Supplementary Material (ESI) for Chemical Communications

Oxidation induced by the antioxidant glutathione (GSH)

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Electronic supplementary information

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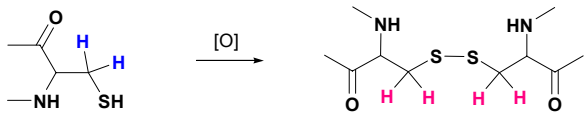
Oxidation reactions

GSH in aqueous solution at pH ca. 7 undergoes very slow oxidation to **GSSG**.[6] On their own in aqueous solution, complexes **1a** and **1b** are stable, even on bubbling with air or oxygen for several hours. In contrast, these complexes are readily oxidized to sulfenates within a few hours (1 - 4 h) when **GSH** is present in solution at the same time; the **GSH** is oxidized to **GSSG** and the reactions are accelerated by bubbling with air. The reactions can be readily followed by NMR spectroscopy, but not monitored whilst bubbling with air. Longer reaction times lead to a displacement of the en ligand, probably by **GSH** or **GSSG**, and to subsequent decomposition of **1a** and **1b**.[10]

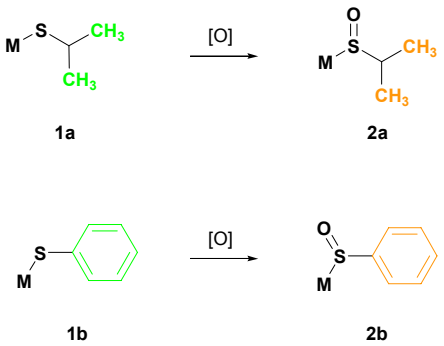
Details of NMR-Experiments

^{1}H NMR spectra were recorded on a Bruker ava600 spectrometer equipped with a triple resonance TXI (^{1}H,^{13}C,^{15}N) *z*-gradient cryo-probe or room temperature TXI (^{1}H, ^{13}C, ^{15}N) triple-axis (*x,y,z*) gradient probehead. Spectra were recorded at 298 K, unless otherwise stated. Suppression of the water signal for 90% H_2O/ 10% D_2O samples was achieved by presaturation or a double-pulsed field-gradient spin-echo routine (DPFGSE).[24] ^{1}H NMR spectra were referenced to dioxane as internal standard (3.71 ppm)[25]. ^{15}N chemical shifts were referenced to NH_4OH as external standard.



GSH GSSG

Scheme S1: The characteristic β-CH_2 NMR resonances of the thiol/disulfide used to assign the redox-state of **GSH**/**GSSG**. For reported assignments see references [26-28].



Scheme S2: Protons (green and orange) whose NMR resonances were used to monitor the thiolato complexes **1a**, **1b** and sulfenato complexes **2a**, **2b** during the oxidation reactions.[10]

Oxidation of [(η^6-HMB)Ru(en)(S-*i*Pr)]$^+$ (1a) using GSH/air, maximum efficiency of oxygen transfer.

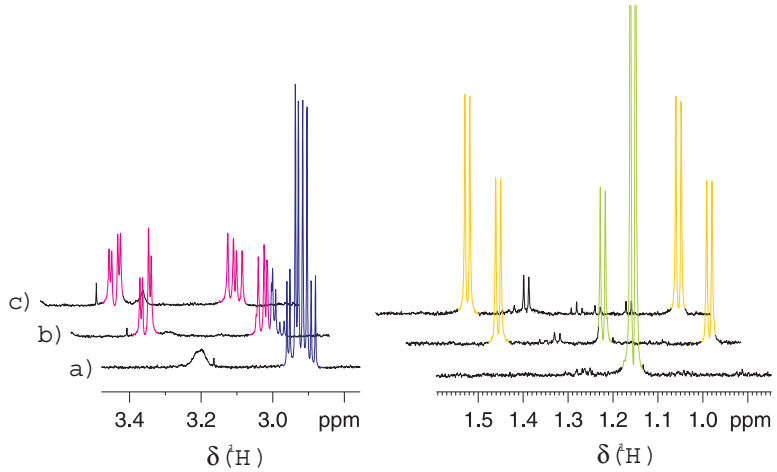


Figure S1: Stacked plot of ^{1}H-NMR spectra for a solution of complex **1a** (0.5 mM) and **GSH** (2.5 mM). a) After mixing, and b) after bubbling air for 4 h, and c) after additional bubbling with air overnight. After the complete oxidation of **GSH**, most of the complex is oxidized to the sulfenato complex [(η^6-HMB)Ru(en)(S(O)-*i*Pr)]$^+$ **2a** together with a small amount of decomposition of products from the starting material. Note that for every transferred oxygen atom, two molecules of **GSH** are oxidized to one molecule of **GSSG** and one water molecule is formed; therefore oxygen transfer is remarkably efficient, ca 35% of the theoretical value. For assignments see Schemes S1 and S2 (colour code: **1a**, **2a**, **GSH**, **GSSG**).

Oxidation using GSSG/air

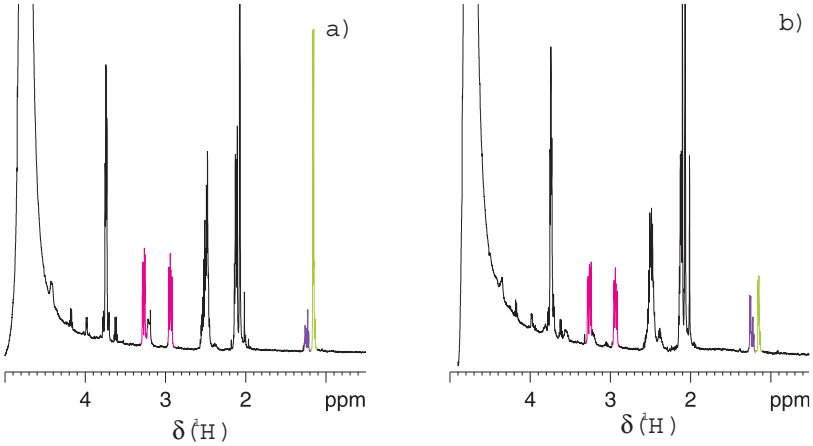


Figure S2: When air was bubbled through a solution of complex **1a** (0.5mM) and **GSSG** (1.25 mM), no oxidation to the sulfenato complex was observed; instead displacement of the en ligand occurred with subsequent formation of various unidentified complexes. For assignments see Schemes S1 and S2 (colour code: **1a**, **2a**, **GSSG**, unidentified complexes).

Competitive oxidation of [(η^6-HMB) R(en) (S-*i*Pr)]$^+$ (1a) and GSH with H_2O_2

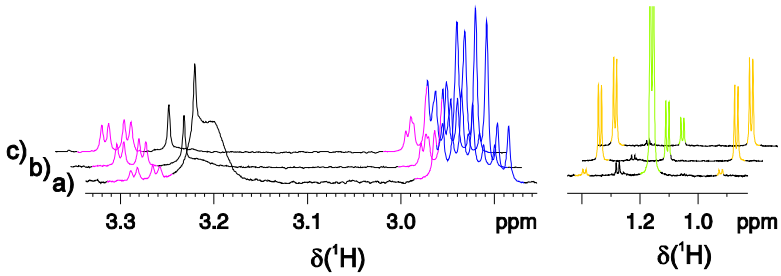


Figure S3: When H_2O_2 (1 mol equiv with respect to GSH) is added to a solution containing **GSH** (1 mM) and complex **1a** (0.5mM), complex **1a** reacts faster than **GSH**. For assignments see Schemes S1 and S2 (**1a**, **2a**, **GSH**, **GSSG**).

Oxidation of [(η^6-*p*-cymene) Ru(en)(S-Ph)]$^+$ (1b) with GSH/air

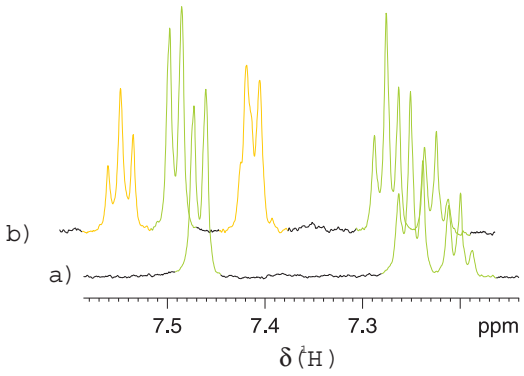


Figure S4: ^{1}H NMR spectra recorded during reactions of 0.5 mM complex **1b** with 2.5 mM **GSH** with air-bubbling for 5 h. Complete oxidation of **GSH** to **GSSG** has occurred; oxidation of complex **1b** is incomplete, but still detectable. The phenyl substituent on the thiolate in **1b** is a weaker electron donor compared to the isopropyl group in **1a** and together with the presence of a weaker arene donor (*p*-cymene compared to hexamethylbenzene) accounts for the slowing down of the reaction. For assignments see Schemes S1 and S2 (**1b**, **2b**).

References

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