Supplementary Information

Ru(II)-dmso Complexes containing Azole-based Ligands: Synthesis, Linkage Isomerism and Catalytic Behaviour

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Keywords: ruthenium /dmso complexes/ azole-based ligands / linkage isomerism / hydration catalysis.

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Table S1. Crystallographic data for complexes 2-5 and 6'.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6'</th>
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<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{10}H_{24}Cl_{2}N_{2}O_{3}RuS_{3}</td>
<td>C_{6}H_{12}Cl_{2}N_{3}O_{3}RuS_{3}</td>
<td>C_{10}H_{22}Cl_{2}F_{3}N_{2}O_{4}RuS_{3}</td>
<td>C_{13}H_{24}BrCl_{2}N_{2}O_{4}RuS_{3}</td>
<td>C_{11}H_{15}Cl_{3}N_{3}ORuS</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>488.46</td>
<td>519.44</td>
<td>560.45</td>
<td>620.40</td>
<td>515.64</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)/c</td>
<td>P21/n</td>
<td>P 21/n</td>
<td>P2(1)/c</td>
<td>P21/c</td>
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<tr>
<td>a [Å]</td>
<td>8.8684(17)</td>
<td>8.396(7)</td>
<td>8.739(3)</td>
<td>12.493(6)</td>
<td>9.969(5)</td>
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<tr>
<td>c [Å]</td>
<td>15.809(3)</td>
<td>14.403(12)</td>
<td>10.690(3)</td>
<td>16.522(6)</td>
<td>11.326(6)</td>
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<tr>
<td>α [°]</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<td>β [°]</td>
<td>102.331(3)</td>
<td>105.773(13)</td>
<td>93.393(6)</td>
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<td>γ [°]</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>V [Å³]</td>
<td>1950.3(6)</td>
<td>1837(3)</td>
<td>2172.9(12)</td>
<td>2195.9(17)</td>
<td>1870.8(16)</td>
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<td><strong>Formula Units/cell</strong></td>
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<tr>
<td><strong>Temp. [K]</strong></td>
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<td>298(2)</td>
<td>298(2)</td>
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<td>100(2)</td>
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<tr>
<td><strong>ρ_{calc} [Mg/m³]</strong></td>
<td>1.664</td>
<td>1.878</td>
<td>1.713</td>
<td>1.877</td>
<td>1.831</td>
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<td><strong>μ [mm⁻¹]</strong></td>
<td>1.407</td>
<td>1.509</td>
<td>1.297</td>
<td>3.083</td>
<td>1.665</td>
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<td><strong>Final R indices, [I&gt;2σ(I)]</strong></td>
<td>R1=0.0256</td>
<td>R1=0.0237</td>
<td>R1=0.0390</td>
<td>R1=0.0387</td>
<td>R1 = 0.0400</td>
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<td>wR2=0.0657</td>
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<td><strong>R indices [all data]</strong></td>
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<td>R1=0.0447</td>
<td>R1=0.0523</td>
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<td>wR2=0.0681</td>
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<td>wR2=0.1229</td>
<td>wR2=0.1052</td>
<td>wR2 = 0.1111</td>
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</table>

R₁ = Σ|F_o| - |F_c|/Σ|F_o|

wR2 = [Σ(w(F_o²-F_c²)²)/Σ(w(F_o²)²)]^½, where w = 1/[σ²(F_o²) + (0.0042P)²] and P=(F_o²+2F_c²)
**Table S2.** Formulas used for the calculation of rate (k) and equilibrium (K) constants.

<table>
<thead>
<tr>
<th>Equations</th>
<th>Description of parameters</th>
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</table>
| \( \frac{i_c}{i_{c2}} = a \cdot \frac{1}{v} + K_{O-S}^{III} \)  
(eq. 1) |  
\( i_c = \) cathodic peak intensity (A)  
\( a = RT/nF, \) with:  
\( R = \) Boltzmann constant (J/(K·mol))  
\( T = \) temperature (K)  
\( n = \) number of exchanged electrons  
\( F = \) Faraday constant (A·s/mol)  
\( v = \) scan rate (V/s)  
\( K = \) equilibrium constant |
| \( \sqrt{v} = \frac{1}{0.471} \cdot \frac{i_d}{nF} \cdot \frac{1}{i_k} + \frac{1.02}{nF} \cdot \frac{i_k}{RT} \)  
(eq. 2) |  
\( i_d = \) diffusional current in the absence of a chemical reaction (= \( i_{a1} \))  
\( i_k = \) measured peak current (= \( i_{c1} \))  
\( l = k_{O-S}^{III} + k_{S-O}^{III} \) |
| \( K^{II} = K^{III} + e^{\frac{F}{RT} \left( E_0^{Ru-S} - E_0^{Ru-O} \right)} \)  
(eq. 3) |  
\( E^0 = \) standard potential |
| \( \ln \left( \frac{i_{a1}}{\sqrt{v}} \right) = k_{O-S}^{II} \cdot \frac{1}{v} + b \)  
(eq. 4) |  
\( b = 0.471 \cdot \frac{1}{RT} \cdot \frac{K_{O-S}^{III}}{K_{O-S}^{III} + k_{S-O}^{III}} \) |
**Scheme S1.** Ru-dmso complexes gathered in entries 3-6 of Table 2.

cis,cis-[RuCl₂(H₃p)(dmso-S)₂]  
trans,cis-[RuCl₂(H₃p)(dmso-S)₂]

trans,cis-[RuCl₂(bpp)(dmso-S)₂]  
out-[Ru(L₂)(trpy)(dmso-S)]⁺
**Figure S1.** NMR spectra of 2, 400 MHz, CD$_2$Cl$_2$: a) $^1$H-NMR; b) $^{13}$C-NMR; c) COSY; d) NOESY; e) $^1$H-$^{13}$C HSQC, f) $^1$H-$^{13}$C HMBC

a)

![NMR spectrum image]

b)

![NMR spectrum image]
Figure S2. NMR spectra of 3, 300 MHz, CD$_2$Cl$_2$: a) $^1$H-NMR; b) $^{13}$C-NMR; c) COSY; d) NOESY; e) $^1$H-$^{13}$C HSQC, f) $^1$H-$^{13}$C HMBC

a)

b)
**Figure S3.** NMR spectra of 4, 300 MHz, CD$_2$Cl$_2$: a) $^1$H-NMR; b) $^{13}$C-NMR; c) COSY; d) NOESY; e) $^1$H-$^{13}$C HSQC, f) $^1$H-$^{13}$C HMBC

![NMR spectra](image-url)
e) 

f)
Figure S4. NMR spectra of 5, 300 MHz, CD$_2$Cl$_2$: a) $^1$H-NMR; b) $^{13}$C-NMR; c) COSY; d) NOESY; e) $^1$H-$^{13}$C HSQC, f) $^1$H-$^{13}$C HMBC, g) $^1$H-NMR with presence of the minor isomer.

a)

b)
**Figure S5.** UV-visible spectra of 2 (blue), 3 (green), 4 (grey) and 5 (red) in CH$_2$Cl$_2$

![UV-visible spectra](image)

**Figure S6.** CV of a) 3 (blue), 4 (black) and 5 (orange) in CH$_3$CN + 0.1 M TBAH.

![CV of a) 3 (blue), 4 (black) and 5 (orange)](image)
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**Figure S11.** Plot of $v^{1/2}$ vs. $i_d/i_k$ to obtain $k_{III}^{S\rightarrow O}$ and $k_{III}^{O\rightarrow S}$ for complex 6.
**Figure S12.** Plot of $\ln(i_{a1}/\nu^{1/2})$ vs. $1/\nu$ to obtain $k_{O\rightarrow S}^{II}$ for complex 2

**Figure S13.** Plot of $\ln(i_{a1}/\nu^{1/2})$ vs. $1/\nu$ to obtain $k_{O\rightarrow S}^{II}$ for complex 6
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