Three dimensional, intramolecular electron transfer through space in [2.2]paracyclophanes with redoxactiv rutheniumvinyl moieties

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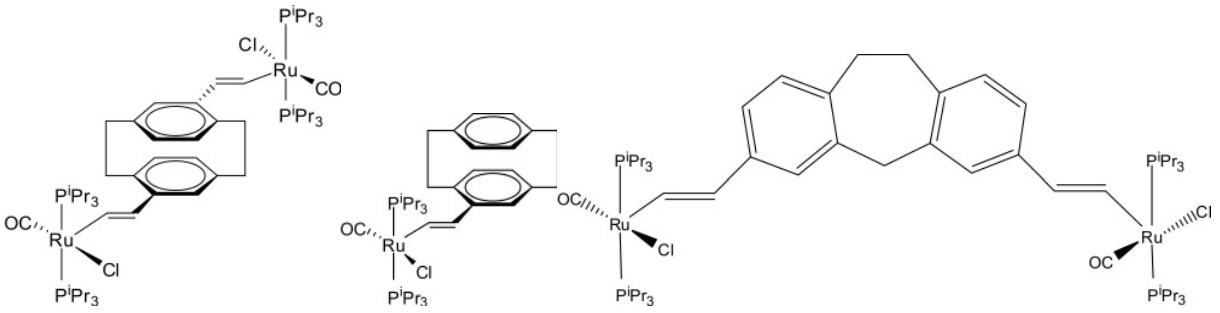
Our topic of research contains electrochemical communication in mixed valent dirutheniumvinyl complexes $\{RuCl(CO)(P^iPr_3)_2\}_2$(pseudoparadivinyl[2.2]-paracyclophane) (**1**) and $\{RuCl(CO)(P^iPr_3)_2\}$(vinyl[2.2]-paracyclophane) (**2**). Both complexes were synthesized by insertion of the alkinyl ligand into the RuH-bond of $RuHCl(CO)(P^iPr_3)_2$ (the so-called hydroruthenation). In a standard OTTLE-cell, the mixed valent species **[$1^{+\cdot}$]** was generated in situ and analyzed towards electronic communication between the ruthenium moieties and the chromophors respectively via IR- and UV/Vis/NIR–spectroelectrochemical measurements. Therefore **2** operated as reference for the identification of the suspected Intervalence-Charge-Transfer-band (IVCT). Furthermore the carbonyl ligands on the ruthenium atoms were used as charge sensitive IR-labels to get better information about the level of delocalization between the metal moieties. For both methods of analyzing electrochemical communication, a discrepancy of values occurred. This assumed a better electronic delocalization in the chromophor through the conjugated π–system between the aryl decks than from one ruthenium moiety to the other. To exclude the possible communication pathway through the σ – bond of the ethylene bridges of **1**, complex **3** was synthesized as "opened" cyclophane complex and analyzed with the same electrochemical methods as **1** and **2**. This complex has a much smaller level of electronic delocalization; therefore we suggested that the electronic communication between the ruthenium moieties of the dinuclear cyclophane complex **1** predominant takes place through space than along the σ – bond of the ethylene bridges.



1 **2** **3**