Electrochemistry of Acetate-, Carbonate-, Sulfate-, and Dihydrogenphosphate-Bridged Dirhodium(II) Complexes

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Complexes, $[Rh_2(B\text{-}B)_4L_2]^n$ (B-B = $CH_3CO_2^-$, L = CH_3CN, H_2O, Cl^-, Br^-, SCN^-; B-B = CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, L = H_2O, Cl^-, Br^-, SCN^-) were prepared and their cyclic voltammograms (CV) and electronic absorption spectra were measured in solution. The CV of the complexes exhibits a reversible one-electron transfer from a metal-based orbital. Constant potential electrolysis at the oxidation peak potential of $[Rh_2(O_2CCH_3)_4(NCCH_3)_2]$ in acetonitrile yielded $[Rh_2(O_2CCH_3)_4(NCCH_3)_2]^+$, a mixed valent Rh(II)–Rh(III) cation complex. The formation of the mixed valent complex was monitored by measuring electronic absorption spectra of the solution *in situ* during the oxidative electrolysis. The reductive electrolysis of the mixed valent complex solution, in the same electrolysis cell, yielded the original electronic absorption spectrum of the starting complex. The changes in the oxidation and reduction potentials of the complexes with different axial ligands, L = H_2O, Cl^-, Br^-, SCN^-, are correlated to the relative energy changes of HOMO and LUMO of the complexes, which indicates the metal-axial ligand σ- and π-bonding interactions. Spectroscopic and CV data indicate that the degree of σ-interaction is $Cl^- > Br^- > SCN^-$, and that of π-interaction is $Br^- > SCN^- > Cl^-$.

Key words: Spectroelectrochemistry, Dirhodium(II) Complexes, Cyclic Voltammetry