Enolate S_NAr of unactivated arenes via [(η⁶-arene)RuCp]^+ intermediates

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Supporting Information

Table of Contents

1. Experimental Detail and Product Characterisation
2. NMR Spectra of Products
3. Crystal and Structural Refinement Data for Complexes 1a, 2a, 2b, 2c and 3c

1. Experimental Detail and Product Characterisation

Commercially available reagents were used as received from suppliers. Solvents were laboratory grade and dried using an appropriate drying agent when required. Prior to use, K₂CO₃ was oven dried at 100 °C for 48 h. Reactions requiring anhydrous conditions were carried out under an atmosphere of dry nitrogen using Schlenk-line techniques. Where appropriate, solvents were degassed using the freeze-thaw cycle method. UV Nail lamp used was a Nailstar 36 Watt Professional UV Nail Lamp.

NMR spectra (1H, 13C, 19F) were recorded on a Varian VXR-400 spectrometer (1H at 399.97 Hz, 13 C at 100.57 MHz, 19F at 376.5 MHz) or a Varian VNMRS-500 spectrometer (1H at 499.73 MHz, 13C at 125.95 MHz). Spectra were recorded at 295 K in commercially available deuterated solvents and referenced internally to the residual solvent proton resonances. Electrospray and high-resolution mass spectrometry were performed on an SQD mass spectrometer with Acquity UPLC.

1a. Ru Sandwich Complexes

[Ru(η⁶-fluorobenzene)(η⁵-cyclopentadienyl)]PF₆ (1a)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Fluorobenzene (38 µL, 0.41 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (133 mg, 0.328 mmol, 92%).
$^1$H (599 MHz, acetone) δ 6.84 – 6.79 (2H, m, H$_2$), 6.46 (2H, tdd, J = 5.5, 2.8, 1.3 Hz, H$_3$), 6.26 (1H, td, J = 5.7, 3.7 Hz, H$_4$), 5.64 (5H, s, H$_5$); $^{13}$C (151 MHz, acetone) δ 137.9 (d, J = 275.3 Hz, C$_1$), 86.1 (s, C$_4$), 85.9 (d, J = 6.4 Hz, C$_3$), 82.6 (s, C$_5$), 78.5 (d, J = 21.2 Hz, C$_6$), $^{19}$F($^1$H) NMR (376 MHz, Acetone) δ -72.4 (d, J = 707.9 Hz, $^{19}$F Counter-ion), -137.6, $^{31}$P (acetone-D$_6$) δ -144.3 (sept., J$_{P-F}$ 707 Hz, P Counter-ion); m/z (HRMS)$^+$ 256.9843 [M-PF$_6]^+$ [M-PF$_6$] (C$_{10}$H$_{11}$F$_9$Ru$^+$ requires 256.9842); Anal. Found (Expected): C 32.26 (32.44); H 2.48 (2.48); N 0.42 (0.00)

[Ru($\eta^6$-chlorobenzene)(η$^5$-cyclopentadienyl])PF$_6$ (1b)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Chlorobenzene (45 µL, 0.40 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (146 mg, 34.4 mmol, 96%).

$^1$H NMR (599 MHz, acetone) δ 6.83 – 6.80 (2H, m, H$_2$), 6.49 (2H, dd, J = 6.4, 5.6 Hz, H$_3$), 6.37 (1H, td, J = 5.7, 0.7 Hz, H$_4$), 5.65 (5H, s, H$_5$), $^{13}$C NMR (151 MHz, acetone) δ 106.60 (s, C$_1$), 88.74 (s, C$_3$), 87.04 (s, C$_4$), 86.59 (s, C$_5$), 83.47 (s, C$_6$), $^{19}$F($^1$H) NMR (376 MHz, Acetone) δ -72.48 (d, J = 707.8 Hz, $^{19}$F Counter-ion), $^{31}$P (acetone-D$_6$) δ -144.3 (sept., J$_{P-F}$ 707 Hz, P Counter-ion); m/z (HRMS)$^+$ 272.9547 [M-PF$_6$] (C$_{10}$H$_{13}$F$_9$Ru$^+$ requires 272.9510); Anal. Found (Expected): C 31.00 (31.18); H 2.41 (2.38); N 0.52 (0.00)

[Ru($\eta^6$-nitrobenzene)(η$^5$-cyclopentadienyl])PF$_6$ (1c)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (150 mg, 0.357 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). Nitrobenzene (41 µL, 0.40 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (135 mg, 0.310 mmol, 87%).

$^1$H NMR (599 MHz, acetone) δ 7.46 – 7.44 (2H, m, H$_2$), 6.79 (2H, dd, J = 6.7, 5.7 Hz, H$_3$), 6.71 (1H, t, J = 5.8 Hz, H$_4$), 5.77 (5H, s, H$_5$), $^{13}$C NMR (151 MHz, acetone) δ 111.4 (s, C$_1$), 88.5 (s, C$_3$), 86.4 (s,
C\(^2\)), 83.7 (s, C\(^5\)), 82.9 (s, C\(^3\)), \(^{19}\)F\(^{(1)}\)H NMR (376 MHz, Acetone) \(\delta\) -72.4 (d, \(J = 707\) Hz, F\(^\text{Counter-ion}\)), \(^{31}\)P (acetone-D6) \(\delta\) -144.3 (sept., \(J_{PF} = 707\) Hz, P\(^\text{Counter-ion}\)); \(m/z\) (HRMS) \(^{283.9788}\) [M-PF\(_6\)] (C\(_{10}\)H\(_{11}\)NO\(_2\)Ru\(^+\) requires 283.9750); Anal. Found (Expected): C 30.31 (30.43); H 2.33 (2.32); N 3.50 (3.23).

\[\text{[Ru}(\eta^6-2\text{-fluorotoluene})(\eta^5\text{-cyclopentadienyl})]PF_6 (2a)\]

Tris(acetonitrile)cyclopentadienylruthenium(III) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Fluorotoluene (30 \(\mu\)L, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered, and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (93.5 mg, 0.222 mmol, 94 %).

\(^1\)H NMR (599 MHz, acetone) \(\delta\) 6.78 (1H, dd, \(J = 6.1, 4.2\) Hz, H\(^6\)), 6.52 (1H, td, \(J = 4.4, 2.2\) Hz, H\(^5\)), 6.34 (1H, tdd, \(J = 6.0, 2.5, 1.1\) Hz, H\(^3\)), 6.19 (1H, td, \(J = 5.7, 3.1\) Hz, H\(^8\)), 5.60 (5H, s, H\(^8\)), 2.50 (3H, d, \(J = 1.6\) Hz, H\(^1\)), \(^{13}\)C NMR (151 MHz, acetone) \(\delta\) 136.2 (d, \(J = 273.3\) Hz, C\(^7\)), 93.8 (d, \(J = 17.3\) Hz, C\(^1\)), 86.9 (d, \(J = 4.0\) Hz, C\(^1\)), 84.5 (s, C\(^4\)), 84.1 (d, \(J = 6.5\) Hz, C\(^5\)), 81.7 (s, C\(^8\)), 76.6 (d, \(J = 22.6\) Hz, C\(^6\)), 13.9 (d, J = 1.1 Hz, C\(^1\)). \(^{19}\)F\(^{(1)}\)H NMR (376 MHz, Acetone) \(\delta\) -72.51 (d, \(J = 707\) Hz, F\(^\text{Counter-ion}\)).

\[\text{[Ru}(\eta^6-2\text{-chlorotoluene})(\eta^5\text{-cyclopentadienyl})]PF_6 (2b)\]

Tris(acetonitrile)cyclopentadienylruthenium(III) hexafluorophosphate (200 mg, 0.472 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Chlorotoluene (62 \(\mu\)L, 0.524 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered, and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (200 mg, 0.458 mmol, 97 %).
$^1$H NMR (599 MHz, acetone) δ 6.84 – 6.74 (1H, m, H$_6$), 6.59 (1H, dd, J = 5.8, 1.0 Hz, H$_7$), 6.38 (1H, td, J = 5.8, 1.0 Hz, H$_4$), 6.29 (1H, td, J = 5.8, 0.7 Hz, H$_3$), 5.59 (5H, s, H$_8$), 2.60 (3H, s, H$_1$), $^{13}$C NMR (151 MHz, acetone) δ 106.7 (s, C$_7$), 102.2 (s, C$_2$), 87.5 (s, C$_3$/6), 87.3 (s, C$_3$/6), 85.3 (s, C$_4$/5), 85.2 (s, C$_4$/5), 82.5 (s, C$_8$), 18.5 (s, C$_1$). $^{19}$F{H} NMR (376 MHz, Acetone) δ -72.54 (d, $J_{F-H}$ = 707 Hz, F.Counter-ion), m/z (HRMS)$^+$ 286.9703 [M-PF$_6$] (C$_{12}$H$_{12}$ClRu$^+$ requires 286.9666); Anal. Found (Expected): C 32.96 (32.93); H 2.84 (2.76); N 0.19 (0.00)

$^{[Ru(η^6-2-nitrotoluene)(η^5-cyclopentadienyl)]PF_6}$ (2c)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Nitrotoluene (31 µL, 0.263 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (94 mg, 0.210 mmol, 89 %).

$^1$H NMR (599 MHz, acetone) δ 7.22 (1H, dd, J = 6.0, 0.7 Hz, H$_6$), 6.72 (1H, d, J = 5.9 Hz, H$_7$), 6.65 (1H, td, J = 6.0, 0.7 Hz, H$_4$), 6.56 (1H, td, J = 5.9, 0.7 Hz, H$_3$), 5.74 (5H, s, H$_8$), 2.70 (3H, s, H$_1$), $^{13}$C NMR (151 MHz, acetone) δ 110.5 (s, C$_1$), 99.9 (s, C$_1$), 89.2 (s, C$_3$), 88.6 (s, C$_4$), 86.2 (s, C$_3$), 85.0 (s, C$_8$), 84.2 (s, C$_6$), 18.8 (s, C$_1$). $^{19}$F{H} NMR (376 MHz, Acetone) δ -72.45 (d, J = 707 Hz, F.Counter-ion), $^{31}$P (acetone-D6) δ -144.3 (sept., $J_{P-F}$ 707 Hz, P.Counter-ion); m/z (HRMS)$^+$ 297.9944 [M-PF$_6$] (C$_{12}$H$_{12}$NO$_2$ClRu$^+$ requires 297.9907); Anal. Found (Expected): C 32.00 (32.15); H 2.67 (2.70); N 3.32 (3.12).

$^{[Ru(η^6-2-fluoro-m-xylene)(η^5-cyclopentadienyl)]PF_6}$ (3a)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Fluoro-m-xylene (33 µL, 0.261 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to
diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (95.6 mg, 0.219 mmol, 94 %)

$^1$H NMR (599 MHz, acetone) $\delta$ 6.37 (2H, dd, $J = 5.6, 3.7$ Hz, H$^4$), 6.09 (1H, td, $J = 5.7, 2.5$ Hz, H$^5$), 5.54 (5H, s, H$^6$), 2.49 (6H, d, $J = 1.7$ Hz, 6H, H$^8$), $^{13}$C NMR (151 MHz, acetone) $\delta$ 136.6 (d, $J = 271.5$ Hz, C$^1$), 93.8 (d, $J = 18.6$ Hz, C$^3$), 86.9 (d, $J = 4.0$ Hz, C$^4$), 84.5 (d, $J = 4.0$ Hz, C$^5$), 82.7 (s, C$^6$), 14.9 (d, $J = 1.4$ Hz, C$^7$), $^{19}$F{H} NMR (376 MHz, Acetone) $\delta$ -72.46 (d, $J = 707$ Hz, F Counter-ion), -146.72 (1F, s, F Arene), $^{31}$P (acetone-D6) $\delta$ -144.3 (sept., $J_{PF} = 707$ Hz, P Counter-ion); $m/z$ (HRMS)$^+$ 285.0150 [M-PF$_6$] (C$_{13}$H$_{14}$F$_9$Ru$^+$ requires 285.0156); Anal. Found (Expected): C 35.70 (35.87); H 3.26 (3.24); N 0.20 (0.00)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (200 mg, 0.472 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Chloro-m-xylene (69 µL, 0.522 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (201 mg, 0.448 mmol, 95 %).

$^1$H NMR (599 MHz, acetone) $\delta$ 6.49 (2H, d, $J = 5.7$ Hz, H$^4$), 6.22 (1H, t, $J = 5.8$ Hz, H$^5$), 5.53 (5H, s, H$^6$), 2.61 (6H, s, H$^8$), $^{13}$C NMR (151 MHz, acetone) $\delta$ 109.3 (s, C$^1$), 102.6 (s, C$^3$), 87.8 (s, C$^4$), 85.3 (s, C$^5$), 83.6 (s, C$^6$), 20.3 (s, C$^7$), $^{19}$F{H} NMR (376 MHz, Acetone) $\delta$ -72.46 (d, $J = 707$ Hz, F Counter-ion), $^{31}$P (acetone-D6) $\delta$ -144.3 (sept., $J_{PF} = 707$ Hz, P Counter-ion); $m/z$ (HRMS)$^+$ 300.9880 [M-PF$_6$] (C$_{13}$H$_{14}$F$_9$Cl$^+$Ru$^+$ requires 300.9860); Anal. Found (Expected): C 34.55 (34.56); H 3.13 (3.12); N 3.23 (3.03)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2-Nitro-m-xylene (35 µL, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction
mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (96 mg, 0.208 mmol, 88%).

$^1$H NMR (599 MHz, acetone) $\delta$ 6.60 (2H, d, $J = 5.9$ Hz, H$_4$), 6.44 (1H, t, $J = 5.9$ Hz, H$_5$), 5.73 (5H, s, H$_6$), 2.53 (6H, s, H$_2$), $^{13}$C NMR (151 MHz, acetone) $\delta$ 111.4 (s, C$_1$), 96.1 (s, C$_3$), 86.2 (s, C$_4$), 85.9 (s, C$_5$), 84.1 (s, C$_6$), 16.0 (s, C$_7$), $^{19}$F $^1$H NMR $\delta$ -71.45 (d, $J = 707$ Hz, F$_{\text{Counter-ion}}$), $^{31}$P (acetone-D$_6$) $\delta$ -144.3 (sept., $J_{PF} 707$ Hz, P$_{\text{Counter-ion}}$); $m/z$ (HRMS) $^+$ 312.0126 [M-PF$_6$]$^{-}$ (C$_{13}$H$_{14}$NO$_2$Ru$^+$ requires 312.0100); Anal. Found (Expected): C 33.63 (33.78); H 3.04 (3.05); N 0.42 (0.00)

[Ru($\eta^6$-1-Chloro-3-fluorobenzene)($\eta^5$-cyclopentadienyl)]PF$_6$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-Chloro-3-fluorobenzene (10 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as an off-white solid (96 mg, 0.82 mmol, 89%).

$^1$H NMR (599 MHz, Acetone-d$_6$) $\delta$ 7.47 – 7.36 (1H, m, H$_2$), 6.86 (1H, ddd, $J = 6.1$, 3.4, 1.5 Hz, H$_3$), 6.75 (1H, ddd, $J = 5.9$, 3.1, 1.1 Hz, H$_4$), 6.62 (1H, td, $J = 6.0$, 2.9 Hz, H$_5$), 5.77 (5H, s, H$_6$), $^{13}$C NMR (151 MHz, Acetone-d$_6$) $\delta$ 137.0 (d, $J = 279.1$ Hz, C$_3$), 104.8 (d, $J = 7.0$ Hz, C$_1$), 87.9 (s, C$_2$), 85.1 (d, $J = 6.5$ Hz, C$_7$), 84.8 (s, C$_4$), 80.5 (d, $J = 23.6$ Hz, C$_5$), 78.2 (d, $J = 21.4$ Hz, C$_6$), $^{19}$F $^1$H NMR (376 MHz, Acetone-D$_6$) $\delta$ -72.51 (d, $J = 707$ Hz, F$_{\text{Counter-ion}}$), -138.07 (1F, s, F$_{\text{Arene}}$), $^{31}$P (acetone-D$_6$) $\delta$ -144.3 (sept., $J_{PF} 707$ Hz, P$_{\text{Counter-ion}}$); $m/z$ (HRMS) $^+$ 290.9451 [M-PF$_6$] (C$_{11}$H$_9$F$_3$Cl$_{35}$Ru$^+$ requires 290.9453).

[Ru($\eta^6$-1-fluoro-3-nitrobenzene)($\eta^5$-cyclopentadienyl)]PF$_6$)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-Fluoro-3-nitrobenzene (12 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to
diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (35 mg, 0.069 mmol, 75 %).

$^1$H NMR (599 MHz, acetone) δ 7.97 (1H, dt, $J = 3.2, 1.3$ Hz, H$^2$), 7.38 (1H, ddd, $J = 6.1, 2.7, 1.2$ Hz, H$^6$), 7.18 (1H, ddd, $J = 6.2, 3.7, 1.5$ Hz, H$^4$), 6.90 (1H, td, $J = 6.2, 2.8$ Hz, H$^5$), 5.90 (5H, s, H$^7$), $^{13}$C NMR (151 MHz, acetone) δ 135.8 (d, $J = 280.5$ Hz, C$^3$), 110.2 (s, C$^1$), 85.1 (s, C$^7$), 84.8 (d, $J = 6.5$ Hz, C$^5$), 82.2 (s, C$^6$), 80.2 (d, $J = 21.5$ Hz, C$^4$), 74.2 (d, $J = 25.6$ Hz, C$^2$), $^{19}$F-$^1$H NMR (376 MHz, Acetone-$D_6$) δ -72.40 (d, $J = 708$ Hz, F Counter-ion), -136.01 (1F, s, F Arene), $^{31}$P (acetone-$D_6$) δ -144.3 (sept., $J_{P-F} = 708$ Hz, P Counter-ion); m/z (HRMS)$^+$ 301.9701 [M-PF$_6$] (C$_{11}$H$_9$NO$_2$F$_9$Ru$^+$ requires 301.9693).

$[\text{Ru(}\eta^6\text{-1-chloro-3-nitrobenzene})(\eta^5\text{-cyclopentadienyl})\text{]}\text{PF}_6$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (40 mg, 0.092 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-Chloro-3-nitrobenzene (12 µL, 0.101 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (36 mg, 0.077 mmol, 83 %).

$^1$H NMR (599 MHz, acetone) δ 7.93 (1H, t, $J = 1.2$ Hz, H$^2$), 7.46 (1H, dd, $J = 6.2, 1.3$ Hz, H$^6$), 7.16 (1H, dd, $J = 6.1, 1.2$ Hz, H$^4$), 6.92 (1H, t, $J = 6.2$ Hz, H$^5$), 5.90 (5H, s, H$^7$), $^{13}$C NMR (151 MHz, acetone) δ 110.9 (s, C$^1$), 105.50 (s, C$^7$), 90.1 (s, C$^4$), 86.0 (s, C$^5$), 85.8 (s, C$^5$), 83.8 (s, C$^7$), 82.5 (s, C$^6$), $^{19}$F-$^1$H NMR (376 MHz, Acetone) δ -72.5 (d, $J = 707$ Hz, F$^{\text{Counter-ion}}$), -136.0 (1F, s, F$^{\text{Arene}}$), $^{31}$P (acetone-$D_6$) δ -144.3 (sept., $J_{P-F} = 708$ Hz, P$^{\text{Counter-ion}}$); m/z (HRMS)$^+$ 314.9413 [M-PF$_6$] (C$_{11}$H$_9$35ClNO$_2$36Ru$^+$ requires 314.9398).

$[\text{Ru(}\eta^6\text{-1-bromo-3-chlorobenzene})(\eta^5\text{-cyclopentadienyl})\text{]}\text{PF}_6$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (60 mg, 0.138 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 1-bromo-3-chlorobenzene (18 µL, 0.152 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise
to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (57 mg, 0.124 mmol, 90%).

$^1$H NMR (599 MHz, acetone-d$_6$) δ 7.39 (1H, t, $J = 1.1$ Hz, H$^1$), 6.86 (2H, ddd, $J = 6.0$, 2.5, 1.1 Hz, H$^4$), 6.58 (1H, t, $J = 5.9$ Hz, H$^5$), 5.74 (5H, s, H$^7$). $^{13}$C NMR (151 MHz, acetone-d$_6$) δ 105.32 (s, C$^3$), 91.12 (s, C$^2$), 89.57 (s, C$^4/6$), 89.09 (s, C$^1$), 87.27 (s, C$^5$), 85.98 (s, C$^4$), 84.73 (s, C$^7$), 19F{H} NMR (376 MHz, Acetone) δ -72.50 (d, $J = 707$ Hz, F$^{Counter-ion}$), -138.07 (1F, s, F$^{Arene}$), $^{31}$P (acetone-D$_6$) δ -144.3 (sept., J$_{P-F}$ 708 Hz, $^{P^{Counter-ion}}$); m/z (HRMS)$^+$ 350.8658 (C$_{11}$H$_9$Cl$_2$Br$_9$Ru$^+$ requires 350.8652).

$^{[Ru(\eta^6-2,5-dichlorotoluene)(\eta^5-cyclopentadienyl)]PF_6}$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 2,5-dichlorotoluene (35 µL, 0.260 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (95 mg, 0.210 mmol, 88%).

$^1$H NMR (599 MHz, Acetone-d$_6$) δ 7.34 (1H, d, $J = 1.3$ Hz, H$^3$), 6.77 (1H, dd, $J = 6.0$, 1.3 Hz, H$^6$), 6.71 (1H, d, $J = 6.0$ Hz, H$^1$), 5.70 (5H, s, H$^7$), 2.56 (3H, s, H$^1$). $^{13}$C NMR (151 MHz, Acetone-d$_6$) δ 106.9 (s, C$^1$), 105.0 (s, C$^6$), 103.0 (s, C$^4$), 89.3 (s, C$^5$), 87.8 (s, C$^{C/6}$), 85.8 (s, C$^4$), 84.7 (s, C$^7$), 18.9 (s, C$^1$), 19F{H} NMR δ -72.52 (d, $J = 707$ Hz, F$^{Counter-ion}$), $^{31}$P (acetone-D$_6$) δ -144.3 (sept., J$_{P-F}$ 707 Hz, $^{P^{Counter-ion}}$); m/z (HRMS)$^+$ 320.9318 (C$_{12}$H$_{11}$Cl$_2$Br$_9$Ru$^+$ requires 320.9314).

$^{[Ru(\eta^6-5-bromo-2-fluoro-1,3-dimethylbenzene)(\eta^5-cyclopentadienyl)]PF_6}$

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (100 mg, 0.236 mmol, 1 eq.) was dissolved in anhydrous 1,2-DCE (8 mL). 5-bromo-2-fluoro-1,3-dimethylbenzene (50 µL, 0.253 mmol, 1.1 eq.) was added and the reaction was stirred at reflux under inert atmosphere overnight.
The reaction mixture was cooled to room temperature, filtered and the filtrate dried in vacuo to give a brown solid. The crude product was dissolved in a minimum of acetonitrile, then added dropwise to diethyl ether (10 mL). The liquid phase was decanted off and the resulting solid dried to give the title compound as a brown solid (109 mg, 0.212 mmol, 90%).

\[\text{[Ru(\eta^6-2-phenylcyclohexane-1,3-dione)(\eta^5-cyclopentadienyl)]PF}_6\]

Potassium carbonate (65.2 mg, 0.472 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu(\eta^6-chlorobenzene)]PF\(_6\) (1b, 100 mg, 0.235 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 40 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as a brown solid (95 mg, 0.191 mmol, 81%).

\[\text{[Ru(\eta^6-2-(2-tolyl)cyclohexane-1,3-dione)(\eta^5-cyclopentadienyl)]PF}_6\]

Potassium carbonate (63.0 mg, 0.456 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu(\eta^6-2-chlorotoluene)]PF\(_6\) (2b, 100 mg, 0.228 mmol, 1 eq.) and anhydrous DMF were
combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as a brown solid (80 mg, 0.156 mmol, 69%).

$^1$H NMR (599 MHz, CD$_2$OD) $\delta$ 6.10 (1H, $d = 5.7$ Hz, H$_{10}$), 5.90 – 5.94 (2H, m, H$_{12/13}$), 5.92 (1H, td, $J = 5.5, 1.2$ Hz, H$_{12}$), 5.27 (5H, s, H$_{11}$), 2.49 – 2.33 (4H, m, H$_{2/3}$), 2.16 (3H, s, H$_9$), 1.97 (2H, $p = 6.5$ Hz, H$_7$), $^{13}$C NMR (151 MHz, CD$_2$OD) $\delta$ 193.2 (s, C$_{6/7}$), 191.8 (s, C$_{15}$), 105.9 (s, C$_8$), 105.5 (s, C$_7$), 102.5 (s, C$^5$), 88.8 (s, C$^{13}$), 86.1 (s, C$^{10}$), 82.9 (s, C$^{12}$), 82.3 (s, C$^{11}$), 79.7 (s, C$_{14}$), 36.4 (s, C$^{2/3}$), 35.8 (s, C$^{2/3}$), 20.8 (s, C$^6$), 18.9 (s, C$^8$), $^{19}$F($^1$H) NMR $\delta$ -72.69 (d, $J = 707$ Hz, P$_{\text{Counter-ion}}$); $m/z$ (HRMS)$^+$ 363.0447 [M-PF$_6$] (C$_{18}$H$_{18}$O$_2$Ru$^+$ requires 363.0461).

$\text{[Ru}^{\eta^6-\text{2-(2-m-xylene)cyclohexane-1,3-dione}(\eta^5-\text{cyclopentadienyl})]\text{PF}_6$

Potassium carbonate (63.0 mg, 0.456 mmol, 2 eq.), 1,3-cyclohexanedione (29 mg, 0.260 mmol, 1.1 eq.), [CpRu($\eta^6$-2-chloro-1,3-dimethylbenzene)]PF$_6$ (3b, 100 mg, 0.220 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the title compound as an impure brown solid (77 mg).

$^1$H NMR (599 MHz, acetone) $\delta$ 5.93 (2H, $d = 5.6$ Hz, H$_{10}$), 5.81 (1H, $t = 5.7$ Hz, H$_{11}$), 5.23 (5H, s, H$_{13}$), 2.22 (4H, ddd, $J = 24.9, 6.8, 5.8$ Hz, H$_{2/3}$), 2.09 (6H, s, H$_9$), 1.89 – 1.82 (2H, m, H$_7$), $^{13}$C NMR (151 MHz, acetone) $\delta$ 189.2 (s, C$^{15}$), 186.6 (s, C$^{4/5}$), 110.0 (s, C$_8$), 102.3 (s, C$_9$), 102.1 (s, C$^6$), 84.9 (s, C$^{12}$), 81.4 (s, C$^{11}$), 79.8 (s, C$^{12}$), 37.6 (s, C$^{2/3}$), 37.4 (s, C$^{2/3}$), 21.7 (s, C$^1$), 19.3 (s, C$^8$), $^{19}$F($^1$H) NMR $\delta$ -72.55 (d, $J = 707$ Hz, P$_{\text{Counter-ion}}$); $^{13}$P (acetone-D$_6$) $\delta$ -145.74 (sept., $J_{P,F} 707$ Hz, P$_{\text{Counter-ion}}$); $m/z$ (HRMS)$^+$ 377.0621 [M-PF$_6$] (C$_{19}$H$_{18}$O$_2$Ru$^+$ requires 377.0618).

1b. general Experimental 1 – base, temperature and solvent screening for S$_4$Ar reaction

To an oven dried Schlenk tube were added [Ru] (1 eq.), 1,3-cyclohexanedione (2 eq.), base (3 eq.) and anhydrous solvent (2 mL). The reaction mixture was heated to the desired temperature for 18 hours, then dried under reduced pressure to give a crude brown residue which was triturated with acetonitrile (3x5 mL), then filtered. The filtrate was dried in vacuum, and the resulting brown
residue dissolved in d₆-acetone and analysed by ¹H NMR. Conversions were calculated by ¹H NMR spectroscopy. Mass spec analysis was used to confirm the presence of any product(s) and/or starting material(s).

1c. Base Screen for SₐAr

| Entry | Base                     | Conversion |
|-------|--------------------------|------------|
| 26    | DBU                      | 30*        |
| 27    | NEt₃                     | Trace      |
| 28    | Pyridine                 | Trace      |
| 29    | DIPEA                    | Trace      |
| 30    | NaH                      | Trace      |
| 31    | KO₂Bu                    | 12         |
| 32    | NaOH                     | 40         |
| 33    | NaHCO₃                   | 36         |
| 34    | (NH₄)₂CO₃                | Trace      |
| 35    | NaOMe                    | Trace      |
| 36    | Na(2,4-di-tert-butylphenoxide) | Trace   |
| 37    | K₂CO₃                    | 67         |

General experimental 2 – Dione scope
Potassium carbonate (9.5 mg, 0.068 mmol, 2 eq.), dione (0.040 mmol, 1.1 eq.), [CpRu(η₆-2-chlorotoluene)]PF₆ (2b, 15 mg, 0.034 mmol, 1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in a minimum of dichloromethane and the solution added dropwise to diethyl ether (5 mL). The solvents were decanted and the residue dried to give the complex.
[Ru(η⁶-2-(2-tolyl)(5,5'-dimethyl)cyclopentane-1,3-dione)(η⁵-cyclopentadienyl)]PF₆

Synthesised via general experimental 2, using 5,5'-dimethylcyclohexane1,3-dione (5.4 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (11.3 mg, 0.021 mmol, 61%).

1H NMR (599 MHz, CD₂OD) δ 6.10 (1H, d, J = 5.6 Hz, H¹¹), 5.98 – 5.95 (1H, m, H¹³), 5.94 – 5.92 (1H, m, H¹³), 5.91 (1H, dd, J = 5.6, 1.0 Hz, H¹²), 5.26 (5H, s, H¹⁴), 2.29 (4H, s, H⁵), 2.15 (3H, s, H²)

13C NMR (151 MHz, CD₂OD) δ 193.4 (s, C⁵), 192.2 (s, C⁶), 106.9 (s, C¹), 106.2 (s, C¹), 103.9 (s, C⁶), 90.3 (s, C¹⁴), 87.6 (s, C¹³), 84.3 (s, C¹), 83.7 (s, C¹⁴), 81.1 (s, C¹⁵), 51.7 (s, C⁴), 51.1 (s, C⁵), 32.2 (s, C¹), 29.3 (s, C¹⁵), 28.5 (s, C¹¹), 20.5 (s, C¹), 19F[¹H] NMR δ -72.58 (d, J = 707 Hz, F¹⁻Counter-ion); m/z (HRMS) 391.0772 [M-PF₆]⁺ C₂₀H₂₃O₇Ru requires 391.0774.

[Ru(η⁶-2-(2-tolyl)(5-ethylacetyl)cyclopentane-1,3-dione)(η⁵-cyclopentadienyl)]PF₆ (1:1 mixture of diastereomers)

Synthesised via general experimental 2, using 5-(ethylacetyl)cyclohexane1,3-dione (7.1 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown solid (12.5 mg, 0.022 mmol, 63%).

1H NMR (599 MHz, CD₂OD) δ 6.07 (1H, dd, J = 8.7, 5.7 Hz, H¹¹), 5.97 – 5.86 (3H, m, H¹⁴/¹⁵, ¹⁶/¹⁷), 5.23 (5H, s, H¹³), 4.14 (2H, dq, J = 14.1, 7.1 Hz, H²), 3.09 – 3.03 (1H, m, H⁵/⁶), 2.78 – 2.68 (1H, m, H⁵/⁶ or ⁶/⁷), 2.63 – 2.54 (3H, m, H⁴/⁵/⁶ or ⁷/⁸), 2.10 (3H, d, J = 34.2 Hz, H¹¹), 1.25 (3H, dt, J = 10.5, 7.1 Hz, H¹⁵), 13C NMR (151 MHz, CD₂OD) δ 190.4 (s, C² or ³/⁴), 190.2 (s, C²/³ or ⁴/⁵), 189.2 (s, C²/³ or ⁴/⁵), 189.0 (s, C²/³ or ⁴/⁵), 174.2 (s, C³/⁴), 174.0 (s, C³/⁴), 105.7 (s, C⁵/⁶), 105.4 (s, C⁹/⁰), 104.9 (s, C¹⁰⁻), 102.5 (s, C¹²⁻), 88.7 (s, C¹⁵¹⁵), 88.6 (s, C¹⁶⁻), 86.4 (s, C¹¹), 86.2 (s, C¹¹), 83.0 (s, C¹⁴), 82.5 (s, C¹⁶⁻), 82.4 (s, C¹⁶), 79.7 (d, J = 2.4 Hz, C¹⁷), 60.5 (s, C²/³), 60.4 (s, C²/³), 38.3 (s, C⁴/⁵ or ⁵/⁶), 38.2 (s, C⁴/⁵ or ⁵/⁶ or ⁶/⁷), 37.9 (s, C⁴/⁵ or ⁵/⁶ or ⁶/⁷), 37.8 (s, C⁴/⁵ or ⁵/⁶ or ⁶/⁷), 37.7 (s, C⁴/⁵ or ⁵/⁶ or ⁶/⁷), 37.5 (s, C⁴/⁵ or ⁵/⁶ or ⁶/⁷), 19.0 (s, C¹¹⁻), 18.9 (s, C¹¹⁻), 13.1 (s, C¹¹⁻), 13.1 (s, C¹¹⁻), 31P NMR (243 MHz, CD₂OD) δ -132.06 – -156.07 (m, p¹⁻Counter-ion),
$^{19}$F$^1$H NMR $\delta$ -74.65 (d, $J = 707.8$ Hz, FCounter-ion); m/z (HRMS)$^*$ 435.0764 [M-PF6] (C$_{21}$H$_{23}$O$_{9}$Ru$^+$ requires 435.0672)

[Ru($\eta^6$-9-(2-tolyl)-3-oxaspiro[5.5]undecane-8,10-dione($\eta^5$-cyclopentadienyl)]PF$_6$

Synthesised via general experimental 2, using 3-oxaspiro[5.5]undecane (6.6 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (14.4 mg, 0.024 mmol, 70 %).

$^1$H NMR (599 MHz, CD$_3$OD) $\delta$ 6.11 (1H, d, $J = 5.7$ Hz, H$^{12}$), 5.98 (1H, t, $J = 5.5$ Hz, H$^{14}$), 2.48 (2H, dd, $J = 16.6, 2.7$ Hz, H$^{4/5}$), 2.42 (2H, dd, $J = 16.4, 2.6$ Hz, H$^{4/5}$), 3.73 (4H, t, $J = 5.5$ Hz, H$^{1}$), 2.48 (2H, dd, $J = 16.6, 2.7$ Hz, H$^{4/5}$), 2.37 (4H, t, $J = 5.5$ Hz, H$^{1}$), 2.14 (3H, s, H$^{10}$), 1.64 (4H, dt, $J = 33.9, 5.4$ Hz, H$^{2, 2'}$), 13C NMR (151 MHz, CD$_3$OD) $\delta$ 192.1 (s, C$^5/6$), 190.9 (s, C$^{5/6}$), 106.5 (s, C$^{8/9}$), 103.8 (s, C$^{12}$), 90.2 (s, C$^{15}$), 87.6 (s, C$^{15}$), 84.4 (s, C$^{14}$), 83.8 (s, C$^{13}$), 81.1 (s, C$^{16}$), 64.7 (s, C$^{1}$), 64.6 (s, C$^{1}$), 48.8 (s, C$^{4/5}$), 48.1 (s, C$^{4/5}$), 38.2 (s, C$^{1}$), 37.5 (s, C$^{2}$), 32.8 (s, C$^{3}$), 20.5 (s, C$^{10}$), $^{19}$F$^{1}$H NMR $\delta$ -72.72 (d, $J = 707$ Hz, FCounter-ion); m/z (HRMS)$^*$ 433.0875 [M-PF6] (C$_{22}$H$_{25}$O$_{9}$Ru$^+$ requires 433.0880).

[Ru($\eta^6$-2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione($\eta^5$-cyclopentadienyl)]PF$_6$

Synthesised via general experimental 2, using 2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione (6.6 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown oil.

$^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 6.02 (1H, d, $J = 5.7$ Hz, H$^{2}$Arene), 5.89 (2H, dd, $J = 3.0, 0.9$ Hz, H$^{2}$Arene), 5.83 (1H, ddd, $J = 5.7, 3.9, 2.6$ Hz, H$^{2}$Arene), 5.17 (5H, s, H$^{15}$), 1.30-1.19 (12H, m, H$^{1, 2}$), m/z (HRMS)$^*$ 421.0875 [M-PF6] (C$_{22}$H$_{25}$O$_{9}$Ru$^+$ requires 421.0880).
[Ru(η⁶-8-(2-tolyl)-1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione)(η⁵-
cyclopentadienyl)]PF₆

Synthesised via general experimental 2, using 1,2,4,5-tetrahydropyrazolo[1,2-
d][1,4,5]oxadiazepine-7,9-dione (6.6 mg, 0.038 mmol. 1.1 eq.). The title compound was isolated
as a yellow foam (14.2 mg, 0.023 mmol, 68%).

¹H NMR (599 MHz, CD₂OD) δ 6.22 (1H, dd, J = 6.0, 0.9 Hz, H¹₁¹), 5.93 (1H, dd, J = 5.7, 0.9 Hz, H¹⁰), 5.32 (5H, s, H²⁵), 3.88 – 3.85 (4H, m, H¹), 3.82 – 3.80 (4H, m, H²), 2.38 (3H, s, H³), ¹³C NMR (151 MHz, CD₂OD) δ 167.1 (s, C⁵), 101.8 (s, C⁶), 100.5 (s, C⁷), 86.7 (s, C⁸), 86.3 (s, C⁹), 83.5 (s, C¹⁰), 82.5 (s, C¹¹), 79.5 (s, C¹²), 79.2 (s, C¹³), 69.7 (s, C¹⁴), 47.7 (s, C¹⁵), 19.1 (s, C¹⁶), ¹⁹F [¹H] NMR δ -72.63 (d, J = 707 Hz, FCounter-ion); m/z (HRMS)⁺ 421.0261 [M-PF₆] (C₁₉H₂₁N₂O₃Ru⁺ requires 421.0268)

[Ru(η⁶-3-(2-tolyl)-1,3-bicyclo[3.2.1]octane-2,4-dione)(η⁵-cyclopentadienyl)]PF₆ (1:1 mixture of diastereomers)

Synthesised via general experimental 2, using 1,3-bicyclo[3.2.1]octane-2,4-dione (6.4 mg, 0.038
mmol, 1.1 eq.). The title compound was isolated as an impure brown oil.

¹H NMR (599 MHz, CD₂OD) δ 6.06 (1H, dd, J = 9.5, 5.7 Hz, H¹⁵/¹⁵'), 5.93 (1H, q, J = 5.6 Hz, H¹₂/¹₂'), 5.88 (2H, ddd, J = 14.6, 9.4, 5.7 Hz, H¹³/¹³', ¹⁴/¹⁴'), 5.27 – 5.21 (5H, m, H¹⁰/¹⁰', ²/²'), 2.83 – 2.74 (2H, m, H¹¹/¹¹' or ²/²'), 2.16 and 2.08 (3H, s, H¹⁰/¹⁰', ²/²'), 2.13 – 2.07 (3H, m, H¹²/¹²' and ³/³'), 1.74 (2H, dd, J = 21.0, 6.6 Hz, H¹¹/¹¹' or ²/²'), 1.55 (1H, dd, J = 23.9, 10.9, 4.3 Hz, H¹³/¹³' or ³/³'), ¹³C NMR (151 MHz, CD₂OD) δ 198.9 (s, C⁶/⁶' or ⁷/⁷'), 198.3 (s, C⁶'/⁶'' or ⁷'/⁷'''), 197.3 (s, C⁵/⁵' or ⁷/⁷'), 197.2 (s, C⁶/⁶' or ⁷/⁷'), 105.2 (s, C⁸/⁸'), 104.7 (s, C⁸'), 102.6 (s, C⁹/⁹'), 102.2 (s, C¹⁰/¹⁰'), 101.2 (s, C¹¹/¹¹'), 100.7 (s, C¹²/¹²'), 88.9 (s, C¹³/¹³' or ¹⁴/¹⁴'), 88.1 (s, C¹³/¹³' or ¹⁴/¹⁴'), 86.3 (s, C¹⁵/¹⁵'), 86.1 (s, C¹⁵/¹⁵'), 83.0 (s, C¹²/¹²'), 82.9 (s, C¹²/¹²'), 82.3 (s, C¹³/¹³' or ¹⁴/¹⁴'), 79.6 (s, C¹⁴/¹⁴'), 79.6 (s, C¹⁴/¹⁴'), 49.5 (s, C¹⁵/¹⁵' or ²/²'), 49.4 (s, C¹⁵/¹⁵' or ²/²'), 48.9 (s, C¹⁶/¹⁶' or ²/²'), 48.8 (s, C¹⁶/¹⁶' or ²/²'), 36.8 (s, C⁵/⁵' or ³/³'), 36.3 (s, C⁵/⁵' or ³/³'), 28.1 and 28.1 (s, C¹/¹' or ²/²'), 27.9 and 27.8 (s, C⁶/⁶'), 19.0 (s, C¹⁰/¹⁰'), 18.3 (s, C¹⁰/¹⁰'), ¹⁹F [¹H] NMR δ -72.58 (d, J = 707 Hz, FCounter-ion); m/z (HRMS)⁺ 389.0602 [M-PF₆] (C₁₉H₂₃O₃Ru⁺ requires 389.0618).
[Ru(η⁶-9-(2-tolyl)-3-methoxy-3-azaspiro[5.5]undecane-8,10-dione)(η⁵-
cyclopentadienyl)]PF₆

Synthesised via general experimental 2, using 3-methoxy-3-azaspiro[5.5]undecane-8,10-dione (8.3 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as a brown solid (18 mg, 0.030 mmol, 63 %).

1H NMR (599 MHz, CD₃OD) δ 6.08 (1H, d, J = 5.7 Hz, H₉), 5.95 (1H, t, J = 5.7 Hz, H₁⁵), 5.92 – 5.88 (2H, m, H₁¹⁶,₁⁸), 5.25 (5H, s, H₅), 3.50 (3H, s, H₁), 3.20-3.12 (2H, m, H₇/₈), 2.68-2.60 (2H, m, H₇/₈), 2.54 (1H, d, J = 16.5 Hz, H₁), 2.40 (1H, d, J = 16.7 Hz, H₁'), 2.31-2.24 (2H, m, H₂/₃), 2.11 (3H, s, H₁₃), 1.95-1.91 (1H, m, H₁), 1.83-1.74 (1H, m, H₁'), 1.60-1.50 (2H, m, H⁴/⁵), 13C NMR (151 MHz, CD₃OD) δ 191.1 (s, C₉/₁₀), 189.8 (s, C₉/₁₀), 105.4 (s, C₁¹/₁₂), 104.9 (s, C₁¹/₁₂), 102.4 (s, C₁₄), 88.8 (s, C₁₈), 86.2 (s, C₁₅), 82.9 (s, C₁₇), 82.4 (s, C₁₈), 79.7 (s, C₁₉), 57.6 (s, C₁), 50.6 (s, C₂/₃), 50.5 (s, C₂/₃), 34.2 (s, C₆), 31.4 (s, C₆), 19.1 (s, C₁³), 19F[¹H] NMR δ -74.76 (d, J = 707 Hz, F₃⁻Counter-ion); m/z (HRMS) 462.1140 [M-PF₆] (C₂₃H₂₈NO₃⁹⁶Ru+ requires 462.1145).

[Ru(η⁶-9-(2-tolyl)-3-methoxy-3-azaspiro[5.5]undecane-8,10-dione)(η⁵-
cyclopentadienyl)]PF₆

Synthesised via general experimental 2, using cyclopentane-1,3-dione (3.8 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown solid.

₁H NMR (599 MHz, CD₃OD) δ 6.12 (1H, d, J = 5.7 Hz, H₉), 6.02-5.96 (2H, m, H₁¹⁶,₁⁸), 5.95 (1H, t, J = 5.7 Hz, H₁⁵), 5.32 (5H, s, H₅), 2.40 (4H, s, H₁), 2.23 (3H, s, H₁'), 13C NMR (151 MHz, CD₃OD) δ 201.4 (s, C₁,₄), 106.0 (s, C₁), 101.3 (s, C₅), 101.0 (s, C₆), 87.1 (s, C₂/₃), 86.6 (s, C₉), 83.5 (s, C₁₁), 82.9 (s, C₁₅), 79.5 (s, C₁₉), 32.3 (s, C₁₁), 18.7 (s, C₁), 19F[¹H] NMR δ -74.76 (d, J = 707 Hz, F₃⁻Counter-ion); m/z (HRMS) 349.0314 [M-PF₆] (C₁₇H₁₇NO₃⁹⁶Ru+ requires 349.0305).
Synthesised via general experimental 2, using acetylacetate (3.8 mg, 0.038 mmol, 1.1 eq.). The title compound was isolated as an impure brown oil (72%).

$^1$H NMR (400 MHz, Acetone) $\delta$ 6.11 (1H, d, $J = 5.3$ Hz, H$_{\text{Arene}}$), 6.01 (1H, d, $J = 5.5$ Hz, H$_{\text{Arene}}$), 5.98 – 5.90 (2H, m, H$_{\text{Arene}}$), 5.29 (5H, s, H$_{13}$), 2.12 (3H, s, H$_{7}$), 2.07 (6H, q, $J = 2.2$ Hz, H$_{1, 5}$). m/z (LRMS)$^+$ 351.20 [M-PF$_6$] ($C_{17}H_{19}O_2$)$_9$Ru$^+$ requires 351.04).

1e. General experimental 3 – Leaving group competition experiments
Potassium carbonate (2 eq.), 1,3-cyclohexanedione (1 eq.), [CpRu($\eta^5$-2-chlorotoluene)]PF$_6$ (1 eq.) and anhydrous DMF were combined in an oven-dried Schlenk flask and stirred at 75 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, then the resulting brown residue was triturated with dichloromethane (3x5 mL) and filtered. The filtrate was dried under reduced pressure, then the brown solid was dissolved in $d_6$-acetone and analysed by $^1$H NMR. Ratios of product(s) were calculated via analysis the $^1$H NMR spectrum and confirmed by analysis of the mass spectrum.
2. NMR Spectra

2a. Ru Sandwich complexes

500 MHz, Acetone-d$_6$, 298K
500 MHz, Acetone-\textit{d}_6, 298K

500 MHz, Acetone-\textit{d}_6, 298K
500 MHz, Acetone-d₆, 298K

\[
\text{NO}_2
\]

\[
\text{PF}_6
\]

500 MHz, Acetone-d₆, 298K

\[
\text{F}
\]

\[
\text{PF}_6
\]
500 MHz, Acetone-$d_6$, 298K

---

500 MHz, Acetone-$d_6$, 298K
500 MHz, Acetone-d₆, 298K
500 MHz, Acetone-$d_6$, 298K

Diagram 1

Diagram 2
500 MHz, Acetone-d₆, 298K

[Diagram of compound with labels Cl, Ru⁺, PF₆, and chemical shifts]

500 MHz, Acetone-d₆, 298K

[Diagram of compound with labels Br, Ru⁺, PF₆, and chemical shifts]
500 MHz, Acetone-d$_6$, 298K

500 MHz, MeOD, 298K
500 MHz, MeOD, 298K
500 MHz, MeOD, 298K

500 MHz, MeOD, 298K
500 MHz, MeOD, 298K
2b. Photolysis of Ru Sandwich Complexes

i. General Experimental

The specified Ru complex (10 mg) was added to a vial and dissolved in 1.5 mL CD$_3$CN. The vial was placed in a Penn M2 photoreactor and irradiated with UV light (365 nm, 60 Hz) for a specified amount of time. The mixture was analysed by $^1$H NMR spectroscopy after 1, 2, 5, 10 and 15 minutes. Formation of free arene was detected by observing disappearance of bound arene signals (ca. 5.8-7 ppm) and emergence of free arene signals (ca. 6.8-8 ppm).

ii. Stacked Photolysis Spectra

![Stacked Photolysis Spectra](Figure S1. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($\eta^6$-2-benzylcyclohexane-1,3-dione)($\eta^5$-cyclopentadienyl)]PF$_6$)
Figure S2. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($\eta^5$-2-(2-tolyl)cyclohexane-1,3-dione)($\eta^5$-cyclopentadienyl)]PF$_6$.
Figure S3. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($\eta^6$-2-(2-m-xylene)cyclohexane-1,3-dione)($\eta^5$-cyclopentadienyl)]PF$_6$

$t = 0$

$t = 10$ min

$t = 5$ min

$[\text{Ru}(\eta^6-\text{2-m-xylene})\text{cyclohexane-1,3-dione})(\eta^5\text{-cyclopentadienyl})]PF_6$
Figure S4. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($^6$-2-tolyl)-5,5'-dimethylcyclohexane-1,3-dione($^5$-cyclopentadienyl)]PF$_6$

$t = 0$
$t = 1$ min
$t = 5$ min
$t = 10$ min
Figure S5. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex
[Ru($\eta^5$-2-(2-tolyl)-(5-ethylacetyl)cyclohexane-1,3-dione)($\eta^5$-cyclopentadienyl)]PF$_6$

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO

$\Delta$  $\triangleright$  HO
Figure S6. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex $[\text{Ru}($η$^6$-2-tolyl)-3-oxaspiro[5,5]undecane-8,10-dione($\eta^5$-cyclopentadienyl)]\text{PF}_6$.
Figure S7. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex $[\text{Ru}$(η$^6$-2,2',6,6'-tetramethyl-4-(2-tolyl)-oxane-3,5-dione)(η$^5$-cyclopentadienyl)]PF$_6$.
Figure S8. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($\eta^6$-8-(2-toly)-1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione($\eta^5$-cyclopentadienyl)]PF$_6$]
Figure S9. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex
$[\text{Ru(η}^6\text{-3-(2-tolyl)-1,3-bicyclo[3.2.1]octane-2,4-dione)(η}^5\text{-cyclopentadienyl)]PF_6]$ with $h\nu$.

$\text{Ru}^{\text{II}}$ + $\text{PF}_6^-$ → $\text{Ru}^{\text{III}}$ + $\text{PF}_6^-$

$t = 0$
$t = 1 \text{ min}$
$t = 2 \text{ min}$
$t = 5 \text{ min}$
$t = 10 \text{ min}$

$\text{d}^3\text{-MeCN}$

$+ [(\text{NCCD}_3)_2\text{RuCp}]\text{PF}_6$
Figure S10. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex
[Ru($\eta^6$-9-(2-toly)-3-methoxy-3-azaspiro[5.5]undecane-8,10-dione($\eta^5$-cyclopentadienyl)]PF$_6$

$t = 0$

$t = 1$ min

$t = 2$ min

$t = 5$ min

$\rightarrow$
Figure S11. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex $[\text{Ru}(\eta^6$-$\eta_6$-9-(2-tolyl)-tert-butyl-8,10-dioxo-3-azaspiro[5.5]undecane-3-carboxylate)(\eta^6$-cyclopentadienyl)]PF$_6$.
Figure S12. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex [Ru($\eta^5$-2-(tolyl)cyclopentanedione)($\eta^5$-cyclopentadienyl)]PF$_6$.
Figure S12. Stacked $^1$H NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of the complex
Ru($\eta^6$-2-(2-tolyl)acetylacetone)($\eta^5$-cyclopentadienyl)]PF$_6$
Section 3. Crystallographic data

The X-ray single crystal data have been collected using λMoKα radiation (λ =0.71073Å) on an Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2)K. The structure was solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [3] and SHELXTL [4] software. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions and refined in riding mode. Crystal data and parameters of refinement are listed in Tables S1-S5. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1546706.
### 3a. Complex 1a

![Complex 1a](image)

Table S1. Crystal data and structure refinement for Ru complex 1a

| Property                              | Value                  |
|----------------------------------------|------------------------|
| **Empirical formula**                  | C₁₁H₁₆F₇PRu            |
| **Formula weight**                     | 407.23                 |
| **Temperature/K**                      | 120.0                  |
| **Crystal system**                     | monoclinic             |
| **Space group**                        | C2                     |
| **a/Å**                                | 8.9922(2)              |
| **b/Å**                                | 9.5814(3)              |
| **c/Å**                                | 7.2372(2)              |
| **α/°**                                | 90                     |
| **β/°**                                | 96.5700(10)            |
| **V/Å³**                               | 619.45(3)              |
| **Z**                                  | 2                      |
| **ρ <sub>calc</sub>/g/cm³**            | 2.183                  |
| **μ/mm⁻¹**                             | 1.467                  |
| **F(000)**                             | 396.0                  |
| **Crystal size/mm³**                   | 0.14 × 0.12 × 0.06     |
| **Radiation**                          | Mo Kα (λ = 0.71073)    |
| **2Θ range for data collection/°**    | 5.666 to 59.986        |
| **Index ranges**                       | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -10 ≤ l ≤ 10 |
| **Reflections collected**              | 6340                   |
| **Independent reflections**            | 1782 [R <sub>int</sub> = 0.0196, R <sub>sigma</sub> = 0.0190] |
| **Data/restraints/parameters**         | 1782/67/126            |
| **Goodness-of-fit on F²**              | 1.089                  |
| **Final R indexes [I>=2σ (I)]**       | R₁ = 0.0210, wR₂ = 0.0507 |
| **Final R indexes [all data]**         | R₁ = 0.0215, wR₂ = 0.0511 |
| **Largest diff. peak/hole / e Å⁻³**    | 0.60/-0.43             |
| **Flack parameter**                    | 0.57(7)                |
### 3b. Complex 1b

![Diagram of complex 1b]

Table S2. Crystal data and structure refinement for Ru complex 1b

| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula              | $\text{C}_{11}\text{H}_{10}\text{ClRu x PF}_6$ |
| Formula weight                 | 423.68                                     |
| Temperature/K                  | 120.0                                      |
| Crystal system                 | monoclinic                                 |
| Space group                    | $\text{P2}_1/n$                            |
| $a$/Å                          | 9.0165(4)                                  |
| $b$/Å                          | 13.3485(6)                                 |
| $c$/Å                          | 10.9347(5)                                 |
| $\alpha$/°                     | 90                                         |
| $\beta$/°                      | 91.0311(18)                                |
| $\gamma$/°                     | 90                                         |
| Volume/Å³                      | 1315.85(10)                                |
| $Z$                            | 4                                          |
| $\rho_{\text{calc}}$/g/cm$^3$  | 2.139                                      |
| $\mu$/mm$^{-1}$                | 1.572                                      |
| $F(000)$                       | 824.0                                      |
| Crystal size/mm$^3$            | 0.19 x 0.11 x 0.07                         |
| Radiation                      | MoKα ($\lambda = 0.71073$)                 |
| 2Θ range for data collection/° | 4.816 to 58.994                            |
| Index ranges                   | $-12 \leq h \leq 12, -18 \leq k \leq 18, -15 \leq l \leq 15$ |
| Reflections collected          | 20662                                      |
| Independent reflections        | 3659 [$R_{\text{int}} = 0.0316$, $R_{\text{sigma}} = 0.0228$] |
| Data/restraints/parameters     | 3659/0/181                                 |
| Goodness-of-fit on $F^2$       | 1.028                                      |
| Final R indexes [I>=2σ (I)]    | $R_1 = 0.0189$, $wR_2 = 0.0398$             |
| Final R indexes [all data]     | $R_1 = 0.0261$, $wR_2 = 0.0417$             |
| Largest diff. peak/hole / e Å$^3$ | 0.39/-0.40                              |
### 3c. Complex 2a

![Complex 2a structure](image)

#### Table S3. Crystal data and structure refinement for Ru complex 2a

| Parameter                  | Value                                      |
|----------------------------|--------------------------------------------|
| Identification code        | 22srv023                                   |
| Empirical formula          | C₁₂H₁₂F₇PRu                                |
| Formula weight             | 421.26                                     |
| Temperature/K              | 120.00                                     |
| Crystal system             | monoclinic                                 |
| Space group                | P2₁/n                                      |
| a/Å                        | 9.0446(3)                                  |
| b/Å                        | 14.1266(4)                                 |
| c/Å                        | 10.6960(3)                                 |
| α/°                        | 90                                         |
| β/°                        | 90.0265(11)                                |
| γ/°                        | 90                                         |
| Volume/Å³                  | 1366.62(7)                                 |
| Z                          | 4                                          |
| ρ calc/g/cm³               | 2.047                                      |
| μ/mm⁻¹                     | 1.334                                      |
| F(000)                     | 824.0                                      |
| Crystal size/mm³           | 0.14 × 0.09 × 0.06                         |
| Radiation                  | Mo Kα (λ = 0.71073)                        |
| 2Θ range for data collection/° | 4.776 to 58.996                           |
| Index ranges               | -12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -14 ≤ l ≤ 14  |
| Reflections collected      | 27182                                      |
| Independent reflections    | 3817 [R_{int} = 0.0388, R_{sigma} = 0.0251]|
| Data/restraints/parameters | 3817/96/240                                |
| Goodness-of-fit on F²      | 1.069                                      |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0292, wR₂ = 0.0676                  |
| Final R indexes [all data] | R₁ = 0.0369, wR₂ = 0.0714                  |
| Largest diff. peak/hole / e Å³ | 0.99/-0.54                              |
### 3d. Complex 2b

![Diagram of Complex 2b]

Table S4. Crystal data and structure refinement for Ru complex 2b

| Property                      | Value                  |
|-------------------------------|------------------------|
| Empirical formula             | C_{12}H_{12}ClF_{6}PRu |
| Formula weight                | 437.71                 |
| Temperature/K                 | 120                    |
| Crystal system                | triclinic              |
| Space group                   | P-1                    |
| a/Å                           | 13.8713(6)             |
| b/Å                           | 13.8734(6)             |
| c/Å                           | 14.9953(7)             |
| α/°                           | 89.4442(16)            |
| β/°                           | 79.4373(16)            |
| γ/°                           | 89.6981(16)            |
| Volume/Å³                     | 2836.7(2)              |
| Z                             | 8                      |
| ρ_{calc}/cm³                  | 2.050                  |
| μ/mm⁻¹                        | 1.462                  |
| F(000)                        | 1712.0                 |
| Crystal size/mm³              | 0.208 × 0.132 × 0.124  |
| Radiation                     | MoKα (λ = 0.71073)     |
| 2θ range for data collection/°| 2.762 to 59.998        |
| Index ranges                  | -19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21 |
| Reflections collected         | 60601                  |
| Independent reflections       | 16458 [R_{int} = 0.0428, R_{sigma} = 0.0439] |
| Data/restraints/parameters    | 16458/0/758            |
| Goodness-of-fit on F²         | 1.059                  |
| Final R indexes [I≥2σ (I)]    | R₁ = 0.0457, wR₂ = 0.1077 |
| Final R indexes [all data]    | R₁ = 0.0658, wR₂ = 0.1230 |
| Largest diff. peak/hole / e Å⁻³| 1.06/-1.20            |
### Table S5. Crystal data and structure refinement for Ru complex 3a

| Parameter                  | Value                                      |
|----------------------------|--------------------------------------------|
| Identification code        | 22srv007                                   |
| Empirical formula          | C_{13}H_{14}F_{7}PRu                       |
| Formula weight             | 435.28                                     |
| Temperature/K              | 120.00                                     |
| Crystal system             | monoclinic                                 |
| Space group                | P2\_1/c                                    |
| a/Å                        | 7.0290(2)                                  |
| b/Å                        | 15.3782(5)                                 |
| c/Å                        | 13.9470(5)                                 |
| α/°                        | 90                                         |
| β/°                        | 103.0623(12)                               |
| γ/°                        | 90                                         |
| Volume/Å³                  | 1468.57(8)                                 |
| Z                          | 4                                          |
| ρ calc./g/cm³              | 1.969                                      |
| μ/mm⁻¹                     | 1.244                                      |
| F(000)                     | 856.0                                      |
| Crystal size/mm³           | 0.15 × 0.07 × 0.02                         |
| Radiation                  | Mo Kα (λ = 0.71073)                        |
| 2θ range for data collection/° | 4 to 59.998                          |
| Index ranges               | -9 ≤ h ≤ 9, -21 ≤ k ≤ 21, -19 ≤ l ≤ 19    |
| Reflections collected      | 26106                                      |
| Independent reflections    | 4275 [R_{int} = 0.0320, R_{sigma} = 0.0220] |
| Data/restraints/parameters | 4275/24/222                               |
| Goodness-of-fit on F²      | 1.089                                      |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0244, wR₂ = 0.0552                   |
| Final R indexes [all data] | R₁ = 0.0276, wR₂ = 0.0565                   |
| Largest diff. peak/hole / e Å⁻³ | 1.35/-0.53                               |
## 3f. Complex 3b

![Complex 3b](image)

### Table S6. Crystal data and structure refinement for Ru complex 3b

| Property                  | Value                                      |
|---------------------------|--------------------------------------------|
| **Empirical formula**     | C_{13}H_{14}ClF_{6}PRu                    |
| **Formula weight**        | 451.73                                     |
| **Temperature/K**         | 120.0                                      |
| **Crystal system**        | monoclinic                                 |
| **Space group**           | P2₁                                         |
| **a/Å**                   | 6.9414(2)                                  |
| **b/Å**                   | 15.3352(4)                                 |
| **c/Å**                   | 7.3463(2)                                  |
| **α/°**                   | 90                                          |
| **β/°**                   | 104.6140(10)                               |
| **γ/°**                   | 90                                          |
| **Volume/Å³**             | 756.70(4)                                  |
| **Z**                     | 2                                           |
| **ρ_{ calc g/cm³}**       | 1.983                                      |
| **μ/mm⁻¹**                | 1.373                                      |
| **F(000)**                | 444.0                                      |
| **Crystal size/mm³**      | 0.13 × 0.11 × 0.06                         |
| **Radiation**             | Mo Kα (λ = 0.71073)                        |
| **2Θ range for data collection/°** | 5.312 to 57.988                          |
| **Index ranges**          | -9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -10 ≤ l ≤ 10    |
| **Reflections collected** | 18388                                      |
| **Independent reflections** | 3986 [R_{int} = 0.0299, R_{sigma} = 0.0240] |
| **Data/restraints/parameters** | 3986/1/202                              |
| **Goodness-of-fit on F²** | 1.047                                      |
| **Final R indexes [>=2σ (I)]** | R₁ = 0.0211, wR₂ = 0.0511                |
| **Final R indexes [all data]** | R₁ = 0.0223, wR₂ = 0.0517                |
| **Largest diff. peak/hole / e Å⁻³** | 2.02/-0.53                                |
| **Flack parameter**       | 0.51(4)                                    |
Table S7. Crystal data and structure refinement for Ru complex 3c

| Property                      | Value                      |
|-------------------------------|----------------------------|
| Empirical formula             | C_{13}H_{14}F_{6}NO_{2}PRu |
| Formula weight                | 462.29                     |
| Temperature/K                 | 120.0                      |
| Crystal system                | monoclinic                 |
| Space group                   | P2_1/c                      |
| a/Å                           | 16.7069(7)                 |
| b/Å                           | 14.2729(6)                 |
| c/Å                           | 14.1391(6)                 |
| α/°                           | 90                         |
| β/°                           | 112.2030(10)               |
| γ/°                           | 90                         |
| Volume/Å^3                    | 3121.6(2)                  |
| Z                             | 8                          |
| \(\rho_{\text{calc}}\)/g/Å^3 | 1.967                      |
| \(\mu\)/mm\(^{-1}\)          | 1.179                      |
| F(000)                        | 1824.0                     |
| Crystal size/mm\(^3\)        | 0.23 × 0.2 × 0.15          |
| Radiation                     | MoKα (λ = 0.71073)         |
| 2θ range for data collection/°| 3.882 to 60                |
| Index ranges                  | -23 ≤ h ≤ 23, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19 |
| Reflections collected         | 52996                      |
| Independent reflections       | 9078 [R_{int} = 0.0295, R_{sigma} = 0.0214] |
| Data/restraints/parameters    | 9078/67/470                |
| Goodness-of-fit on F^2        | 1.046                      |
| Final R indexes [I≥2σ (I)]    | R_1 = 0.0249, wR_1 = 0.0572 |
| Final R indexes [all data]    | R_1 = 0.0293, wR_2 = 0.0593 |
| Largest diff. peak/hole / e Å\(^{-3}\) | 0.85/-0.77          |