Nucleophilic Trifluoromethylation of Unactivated Arenes

Jack A Pike, James W Walton

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1. NMR Spectra for Photolysis of Complex 2

Figure S1. Stacked $^1$H-NMR spectra (CD$_3$CN, 298 K, 400 MHz) for the photolysis of complex 2.
2. Experimental Detail and Product Characterisation

General Information

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, KF was oven dried at 100 °C for 48 h. Reactions requiring anhydrous conditions were carried out under an atmosphere of dry argon using Schlenk-line techniques. Where appropriate, solvents were sparged with argon or degassed using the freeze-thaw cycle method. Thin-layer chromatography was carried out on silica plates (Merck 5554) or neutral alumina plates (Merck Art 5550) and visualized under UV (254/365 nm) irradiation or by staining with potassium permanganate solutions. Preparative column chromatography was carried out using silica (Merck Silica Gel 60, 230400 mesh) or neutral alumina (Merck Aluminium Oxide 90, activity II-III, 70230 mesh), pre-soaked in ethyl acetate.

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-700 spectrometer (1H at 699.73 MHz, 13C at 175.95 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 a Thermo-Finnigan LTQ FT system using acetonitrile as the carrier solvent

![Chemical Structure](image)

[Ru(η⁶-nitrobenzene)(η⁵-cyclopentadienyl)]PF₆ (I)

To a solution of nitrobenzene (63 mg, 53 µL, 0.507 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (9 mL) at 80 °C was added [Ru(NCMe)₃Cp]PF₆ (200 mg, 0.461 mmol). The resulting solution was heated to reflux for 16 hours under an inert atmosphere, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et₂O. The green solid was isolated by filtration,
rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the \textit{title compound} as a light brown solid (187 mg, 93%); \(\delta_H\) (acetone-D\textsubscript{6}) 7.46 (2H, dt, \(^3J_{H-H}\) 6.0 Hz, \(^4J_{H-H}\) 2.0 Hz, H\textsuperscript{2}), 6.79 (2H, tt, \(^3J_{H-H}\) 6.0 Hz, \(^4J_{H-H}\) 2.0 Hz, H\textsuperscript{4}), 6.70 (1H, tt, \(^3J_{H-H}\) 6.0 Hz, \(^4J_{H-H}\) 2.0 Hz, H\textsuperscript{3}); \(\delta_C\) (acetone-D\textsubscript{6}) 111.4 (1C, s, C\textsuperscript{1}), 88.5 (1C, s, C\textsuperscript{4}), 86.5 (2C, s, C\textsuperscript{3}), 83.7 (5C, s, C\textsuperscript{5}), 82.9 (2C, s, C\textsuperscript{2}); \(\delta_P\) (acetone-D\textsubscript{6}) -144.3 (sept., \(^{J_P-F}\) 707 Hz); \(m/z\) (HRMS\textsuperscript{+}) 283.9788 \([M-PF\textsubscript{6}]^+\) (C\textsubscript{11}H\textsubscript{10}NO\textsubscript{2}\textsuperscript{96}Ru requires 283.9787); Anal. Found (Expected): C 30.47 (30.43); H 2.34 (2.32); N 3.37 (3.23).

\[\text{Ru}(\eta^6-\alpha,\alpha,\alpha\text{-trifluorotoluene})(\eta^5\text{-cyclopentadienyl})\text{PF}_6\] (2)

[Ru(\eta^6-nitrobenzene)(\eta^5\text{-cyclopentadiene})\text{PF}_6] (100 mg, 0.230 mmol) was dissolved in anhydrous DMF (5 mL). Oven dried potassium fluoride (15 mg, 0.253 mmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (36 mg, 37.4 µL, 0.253 mmol, 1.1 equiv) were added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column chromatography (silica, acetonitrile : 5\% MeOH) gave the \textit{title compound} as a brown solid (33 mg, 31%); \(\delta_H\) (acetone-D\textsubscript{6}) 6.86 – 6.82 (2H, dt, \(^3J_{H-H}\) 6.0 Hz, \(^4J_{H-H}\) 2.0 Hz, \(^4J_{H-H}\) 1.5 Hz H\textsuperscript{3}), 6.64 – 6.61 (3H, m, H\textsuperscript{4 and 5}), 5.70 (5H, s, H\textsuperscript{6}); \(\delta_C\) (acetone-D\textsubscript{6}) 123.2 (1C, q, \(^{1J_C-F}\) 274 Hz, C\textsuperscript{1}), 91.8 (1C, q, \(^{2J_C-F}\) 38 Hz, C\textsuperscript{2}), 87.8 (1C, s, C\textsuperscript{3}), 86.2 (2C, s, C\textsuperscript{4}), 83.6 (2C, q, \(^{3J_C-F}\) 3 Hz, C\textsuperscript{5}), 82.6 (5C, s, C\textsuperscript{6}); \(\delta_F\) (acetone-D\textsubscript{6}) -62.33 (3F, s, F\text{arene}), -72.6 (6F, d, \(^{J_F-P}\) 707 Hz, F\text{counterion}); \(m/z\) (HRMS\textsuperscript{+}) 306.9812 \([M-PF\textsubscript{6}]^+\) (C\textsubscript{12}H\textsubscript{10}F\textsubscript{3}\textsuperscript{96}Ru requires 306.9811) \(R_f = 0.17\) (silica, acetonitrile : 5\% MeOH); Anal. Found (Expected): C 31.69 (31.52); H 2.21 (2.20); N 0.26 (0.00).

\[\text{Ru}(\eta^4\text{-1-nitro-2-trifluoromethylcyclohexadienyl})(\eta^5\text{-cyclopentadienyl})\] (3)
[Ru(η⁶-nitrobenzene)(η⁵-cyclopentadiene)]PF₆ (100 mg, 0.230 mmol) was dissolved in anhydrous DMF (5 mL). Oven dried potassium fluoride (15 mg, 0.253 mmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (36 mg, 37.4 µL, 0.253 mmol, 1.1 equiv) was added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column chromatography (silica, pet. ether : 20% EtOAc) gave the title compound as a yellow oil (27 mg, 32%); δH (acetone-D₆) 6.19 (1H, td, 3Jₕ-ₕ 5.5 Hz, 4Jₕ-ₕ 1.5 Hz, H₅), 6.09 (1H, ddd, 3Jₕ-ₕ 5.5 Hz, 4Jₕ-ₕ 1.5 Hz, H₆), 5.09 (1H, t, 3Jₕ-ₕ 5.5 Hz, H₄), 4.96 (5H, s, H₈), 4.48 (1H, qdd, 3Jₕ-F 8.0 Hz, 3Jₕ-H 6.5 Hz, 4Jₕ-H 1.5 Hz, H₂), 3.76 (1H, dt, 3Jₕ-H 6.0 Hz, 4Jₕ-H 1.5 Hz, H₃); δC (acetone-D₆) 124.1 (1C, q, 1Jₖ-F 287 Hz, C₁), 81.0 (1C, s, C₄), 80.6 (1C, s, C₅), 79.4 (5C, s, C₈), 75.1 (1C, s, C₆), 62.0 (1C, m, C₇), 43.4 (1C, q, 2Jₖ-C 29 Hz, C₂), 28.3 (1C, q, 1Jₖ-C 2 Hz, C₃); δF (acetone-D₆) -76.4 (3F, d, 3Jₖ-F 8.0 Hz); m/z (HRMS+) 353.9818 [M+H]+ (C₁₂H₁₁F₃NO₂⁹⁶Ru requires 353.9818), 306.9811 [M-NO2]+ (C₁₂H₁₀F₃⁹⁶Ru requires 306.9811), Rf = 0.28 (silica, pet. ether : 20% EtOAc); tR (RP-HPLC) column 1: 3.36 min, purity >99%; column 2: 3.56 min, purity >99%.

2-Trifluoromethyl-nitrobenzene

To an oven dried Schlenk tube, [Ru(η⁵-1-nitro-2-trifluoromethylcyclohexadienyl)(η⁵-cyclopentadiene)] (20 mg, 55.8 µmol) was added and dissolved in anhydrous deuterated acetonitrile (1 mL). To this, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (15 mg, 66.9 µmol, 1.2 equiv) was added and the mixture was stirred at room temperature for 24 hours. ¹H- and ¹⁹F-NMR showed confirmation of quantitative conversion to free arene using an external standard of α,α,α-trifluorotoluene (10 mg, quantitative); δH (acetonitrile-D₃) 8.00 (1H, m), 7.96 (1H, m), 7.89 (2H, m); δF (acetonitrile-D₃) -60.2 (3F, m).
**a,a,a-Trifluorotoluene**

To a quartz NMR tube, [Ru(η⁶-a,a,a-trifluorotoluene)(η⁵-cyclopentadienyl)]PF₆ (20 mg, 43.7 µmol) was added and dissolved in anhydrous deuterated acetonitrile (0.8 mL). The mixture was irradiated under UV lamp (365 mn, 36 W) for 27 hours to give the title compound in a quantitative conversion (see NMR spectrum S1). δ_H (acetonitrile-D₃) 7.73 (2H, m, H₁), 7.68 (1H, t, J_H-H 7.5, H₃) 7.60 (2H, t, J_H-H 7.5, H²); δ_F (acetonitrile-D₃) -63.2 (3F, m).

![Chemical Structure](image)

**[Ru(η⁶-4-nitrotoluene)(η⁵-cyclopentadienyl)]PF₆**

To a solution of 4-nitrotoluene (19 mg, 0.138 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (4 mL) at 80 °C was added [Ru(NCMe)₃Cp]PF₆ (50 mg, 0.115 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et₂O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound as a light brown solid (56 mg, 91%). δ_H (acetone-D₆) 7.39 (2H, d, J_H-H 6.5 Hz, H²), 6.77 (2H, d, J_H-H 6.5 Hz, H³), 5.73 (5H, s, H⁶), 2.54 (3H, s, H⁵); δ_C (acetone-D₆) 110.5 (1C, s, C¹), 105.8 (1C, s, C⁴), 88.6 (2C, s, C³), 87.6 (1C, s, C⁵), 83.3 (5C, s, C⁶), 72.9 (1C, s, C²); δ_P (acetone-D₆) -144.3 (sept, J_P-F 713 Hz); δ_F (acetone-D₆) -72.2 (d, J_F-P 713 Hz); m/z (HRMS⁺) 297.9946 [M – PF₆]^+ (C₁₂H₁₂NO₂⁶⁶Ru requires 297.9944); Anal. Found (Expected): C 31.38 (32.15); H 2.71 (2.70); N 3.30 (3.12).

![Chemical Structure](image)

**[Ru(η⁶-benzonitrile)(η⁵-cyclopentadienyl)]PF₆**

To a solution of benzonitrile (26 mg, 26 µL, 0.253 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (6 mL) at 80 °C was added [Ru(NCMe)₃Cp]PF₆ (100 mg, 0.230 mmol). The
resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et$_2$O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound as a light brown solid (85 mg, 89%).

δ$_H$ (acetone-D$_6$) 6.89 (2H, dt, $^3$J$_{H-H}$ 6.0 Hz, $^4$J$_{H-H}$ 1.5 Hz, H$^3$), 6.65 (2H, tt, $^3$J$_{H-H}$ 6.0 Hz, $^4$J$_{H-H}$ 1.5 Hz, H$^4$), 6.61 (1H, $^3$J$_{H-H}$ 6.0 Hz, $^4$J$_{H-H}$ 1.5 Hz, H$^5$), 5.77 (5H, s, H$^6$); δ$_C$ (acetone-D$_6$) 115.3 (1C, s, C$^1$), 88.6 (2C, s, C$^3$), 87.6 (1C, s, C$^5$), 86.7 (2C, s, C$^4$), 83.3 (5C, s, C$^6$), 72.9 (1C, s, C$^2$); δ$_F$ (acetone-D$_6$) -144.3 (sept, $^1$J$_{F-P}$ 713 Hz); m/z (HRMS$^+$) 263.9888 [M – PF$_6$]$^+$ (C$_{12}$H$_{10}$N$_9$Ru requires 263.9889); Anal. Found (Expected): C 34.85 (34.79); H 2.56 (2.43); N 3.43 (3.38).

[Ru(η$^5$-1-cyano-2-trifluoromethylcyclohexadienyl)(η$^5$-cyclopentadiene)](4b)

[Ru(η$^6$-benzonitrile)(η$^5$-cyclopentadiene)]PF$_6$ (20 mg, 48.3 µmol) was dissolved in anhydrous DMF (3 mL). Oven dried potassium fluoride (4 mg, 53.1 µmol, 1.1 equiv) and trimethyl(trifluoromethyl)silane (8 mg, 9 µL, 53.1 µmol, 1.1 equiv) was added. The mixture was stirred at 0 °C under argon atmosphere for 8 hours. Purification by column chromatography (silica, pet. ether : 20% EtOAc) gave the title compound as a brown oil (6 mg, 20%).

δ$_H$ (acetone-D$_6$) 6.13 (1H, td, $^3$J$_{H-H}$ 5.5 Hz, $^4$J$_{H-H}$ 1.0 Hz, H$^3$), 5.25 (1H, d, $^3$J$_{H-H}$ 5.5 Hz, H$^6$), 5.05 (5H, s, H$^9$), 4.94 (1H, t, $^3$J$_{H-H}$ 5.5 Hz, H$^4$), 3.48 (1H, qdd, $^3$J$_{H-F}$ 7.5 Hz, $^4$J$_{H-H}$ 1.5 Hz, H$^5$), 3.33 (1H, t, $^3$J$_{H-H}$ 5.5 Hz, H$^3$); δ$_C$ (acetone-D$_6$) 124.1 (1C, q, $^1$J$_{C-F}$ 286 Hz, C$^1$), 123.2 (1C, m, C$^8$), 81.9 (1C, s, C$^5$), 80.4 (1C, s, C$^4$), 79.0 (5C, s, C$^9$), 78.8 (1C, s, C$^6$), 44.2 (1C, q, $^2$J$_{C-F}$ 29 Hz, C$^2$), 24.1 (1C, q, $^1$J$_{C-F}$ 2 Hz, C$^3$), 7.07 (1C, s, C$^7$); δ$_F$ (acetone-D$_6$) -78.7 (3F, d, $^3$J$_{F-H}$ 8.0 Hz); m/z (HRMS$^+$) 333.9921 [M+H]$^+$ (C$_{13}$H$_{11}$F$_3$N$_9$Ru requires 333.9920), R$_f$ = 0.24 (silica, pet. ether : 20% EtOAc).
To a solution of benzoic acid (17 mg, 0.138 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (6 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF$_6$ (50 mg, 0.115 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et$_2$O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound as a light brown solid (47 mg, 94%). $\delta_H$ (acetone-D$_6$) 6.88 (2H, d, $^3J_{H-H}$ 6.0 Hz, H$^3$), 6.56 (2H, t, $^3J_{H-H}$ 6.0 Hz, H$^4$), 6.53 (1H, $^3J_{H-H}$ 6.0 Hz, H$^5$), 5.60 (5H, s, H$^6$); $\delta_C$ (acetone-D$_6$) 165.3 (1C, s, C$^1$), 88.5 (1C, s, C$^2$), 87.3 (1C, s, C$^5$), 86.7 (2C, s, C$^3$), 86.5 (2C, s, C$^4$), 81.8 (5C, s, C$^6$); $\delta_P$ (acetone-D$_6$) -144.3 (sept, $^1J_{P-F}$ 713 Hz); $\delta_F$ (acetone-D$_6$) -72.2 (d, $^1J_{F-P}$ 713 Hz); m/z (HRMS$^+$) 282.9834 [M – PF$_6$]$^+$ ($C_{12}H_{11}O_2$)$_{N6}$Ru requires 282.9835); Anal. Found (Expected) for C$_{12}$H$_{11}$F$_6$O$_2$PRu(MeCN)$_{0.15}$: C 33.95 (33.62); H 2.70 (2.63); N 0.27 (0.48).

To a solution of 4-chlorotoluene (48 mg, 45 µL, 0.380 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (8 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF$_6$ (150 mg, 0.345 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et$_2$O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound
as a light brown solid (147 mg, 97%). $\delta_H$ (acetone-D$_6$) 6.81 – 6.74 (2H, m, H$_2$), 6.55 – 6.48 (2H, m, H$_3$), 5.63 (5H, s, H$_6$), 2.42 (3H, s, H$_5$); $\delta_C$ (acetone-D$_6$) 104.7 (1C, s, C$_1$), 102.6 (1C, s, C$_4$), 87.2 (2C, s, C$_{2/3}$), 86.9 (2C, s, C$_{2/3}$), 83.0 (5C, s, C$_6$), 20.0 (1C, s, C$_5$); $\delta_P$ (acetone-D$_6$) -144.3 (sept, $^1J_{P-F}$ 713 Hz); $\delta_F$ (acetone-D$_6$) -72.2 (d, $^1J_{F-P}$ 713 Hz); m/z (HRMS$^+$) 286.9705 [M – PF$_6$]$^+$ (C$_{12}$H$_{13}$Cl$_9$Ru requires 286.9704).

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

To a solution of toluene (24 mg, 27 µL, 0.253 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (5 mL) at 80 °C was added [Ru(NCMe)$_3$Cp]PF$_6$ (100 mg, 0.230 mmol). The resulting solution was heated to reflux for 16 hours, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et$_2$O. The light brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound as a light brown solid (87 mg, 94%). $\delta_H$ (acetone-D$_6$) 6.35-6.38 (2H, m, H$_3$), 6.27-6.32 (2H, m, H$_4$), 6.22-6.26 (1H, m, H$_5$), 5.51 (5H, s, H$_6$), 2.39 (3H, s, H$_5$); $\delta_C$ (acetone-D$_6$) 102.6 (1C, s, C$_2$), 87.2 (2C, s, C$_3$), 85.4 (2C, s, C$_4$), 84.7 (1C, s, C$_5$), 80.5 (5C, s, C$_6$), 19.7 (1C, s, C$_1$); $\delta_P$ (acetone-D$_6$) -144.3 (sept, $^1J_{P-F}$ 713 Hz); $\delta_F$ (acetone-D$_6$) -72.2 (d, $^1J_{F-P}$ 713 Hz); m/z (ESI$^+$) 253.0098 [M-PF$_6$]$^+$ (C$_{12}$H$_{13}$Cl$_9$Ru requires 253.0093). Anal. Found (Expected): C 35.67 (35.74); H 3.36 (3.25); N 0.32 (0.00).

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

The reaction is a modification of the existing literature procedure.$^1$ A 100 mL oven dried round-bottom flask equipped with a stir-bar was charged with finely ground potassium carbonate (0.83 g, 6.00 mmol, 6.0 equiv) and the flask flame-dried under vacuum. After
cooling to room temperature, the flask was further charged with [(C₆H₆)RuCl₂]₂ (0.50 g, 1.00 mmol) and a reflux condenser added. Ethanol (30 mL) was then added, followed by freshly cracked cyclopentadiene (1.5 mL, 18.0 mmol, 18 equiv). The resulting heterogeneous brown mixture was then warmed to 85 °C with rapid stirring. After approximately 16 h, the reaction mixture was cooled to room temperature and filtered through a plug of Celite, and the Celite rinsed with a further 25 mL of ethanol. The dark yellow filtrate was concentrated to 20 mL, then an aqueous solution of NH₄PF₆ (0.68 g, 4.20 mmol, 4.2 equiv, in 10 mL of H₂O) was added, resulting in the immediate formation of a tan precipitate. The remaining ethanol was removed under reduced pressure and the resulting suspension cooled for several hours. The mixture was then filtered and the tan solid dried under vacuum. The crude product was subsequently dissolved in a minimum of acetonitrile and diethyl ether added dropwise until precipitate formation was no longer observed. This mixture was cooled for several hours before being filtered to give the title compound as a light brown solid 0.718 g (92%). The product is spectroscopically identical to the known \([\eta^6\text{-C}_6\text{H}_6]\text{Ru(C}_5\text{H}_5])\text{PF}_6^2\) and is pure by \(^1\text{H}\) NMR spectroscopy to the limits of detection. \(\delta\text{H (acetone-D}_6\) 6.36 (6H, s, H₁), 5.56 (5H, s, H₂).

To a solution of fluorobenzene (48 mg, 47 µL, 0.507 mmol, 1.1 equiv) in degassed 1,2-dichloroethane (9 mL) at 80 °C was added \([\text{Ru(NCMe)}_3\text{Cp}]\text{PF}_6\) (200 mg, 0.461 mmol). The resulting solution was heated to reflux for 16 hours under an inert atmosphere, allowed to cool to room temperature and filtered. The filtrate was concentrated in vacuo, redissolved in a minimum of MeCN and added dropwise to Et₂O. The brown precipitate was isolated by filtration, rinsed with ether, dissolved in MeCN, concentrated in vacuo and dried under vacuum to give the title compound as a brown solid (153 mg, 82%); \(\delta\text{H (acetone-D}_6\) 6.82 (2H, dd, \(^3\text{J}_\text{H-H} 6.0\) Hz, \(^3\text{J}_\text{H-F} 4.5\) Hz, H²), 6.47 (2H, td, \(^3\text{J}_\text{H-H} 6.0\) Hz, \(^4\text{J}_\text{H-F} 4.0\) Hz, H³), 6.27 (1H, td, \(^3\text{J}_\text{H-H} 6.0\) Hz, \(^5\text{J}_\text{H-F} 3.5\) Hz, H⁴) 5.65 (5H, s, H⁵); \(\delta\text{C (acetone-D}_6\) 136.9 (1C, d, \(^1\text{J}_{\text{C-F}} 217\) Hz, C¹), 85.2 (1C, s, C⁴), 84.9 (2C, d, \(^3\text{J}_{\text{C-F}} 6\) Hz, C³), 81.6 (5C, s, C⁵), 77.4 (2C, d, \(^2\text{J}_{\text{C-F}} 21\) Hz, C²); \(\delta\text{F}
(acetone-D$_6$) $-72.6$ (6F, d, $^1$J$_{F-P}$ 707 Hz, F$_{\text{counterion}}$), $-137.5$ (1F, m, F$_{\text{arene}}$); $\delta_P$ (acetone-D$_6$) $-144.3$ (sept., $J_{P,F}$ 707 Hz); $m/z$ (HRMS$^+$) 256.9836 [M-PF$_6]^+$ (C$_{11}$H$_{10}$F$_9$Ru requires 256.9842). Anal. Found (Expected): C 32.56 (32.44); H 2.52 (2.48); N 0.25 (0.00).
3. NMR spectra of Products

\[ ^1H \text{NMR CO(CD}_3\text{)}_2 \text{RuPF}_6 \text{NO}_2 \text{ 400 MHz} \]
$^1$H NMR
CO(CD$_3$)$_2$
400 MHz
$^{1}\text{H NMR}$

CO($\text{CD}_3)_2$

400 MHz
$^{1} \text{H NMR}$

$\text{CO(CD}_2\text{)}_2$

$400 \text{ MHz}$
$^1$H NMR (COCD$_3$) 400 MHz

RuPF$_6$CN
$^{1}H$ NMR
CO(CD$_3$)$_2$
400 MHz
$^1$H NMR

$\text{CO(CD}_3\text{)}_2$

400 MHz
4. **HPLC Methods and Traces:**

Chromatograms of complex 3 were analysed using a Waters Arc HPLC system with PDA detector. Gradient analysis 90% water, 10% acetonitrile ---3.5 minutes--- 95% Acetonitrile, 5% water through column 1 (Waters Coretecs C18 2.7um 4.6x50mm column) and column 2 (ACE Excel 3um, C18PFP, 4.6x50mm).

**Complex 3, column 1:**

\[ ^1H \text{ NMR} \]

CO(CD\textsubscript{3})\textsubscript{2}

400 MHz
The X-ray single crystal data have been collected using λMoKα radiation (λ =0.71073 Å) 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 F² 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 Table S1. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1546706.

1. **Table S1. Crystal data and structure refinement for 1**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{11}H_{10}NO_{2}Ru x PF_{6}</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
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</tr>
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<td><strong>Temperature/K</strong></td>
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<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Space group</strong></td>
<td>P2_{1}/n</td>
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<tr>
<td><strong>b/Å</strong></td>
<td>12.4722(2)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>13.2874(3)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>90.00</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>91.5709(18)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>90.00</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>1353.72(5)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ_{calc}/g/cm³</strong></td>
<td>2.131</td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
<td>1.352</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>848.0</td>
</tr>
<tr>
<td><strong>Crystal size/mm³</strong></td>
<td>0.38 × 0.31 × 0.23</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td><strong>2Θ range for data collection/°</strong></td>
<td>4.48 to 60</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>20965</td>
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<tr>
<td><strong>Independent reflections</strong></td>
<td>3953 [R_{int} = 0.0336, R_{sigma} = 0.0243]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>3953/0/199</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.073</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
<td>R₁ = 0.0368, wR₂ = 0.0975</td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
<td>R₁ = 0.0447, wR₂ = 0.1033</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
<td>1.29/-0.95</td>
</tr>
</tbody>
</table>
References


