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Synthesis of a Ruthenium Bis-Terpyridine Derivative

Ashini Patel
Lehigh University

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Introduction

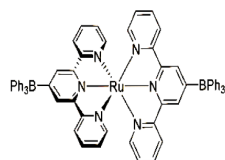
A metal complex is an acid-base adduct in which a central metal acts as a Lewis acid and accepts electrons from the surrounding ligands which act as Lewis bases. Transition metals form complexes because they have unfilled d-orbitals which are filled by ligand electrons to form dative bonds. In these dative bonds electron density is shared between the central metal and the ligand.

Metal complexes have a number of properties. They can be either paramagnetic or diamagnetic. Paramagnetic compounds have unpaired electrons in their molecular orbitals while diamagnetic compounds have only electron pairs. Metal complexes also have optical properties, and are usually vividly colored. These optical properties are due to electron or charge transfers between the metal and the ligand. If the energies required for these electron transitions are in the visible spectrum the metal compound will be colored. For example, Ruthenium complexes are characteristically red in color because the energy absorbed for a metal to ligand charge transfer correlates to the color green. Therefore the complimentary color, red, is reflected by ruthenium complexes. Like all molecules, metal complexes can also be characterized by their shape and stability.

Metals complexes play an essential role in many biochemical processes. One example of a biologically important metal complex is the Heme group which acts as the active site of the hemoglobin protein. The hemoglobin protein is responsible for carrying oxygen throughout the body, from the lungs and to the circulatory system. The Heme group is an Iron complex. The central Iron is surrounded by a porphyrin ring. The central Iron is able to bind to O₂ molecule and carry it around the body. The binding of oxygen changes the oxidation state of the Iron from (2+) to (3+). The oxidation state of a metal refers to that metal's ability to form chemical bonds. When Iron coordinates with one oxygen molecule it is oxidized and cannot bind to another oxygen molecule until it is reduced. The optical properties of the Heme group changes with oxidation. The coordination of oxygen to Iron results in the Heme group changing from a blue color to a red. Most metal complexes have interchangeable oxidation states. The oxidation and reduction of transition metals and ligands refer to the respective loss or gain of electrons. Metal complexes are useful for catalysis due to their ability to readily and reversibly give or accept electrons.

A catalyst is a species that increases the rate of a reaction by stabilizing the transition state and therefore lowers the activation energy of a reaction. A catalyst does not undergo any permanent chemical change during the reaction and is recovered at the end of a reaction. Metal complexes are good catalysts because they can readily give and accept electrons. If a transition state is electron poor the metal complex can donate electron density and if the transition state is electron rich the metal can accept electron density. Transition metals can also form complexes with reactants and bring them together to increase the collision frequency between reactants.

Most metal catalysts use precious metals but these metals are rare and expensive so they are hard to use in large scale industrial catalysis.



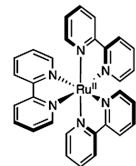
Objective

To coordinate Ruthenium metal with an anionic Terpyridine derivative ligand. Furthermore, in order to photocatalyze synthetically useful reactions like reductive eliminations we aim to modify the Terpyridine ligand to make it a strong oxidant which can be irreversibly reduced

Background

The Terpyridine ligand is a common tridentate ligand. Due to its conjugated ring system, it can absorb light. This property can be used for photoredox catalysis, this process is selective and controllable because depending on the type of Terpyridine complex only a specific wavelength of light will be absorbed by the metal complex and this absorption can occur in mild conditions. The photoexcitation of an electron can form reactive radical intermediates or allow for single-electron transfers with the substrate.

A well studied photocatalyst is Tris-bipyridyl Ruthenium(II)^[1]. This metal complex absorbs light at the wavelength of 452 nm which is in the visible range. When this complex is excited by light it is a strong single electron transfer reagent. Contrastingly, when this complex is in its ground state it is a poor oxidant or reductant.

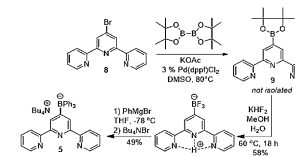


Ru(bpy)₃²⁺

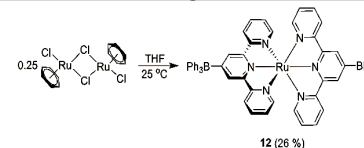
When this molecule absorbs light, an electron from the Ruthenium d-orbital is transferred to a high energy pi-star orbital of the ligand. This metal to ligand charge transfer, oxidizes ruthenium to a (III) state and the bipyridyl ligand has been effectively reduced. The photoexcitation of the Ru(bpy)₃ complex makes both reduction and oxidation more favorable. This is because when the excited catalyst acts as an oxidant, the electron it gains is placed into the t_{2g} binding d-orbital. When the complex acts as a reductant an electron is taken from the high energy pi* orbital. This photo catalyst can take part in either an oxidative or reductive quenching cycle. The redox potentials can be manipulated through ligand substitutions. Electron donating additions to the ligand will make the photocatalyst a stronger reductant and electron withdrawing groups will make the complex a stronger oxidant. The photocatalytic properties of Bipyridine extends to Terpyridine ligands as well.

In addition to being excitable by visible light, the polypyridine backbone of Terpyridine can act as an electron reservoir in reducing systems so it is a suitable ligand for non-innocent redox reactions. A non-innocent ligand plays a role in determining the oxidation state of the metal center, because it can accept or give electrons. Non-innocent ligands are active in redox transformations. Contrastingly, innocent ligands have clearly defined metal oxidation states and redox transformations are metal centered. Lastly, a Triphenyl borane is added to the Terpyridine to create an anionic derivative. Anionic ligands have shown to yield electron-richer metal complexes^[2]. This substituted anionic ligand also will coordinate to the same metal differently relative to the unsubstituted neutral Terpyridine ligand.

Synthesis of Anionic Terpyridine Derivative^[3]



Coordination of Novel Ligand with Ruthenium Metal



12 (26 %)

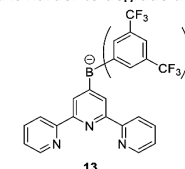
Conclusion and Continuing Work

We successfully were able to coordinate the novel anionic Terpyridine derivative ligand with Ruthenium by reacting 4 equivalents of our ligand with a Ruthenium (II) chloride dimer in a tetrahydrofuran solvent at room temperature. The purity of the product was confirmed with elemental analysis. The paramagnetic properties of our metal complex would have lowered the resolution of any NMR (nuclear magnetic resonance spectroscopy) results collected.

To study the electrochemical properties of the novel ligand a CV was run. Cyclic Voltammetry of the free ligand using Ferrocene as a standard shows that the Terpyridine derivative is irreversibly oxidized at a potential of 0.5 V. DFT, or density functional theory tells us that the HOMO orbital that would be involved with an oxidation reaction is localized at the triphenyl borane. Therefore just like for Tris-bipyridyl Ruthenium (II), by adding electron withdrawing groups, like trifluoromethyl, to the phenyl will make the catalyst a better oxidant. In concept this electron withdrawing group should lower the energy of the HOMO orbital and allow the ligand to be irreversibly reduced.

The trifluoromethyl functional group is not only an electron withdrawing group but it is also used in a great deal of medicinal chemistry^[4]. Replacing labile hydrogen atoms of pharmaceuticals with fluorine usually reduces its potency and bioavailability^[5] because the C-F bond is harder to degrade than the C-H bond. Our fluorinated ligand hopefully can be used as a fluorinating agent via an irreversible reductive elimination which would transfer the trifluoromethyl group to a molecule.

To achieve this we currently are trying to change the last Grignard reactant in the last reaction in the previously established anionic Terpyridine derivative synthesis pathway^[3].



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References

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