INTRAMOLECULAR ENERGY TRANSFER REACTIONS IN
POLYMETALLIC [complexes]

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PROGRESS REPORT FOR THE PERIOD
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PROGRESS REPORT

1. Excited-State Energy Transfer

Our major effort in energy transfer has been an attempt to sensitize the photoelimination of molecular hydrogen from a bimetallic, metal-dihydride complex. These complexes have most recently involved highly-absorbing, antenna fragments such as cyanoferrate(II) or azineruthenium(II) centers, bi- or tridentate azine bridging ligands, and a cobalt-phosphine-dihydride reactive fragment. In cases where bidentate bridging ligands were used, such as 2,2'-bipyrimidine (bpm), 2,3-bis(2-pyridyl)pyrazine (dpp) or 2,3-bis(2-pyridyl)quinoxaline (dpq), the stability of the bridge between the antenna and the cobalt hydride. At this point in time, we have been unable to stabilize the cobalt hydride to an antenna fragment through a bidentate bridge.

A stabilized trimetallic complex can be made with 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpp) as the bridging ligand. Unfortunately, the complexes formed with this bridging ligand have only one vacant site for a phosphine ligand on the cobalt hydride fragment. Thus, complexes such as $(\text{tpy})\text{Ru}(\text{tpp})\text{Co}(\text{PPhEt}_2)\text{H}_2^{3+}$, $(\text{NC})_3\text{Fe}(\text{tpp})\text{Co}(\text{PPhEt}_2)\text{H}_2$ and $(\text{NC})_3\text{Fe}(\text{tpp})\text{Co}(\text{PPh}_3)\text{H}_2$ (tpy - 2,2':6',2''-terpyridine) undergo photoinduced reductive elimination of H_2 , but also have the competing thermal loss associated with having only one phosphine ligand on the cobalt hydride metal center.

Since the only stable complex of the cobalt dihydride formed thus far is the parent, monometallic system, $\text{Co}(\text{bpy})(\text{PPhEt}_2)_2\text{H}_2^+$, we are

attempting to mimic this fragment in a bimetallic complex. The bridging ligand we have prepared and are using is bbpy (illustrated below).

bbpy

Currently, we are preparing $(bpy)_2Ru(bbpy)Co(PPhEt_2)_2H_2^{3+}$ which should mimic the monometallic cobalt hydride, except that a covalently linked ruthenium(II) azine center should be close enough to act as an intramolecular energy-transfer catalyst.

2. Excited-State Electron Transfer (Charge Separation)

We have prepared a series of diad and triad complexes in order to sustain charge separation in an artificial photosynthetic system. The triad systems have the following general formula:

The projected role of the $(BL)Ru(bpy)(BL')$ moiety is photon absorber, MQ^+ is an electron acceptor, and $(NC)_4Fe(BL)$ is the electron donor.

The diad molecules which were prepared are a simplified version of the molecules depicted above:

The projected role of the $(BL)Ru(tpy)(MQ^+)$ is that of photon absorber while $(NC)_4Fe(BL)$ and MQ^+ are electron donor and acceptor, respectively, as before. Typically, compounds containing the tpy ligand bound to $Ru(II)$ have not been used as antenna fragments because of the short lifetime of $Ru(tpy)_2^{2+}$ in fluid solution at room temperature.

Recently, we have measured the lifetime of a series of $Ru(tpy)(bpy)L$ complexes, where L is acetonitrile, pyridine, cyanoacetylene, cyanophenylacetylene, phenylpyridyl-acetylene, dipyritylacetylene and pyridylacetylene. Each of these complexes has a lifetime between 700 ns and 1.3 μs at room temperature in DMF. The long-lived nature of these species opens up a new dimension in long-lived $Ru(II)$ sensitizers.

In order to look at models for the diad and triad systems, all systems were prepared with 4,4'-bipyridine substituted for MQ^+ . The lack of a methylated nitrogen on the remote pyridine ring eliminates the electron acceptor from the system. All complexes with 4,4'-bipyridine in place of MQ^+ and $BL = dpp$, undergo emission (Ru -based) at room temperature. For $BL = bpm$, no emission is observed in the 4,4'-bipyridine complex as expected in previous studies on $(bpy)_2Ru^{II}(dpp)Fe^{II}(CN)_4$ and $(bpy)_2Ru^{II}(bpm)Fe^{II}(CN)_4$. However, in all cases, methylation to give MQ^+ in either diad or triad with $BL = dpp$ quenches the emission. Our interpretation is that the electron acceptor is quenching the emission *via* electron transfer.

We attempted to measure transients in the diad and triad systems by nanosecond transient absorbance. These measurements were carried out at Notre Dame Radiation Laboratory with the assistance of Dr. Guillermo Ferraudi. In all cases, no transients were observed for the $MQ^\bullet$ radical, which is expected in the charge separated species. Our conclusion is that

either charge separation is not occurring (a hypothesis not consistent with emission studies) or that charge recombination is faster than the nanosecond time scale.

On the basis of this latter interpretation, we are continuing to study the lengthening of the covalent bridge between the antenna and the electron acceptor. A previous complex we prepared was the Cu(II) polymer shown below:

This polymer is a semiconductor and we are now attempting to place this species synthetically between a $(bpy)_2Ru(bpm)$ absorbing fragment and a dihydroxyquinone electron acceptor. In addition, we have taken a Cu(II)(hfac) system, hfac = hexafluoroacetylacetonato, and bridged these units with the following four ligands:

The selection of these four ligands gives us flexibility in varying electron coupling and metal-metal distance in preparing mediating polymeric bridges.

Many of these studies are just getting to the point where they can be published. Our lifetime apparatus was down for many months and has

just been repaired totally this fall. Therefore, while some reprints are attached, preprints and reprints pertaining to the work described herein will be included with the next progress report.

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