**Supplementary material**

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Table S1. Crystal Data for structures 6-8.

<table>
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<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>empirical formula</td>
<td>C_{13}H_{10}Cl_{4}N_{2}O_{2}Ru</td>
<td>C_{12}H_{8}Br_{2}N_{2}O_{2}Ru</td>
<td>C_{12}H_{12}I_{2}N_{2}O_{2}Ru</td>
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<td>fw</td>
<td>469.10</td>
<td>473.09</td>
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<tr>
<td>temp (K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td>λ(Å)</td>
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<td>0.71073</td>
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<td>cryst syst</td>
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<td>Monoclinic</td>
<td>Orthorhombic</td>
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<tr>
<td>space group</td>
<td>P</td>
<td>Pn</td>
<td>Pbca</td>
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<tr>
<td>a (Å)</td>
<td>6.4683(3)</td>
<td>8.3627(6)</td>
<td>13.7231(15)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.3842(5)</td>
<td>6.9269(5)</td>
<td>11.9220(13)</td>
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<tr>
<td>c (Å)</td>
<td>21.1414(9)</td>
<td>12.7050(9)</td>
<td>18.0712(19)</td>
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<tr>
<td>α (deg)</td>
<td>89.106(2)</td>
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<td>90</td>
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<tr>
<td>β (deg)</td>
<td>83.451(2)</td>
<td>103.490(2)</td>
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<td>γ (deg)</td>
<td>87.535(2)</td>
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<td>90</td>
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<td>V (Å³)</td>
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<td>715.66(9)</td>
<td>2956.6(6)</td>
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<td>Z</td>
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<td>2</td>
<td>8</td>
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<tr>
<td>ρ_{calc} (Mg/m³)</td>
<td>1.854</td>
<td>2.195</td>
<td>2.566</td>
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<td>μ(Mo Kα) (mm⁻¹)</td>
<td>1.574</td>
<td>6.676</td>
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<tr>
<td>No. reflns.</td>
<td>42866</td>
<td>6862</td>
<td>47635</td>
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<td>Unique reflns.</td>
<td>12621</td>
<td>3189</td>
<td>4306</td>
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<tr>
<td>GOOF (F²)</td>
<td>1.035</td>
<td>1.011</td>
<td>1.040</td>
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<tr>
<td>R_{int}</td>
<td>0.0267</td>
<td>0.0240</td>
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<tr>
<td>R1 (I ≥ 2σ)</td>
<td>0.0297</td>
<td>0.0235</td>
<td>0.0236</td>
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<tr>
<td>wR2 (I ≥ 2σ)</td>
<td>0.0703</td>
<td>0.0552</td>
<td>0.0531</td>
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</table>

R1 = \sum ||F_o||-|F_c||/\sum |F_o|, \quad wR2 = [\sum [w(F_o^2-F_c^2)^2)]^{1/2} \sum [w(F_o^2)]^{1/2}.

Figure S1. Thermal ellipsoid plot and atomic numbering of structure 1. The ellipsoids are drawn at the 50% probability level.
**Figure S2.** Thermal ellipsoid plot and atomic numbering of structure 2. The ellipsoids are drawn at the 50% probability level.

**Figure S3.** Thermal ellipsoid plot and atomic numbering of structure 3. The ellipsoids are drawn at the 50% probability level.

**Figure S4.** Thermal ellipsoid plot and atomic numbering of structure 4. The ellipsoids are drawn at the 50% probability level.
Figure S5. Thermal ellipsoid plot and atomic numbering of structure 5. The ellipsoids are drawn at the 50% probability level.

Figure S6. Thermal ellipsoid plot and atomic numbering of structure 6. The ellipsoids are drawn at the 50% probability level.

Figure S7. Thermal ellipsoid plot and atomic numbering of structure 7. The ellipsoids are drawn at the 50% probability level.
Figure S8. Thermal ellipsoid plot and atomic numbering of structure 8. The ellipsoids are drawn at the 50% probability level.

Figure S9. Bond critical points and bond paths for 1.
The green dots denote the bond critical points.

Figure S10. Bond critical points and bond paths for 2.
The green dots denote the bond critical points.
Figure S11. Bond critical points and bond paths for 3. The green dots denote the bond critical points.

Figure S12. Bond critical points and bond paths for 4. The green dots denote the bond critical points.
Figure S13. Bond critical points and bond paths for 5. The green dots denote the bond critical points.

Figure S14. Properties of the electron density at the N–I bond critical point in the adduct of Py and I₂.