S1.

**Figure S1a.** Stoichiometric reactions with MCPBA in MeCN and MeOH. ESI-MS of product of stoichiometric reaction of MCPBA with 1, in MeCN, showing small yields of both di-oxygenate 3, (M+32) and the S-extruded monothiocarbamate 4, (M-16).

**Figure S1b.** ESI-MS of product of stoichiometric reaction of MCPBA with 1, in MeOH, showing small yields of mono-oxygenate 3.
**Figure S2.** Electronic absorbance spectra for compounds 1-4. Scale in nanometers, spectra are not normalized, approximately equivalent concentrations ca. 1 mM. Epsilon vs. lambda data are given in Table 1 of the text.
Figure S3. IR spectra of Ru complexes. The IR spectrum of the 1 exhibited the characteristic bands of 2,2'-bipyridine (728, 842,1443 and 1600 cm\(^{-1}\)) and DTC (at 1522 and 974 cm\(^{-1}\)). The ν(CN) stretch absorbances for all complexes were higher than that of the free ligand (ca 1480 cm\(^{-1}\)), implying a greater contribution of the dithiolate tautomer with a partial C-N double bond. The IR spectra of 3 displayed the highest ν(CN) stretch.
Figure S4. Cyclic voltammograms of compounds 1-4, conditions, measured vs. Ag/AgCl reference at glassy carbon electrode in 0.1M $[n$-Bu$_4$N][PF$_6$]/CH$_3$CN; scan rate = 250 mV/s.
S5.
1D and 2D H NMR spectra of compound 1.
S6.

2D H NMR of compound 3.
S7.
Partial assignment of H NMR spectra of compound 4.

$^1$H NMR $\delta$ 9.94

$^1$H NMR $\delta$ 9.38
2D H NMR of compound 2b.

$O,S$-bound $2b$
Figure S9. Low temperature NMR of compound 2b.
Both 2a & 2b show a broad peak for the methyl groups at RT. In the 2a spectra shown below, the peak gradually split into two singlets as temperature decreases.
S10.

**Figure S10.** Computer generated models of the four diastereomeric forms of 2a.
S11.
Figure S11. NMR characterization of the product of the anaerobic reaction of the peroxodithiocarbamate 2a with O-atom acceptor, PEt₃, as illustrated by the equation below. The 3¹P NMR spectra clearly shows the generation of OPEt₃; the ¹H NMR of the reaction solution is consistent with the dithiocarbamate complex 1 as the only Ru-containing product of the reaction.

![Chemical Structures](image)

![NMR Spectra](image)