Bimetallic Ruthenium Vinyl Complexes Bridged by Electronic Substituent Phenylenes: Spectroelectrochemical and Computational Studies

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A combination of *in-situ* IR and UV/vis/NIR spectroelectrochemistry and DFT/TDDFT calculations have been employed to explore the spectroscopic and electronic properties of a series of dinuclear ruthenium vinyl complexes **1a-1d** [RuCl(CO)(PMe₃)₃]₂(μ -CH=CH-Ar-CH=CH) (Ar = C₆H₂(CH₃)_{2-2,5} (**1a**), C₆H₂(OCH₃)_{2-2,5} (**1b**), C₆H₂F_{2-2,5} (**1c**) and C₆H₂(CF₃)_{2-2,5} (**1d**)). The spectroelectrochemical results combined with theoretical calculations reveal that there are no real electronic couplings between two ruthenium centers for **1a-1d** despite high half-wave potential splittings observed. The complexes **1a-1d** are characterized by localized oxidations of the bridging ligands and electron-releasing substituents render these localized oxidation processes more facile. In addition, the observed strong near-IR absorptions of [**1a**]⁺ and [**1b**]⁺ are mainly attributed to the metal-to-ligand charge-transfer (MLCT) transitions.

Keywords: Ruthenium Vinyl Complexes, Electronic Substituent, DFT Calculations, Phenylene Bridge.

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