Electronic Supplementary Information for Dalton Transactions

Supporting Information

Fe-S complexes containing five-membered heterocycles: novel models for the active site of hydrogenases with unusual low reduction potential

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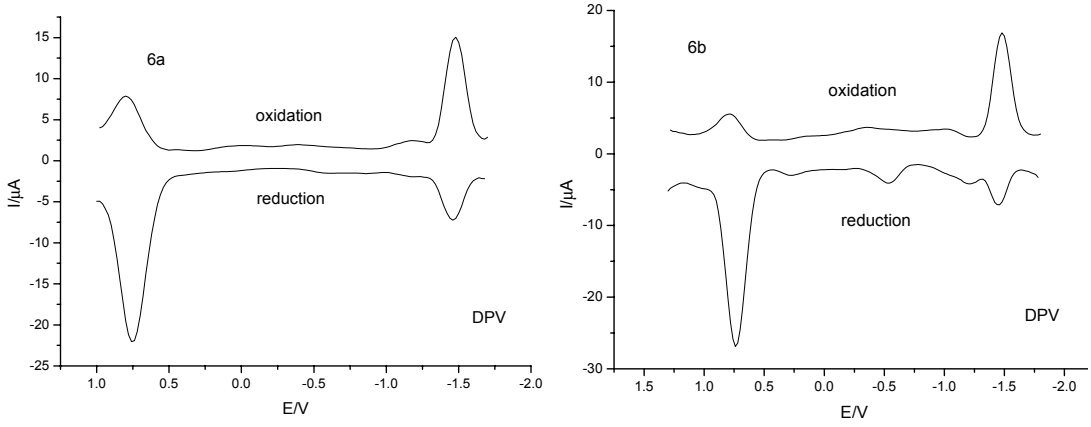
Electrochemistry Studies of Complexes 6a-6c: Acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was dried with molecular sieves and then freshly distilled from CaH_2 under N_2. A solution of 0.1 m *n*Bu4NPF6 (Fluka, electrochemical grade) in CH_3CN was used as electrolyte, which was degassed by bubbling with dry CO or argon for 10 min before measurement. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV/s. Diferrential Pulse Voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3- and 1-μm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag^+ electrode (0.01 m $AgNO_3$ in CH_3CN) and the auxiliary electrode was a platinum wire.



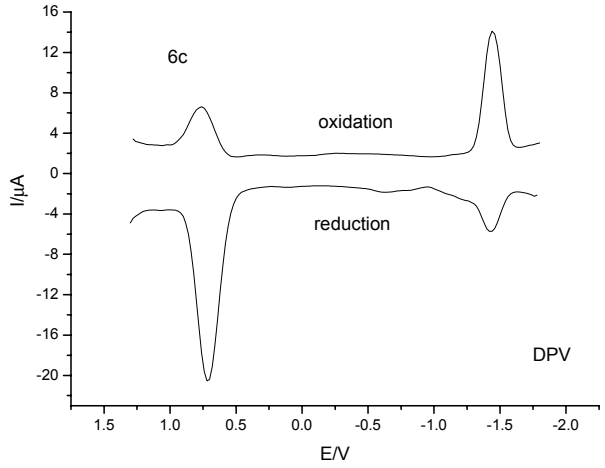


Figure 1 Differential Pulse Voltammograms (DPV) of **6a**, **6b** and **6c** Sample concentration is 1.0 mmol in 0.05 M *n*-Bu_4NPF_6/CH_3CN, scan rate 100 mVs^{-1}, working electrode: glassy carbon, surface area: 0.017 cm^2, reference electrode: Ag/Ag^+. All potentials are *versus* Fc/Fc^+

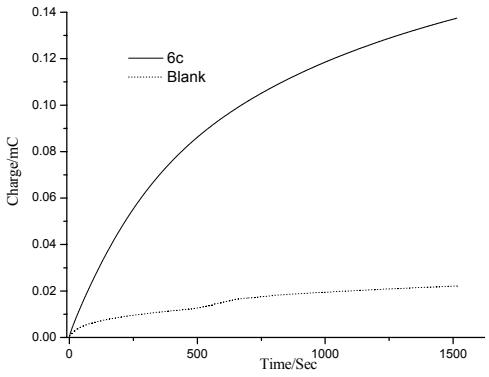


Figure 2 Coulometry for bulk electrolysis at a graphite electrode in the presence of **6c** (—) and blank (···). The electrolysis potential: 0.83 V; the measurement was made on 4mM solutions in CH_3CN.

Bulk Electrolysis

Controlled potential electrolysis was performed in a closed cell, with a glassy carbon working electrode (R = 0.2cm, and L = 0.8 cm; surface area: *ca* 1.14 cm^2). The electrolyte solution was degased by bubbling with dry N_2 for 10 min before measurement. Bubbles got out from the surface of the glassy carbon disk were carefully taken out by syringe for GC analysis, proved to be the molecular hydrogen. Gas chromatography was performed with a GC7890 instrument under isothermal conditions with nitrogen as a carrier gas and a thermal conductivity detector (TCD).

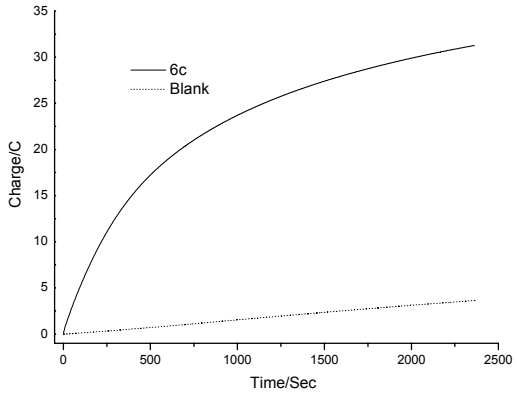


Figure 3 Coulometry for bulk electrolysis of $HClO_4$ (50 mM) at a graphite electrode in the presence of **6c** (—) and blank (⋯). The electrolysis potential: −1.2 V; the measurement was made on 5mM solutions in CH_3CN.