Final Technical Report

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"Further Studies on Photocatalytic Water Decomposition"

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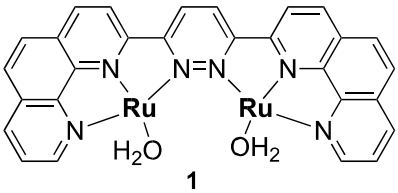
The initial ideas underlying this project were first developed during a sabbatical by RT as a Senior Fulbright Scholar in the laboratory of Professor Jean-Marie Lehn at the University of Strasbourg. Professor Lehn had recently been awarded the Nobel Prize for his work on Supramolecular Chemistry. The project, as it was originally proposed upon my return to Houston, involved using the excited state of an appropriate photocatalyst to bring about the bond-breaking (O-H) and bond making (O=O and H-H) steps involved in water decomposition. The original idea was to design a bridging ligand that would hold two Ru(II) centers such that the two Ru-O species would interact in a favorable manner (**1**). We discovered that when **1** was exposed to Ce(IV) as a sacrificial electron acceptor, tiny oxygen bubbles were readily observed. Even more remarkable, however, was the observation that a mononuclear complex such as **2** was also active as a water oxidation catalyst. This simple observation opened the flood gates for the development of a whole new approach to catalyst design. The so-called "nucleophilic attack" mechanism was proposed. It was suggested that Ru(IV)=O was sufficiently electrophilic to be attacked by water leading to formation of the critical O-O bond.



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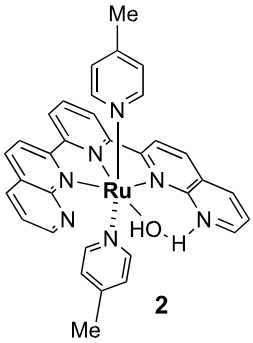


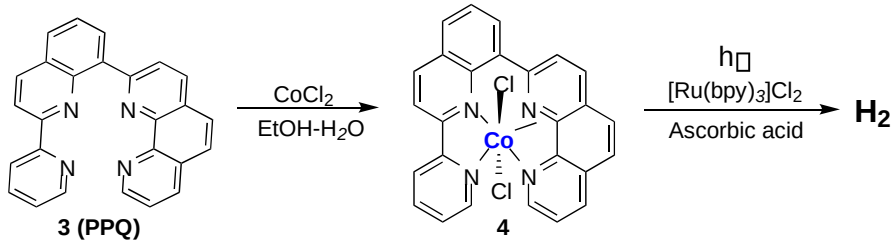
2

We discovered that photochemically generated Ru(III) could also serve as an electron acceptor and thus we were able to use light to initiate photooxidation of a metal bound water molecule. Unfortunately a stoichiometric electron acceptor was still required.

A single crystal X-ray analysis of **2** revealed an intramolecular N-H bond involving a non-coordinated nitrogen on the 1,8-naphthyridine nucleus. This observation suggested the possibility of intramolecular assistance to the O-H bond cleavage. We are currently considering

the possible role of an internal base to assist in the deprotonation step. In particular we are considering the likelihood of a seven-coordinate trigonal bipyramid Ru species. There is precedent for such species.

A persistent problem associated with our approach to ligand design is the necessity for a stroichiometric oxidizing agent (Ce(IV)). This requirement precluded the development of a truly catalytic species. The obvious solution is that we need to make oxygen and hydrogen concurrently. By comparison with the oxidation process, water reduction should be much simpler. It must involve the elementary process of proton reduction. A variety of transition metals have been explored in this regard. One of the more active systems involves Co(II). Co(II) complexes prefer a square planar geometry with an internal bite angle of about 90°. We were able to make a slight variation in our polypyridyl ligands to provide a more square-planar environment. This was accomplished by replacing a pyridyl binding unit with a quinoline-2,8diyl, effectively increasing the size of one chelate ring from five atoms to six. We named the parent member of this family PPQ (pyridyl-phenanthrolinyl-quinoline). The resulting complex with Co(II) uses $[Ru(bpy)_3]^{2+}$ as a photosensitizer and ascorbic acid as a sacrificial electron donor to reduce water and give hydrogen. Interestingly, the same ligand with Ru(II) is a good catalyst for water oxidation and also provides oxygen when Fe(II) is used as the active metal.

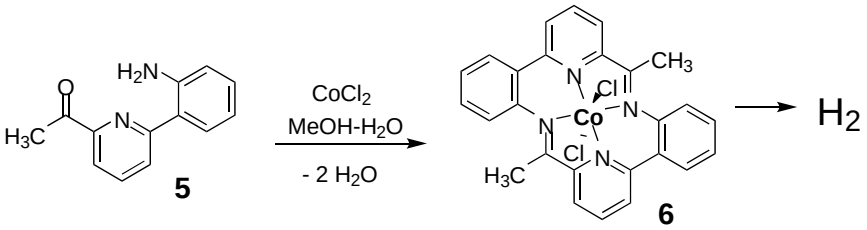


3 (PPQ) **4**

A critical factor in the development of an effective water decomposition catalyst involves a better understanding of the catalyst deactivation process. For example we have discovered that the central pyridazine ring in catalyst **1** may be oxidatively cleaved into two equivalent pieces and each of these can function as an effective catalyst. Since a secondary product may indeed be the active species, care must be taken in the use of strong sacrificial reagents.

We have discovered that an appropriate anilino-acetyl pyyridine can cyclodimerize to form what is effectively a cyclotetrapyridine analog. The Co(II) ion acts as a template for the cyclodehydration that leads to **6**. No cyclization at all is observed in the absence of the templating metal. Since metal complexes of Co(II) are effective in water reduction, the method

allows for the direct formation of the catalytically active species without the need for an intermediate ligand synthesis step. This approach holds promise for self-assembly type chemistry as well as self-repair.



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