# Electronic Supplementary Information for

## Synthesis and characterisation of ruthenium-nitrosyl complexes in oxygen-rich ligand environments.

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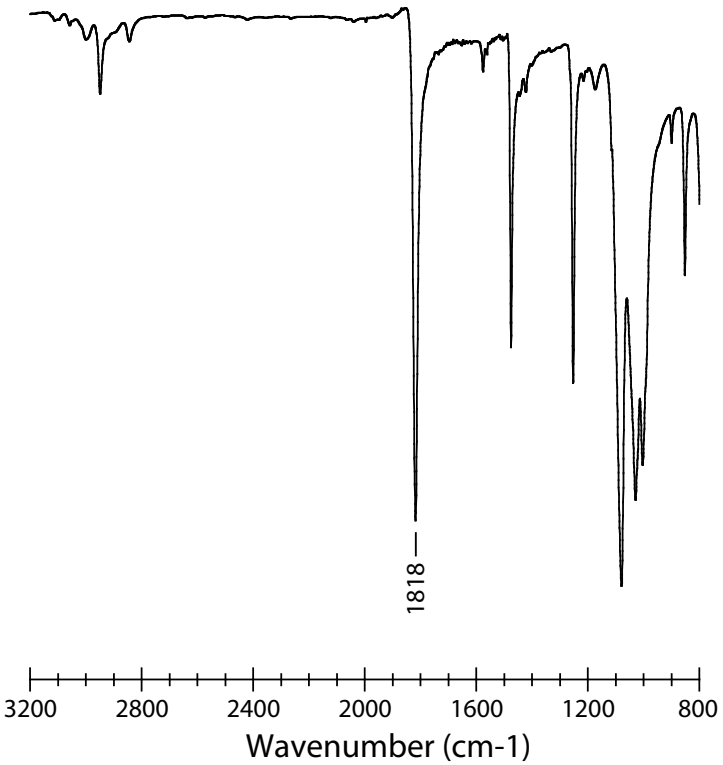


**Figure S1.** Infrared spectrum of [Ru($L_{OMe}$)(NO)($H_4$Cat)] (**1**) as a thin film on NaCl.

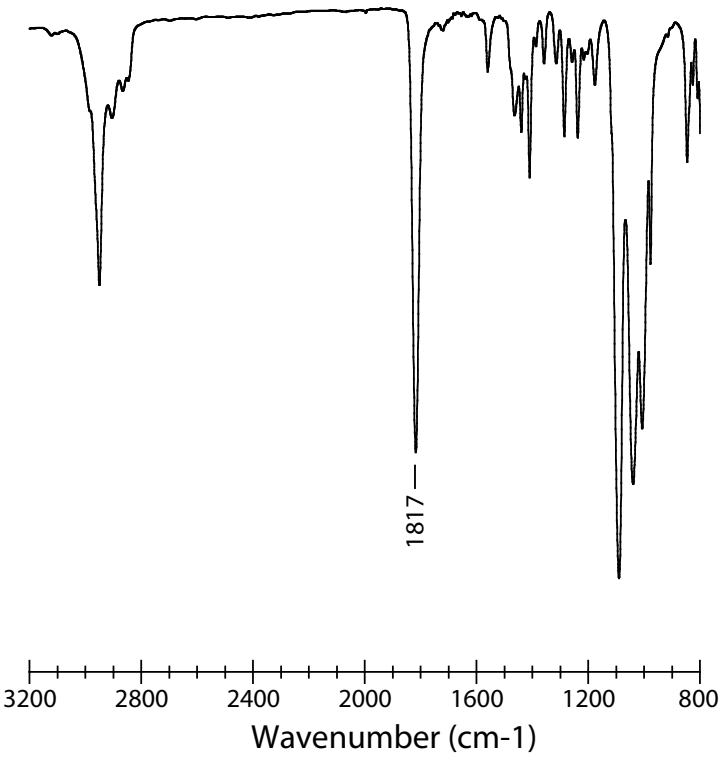


**Figure S2.** Infrared spectrum of [Ru($L_{OMe}$)(NO)($^t$Bu$_2$Cat)] (**2**) as a thin film on NaCl.

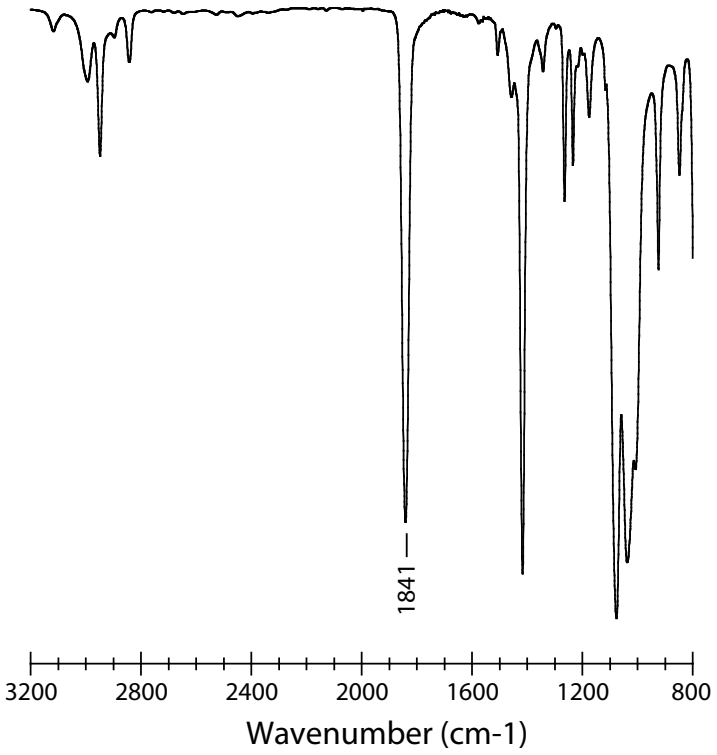


**Figure S3.** Infrared spectrum of [Ru($L_{OMe}$)(NO)($Br_4$Cat)] (**3**) as a thin film on NaCl.

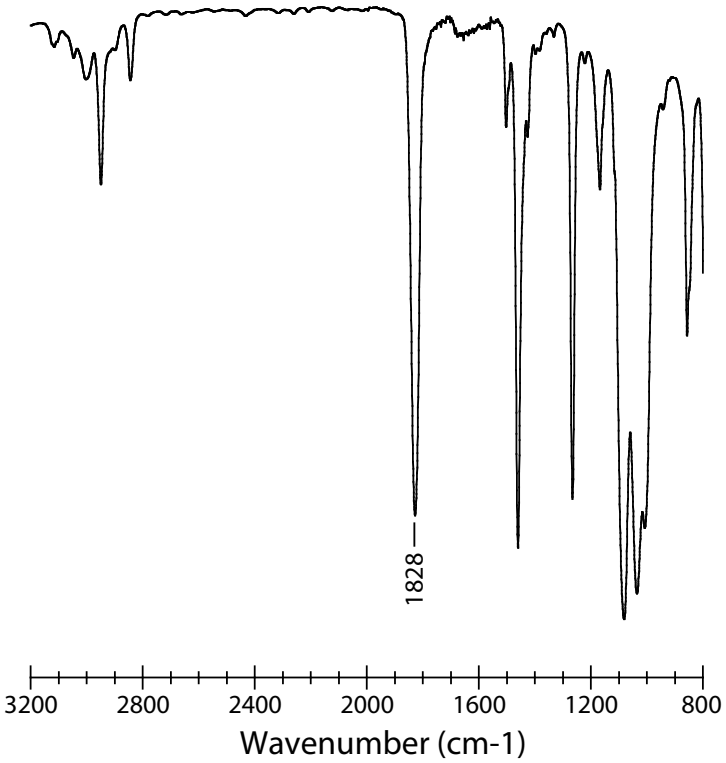


**Figure S4.** Infrared spectrum of [Ru($L_{OMe}$)(NO)(NaphCat)] (**4**) as a thin film on NaCl.

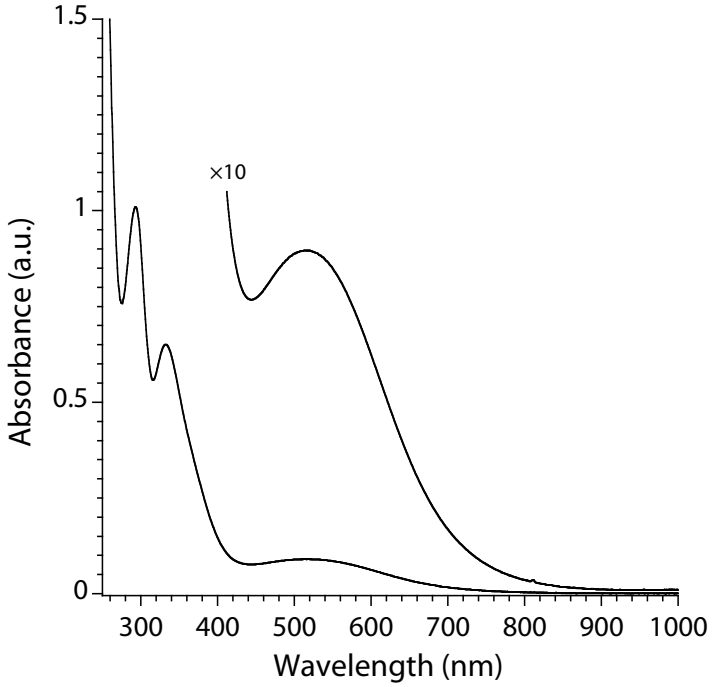


**Figure S5.** Electronic absorption spectrum of [Ru($L_{OMe}$)(NO)($H_4$Cat)] (**1**) in dichloromethane.

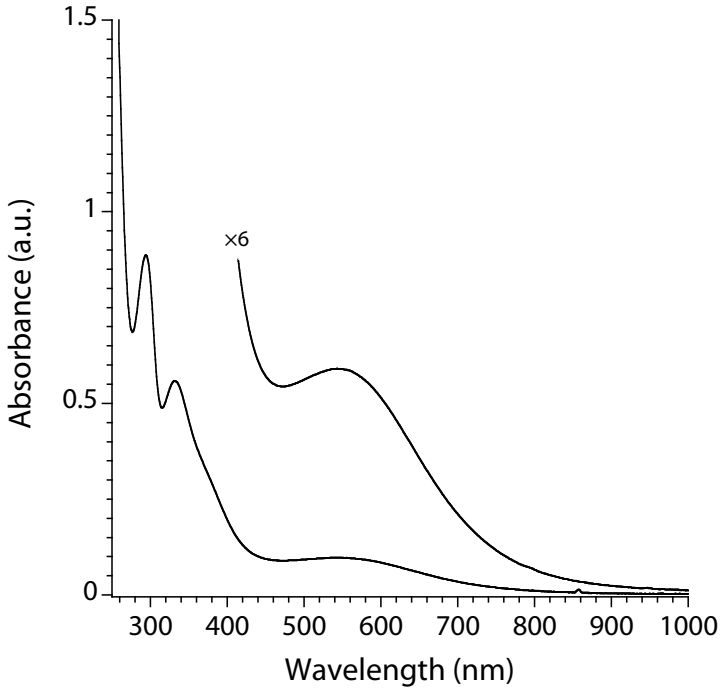


**Figure S6.** Electronic absorption specturm of [Ru($L_{OMe}$)(NO)($^t$Bu$_2$Cat)] (**2**) in dichloromethane.

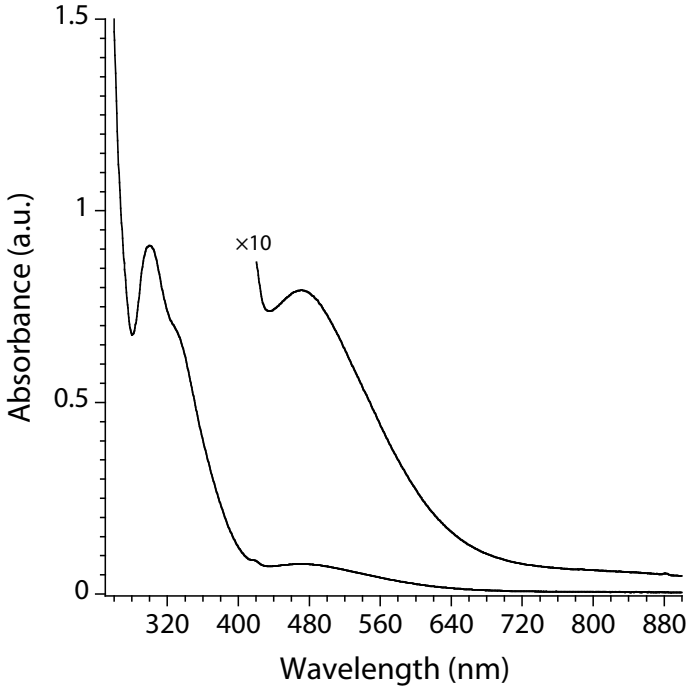


**Figure S7.** Electronic absorption spectrum of [Ru($L_{OMe}$)(NO)($Br_4$Cat)] (**3**) in dichloromethane.

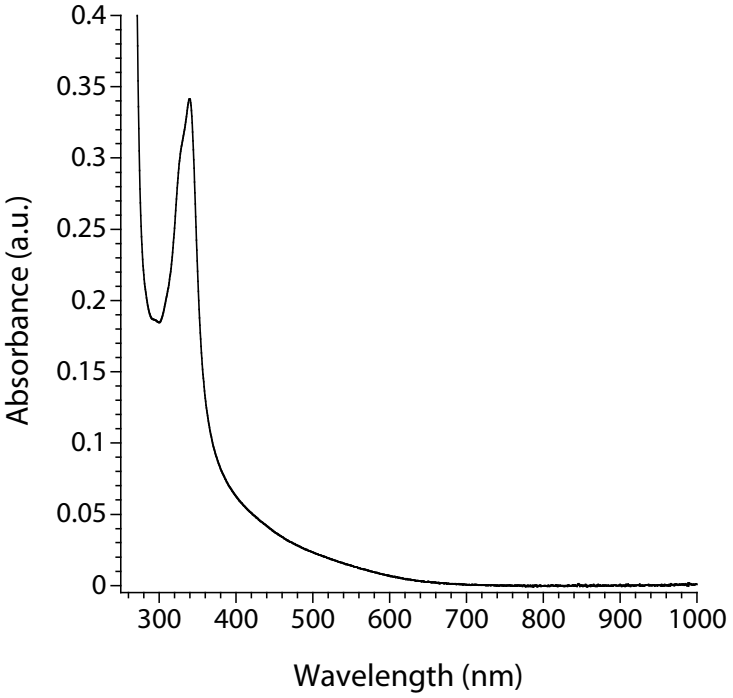


**Figure S8.** Electronic absorption spectrum of [Ru($L_{OMe}$)(NO)(NaphCat)] (**4**) in dichloromethane.

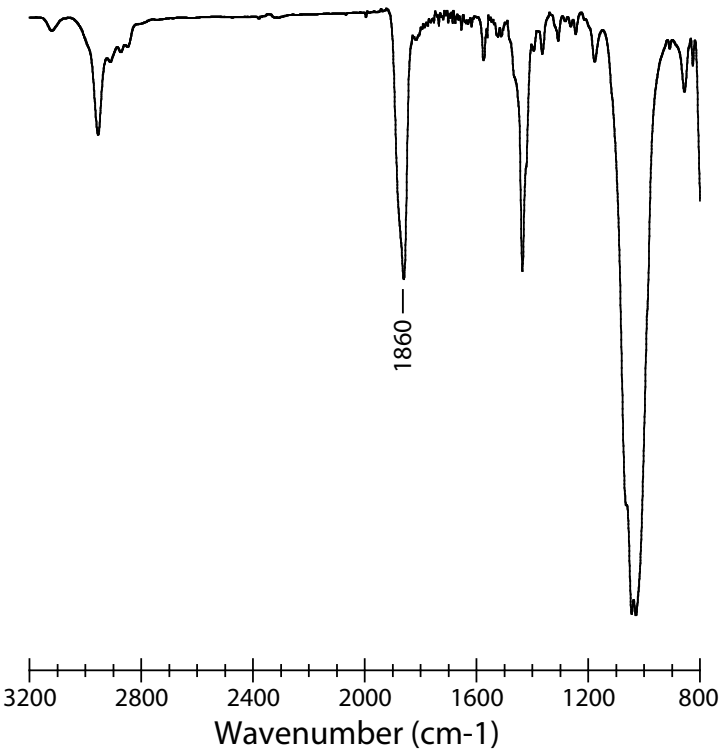


**Figure S9.** Infrared spectrum of [Ru($L_{OMe}$)(NO)($^t$Bu$_2$cat)]($BF_4$) (**2**$^+$) as a thin film on NaCl.

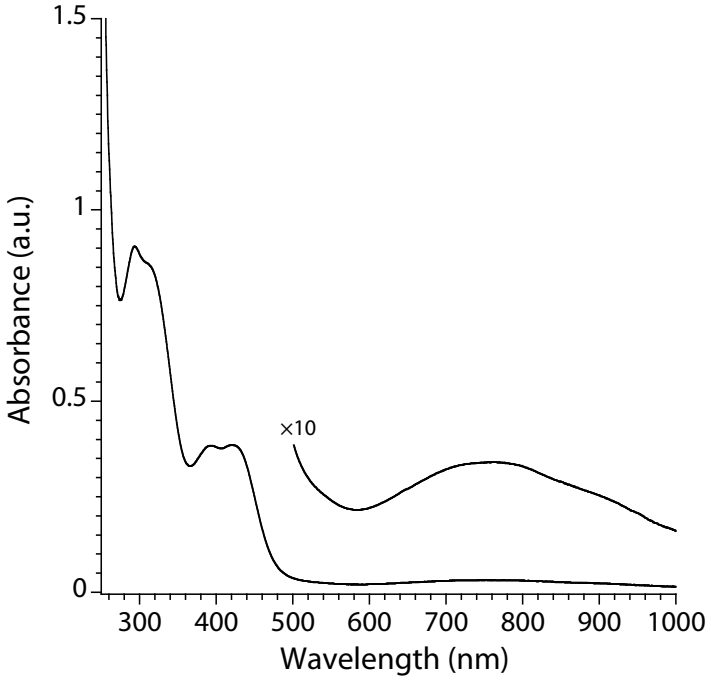


**Figure S10.** Electronic absorption spectrum of [Ru($L_{OMe}$)(NO)($^t$Bu$_2$cat)]($BF_4$) (**2**$^+$) in dichloromethane.

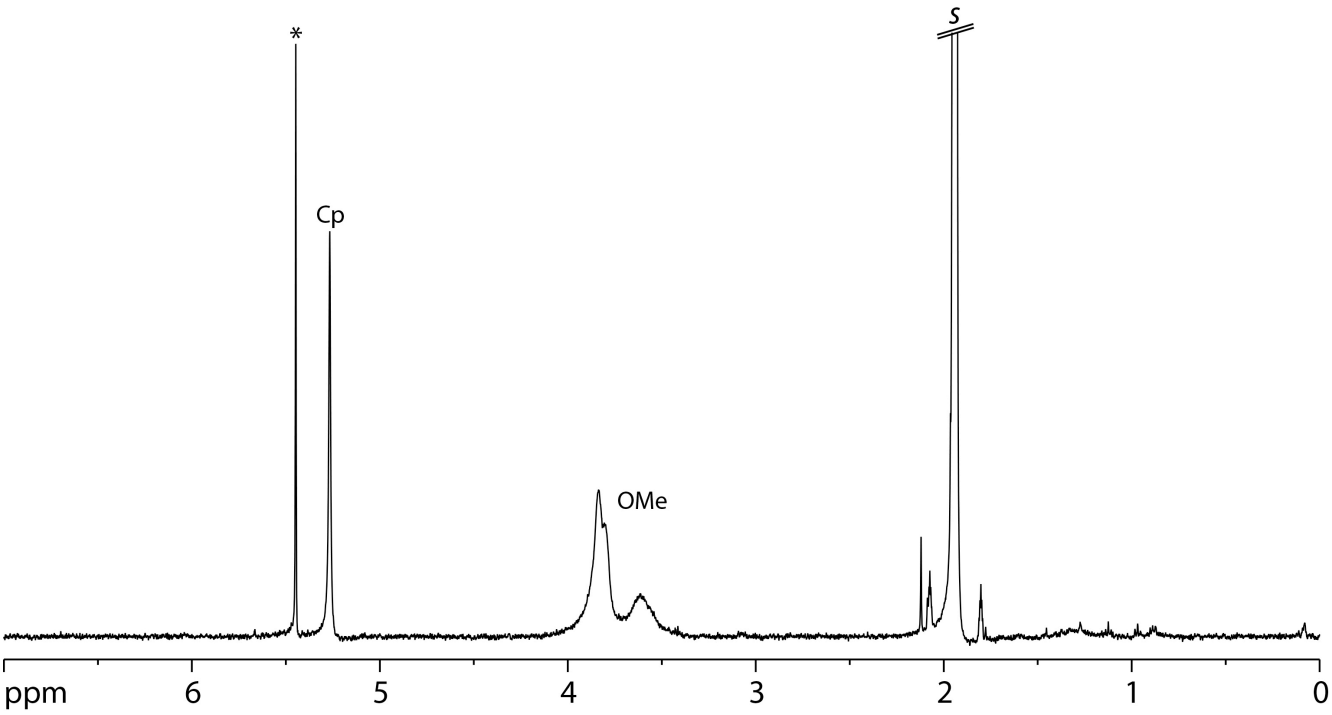


**Figure S11.** 500 MHz $^1$H NMR spectrum of crude [Ru($L_{OMe}$)(NO)($^t$Bu$_2$cat)]($BF_4$) (**2**$^+$) in acetonitrile-*d*3 (*s*). Asterisk denotes resonance due to residual dichloromethane.

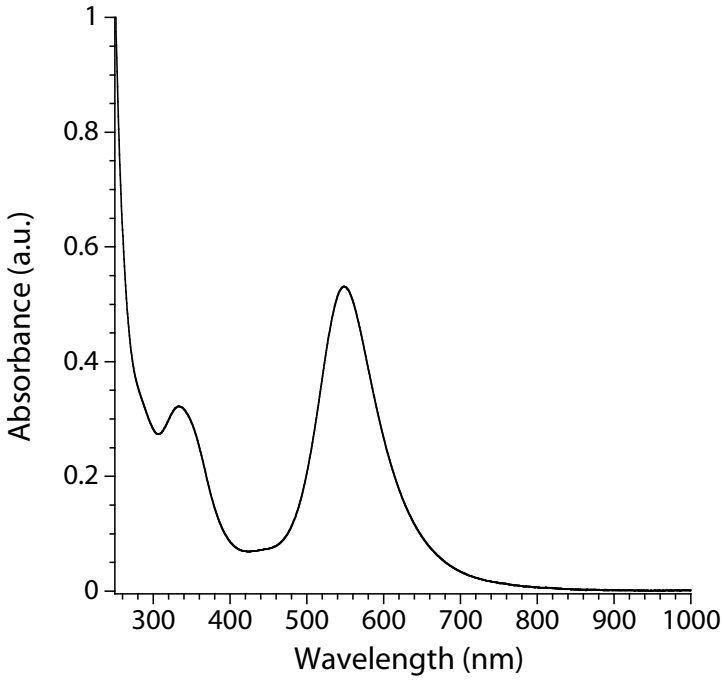


**Figure S12.** Electronic absorption spectrum of [Ru($L_{OMe}$)($NCCH_3$)($^t$Bu$_2$quin)]($BF_4$) (**5**$^+$) in dichloromethane obtained by photolysis of **2**$^+$ in acetonitrile.

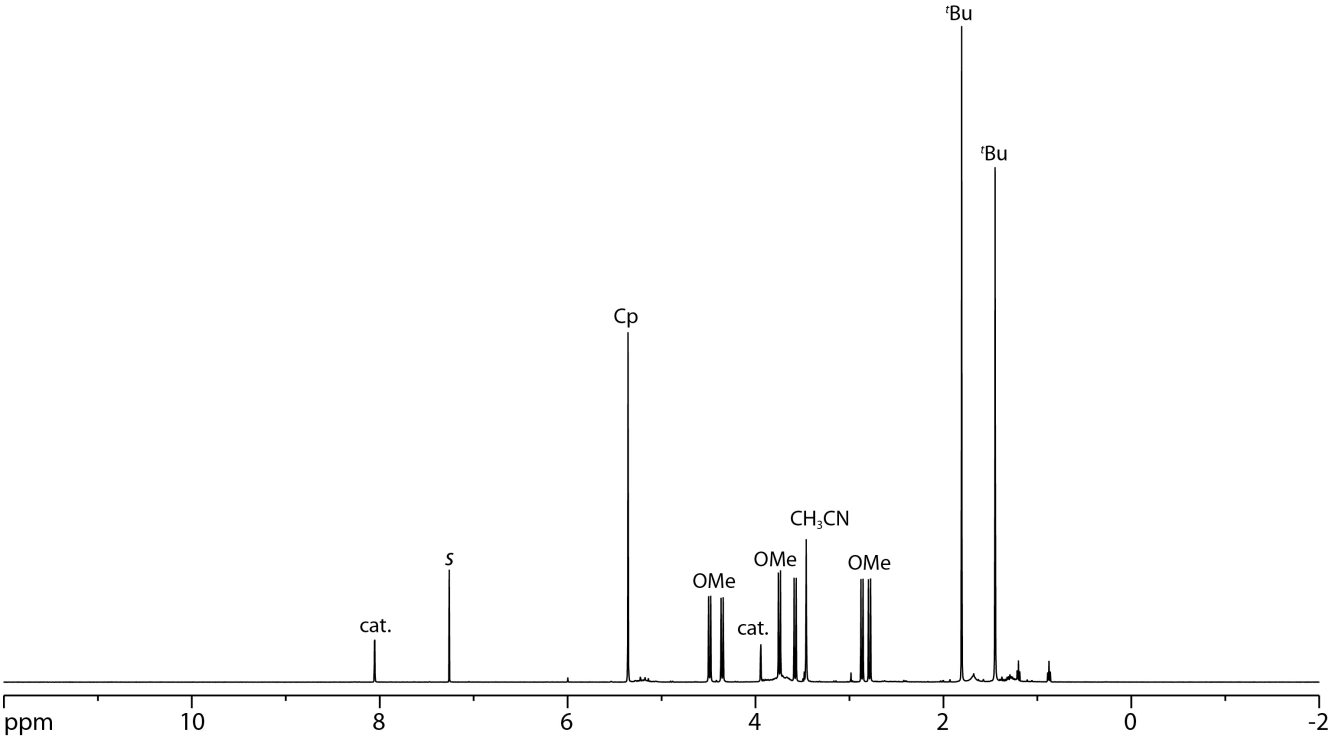


**Figure S13.** 500 MHz $^1$H NMR spectrum ($CDCl_3$) of [Ru($L_{OMe}$)($NCCH_3$)($^t$Bu$_2$quin)]($BF_4$) (**5**$^+$) obtained by photolysis of **2**$^+$ in acetonitrile.

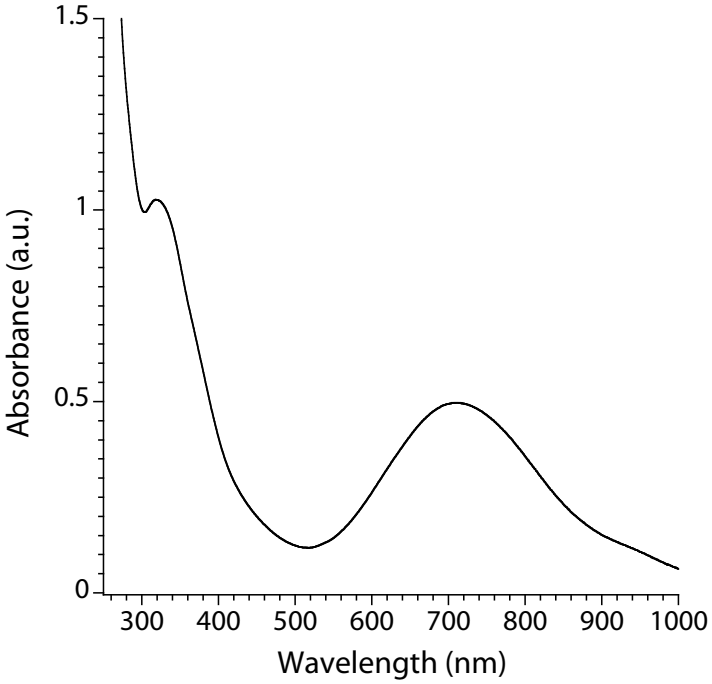


**Figure S14.** Electronic absorption specturm of [Ru($L_{OMe}$)($NCCH_3$)($Br_4$cat)] (**6**) in dichloromethane.

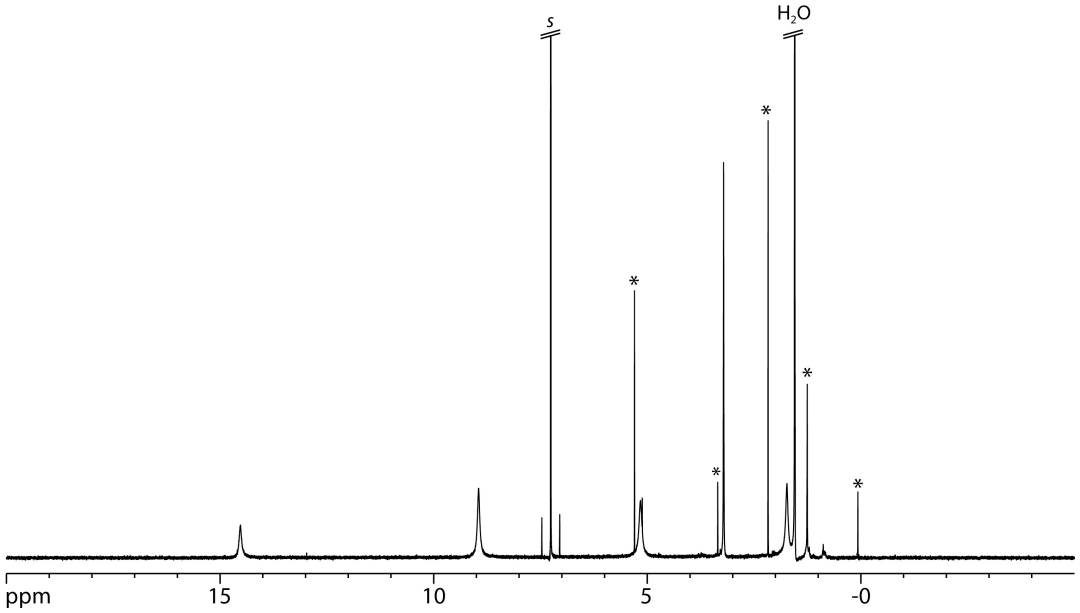


**Figure S15.** 500 MHz $^1$H NMR spectrum ($CDCl_3$) of [Ru($L_{OMe}$)($NCCH_3$)($Br_4$cat)] (**6**) obtained by photolysis of **3** in a mixture of dichloroethane and acetonitrile. Asterisks denote resonances due to residual dichloromethane, dichloroethane, acetone and grease.

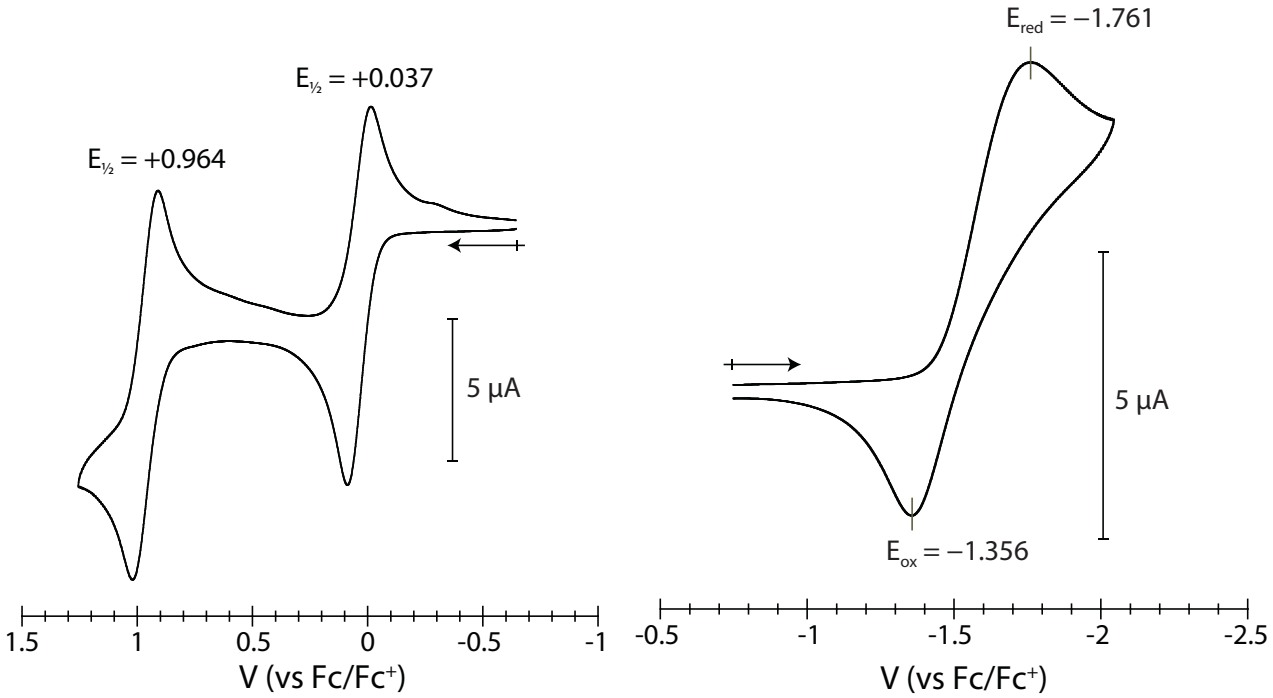


**Figure S16.** Anodic (left) and cathodic (right) portions of the cyclic voltammogram of [Ru($L_{OMe}$)(NO)($H_4$cat)] (**1**) at a Pt electrode in dichloromethane. The scan rate is 50 mV/s and the supporting electrolyte is 0.1 M $Bu_4NPF_6$.

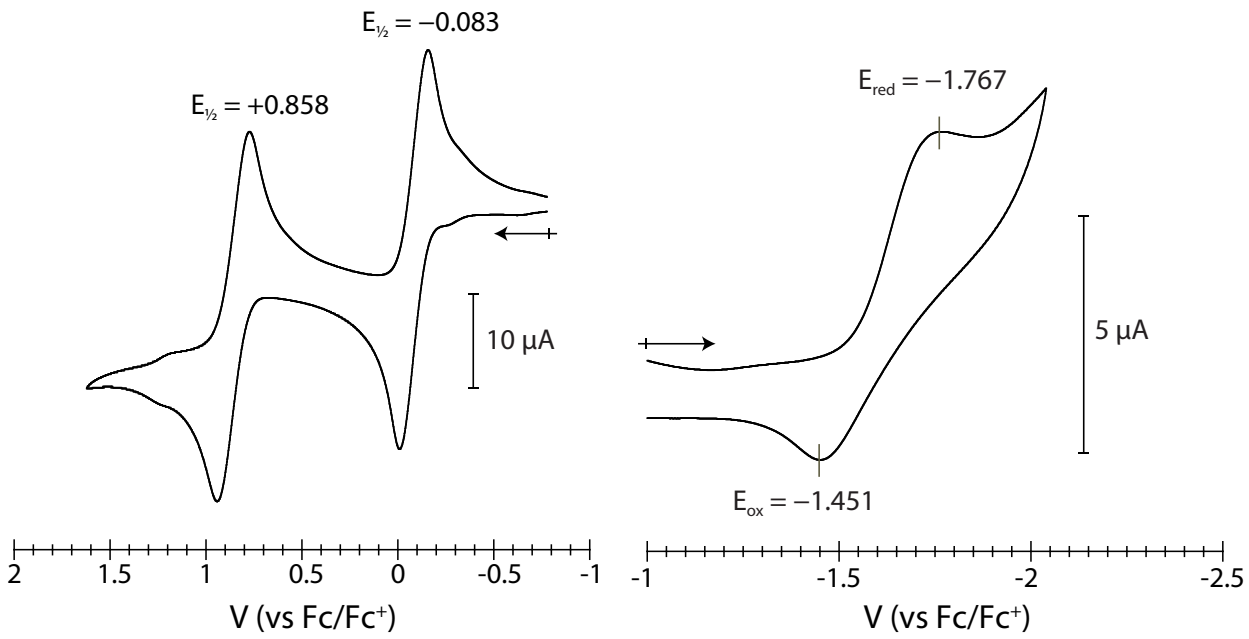


**Figure S17.** Anodic (left) and cathodic (right) portions of the cyclic voltammogram of [Ru($L_{OMe}$)(NO)($^t$Bu$_2$cat)] (**2**) at a Pt electrode in dichloromethane. The scan rate is 50 mV/s and the supporting electrolyte is 0.1 M $Bu_4NPF_6$.

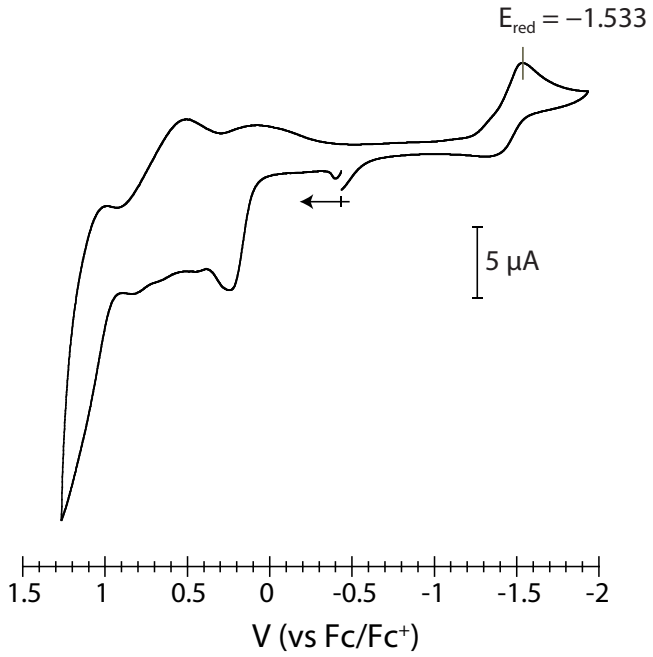


**Figure S18.** Cyclic voltammogram of [Ru($L_{OMe}$)(NO)(Naphcat)] (**4**) at a Pt electrode in dichloromethane. The scan rate is 50 mV/s and the supporting electrolyte is 0.1 M $Bu_4NPF_6$.

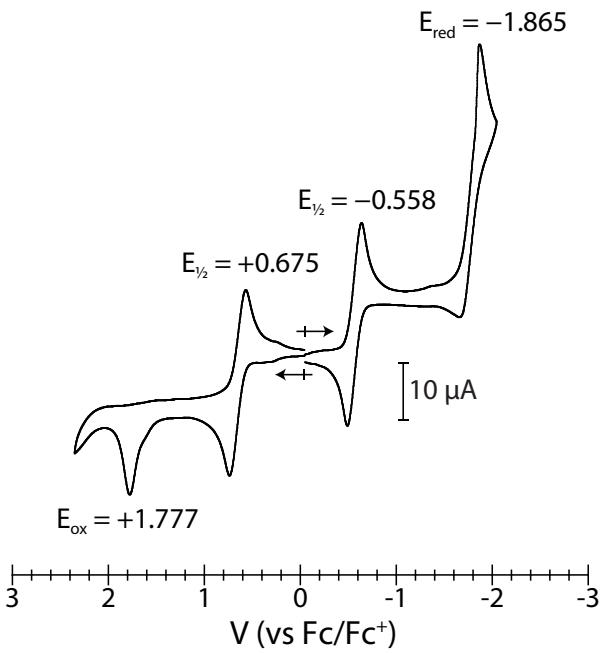


**Figure S19.** Cyclic voltammograms of [Ru($L_{OMe}$)(CH3CN)($^t$Bu$_2$quin)]($BF_4$) (**5+**) at a Pt electrode in dichloromethane. The scan rate is 50 mV/s and the supporting electrolyte is 0.1 M $Bu_4NPF_6$.

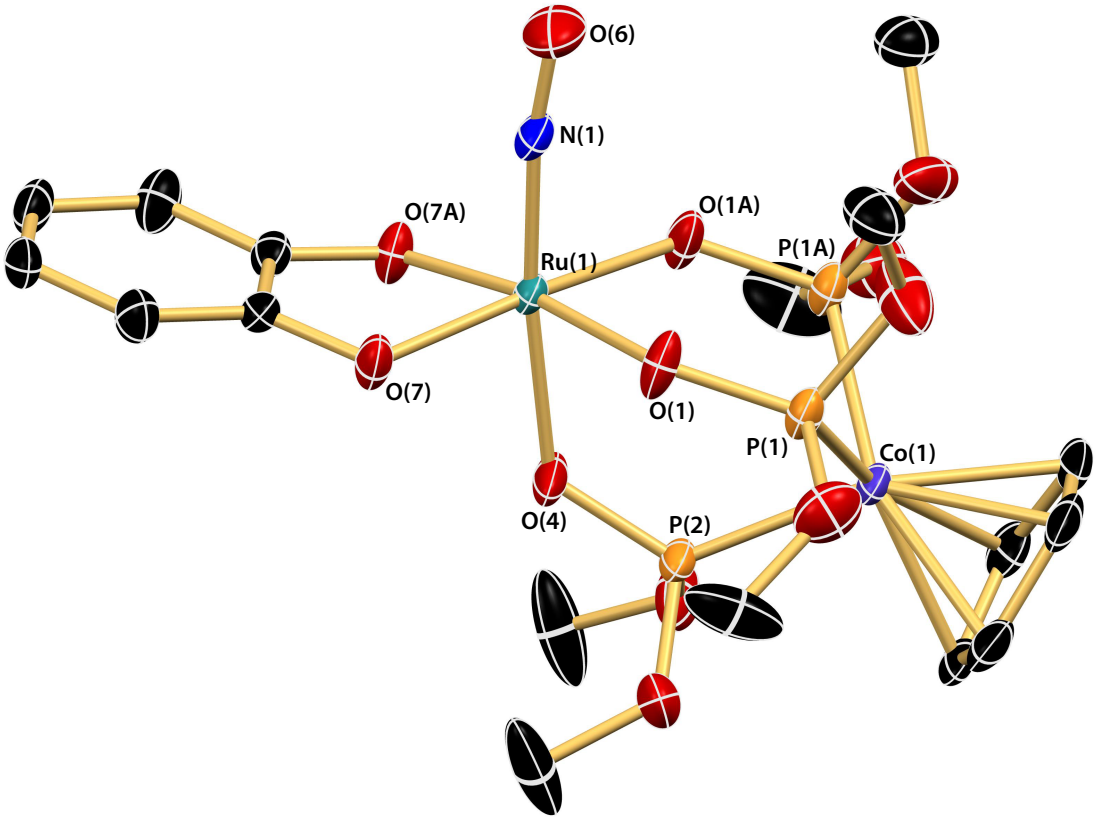


**Figure S20.** Thermal ellipsoid rendering (50%) of [Ru($L_{OMe}$)(NO)($H_4$cat)] (**1**). Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)-N(1) = 1.720(5); Ru(1)-O(7) = 1.986(3); Ru(1)-O(avg) = 2.062(4); N(1)-O(12) = 1.166(7); Ru(1)-N(1)-O(12) = 171.4(4).

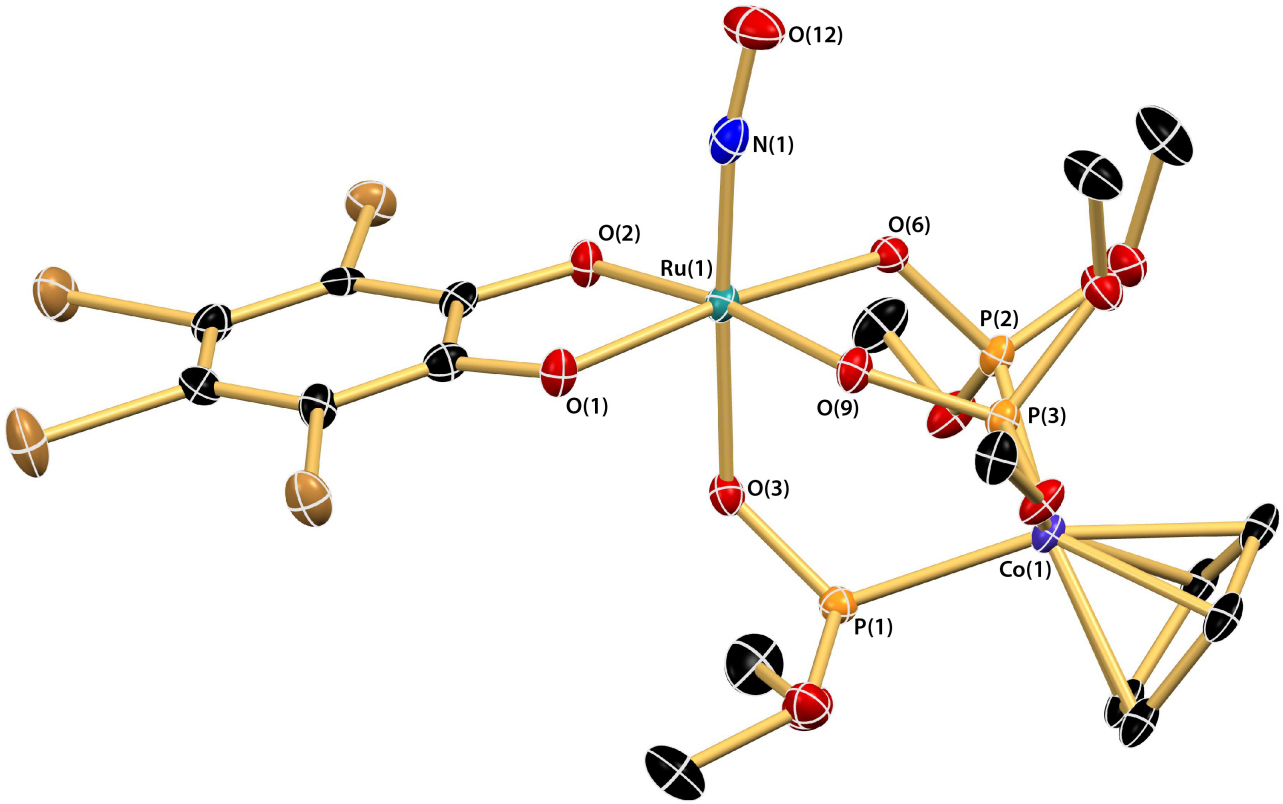


**Figure S21.** Thermal ellipsoid rendering (50%) of one of the two cyrstallographically independent molecules of [Ru($L_{OMe}$)(NO)($Br_4$cat)] (**3**) in the assymetric unit. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)-N(1) = 1.721(6); Ru(1)-O(1) = 2.018(4); Ru(1)-O(2) = 2.012(4); Ru(1)-O(avg) = 2.073(4); N(1)-O(12) = 1.188(7); Ru(1)-N(1)-O(12) = 170.2(5).

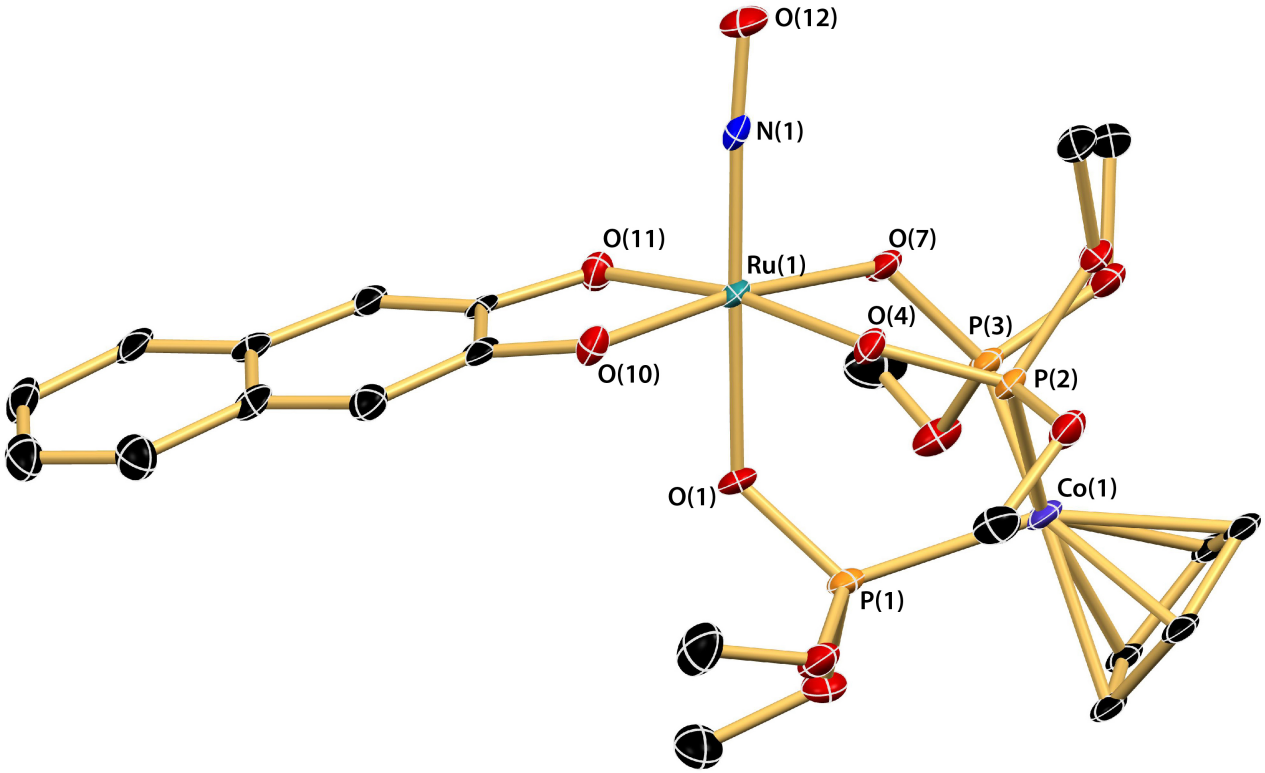


**Figure S22.** Thermal ellipsoid rendering (50%) of [Ru($L_{OMe}$)(NO)(Naphcat)] (**4**). Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)-N(1) = 1.720(3); Ru(1)-O(10) = 1.980(3); Ru(1)-O(11) = 1.982(3); Ru(1)-O(avg) = 2.063(3); N(1)-O(12) = 1.162(4); Ru(1)-N(1)-O(12) = 176.2(3).

**Table S1.** Crystallographic data and refinement parameters for compounds **1**-**3**.[‡]

| **Compound** | **1** | **2** | **3**[§] |
|---|---|---|---|
| Empirical formula | $C_{17}H_{27}NCoO_{12}P_3Ru$ | $C_{25}H_{43}NCoO_{12}P_3Ru$ | $C_{17}H_{23}NBr_4CoO_{12}P_3Ru$ |
| Formula weight (g/mol) | 690.31 | 802.54 | 1005.91 |
| Temperature (K) | 98(2) | 98(2) | 98(2) |
| Crystal system, space group | Orthorhombic *P*nma | Orthorhombic *P*bca | Orthorhombic *P*ca2$_1$ |
| Unit cell dimensions (Å, deg) | $a$ = 16.740(3)<br>$b$ = 11.664(2)<br>$c$ = 12.351(2) | $a$ = 16.170(3)<br>$b$ = 17.167(3)<br>$c$ = 24.094(4) | $a$ = 24.071(3)<br>$b$ = 14.2382(17)<br>$c$ = 17.677(2) |
| Volume (Å$^3$) | 2411.6(7) | 6688(2) | 6058.5(13) |
| Z | 4 | 8 | 8 |
| Calculated density (g/cm$^3$) | 1.901 | 1.594 | 2.206 |
| Absorption coefficient (mm$^{-1}$) | 1.576 | 1.149 | 6.536 |
| F(000) | 1392 | 3296 | 3872 |
| Crystal size (mm) | 0.16 × 0.06 × 0.02 | 0.33 × 0.30 × 0.10 | 0.30 × 0.23 × 0.13 |
| Θ range | 2.40 to 27.50º | 3.03 to 25.50º | 2.98 to 27.43º |
| Limiting indices | $-21 \le h \le 21$,<br>$-15 \le k \le 11$,<br>$-16 \le l \le 16$ | $-19 \le h \le 19$,<br>$-20 \le k \le 20$,<br>$-29 \le l \le 27$ | $-30 \le h \le 30$,<br>$-18 \le k \le 18$,<br>$-22 \le l \le 21$ |
| Reflections collected / unique | 17093 / 2896<br>[$R_{int}$ = 0.0628] | 42240 / 6203<br>[$R_{int}$ = 0.0661] | 45644 / 12832<br>[$R_{int}$ = 0.0485] |
| Completeness to Θ | 99.9% | 99.7% | 99.8% |
| Absorption correction | multi-scan ABSCOR | multi-scan ABSCOR | multi-scan ABSCOR |
| Min. and max transmission | 0.749 and 1.000 | 0.449 and 1.000 | 0.594 and 1.000 |
| Data / restraints / parameters | 2896 / 0 / 169 | 6203 / 0 / 400 | 12832 / 1 / 692 |
| Goodness-of-fit on F$^2$ | 1.013 | 1.047 | 1.060 |
| Final R indices [I > 2σ(I)] | $R_1$ = 0.0454,<br>$wR_2$ = 0.1228 | $R_1$ = 0.0432,<br>$wR_2$ = 0.1091 | $R_1$ = 0.0308,<br>$wR_2$ = 0.0557 |
| R indices (all data) | $R_1$ = 0.0493,<br>$wR_2$ = 0.1264 | $R_1$ = 0.0497,<br>$wR_2$ = 0.1138 | $R_1$ = 0.0397,<br>$wR_2$ = 0.0577 |
| Largest diff. peak and hole (e·Å$^{-3}$) | 2.124 and –0.795 | 1.210 and –1.053 | 0.552 and –0.583 |

[‡]Refinement method was full-matrix least-squares on F$^2$; wavelength = 0.71073 Å. $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{½}$. [§]Compound **3** was refined as an inversion twin.

**Table S2.** Crystallographic data and refinement parameters for compounds **4** and **7**.[‡]

| **Compound** | **4** | **7** |
|---|---|---|
| Empirical formula | $C_{21}H_{29}NCoO_{12}P_3Ru$ | $C_{22}H_{44}N_3CoF_6O_{18}P_3RuS_2$ |
| Formula weight (g/mol) | 690.31 | 802.54 |
| Temperature (K) | 98(2) | 298(2) |
| Crystal system, space group | Monoclinic $P2_1/c$ | Monoclinic $Cc$ |
| Unit cell dimensions (Å, deg) | $a$ = 10.4496(16)<br>$b$ = 11.5244(17)<br>$c$ = 22.855(4)<br>$\beta$ = 97.413(3) | $a$ = 20.084(3)<br>$b$ = 12.6011(17)<br>$c$ = 16.863(2)<br>$\beta$ = 93.902(2) |
| Volume (Å$^3$) | 2729.3(7) | 4257.8(10) |
| Z | 4 | 4 |
| Calculated density (g/cm$^3$) | 1.802 | 1.669 |
| Absorption coefficient (mm$^{-1}$) | 1.399 | 1.050 |
| F(000) | 1496 | 2172 |
| Crystal size (mm) | 0.18 × 0.17 × 0.10 | 0.50 × 0.44 × 0.30 |
| Θ range | 1.965 to 25.500º | 3.453 to 25.049º |
| Limiting indices | $-12 \le h \le 7$,<br>$-13 \le k \le 13$,<br>$-23 \le l \le 27$ | $-23 \le h \le 23$,<br>$-13 \le k \le 15$,<br>$-20 \le l \le 20$ |
| Reflections collected / unique | 36848 / 5033<br>[$R_{int}$ = 0.0759] | 12678 / 6982<br>[$R_{int}$ = 0.0473] |
| Completeness to Θ | 99.3% | 99.1% |
| Absorption correction | multi-scan ABSCOR | multi-scan ABSCOR |
| Min. and max transmission | 0.430 and 1.000 | 0.449 and 1.000 |
| Data / restraints / parameters | 5033 / 0 / 328 | 6982 / 2 / 517 |
| Goodness-of-fit on $F^2$ | 1.058 | 1.000 |
| Final R indices [I > 2σ(I)] | $R_1$ = 0.0478,<br>$wR_2$ = 0.1212 | $R_1$ = 0.0485,<br>$wR_2$ = 0.1222 |
| R indices (all data) | $R_1$ = 0.0515,<br>$wR_2$ = 0.1258 | $R_1$ = 0.0493,<br>$wR_2$ = 0.1236 |
| Largest diff. peak and hole (e·Å$^{-3}$) | 1.291 and –1.788 | 0.696 and –0.836 |

[‡]Refinement method was full-matrix least-squares on $F^2$; wavelength = 0.71073 Å. $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{½}$.