Investigations on the Redox-Photochromism of Rhodium Acetonitrile Complexes

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The spectroscopic and photochromic properties of the dinuclear rhodium complex $Rh_2L_{10}X_4$ ($L=CH_3CN, X^-=BF_4^-$) have been studied in acetonitrile solution. A reversible wavelength-dependent photoredox disproportionation of the dark-equilibrated dirhodium(II) compound occurs upon irradiation with quantum yields of $\phi=0.04$ at 254 nm and $\phi=0.60$ at 436 nm, respectively. While the photolysis products show conspicuous aggregation phenomena at higher concentrations, a straightforward pseudo-bimolecular recombination of the metastable fragments following second-order kinetics was observed in 5×10^{-5} M solution with k=0.18 l mol^{-1} s⁻¹ at 295 K. Both spectroscopic and kinetic results are consistent with the heterolytic formation of mononuclear rhodium(I) and rhodium(III) acetonitrile complexes in the course of the photochemical reaction.

Key words: Photochemistry, Rhodium Complexes, Electronic Spectra, Redox Reactions, Photochromism