RU(II) POLYPYRIDINE COMPLEXES THAT CATALYZE WATER OXIDATION

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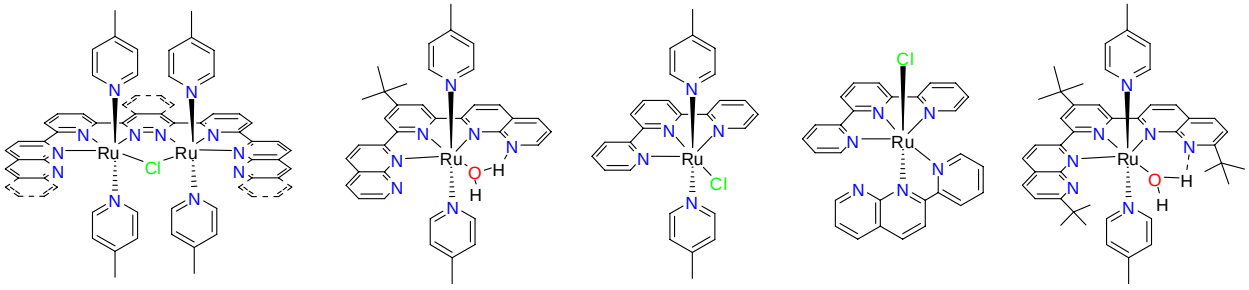
We have reported that a series of Ru(II) dimer with structures similar to **1** and mononuclear Ru(II) complexes with structures similar to **2** in the presence of Ce(IV) as a sacrificial oxidant catalyze the oxidation of water to produce dioxygen.[1,2]

To establish a structure-activity correlation that would help in optimization of catalyst performance and provide some understanding of mechanism, we are following a synthetic approach to explore a wide variety of Ru(II) pyridine and polypyridine complexes. The structure of the diruthenium complex **1** has been varied both in the central linker as well as the peripheral binding unit of the bridging ligands and the axial monodentate. Variation of the bridging ligand does not significantly change the catalytic activity of the complexes, while variation of the axial monodentates produces dramatic influence. Complexes with *N*-methylimidazole at the axial sites do not catalyze water oxidation at all.

Systematic variation of the mononuclear catalyst **2** using mono-, bi-, tri-, and tetrapyridine have lead to the discovery of new Ru(II) catalysts such as **3** and **4**. The mononuclear complexes show considerable catalytic activity. Complex **5** with two bulky *t*-butyls at the bay entrance showing the same catalytic activity as its parent 2 provides an evidence supporting mononuclear catalytic mechanism.



1 **2** **3** **4** **5**

Figure 1. Ru(II) catalysts with charges omitted for clarity

References:

1. Deng, Z.; Tseng, H.-W.; Zong, R.; Wang, D.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 1835-1848.

2. Zhang, G.; Zong, R.; Tseng, H.-W.; Thummel, R. P. *Inorg. Chem.* **2008**, *47*, 990-998.