colour of the solid changed from bright yellow to pale yellow then turned dark orange. The

CO balloon was removed and the orange solid was collected by filtration and washed with pentane (3 x 5mL) and dried *in vacuo*. Yield: 0.128 g; 88%.

ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 546.00 ([M]$^+$, 100), 517.90 ([M-CO]$^+$, 77), 489.93 ([M-2CO]$^+$, 25) amu; calculated for $[C_{29}H_{25}N_5O_3Rh]^+$ = 546.10 amu.

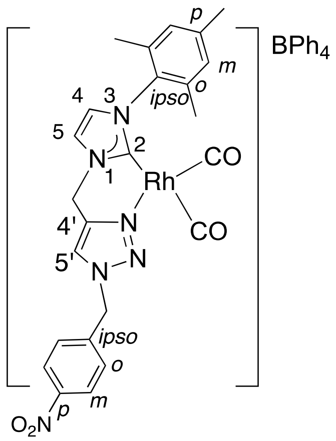
Elemental analysis: found: C, 68.18; H, 5.20 and N, 8.19; calculated for $C_{49}H_{45}BN_5O_3Rh$: C, 67.99; H, 5.24 and N, 8.09 %.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39 (br m, 8H, *o*-C**H** of BPh$_4$), 7.20 (m (apparent d, ^3J = 8.4 Hz), 2H, *o*-C**H** of PhOCH$_3$), 7.04 (s, 2H, *m*-C**H** of Mes), 6.98 (t, ^3J = 7.50 Hz, 8H, *m*-C**H** of BPh$_4$), 6.93 (d, ^3J = 1.70 Hz, 1H, Im-**H**4), 6.92 (m (apparent d, ^3J = 8.7 Hz), 2H, *m*-C**H** of PhOCH$_3$), 6.84 (1H, Im-**H**5, overlapped with the next resonance), 6.83 (t, ^3J = 7.5 Hz, 4H, *p*-C**H** of BPh$_4$), 6.42 (s, 1H, Tz-**H**5’), 5.23 (s, 2H, TzN-C**H**$_2$), 4.31 (s, 2H, ImNC**H**$_2$), 3.81 (s, 3H, OCH$_3$), 2.37 (s, 3H, *p*-CC**H**$_3$), 2.02 (s, 6H, *o*-CC**H**$_3$) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 184.74 (d, $^1J_{Rh\text{-}C}$ = 59.5 Hz, **C**O), 184.68 (d, $^1J_{Rh\text{-}C}$ = 65.5 Hz, **C**O), 172.17 (d, $^1J_{Rh\text{-}C}$ = 47.0 Hz, Im-**C**2), 164.42 (q, $^1J_{B\text{-}C}$ = 49.2 Hz, *ipso*-**C** of BPh$_4$), 161.02 (**C**OCH$_3$ of PhOCH$_3$), 141.14 (*p*-**C**CH$_3$ of Mes), 140.30 (s, Tz-**C**4’), 136.29 (*o*-**C**H of BPh$_4$), 136.04 (*o*-**C** of Mes), 135.34 (*ipso*-N**C** of Mes), 130.70 (*o*-**C**H of PhOCH$_3$), 129.87 (*m*-**C**H of Mes), 126.28 (br s, *m*-**C** of BPh$_4$), 124.62 (*ipso*-**C**CH$_2$ of PhOCH$_3$), 123.95 (Im-**C**5), 123.86 (Tz-**C**5’), 123.29 (Im-**C**4), 122.42 (*p*-**C**H of BPh$_4$), 115.02 (*m*-**C**H of PhOCH$_3$), 55.83 (O**C**H$_3$), 55.77 (TzN-**C**H$_2$), 44.62 (ImN-**C**H$_2$), 21.27 (*p*C-**C**H$_3$), 18.32 (*o*-C**C**H$_3$) ppm.

FTIR (dcm): *ν* (CO): 2096 and 2035 cm^{-1}.

B.5 Synthesis of [Rh(MesCaTBnNO$_2$)(CO)$_2$]BPh$_4$ (**3c**)



Methanol (7 mL) and pentane (20 mL) were added to a Schlenk flask containing [Rh(MesCaTBnNO$_2$)(COD)]BPh$_4$ (**2c**, 0.160 g, 0.169 mmol). The reaction mixture was degassed *via* three cycles of freeze-pump-thaw. The reaction mixture was then put under an atmosphere of carbon monoxide using a balloon for two hours, during which time the colour of the solid changed from greenish yellow to creamy yellow. Yield: 0.121 g, 89%.

ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 560.85 ([M]$^+$, 100); calculated for $C_{24}H_{22}N_6O_4Rh$: 561.08 amu.

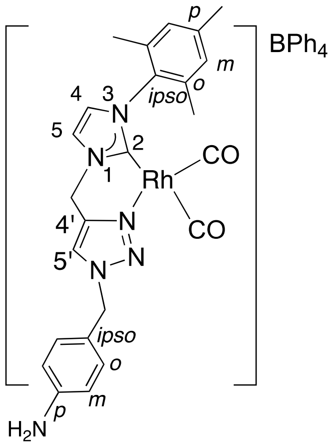
Elemental analysis, found: C, 65.42, H, 4.84 and N, 9.73; calculated for $C_{48}H_{42}BN_6O_4Rh$: C, 65.47; H, 4.81 and N, 9.54 %.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (d, ^3J = 8.70 Hz, 2H, *m*-C**H** of PhNO$_2$), 7.41 (br s, 8H, *o*-C**H** of BPh$_4$), 7.28 (d, ^3J = 8.70 Hz, 2H, *o*-C**H** of PhNO$_2$), 7.05 (s, 2H, *m*-C**H** of Mes), 6.98 (s, 1H, Im-**H**5), 6.97 (t, J = 7.40 Hz, 9H, *m*-C**H** of BPh$_4$ and Im-**H**4), 6.81 (t, ^3J = 7.10 Hz, 4H, *p*-C**H** of BPh$_4$), 6.01 (s, 1H, Tz-**H**5'), 5.16 (s, 2H, TzN-C**H**$_2$), 4.42 (s, 2H, ImN-C**H**$_2$), 2.37 (s, 3H, *p*-CC**H**$_3$), 2.04 (s, 6H, *o*-CC**H**$_3$) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 184.57 (d, $^1J_{Rh\text{-}C}$ = 53.9 Hz, **C**O), 184.49 (d, $^1J_{Rh\text{-}C}$ = 70.0 Hz, **C**O), 172.18 (d, $^1J_{Rh\text{-}C}$ = 46.9 Hz, Im-**C**2), 164.45 (q, $^1J_{B\text{-}C}$ = 48.90 Hz, *ipso*-**C** of BPh$_4$), 148.79 (**C**NO$_2$), 141.23 (*p*-**C** of Mes), 140.43 (d, $^2J_{Rh\text{-}C}$ = 1.40 Hz, Tz-**C**4'), 139.71 (*ipso*-**C** of PhNO$_2$), 136.25 (br s, *o*-**C**H of BPh$_4$), 135.99 (*o*-**C** of Mes), 135.28 (*ipso*-**C** of Mes), 129.72 (*o*-**C**H of PhNO$_2$), 129.61 (*m*-**C**H of Mes), 126.36 (q, ^3J = 2.8 Hz, *m*-**C**H of BPh$_4$), 124.87 (Tz-**C5'**), 124.63 (*m*-**C**H of PhNO$_2$), 123.92 (**C**4), 123.50 (Im-**C**5), 122.53 (*p*-**C**H of BPh$_4$), 54.71 (TzN-**C**H$_2$), 44.67 (ImN-**C**H$_2$), 21.27 (*p*-C**C**H$_3$), 18.32 (*o*-C**C**H$_3$) ppm.

FTIR (dcm): *v* (CO): 2096 and 2035 cm^{-1}.

*B.6 Synthesis of [Rh(MesCaTBnNH$_2$)(CO)$_2$]BPh$_4$ (**3d**)*



Methanol (3 mL) and pentane (20 mL) were added to a Schlenk flask containing [Rh(MesCaTBnNH$_2$)(COD)]BPh$_4$ (**2d**, 0.153 g, 0.169 mmol). The reaction mixture was degassed *via* three cycles of freeze-pump-thaw. The reaction mixture was then put under an atmosphere of carbon monoxide using a balloon for two hours, during which time the colour of the solid changed from greenish yellow to very pale greenish yellow. Yield: 0.119 g, 83%.

ESI-MS (ESI$^+$, MeOH) *m/z* (assignment, %): 530.83 ([M]$^+$, 100), 502.73 ([M-CO]$^+$, 70); calculated for [M = $C_{24}H_{24}N_6O_2Rh$]: 531.10 and [M-CO]$^+$ = 503.11 amu.

Elemental analysis: found: C, 66.75, H, 5.20 and N, 10.03; calculated for $C_{48}H_{44}BN_6O_2Rh.H_2O$: C, 66.37; H, 5.34 and N, 9.67 %.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.37 (br s, 8H, *o*-C**H** of BPh$_4$), 7.07 (m (apparent d, ^3J = 8.70 Hz), 2H *m*-C**H** of PhNH$_2$), 7.04 (s, 2H, *m*-C**H** of Mes), 6.95 (t, ^3J = 7.50 Hz, 8H, *m*-C**H** of BPh$_4$), 6.93 (d, ^3J = 1.8 Hz, 1H, Im-**H**4), 6.84 (d, ^3J = 1.8 Hz, 1H, Im-**H**5), 6.81 (t, ^3J = 7.5 Hz, 4H, *p*-C**H** of BPh$_4$), 6.66 (m (apparent d, ^3J = 8.70 Hz), 2H, *o*-C**H** of PhNH$_2$), 6.59 (s, 1H, Tz-**H**5’), 5.22 (s, 2H, TzN-C**H**$_2$), 4.32 (s, 2H, ImN-C**H**$_2$), 3.88 (br s, 2H, N**H**$_2$), 2.37 (s, 3H, *p*-CC**H**$_3$), 2.04 (s, 6H, *o*-CC**H**$_3$) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): The 13C NMR data were not acquired as the sample slowly decomposed in a DCM-*d*$_2$ solution overnight.

FTIR (dcm): *v* (CO): 2095 and 2034 cm^{-1}.

B.7 Summary of νCO (cm^{-1}) and δ(CO)(ppm) values for complexes ***3a-d***

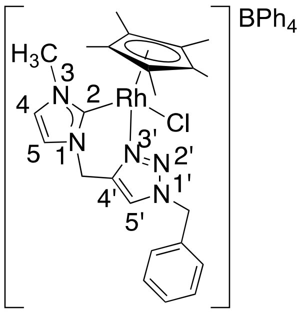
Table S1: νCO[a] and *δ*(CO)[b] of complexes **3a-d**.

Complex	***ν*CO**	***δ*(CO)**[b]
[Rh(MesCaTBn)(CO)$_2$BPh$_4$ (**3a**)	2095; 2034	184.29 (d, $^1J_{\text{Rh-C}}$ = 60.5 Hz), 184.23 (d, $^1J_{\text{Rh-C}}$ = 68.8 Hz)
[Rh(MesCaTBnOMe)(CO)$_2$BPh$_4$ (**3b**)	2096; 2035	184.74 (d, $^1J_{\text{Rh-C}}$ = 59.5 Hz), 184.68 (d, $^1J_{\text{Rh-C}}$ = 65.5 Hz)
[Rh(MesCaTBnNO$_2$)(CO)$_2$BPh$_4$ (**3c**)	2096; 2035	184.57 (d, $J_{\text{Rh-C}}$ = 53.9 Hz), 184.49 (d, $J_{\text{Rh-C}}$ = 70 Hz)
[Rh(MesCaTBnNH$_2$)(CO)$_2$BPh$_4$ (**3d**)	2095; 2034	n/a

[a] FTIR spectra were acquired as dichloromethane. [b] NMR spectra were acquired in dichloromethane-*d*$_2$.

Part C: Synthesis of Cationic Rh(III) and Ir(III) Complexes

C.1 Synthesis of [Rh(CH_3CaTBn)(Cp)Cl]BPh_4 (**4b**)*

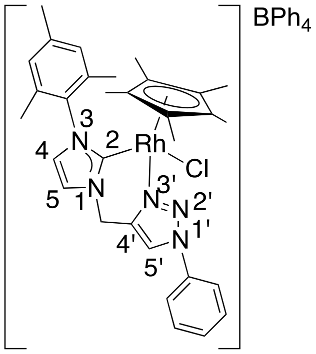


To a solution of [MeCaTBn]BPh_4 (**1e**, 0.287 g, 0.50 mmol) in the acetone (25ml), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed for 3 hours. [RhCp*Cl_2]$_2$ (0.155 g, 0.25 mmol) was added and reaction mixture was refluxed for 1h and stirred over night at room temperature followed by filtration through the Celite. The solvent was removed *in vacuo* to afford brown solid. The solid was dissolved in DCM (4 ml) and pentane (about 15 ml) was added until a yellow precipitate was formed. This suspension was cooled down in an ice bath to further precipitation of the product, which was filtered and dried under vacuum. Yield: 0.288 g, 68%.

Elemental analysis, found: C, 58.3; H, 5.02; N, 6.91; calculated for: $C_{48}H_{49}BClN_5Rh$ + 2 CH_2Cl_2 + 1 H_2O: C, 58.14; H, 5.37; N, 6.78 %.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.43 (m, 11H, *o*-C**H** of BPh_4, *m*-C**H** and *p*-C**H** of Ph), 7.23 (m, 2H, *o*-C**H** of Ph), 7.00 (m, 9H, *m*-C**H** of BPh_4 and Im-**H**4), 6.87 (m, 4H, *p*-C**H** of BPh_4), 6.72 (s, 1H, Im-**H**5), 6.39 (s, 1H, Tz-**H**5'), 5.46 (d, ^2J = 14.4 Hz, 1H, TzN-C**H**H), 5.28 (d, ^2J =14.4 Hz, 1H, TzN-CH**H**), 4.10 (d, ^2J = 16.4 Hz, 1H, ImN-C**H**H), 3.98 (d, ^2J =16.4 Hz, 1H, ImN-CH**H**), 3.83 (s, 3H, C**H**$_3$), 1.56 (s, 15H, C**H**$_3$ of Cp*) ppm.

C.2 Synthesis of [Rh(MesCaTPh)(Cp)Cl]BPh_4 (**4c**)*



To a solution of [MesCaTPh]Br (**1i**, 0.212 g, 0.50 mmol) in the acetone (25 ml), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed for 3h under nitrogen. The reaction mixture was cooled to RT and [RhCp*Cl_2]$_2$ (0.155 g, 0.25 mmol) was added. The mixture was refluxed for 1h and stirred overnight at room temperature. NaBPh_4 (0.171 g, 0.50 mmol) was added and reaction mixture was stirred for another

30 min, followed by filtration through Celite. The solvent was removed *in vacuo* to afford a brown solid. The solid was re-dissolved in DCM (4 ml) and pentane (about 15 ml) was added to form a yellow precipitate. This suspension was cooled down in an ice bath to induce crystallization of the product, which as filtered and dried under vacuum. Crystals suitable for a single crystal structure analysis were obtained by slow diffusion of *n*-pentane into a concentrated DCM solution of the complex. Yield: 0.337 g, 72%; m.p. 147 ^{o}C.

ESI-MS (ESI$^+$, MeCN), *m/z* (%, assignment): 616.17 (100, M); calculated for $[C_{31}H_{36}ClN_5Rh]^+$ = 616.17 amu.

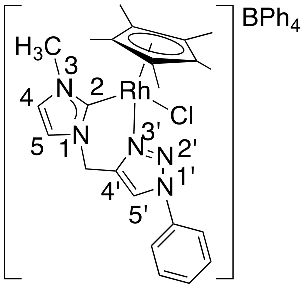
Elemental analysis, found: C, 67.54; H, 5.57; N, 7.27;

Anal. Calcd. $C_{55}H_{56}BClN_5Rh + 2H_2O$: C, 67.94; H, 6.22; N, 7.20;

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.57 (m, 5H, C**H** of Ph), 7.42 (m, 8H, *o*-C**H** of BPh_4), 7.01 (m, 9H, *m*-C**H** of BPh_4, and Tz-**H**5'), 6.97 (m, 3H, m_1-C**H**, m_2-C**H**, and Im-**H**4), 6.84 (m, 5H, *p*-C**H** of BPh_4, and Im-**H**5), 4.69 (d, ^2J = 16.0 Hz, 1H, ImN-C**H**H), 4.33 (d, ^2J = 16.0 Hz, 1H, ImN-CH**H**), 2.35 (s, 3H, *p*-C**H**$_3$ of Mes), 2.14 (s, 3H, o_1-C**H**$_3$ of Mes), 1.95 (s, 3H, o_2-C**H**$_3$ of Mes), 1.42 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 169.1 (d, **C**2), 164.7 (q, *ipso*-**C** of BPh_4), 141.8 (Tz-**C**4'), 140.4 (*p*-**C** of Mes), 139.1 (o_2-**C** of Mes), 136.5 (**C**-N of Ph), 136.4 (*o*-**C**H of BPh_4), 135.9 (*ipso*-**C** of Mes), 135.2 (o_1-**C** of Mes), 130.6 (*m*-**C**H and *p*-**C**H), 130.0 (s, m_2-**C** of Mes), 128.7 (m_1-**C** of Mes), 126.4 (*m*-**C**H of BPh_4), 126.3 (**C**5), 124.7 (**C**4), 122.7 (*p*-**C**H of BPh_4), 122.4 (Tz-C5'), 121,4 (*o*-**C**H of Ph), 99.1 (**C**-CH$_3$ of Cp*), 45.2 (ImN-**C**H$_2$), 21.4 (*p*-C**C**H$_3$ of Mes), 20.2 (o_2-C**C**H$_3$ of Mes), 19.4 (o_1-C**C**H$_3$ of Mes), 10.0 (**C**H$_3$ of Cp*) ppm.

C.3 Synthesis of [Rh(MeCaTPh)(Cp)Cl]BPh$_4$ (**4d**)*



To a solution of the ligand precursor [MeCaTPh]BPh$_4$ (**1g**, 0.280 g, 0.50 mmol) in acetone (25ml), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed under nitrogen for 3 hours. [RhCp*Cl$_2$]$_2$ (0.155 g, 0.25 mmol) was added and the reaction mixture was refluxed for 1h and stirred over night at room temperature. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo* to afford a brown solid. The solid was re-dissolved in DCM (4 ml) and pentane (about 15 ml) was added until a yellow precipitate was formed. This suspension was cooled down in an ice bath to induce further crystallization of the product. The product which was filtered, washed with 10 ml of methanol to remove excess of NaBPh$_4$, and dried under vacuum. Yield: 0.179 g, 43 %.

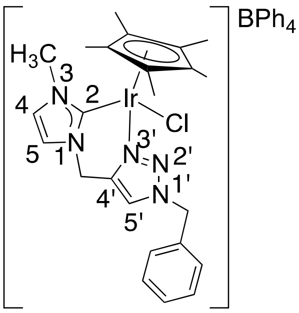
ESI-MS (ESI$^+$, MeOH), *m/z* (%, assignment): 512.11 (100, M); calculated for $C_{23}H_{28}ClN_5Rh$: 512.11 amu.

Elemental analysis, found: C, 66.24; H, 5.70; N, 8.28; calculated for $C_{47}H_{48}BClN_5Rh$ + H_2O: C, 66.40; H, 5.93; N, 8.24 %.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.58 (m, 5H, C**H** of Ph), 7.41 (br s, 8H, *o*-C**H** of BPh$_4$), 7.06 (d, $^3J_{H5\text{-}H4}$ = 1.9 Hz, 1H, **H**4), 7.01 (m, 9H, *m*-C**H** of BPh$_4$ and Tz-**H**5'), 6.90 (d, ^3J = 1.9 Hz, 1H, **H**4), 6.85 (m, 4H, *p*-C**H** of BPh$_4$), 4.46 (d, ^2J = 16.1 Hz, 1H, ImN-C**H**H), 4.34 (d, ^2J_H = 15.7 Hz, 1H, Im-NCH**H**), 3.88 (s, 3H, C**H**$_3$) 1.66 (s, 15H, C**H**$_3$ of Cp*) ppm.

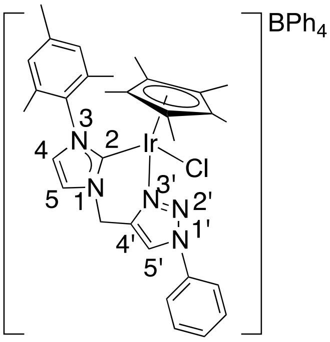
^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): δ 168.1 (d, **C**2), 163.9 (q, *ipso*-**C** of BPh$_4$), 140.8 (**C**4'), 135.8 (*o*-**C**H of BPh$_4$), 135.7 (*ipso*-**C** of Ph), 130.3 (*m*-**C**H of Ph), 129.9 (*p*-**C**H of Ph), 125.8 (*m*-**C**H of BPh$_4$), 123.7 (Im-**C**4), 123.5 (Im-**C**5), 122.1 (*p*-**C** of BPh$_4$), 121.9 (Tz-**C**5'), 120.8 (*o*-**C**H of Ph), 98.4 (d, **C**-CH$_3$ of Cp*), 43.5 (Im-**C**HH), 38.0 (C**H**$_3$), 9.4 (**C**H$_3$ of Cp*) ppm.

C.4 Synthesis of [Ir(MeCaTBn)(Cp)Cl]BPh$_4$ (**5b**)*



The synthesis of this complex was conducted in a similar fashion for the synthesis of complex **5a**. Only a small number of X-ray quality crystals were obtained for this compound and the solid state structure of **5b** was determined however full characterization was not performed.

C.4 Synthesis of [Ir(MesCaTPh)(Cp)Cl]BPh$_4$ (**5c**)*



To a solution of the ligand [MesCaTPh]Br (**1i**, 0.212 g, 0.50 mmol) in the acetone (25ml), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed for 3h under nitrogen. The reaction mixture was cooled to RT and [IrCp*Cl$_2$]$_2$ (0.199 g, 0.25 mmol) was added. The mixture was refluxed for 1h and stirred over night at room temperature. NaBPh$_4$ (0.171 g, 0.50 mmol) was added and reaction mixture was stirred for another 30 min, followed by filtration through Celite. The solvent was removed *in vacuo* to afford brown solid. The solid was redissolved in DCM (4 ml) and pentane (15 ml) was added to form a yellow precipitate. This suspension was cooled down in an ice bath to induce further crystallization of the product which was filtered and dried under vacuum. Yield: 0.335 g, 65%.

ESI-MS (ESI$^+$, MeOH), *m/z* (%, assignment): 706.23 (100, M); 365.15 (100) [2Na$^+$ + BPh$_4^-$]$^+$; calculated for: $C_{31}H_{36}ClIrN_5$: 706.23 amu.

Elemental analysis, found: found: C, 61.54; H, 5.33; N, 6.61; calculated for: $C_{55}H_{56}BClIrN_5$ + $3H_2O$: C, 61.19; H, 5.79; N, 6.49 %.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.58 (s, 1H, Tz-**H**5'), 7.63 (d, ^3J = 7.8 Hz, 2H, *o*-C**H** of Ph), 7.53 (br s, 1H, Im-**H**5), 7.39 (dd, ^3J = 7.8 Hz, ^3J = 7.3 Hz, 2H, *m*-C**H** of Ph), 7.33 (t, ^3J = 7.3 Hz, 1H, *p*-C**H** of Ph), 7.04 (br s, 8H, *o*-C**H** of BPh$_4$), 7.02 (br s, 1H, Im-**H**4), 6.75 (s, 1H, m_1-C**H** of Mes), 6.66 (s, 1H, m_2-C**H** of Mes), 6.62 (m, 8H, *m*-C**H** of BPh$_4$), 6.47 (m, 4H, *p*-C**H** of BPh$_4$), 5.59 (d, ^2J

= 15.7 Hz, 1H, ImN-C**H**H), 4.49 (d, 1H, ^2J =15.7 Hz, Im-CH**H**), 2.03 (s, 3H, *p*-C**H**$_3$ of Mes), 1.90 (s, 3H, *o$_1$*-C**H**$_3$ of Mes), 1.74 (s, 3H, *o$_2$*-C**H**$_3$ of Mes), 1.28 (s, 15H, C**H**$_3$ of Cp*) ppm.

^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): *δ* 164.0 (q, *ipso*-**C** of BPh$_4$), 152.7 (d, Im-**C**2), 141.6 (Tz-**C**4’), 138.9 (*p*-**C** of Mes), 138.4 (*o$_2$*-**C** of Mes), 136.3 (*ipso*-**C**N of Ph), 136.1 (*o*-**C**H of BPh$_4$), 135.5 (*ipso*-**C**N of Mes), 135.1 (*o*$_1$-**C** of Mes), 130.2 (*p*-**C**H of Ph), 130.1 (*m*-**C**H of Ph), 129.1 (*m*$_2$-**C** of Mes), 127.7 (*m$_1$*-**C** of Mes), 125.6 (Im-**C**4), 125.1 (*m*-**C**H of BPh$_4$), 123.6 (Im-**C**5), 122.2 (Tz-**C**5’), 121.3 (*p*-**C**H of BPh$_4$), 121.0 (*o*-**C**H of Ph), 91.4 (d, **C**CH$_3$ of Cp*), 45.1 (ImN-**C**H$_2$), 20.0 (*p*-**C**H$_3$ of Mes), 19.5 (*o$_2$*-**C**H$_3$ of Mes), 18.4 (*o$_1$*-**C**H$_3$ of Mes), 8.6 (s, **C**H$_3$ of Cp*) ppm.

Part D: X-ray Crystallography

D.1 X-ray Crystallographic Data

Table S2: Crystallographic data for [MesCaTBnNO$_2$]BPh$_4$ (**1c**), [Rh(MesCaTBn)(COD)]BPh$_4$ (**2a**), [Rh(MesCaTBnOMe)(COD)]BPh$_4$ (**2b**), [Rh(MesCaTBnNO$_2$)(COD)]BPh$_4$ (**2c**), [Rh(MesCaTBnNH$_2$)(COD)]BPh$_4$ (**2d**), [Rh(MesCaTBn)(CO)$_2$]BPh$_4$ (**3a**) and [Rh(MesCaTBnOMe)(CO)$_2$]BPh$_4$ (**3b**)

	1c	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**
Chemical formula	$C_{22}H_{23}N_6O_2\cdot C_{24}H_{20}B$	$C_{30}H_{35}N_5Rh\cdot C_{24}H_{20}B$	$C_{31}H_{37}N_5ORh\cdot C_{24}H_{20}B$	$C_{30}H_{34}N_6O_2Rh\cdot C_{24}H_{20}B$	$C_{34}H_{36}N_6Rh\cdot C_{24}H_{20}B$	$C_{24}H_{23}N_5O_2Rh\cdot C_{24}H_{20}B$	$C_{25}H_{25}N_5O_3Rh\cdot C_{24}H_{20}B$
M (g mol^{-1})	722.67	887.75	917.78	932.75	902.77	835.59	865.62
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/c$
Crystal habit	Yellow plates	Yellow plates	Yellow plates	Yellow plates	Thin yellow plates	Red orange plates	Dark red square plates
Temperature (K)	150	150	150	150	150	150	150
a (Å)	20.119(3)	10.8373(3),	11.0626(7)	11.0520(5)	11.0540(4)	15.4027(11)	17.012(4)
b (Å)	9.3929(13)	15.3768(4),	15.0649(4)	15.3218(6)	15.1556(6)	16.4453(15)	16.520(4)
c (Å)	21.433 (4)	15.4028(5)	15.9240(3)	15.4565(7)	15.2020(6)	33.125 (3)	14.645(2)
α (°)	90	113.222 (2),	114.270(1)	113.899(2)	112.774(2)	90	90
β (°)	105.532(6)	90.921(1),	99.407(1)	90.403(2)	102.466(2)	90	90.01(1)
γ (°)	90	102.211(1)	98.559 (1)	101.927(2)	90.891(2)	90	90
V (Å^3)	3902.4(11)	2291.27(11)	2316.89(16)	2329.20(17)	2278.94(15)	8390.7(12)	4115.8(15)
Z	4	2	2	2	2	8	4
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	0.08	0.42	0.41	0.42	0.42	0.45	0.47
Crystal size (mm)	0.16×0.08×0.03	0.32×0.14×0.09	0.32×0.22×0.12	0.21×0.19×0.04	0.43×0.17×0.07	0.28×0.09×0.04	0.29×0.23×0.09
T_{min}, T_{max}	0.988, 0.998	0.878, 0.963	0.880, 0.950	0.917, 0.983	0.842, 0.972	0.886, 0.984	0.875, 0.960
Refl. measured	28144	32636	28873	31253	31905	34660	29045
Unique reflections	6864	7984	8046	8091	7968	7389	7168
Obsd. Reflections [I > 2σ(I)]	2578	7058	7337	6144	6463	2965	5248
R_{int}	0.219	0.046	0.052	0.058	0.054	0.210	0.072
$R[F^2 > 2\sigma(F^2)]$	0.066	0.031	0.027	0.051	0.036	0.061	29045
$wR(F^2)$	0.157	0.077	0.070	0.130	0.090	0.118	7168
S	0.95	1.04	1.07	1.03	1.02	0.94	5248
Reflections used	6864	7984	8046	8091	7968	7389	7168
Parameters	500	553	572	556	550	517	549
Restraints	0	0	0	0	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, -0.30	1.13, -0.40	0.38, -0.39	1.41, -0.61	0.73, -0.65	0.46, -0.67	0.31, -0.37

Table S3: Crystallographic data for [Rh(MesCaTBn)(Cp*)Cl]BPh$_4$ (**4a**), [Rh(MeCaTBn)(Cp*)Cl]BPh$_4$ (**4b**), [Rh(MesCaTPh)(Cp*)Cl]BPh$_4$ (**4c**), [Rh(MeCaTPh)(Cp*)Cl]BPh$_4$ (**4d**), [Ir(MesCaTBn)(Cp*)Cl]BPh$_4$ (**5a**) and [Rh(MeCaTPh)(Cp*)Cl]BPh$_4$ (**5b**).

	4a	**4b**	**4c**	**4d**	**5a**	**5b**
Chemical formula	$C_{32}H_{38}ClN_5Rh\cdot C_{24}H_{20}B\cdot 2(CH_2Cl_2)$	$C_{24}H_{30}ClN_5Rh\cdot C_{24}H_{20}B\cdot C_2H_2Cl_4$	$2(C_{31}H_{36}ClN_5Rh)\cdot 2(C_{24}H_{20}B)\cdot CH_2Cl_2$	$C_{23}H_{28}ClN_5Rh\cdot C_{24}H_{20}B$	$C_{32}H_{38}ClIrN_5\cdot C_{24}H_{20}B\cdot 2(CH_2Cl_2)$	$C_{24}H_{30}ClIrN_5\cdot C_{24}H_{20}B\cdot CH_2Cl_2$
M (g mol^{-1})	1120.10	1013.94	1957.36	832.07	1209.39	1020.32
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Crystal habit	Orange blocks	Yellow orange blocks	Dark orange plates	Yellow square plates	Yellow blocks	Light yellow blocks
Temperature (K)	155	156	150	160	155	160
a (Å)	13.4167(5)	11.3706(5)	15.2978(8)	12.3833(9)	13.4189(7)	13.1491(5)
b (Å)	13.6538(5)	12.6307 (5)	12.1192(7)	24.7571(17)	13.6633(7)	13.3892(5)
c (Å)	14.7446(5)	17.3968 (7)	26.5776(14)	13.1128(9)	14.7206(8)	13.8083(5)
α (°)	89.616(2)	95.456(2)	90	90	89.731(2)	67.185(1)
β (°)	83.727(2)	101.823(2)	96.241(2)	92.980(2)	83.712(2)	87.363(2)
γ (°)	85.346(2)	104.458(2)	90	90	85.488 (2)	88.838 (2)
V (Å^3)	2676.02(17)	2339.69(17)	4898.2(5)	4014.6(5)	2674.4(2)	2238.45(14)
Z	2	2	2	4	2	2
Radiation type	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$
μ (mm^{-1})	0.61	0.69	0.50	0.53	2.79	3.20
Crystal size (mm)	0.36×0.22×0.09	0.25×0.17×0.08	0.28×0.19×0.10	0.28×0.25×0.09	0.24×0.17×0.14	0.23× 0.23×0.15
T_{min}, T_{max}	0808, 0.948	0.849, 0.944	0.888, 0.959	0.866, 0.955	0.557, 0.698	0.528, 0.645
Refl. measured	28228	29804	49243	30243	36887	49473
Unique reflections	9163	8053	8609	7047	9359	7871
Obsd. Reflections [I > 2σ(I)]	8012	7389	7228	5955	8757	7458
R_{int}	0.034	0.030	0.026	0.044	0.023	0.051
R[$F^2 > 2\sigma(F^2)$]	0.033,	0.025	0.067	0.027	0.019	0.020
$wR(F^2)$	0.085	0.063	0.203	0.072	0.050	0.052
S	1.05	1.03	1.04	1.04	1.07	1.06
Reflections used	9163	8053	8609	7047	9359	7871
Parameters	639	565	603	502	639	538
Restraints	0	0	4	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.75, -0.80	0.52, -0.56	2.05, -0.57	0.32, -0.63	1.02, -0.82	0.91, -0.83

D.2. ORTEP Diagrams of ***2b-d*****;** ***3b*****;** ***4c-d*** *and* ***5a-b***

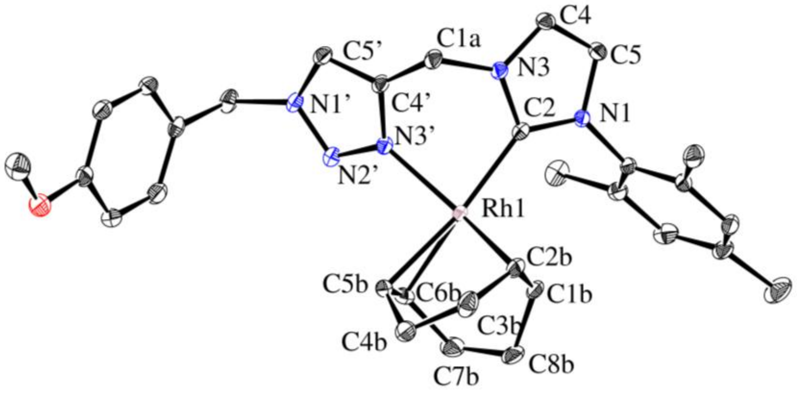


Figure S1: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MesCaTBnOMe)(COD)]BPh_4 (**2b**) at 40% thermal ellipsoids for the non hydrogen atoms.

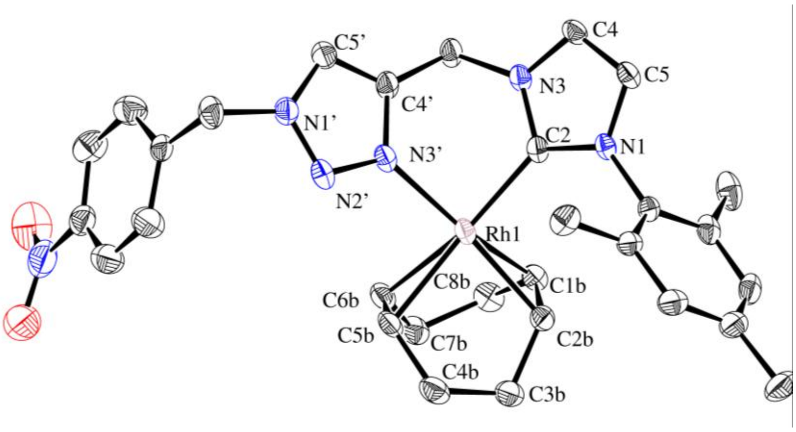


Figure S2: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MesCaTBnNO_2)(COD)]BPh_4 (**2c**) at 40% thermal ellipsoids for the non hydrogen atoms.

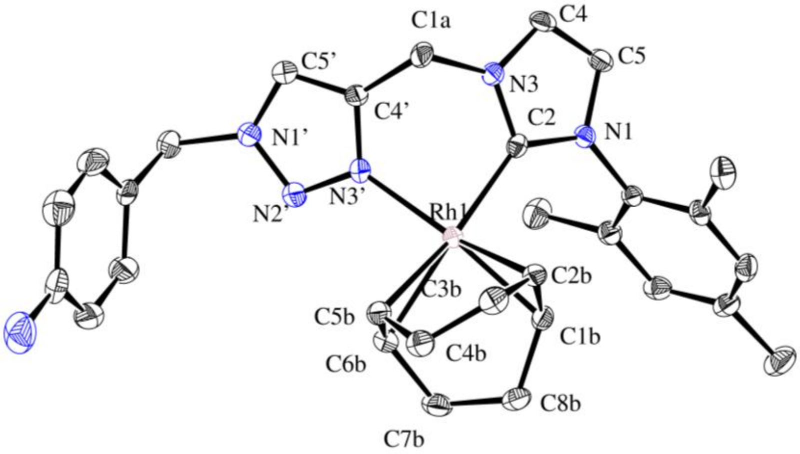


Figure S3: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MesCaTBnNH_2)(COD)]BPh_4 (**2d**) at 40% thermal ellipsoids for the non hydrogen atoms.

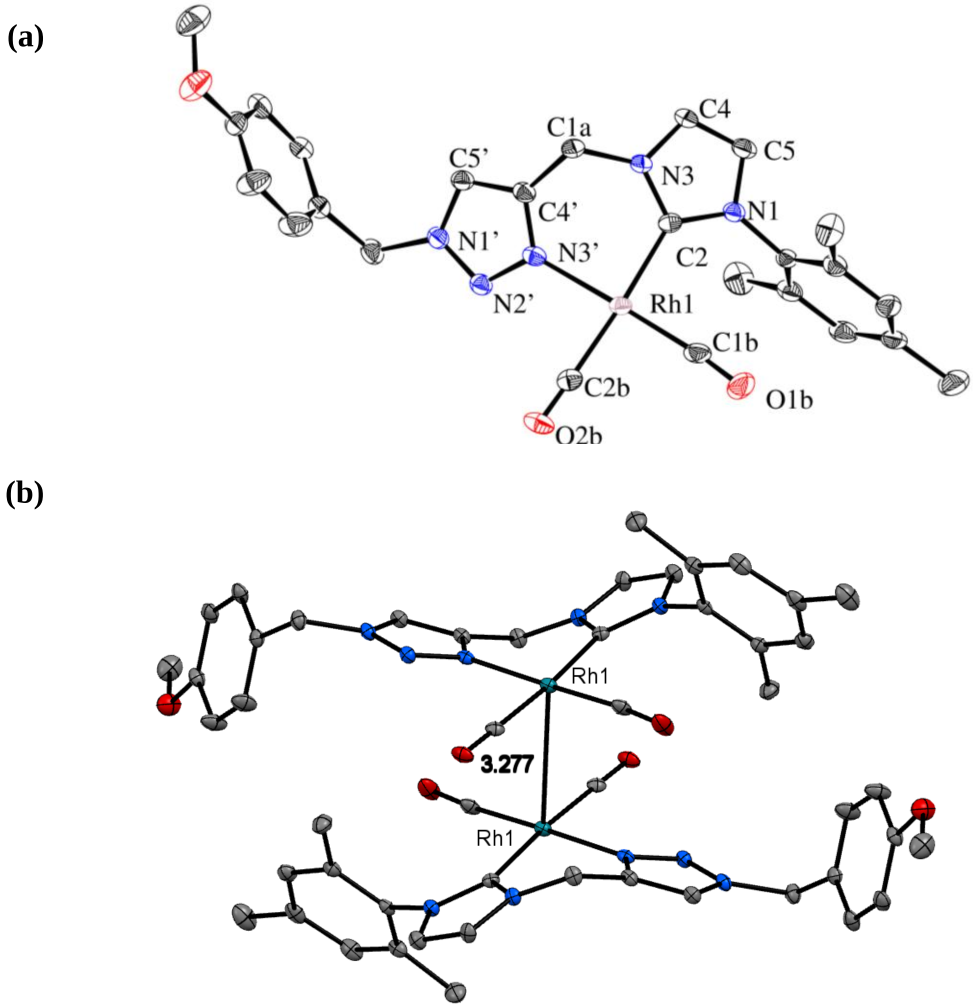


Figure S4: ORTEP depiction of: (a) the cationic fragment of the single crystal solid state structure of [Rh(MesCaTBnOMe)(CO)$_2$]BPh$_4$ (**3b**) at 40% thermal ellipsoids for the non hydrogen atoms and (b) the stacking of two molecules in the unit cell showing a strong interaction (Rh-Rh = 3.277 Å) between the two Rh centres. The phenyl ring bearing the O-CH$_3$ substitution shows conformational disorder over two positions of unequal occupancies (0.70 and 0.30). However, the minor site of disordered position is omitted for the figure depicting dimeric association for the sake of clarity.

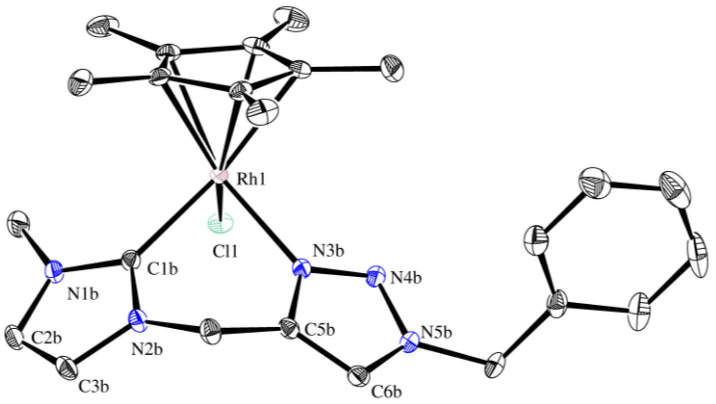


Figure S5: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MeCaTBn)(Cp*)Cl]BPh_4 (**4b**) at 40% thermal ellipsoids for the non hydrogen atoms.

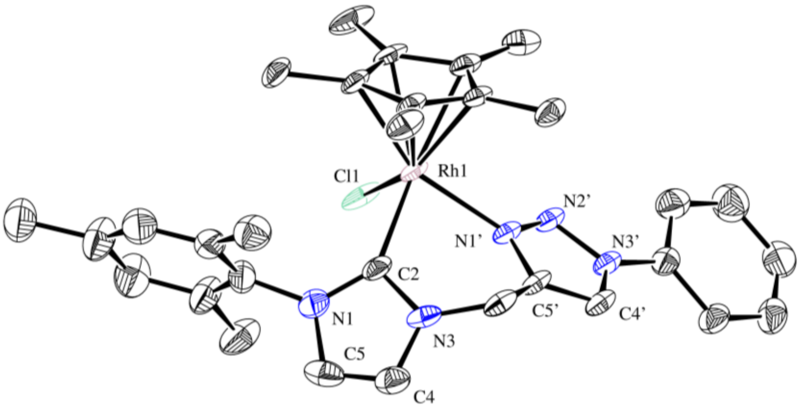


Figure S6: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MesCaTPh)(Cp*)Cl]BPh_4 (**4c**) at 40% thermal ellipsoids for the non hydrogen atoms.

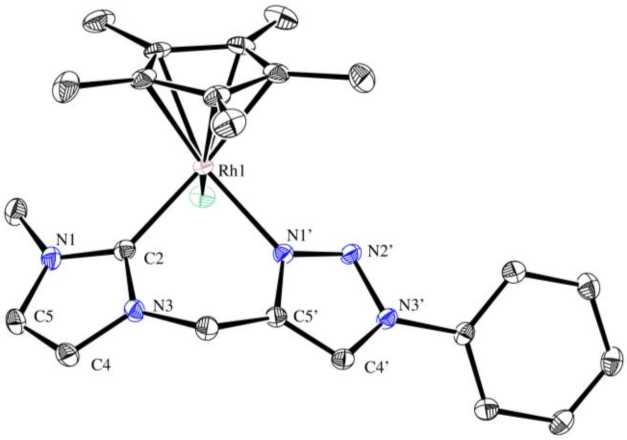


Figure S7: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Rh(MeCaTPh)(Cp*)Cl]BPh_4 (**4d**) at 40% thermal ellipsoids for the non hydrogen atoms.

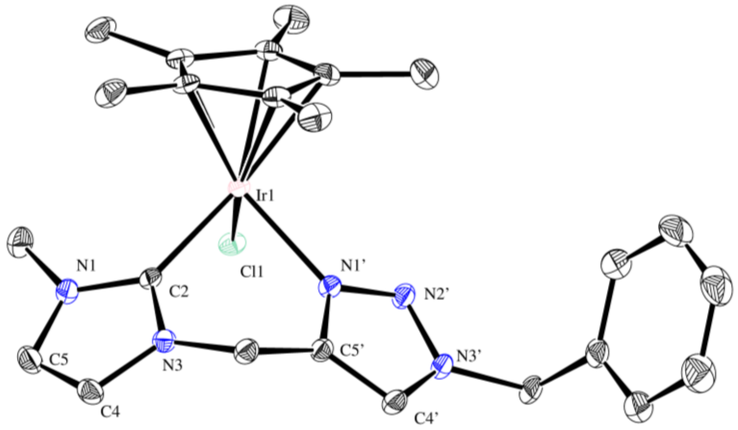


Figure S8: ORTEP depiction of the cationic fragment of the single crystal solid state structure of [Ir(MeCaTBn)(Cp*)Cl]BPh$_4$ (**5b**) at 40% thermal ellipsoids for the non hydrogen atoms.

References

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