

S1 Experimental

S1.1. Instrumentation and Electrodes for Voltammetry

Voltammetric measurements were carried out using a standard three-electrode arrangement containing a platinum wire counter electrode, a Ag/Ag^+ (CH_3CN , 10mM AgNO_3) double junction reference electrode, and in-house built platinum or glassy carbon disk working electrodes of different sizes. A Metrohm 628-10 assembly was used for the rotating-disk electrode measurements. CYSY-1R (Cypress Systems) or BAS100 (Bio Analytical Systems) electrochemical systems were used to obtain the voltammograms. The potential of the reference electrode was calibrated against that of the ferrocene/ferrocenium (Fc/Fc^+) redox couple via measurement of the ferrocene oxidation process under identical conditions (technique, temperature, solvent and electrolyte) being used in the study of interest. Before each experiment, the working electrode was polished with an aqueous aluminium oxide ($0.3\mu\text{m}$) slurry and rinsed with acetone. Oxygen was removed by purging the solutions with high purity nitrogen or argon.

S1.2. Instrumentation and Electrodes for Bulk Electrolysis

The bulk electrolysis platinum electrode cell was in-house built and had the appearance of a beaker ($\approx 25\text{mL}$ total volume, $\approx 5\text{cm}$ diameter) into which a glass cylinder with frit at bottom was placed ($\approx 12\text{mL}$ total volume). The working and counter electrodes were both cylindrical large surface area platinum gauze basket designs. The working electrode was placed inside the glass cylinder containing the frit, along with the solvent, electrolyte and analyte of interest. The Ag/Ag^+ reference electrode also was placed inside the inner compartment and the counter electrode was placed in the outer compartment which was filled only with the solvent-electrolyte mixture. The lid to the cell contained five inlets/outlets to allow additional electrodes to be placed into the inner solution so that monitoring of the course of bulk electrolysis experiments was feasible and to permit electrical contact with the working,

reference and counter electrodes to be made. For gas chromatographic determination of hydrogen gas generated during electrolysis, the lid was sealed by paraffin film and the inlets by rubber septa.

Bulk electrolysis at platinum was usually conducted with sample volumes of 5–11 mL (inner compartment). During the electrolysis, the solutions in both compartments were vigorously stirred. Exhaustive electrolysis was said to have occurred when the charge passed per minute was less than 1% of the charge passed in the first minute. This definition typically resulted in electrolysis times of 15–20 minutes for a one-electron process.

Bulk electrolysis at glassy carbon electrodes utilized an identical setup as described above and a cylindrical single piece glassy carbon working electrode.

S1.3. Instrumentation for other Techniques

Optically transparent thin-layer electrolysis (OTTLE) experiments were carried out at a platinum gauze electrode, a 1 mm quartz cuvette and a Varian Cary 5 NIR/VIS/UV spectrometer. The detailed experimental setup is described elsewhere.¹ For gas chromatographic measurements, a Varian 3700 gas chromatograph equipped with a carboxsphere 80/100 9'x $\frac{1}{8}$ " s.s. column and a TCD detector was used. Under conditions where $T_{\text{col}}=40^{\circ}\text{C}$, $T_{\text{valve}}=100^{\circ}\text{C}$, $T_{\text{TCD}}=200^{\circ}\text{C}$ and flow rate = 27 mL min^{-1} (He), dihydrogen had a retention time of $53\pm 2\text{ s}$. The MOPAC-97 software package (Fujitsu Ltd., Tokyo, Japan) was used for molecular orbital calculations. All calculations employed the semiempirical MNDO-PM3 Hamiltonian.

S1.4. Reagents and Compounds

Dimethylformamide (DMF) used for electrochemical and spectroscopic measurements was of HPLC grade (Mallinckrodt, ChromAR) and received with 0.005% water content and treated with activated 3 Å molecular sieves prior to experiments to reduce the water content. An aqueous 40% tetrabutylammonium hydroxide, $\text{Bu}_4\text{N}(\text{OH})$, solution and 48% aqueous

HBF_4 were purchased from Aldrich and used as received. The electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), was prepared according to a literature method² and dried in vacuum at 90°C for 10 hours. *cis*- $\text{L}_2\text{Ru}(\text{NCS})_2$ ^{3, 4} and *cis*- $\text{L}_2\text{Ru}(\text{CN})_2$ ^{5, 6} were synthesized as described elsewhere. NMR data confirmed that both compounds were present in the *cis* configuration (although for convenience the *cis* prefix notation will be omitted in further discussion) and that $\text{L}_2\text{Ru}(\text{NCS})_2$ was present predominately as the diisothiocyanate linkage isomer with $\leq 4\%$ of the mixed bond N-,S- linkage isomer being present.

Reference List

(Supporting Information)

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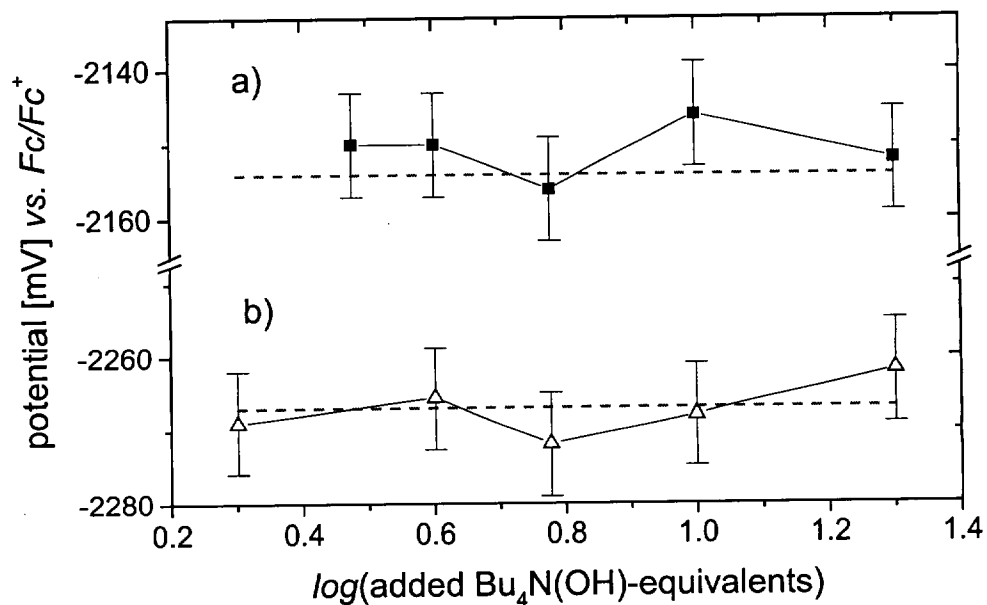


Figure S1: Dependence of $\text{Bu}_4\text{N}(\text{OH})$ concentration on the reversible half-wave potential for the reduction process of $[(\text{H}_{2-x/2}\text{-dcbpy})^{x/2-}]_2\text{RuX}_2]^{x-}$. Horizontal dashed lines indicate the reversible half-wave potential obtained after exhaustive controlled potential reductive electrolysis. a) $(\text{H}_2\text{-dcbpy})_2\text{Ru}(\text{NCS})_2$ b) $(\text{H}_2\text{-dcbpy})_2\text{Ru}(\text{CN})_2$.