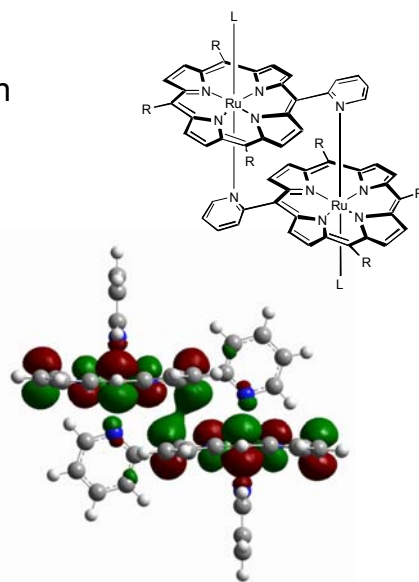
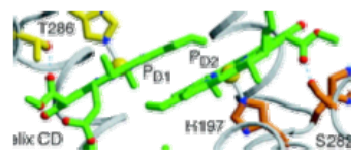


Synthesis of Osmium Porphyrin Dimers for Experimental Studies of Metal Coupling

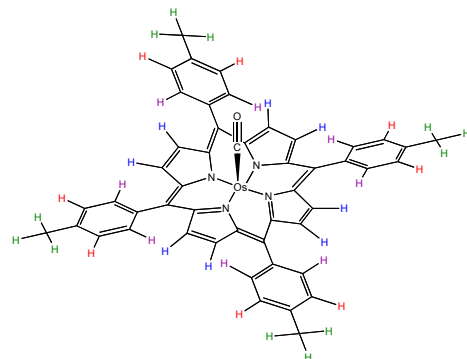
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Background. Metalloporphyrins are present in a variety of biologically relevant molecules. The low-energy sink in chlorophyll, the special pair, (shown at right) is comprised of two magnesium porphyrins in the slipped-disk or cofacial conformation. The process of electron transfer, as in photosynthesis, can be understood from the kinetics of electron transfer, which is largely governed by the metal-metal electronic coupling, HDA. Koopmans' Theorem-Generalized Mulliken-Hush theory has been developed as a method for calculating HDA; experimental values are necessary for comparison with theoretical ones. Ruthenium cofacial dimers have been synthesized and their HDA experimentally determined by Amanda Hickman '07.

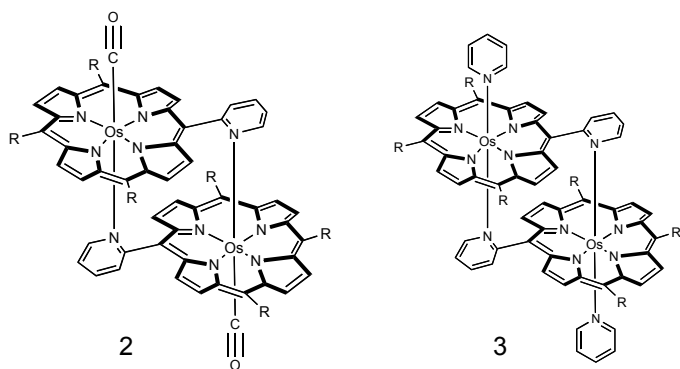


Approach. Organometallic synthesis and column chromatography, with characterization via uv-vis, IR, and ¹HNMR spectroscopy and cyclic voltammetry.

Results. The carbonyl-capped osmium monomer (**1**) synthesis via oxidative metallation requires inert conditions yet side products with different osmium oxidation states or different ligands may be formed. Initial ¹HNMR and uv-vis spectroscopy suggest that the carbonyl-capped dimer [Os(2-PytB₃P)(CO)]₂ (**2**) has been successfully synthesized via a reductive metallation pathway.



1



Future Work. Further characterization of the carbonyl-capped dimer, photolysis of **2** to the pyridine-capped dimer **3**, and oxidative titration with near-infrared analysis to obtain experimental values for calculating metal coupling in the cofacial dimers via eqn 1.

$$H_{DA} (cm^{-1}) = 2.05 \cdot 10^{-2} \frac{\bar{v}}{r} \left[\frac{\epsilon_{\max} \Delta \bar{v}}{\bar{v}_{\max}} \right]^{1/2}$$

Eqn 1

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