# Electronic supplementary information

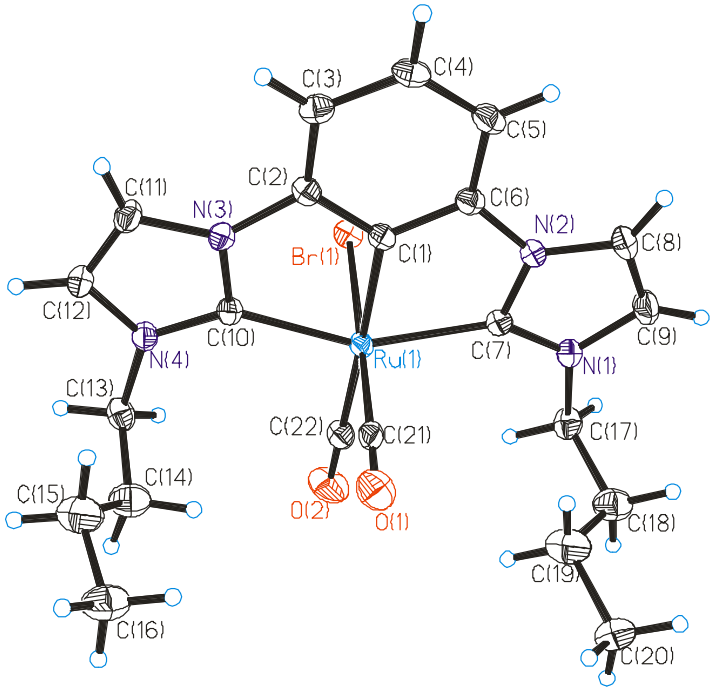


Figure S1. ORTEP plot (30 % probability ellipsoids) of **2b**. $PF_6$ anion is omitted for clarity.

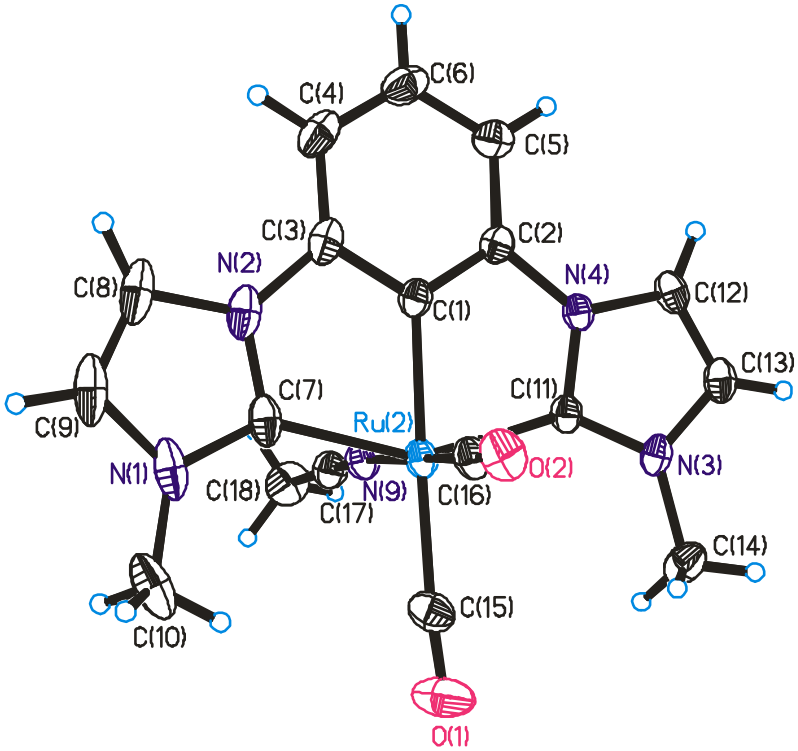


Figure S2. ORTEP plot (30 % probability ellipsoids) of **3a**. $PF_6$ anion is omitted for clarity.

Table S1. Crystal and data collection parameters for complexes **2a**, **2b**, **3a**, **3b**, **4a**, **5a**, **6a**, and **7a**

| | **2a** | **2b** | **3a** | **3b** · $CH_3CN$ | **4a** · $CH_3CN$ · 0.5aetone | **5a** | **6a** | **7a** |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_{16}H_{13}IN_4O_2Ru$ | $C_{22}H_{25}BrN_4O_2Ru$ | $C_{18}H_{16}F_6N_5O_2PRu$ | $C_{26}H_{31}F_6N_6O_2PRu$ | $C_{45}H_{50}F_{12}N_{14}O_3P_2Ru_2$ | $C_{25}H_{21}I\ N_6ORu$ | $C_{22}H_{21}F_6N_6O_2PRu$ | $C_{21}H_{21}F_6N_6OPRu$ |
| Formula weight | 521.2 | 558.44 | 580.40 | 705.61 | 1327.07 | 649.45 | 647.49 | 619.48 |
| Crystal size ($mm^3$) | 0.38x0.26x0.25 | 0.33x0.33x0.11 | 0.19x0.18x0.15 | 0.52x0.28x0.23 | 0.30x0.27x0.19 | 0.12x0.03x0.02 | 0.22x0.22x0.15 | 0.35x0.32x0.22 |
| T (K) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) |
| Crystal system | Monoclinic | Orthorhombic | Triclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2(1)/n | Pbca | Pī | Pī | P2(1) | P2(1)/n | P2(1)/c | P2(1)/c |
| *a* (Å) | 10.5225(6) | 13.5343(7) | 8.2596(2) | 8.6684(4) | 8.2987(12) | 8.4655(5) | 12.3335(3) | 10.9243(7) |
| *b* (Å) | 13.9073(8) | 16.3150(8) | 11.7151(3) | 11.7651(5) | 38.281(5) | 15.8272(9) | 8.1254(2) | 14.5417(10) |
| *c* (Å) | 12.1595(7) | 20.3240(10) | 11.9249(3) | 15.6709(6) | 8.8978(13) | 18.9515(11) | 25.8414(7) | 15.1796(10) |
| $\alpha$ ($^O$) | 90 | 90 | 79.4890(10) | 84.505(2) | 90 | 90 | 90 | 90 |
| $\beta$ ($^O$) | 92.3560(10) | 90 | 70.5020(10) | 89.649(2) | 92.463(4) | 100.909(2) | 102.3980(10) | 94.9790(10) |
| $\gamma$ ($^O$) | 90 | 90 | 88.6630(10) | 81.020(2) | 90 | 90 | 90 | 90 |
| *V* ($Å^3$) | 1783.23(18) | 4487.8(4) | 1068.58(5) | 1571.28(12) | 2824.1(7) | 2493.3(3) | 2529.29(11) | 2402.3(3) |
| *Z* | 4 | 8 | 2 | 2 | 2 | 4 | 4 | 4 |
| $D_{calc}$ (g $cm^{-3}$) | 1.942 | 1.653 | 1.804 | 1.491 | 1.561 | 1.738 | 1.706 | 1.721 |
| $\mu$ ($mm^{-1}$) | 2.626 | 2.505 | 0.887 | 0.619 | 0.683 | 1.897 | 0.761 | 0.793 |
| $\theta$ Range/$^o$ | 2.22—26.42 | 2.00—30.33 | 1.77—30.72 | 1.76—30.81 | 2.13—25.00 | 1.69—26.43 | 1.61—25.00 | 1.87—30.65 |
| Reflections collected / unique | 20585 / 3665 [R(int) = 0.035] | 38935 / 6662 [R(int) = 0.0450] | 22259 / 6567 [R(int) = 0.0305] | 33472 / 9774 [R(int) = 0.0373] | 16592 / 8325 [R(int) = 0.0295] | 24610 /5115 [R(int) = 0.0470] | 28945 / 4470 [R(int) = 0.0303] | 42382 / 7410 [R(int) = 0.0301] |
| data/ restraints/ parameters | 3665 / 1 / 219 | 6662 /0 / 261 | 6567 / 0 / 318 | 9774 / 36 / 408 | 8325 / 1 /740 | 5115 / 0 / 249 | 4470 / 0 / 388 | 7410 / 0 / 345 |
| Goodness-of-fit on $F^2$ | 1.067 | 1.055 | 1.028 | 1.026 | 1.067 | 1.028 | 1.046 | 1.048 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0362, $wR_2$ = 0.1008 | $R_1$ = 0.0416, $wR_2$ = 0.1071 | $R_1$ = 0.0339, $wR_2$ = 0.0885 | $R_1$ = 0.0405, $wR_2$ = 0.1063 | $R_1$ = 0.0409, $wR_2$ = 0.0912 | $R_1$ = 0.0495, $wR_2$ = 0.1206 | $R_1$ = 0.0264, $wR_2$ = 0.0667 | $R_1$ = 0.0322, $wR_2$ = 0.0886 |
| $R_1/wR_2$ indices (all data) | 0.0474 / 0.1087 | 0.0607/ 0.1171 | 0.0408/ 0.0945 | 0.0580 / 0.1161 | 0.0443/ 0.0931 | 0.0710 / 0.1343 | 0.0331 / 0.0712 | 0.0408 / 0.0978 |
| Largest diff. peak and hole($e·Å^{-3}$) | 1.077 and -0.952 | 2.370 and -1.356 | 0.758 and -0.514 | 0.729 and -0.487 | 0.538 and -1.079 | 1.448 and -1.335 | 0.418 and -0.308 | 0.637 and -0.463 |

Electronic Supplementary Material (ESI) for Dalton Transactions