

Contribution to the science behind alternative energy utilization: Developing the fundamental chemistry behind solar energy conversion using Ni, Pd, Pt metal complexes and small molecule activation.

Introduction

Increasing energy demands and depletion of fossil fuel resources worldwide demands the immediate attention of science in general and chemistry specifically to develop alternative sources of reliable energy. At our current rate of consumption, 500 million-year-old fossil fuel sources will run dry in less than 100 years⁰. Carbon dioxide emissions are at an all time high and are projected to increase at an alarming rate by 2100⁰. Our future security and even the sustainability of life depend on a change in these global energy trends.

Despite a clear impetus for the establishment of clean, efficient, alternative energy sources, progress has been slow since current technologies cannot yet maximize the efficiency of many proposed energy sources. Solar energy is a promising alternative energy source because it is environmentally friendly and is virtually unlimited in supply. However, before solar energy can be harnessed efficiently, we must first gain a better understanding of how chemistry can be used to harness light energy. In nature, green plants harness sunlight to drive the conversion of CO₂ and H₂O into O₂ and simple carbohydrates. An attractive artificial photosynthetic strategy could harness sunlight to split water into H₂ and O₂ via the multi-electron reactions shown in Figure 1. While sunlight may be used to provide the thermodynamic driving force for these processes, synthetic molecules capable of promoting the specific bond breaking and bond-making reactions do not exist. This research proposal will develop new transition metal complexes and explore fundamental reaction chemistry related to the problem of photochemical hydrogen and oxygen production from aqueous solution.

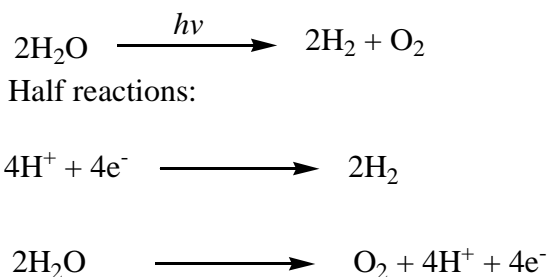


Figure 1. Redox reactions of water being split into its component molecules.
Adapted from Nocera et.al¹.

To realize a strategy for cleaving water to produce hydrogen and oxygen gas, two gigantic obstacles must be overcome. The first is a thermodynamic one. Since water is a combustion byproduct, it is a very stable and energy-poor molecule; conversion to hydrogen and oxygen requires a massive input of energy (251 kJ mol⁻¹, or 4.17x10⁻¹⁹ J/molecule of H₂O). Sunlight may be used for this purpose, as one photon of sunlight can provide the necessary energy input to split one water molecule. The second obstacle is harnessing this energy in a catalyst capable of promoting the multi-electron bond-breaking and bond-forming steps needed to transform water into hydrogen and oxygen. The fundamentals of this multi-electron reactivity have yet to be fully developed. However, families of transition metal complexes containing redox-active ligands provide a logical platform for targeting such reactivity.²⁻³

Proposed Research

One strategy for developing transition metal complexes capable of mediating multi-electron bond activation reactions is to design redox activity into both the metal center and the auxiliary ligand set. In this program, systems of the type $M^{II}(isq)_2$ ($M = Ni, Pd, Pt$; $isq^- = 4,6$ -di-*tert*-butyl-2-arylimino-semiquinonate) will be investigated in small molecule activation and substitution reactions related to artificial photosynthesis. The isq^- ligand is a mono-anionic radical ligand capable of chelating metal ions such as nickel(II), palladium(II), and platinum(II). Reduction of the isq^- ligand affords the dianionic ap^{2-} (4,6-di-*tert*-butyl-2-arylamidophenolate) form, while oxidation of the isq^- ligand affords the neutral iq ($iq = 4,6$ -di-*tert*-butyl-2-aryliminoquinone) form (Fig 2a). Harnessing this ligand-centered redox activity, it has been shown that complexes of the type $M^{II}(isq)_2$ can be oxidized or reduced by two electrons³ resulting in a homologous four-electron series of complexes shown in Figure 2b.

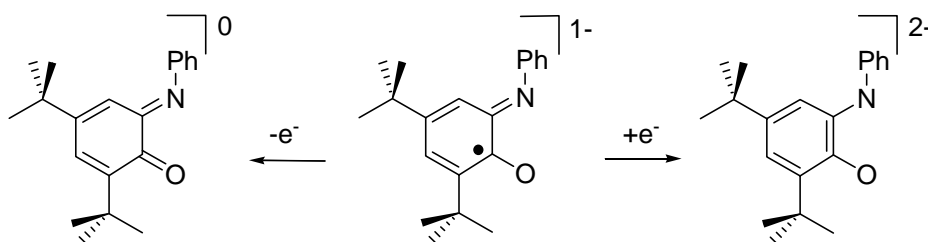


Figure 2a. Neutral, anionic and dianionic forms (respectively, left to right) of isq ligand.

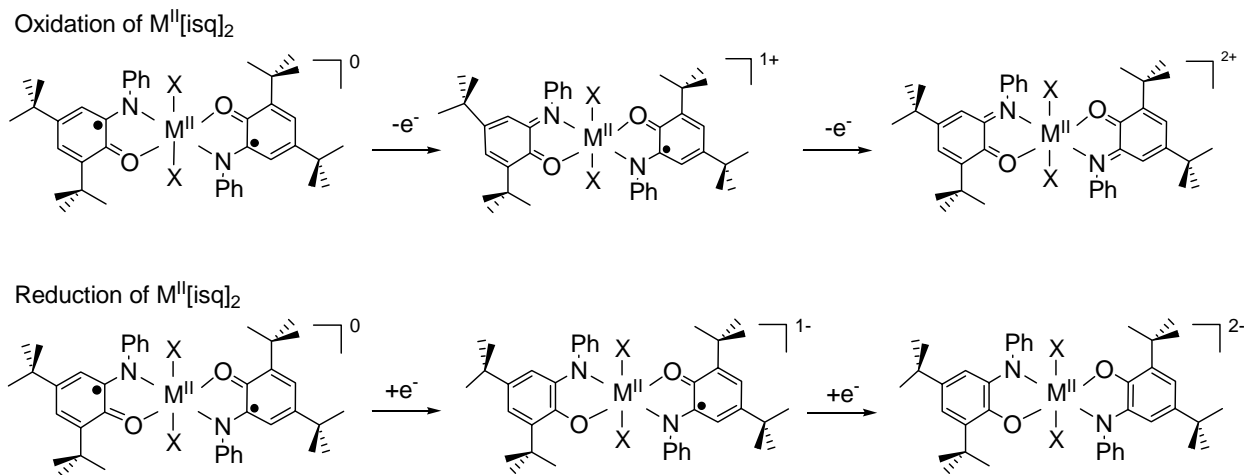


Figure 2b. Four electron series of complexes, derived from either oxidation or reduction of $M^{II}(isq)_2$.

Our initial efforts will focus on developing the oxidative addition reactivity of the $M^{II}(isq)_2$ family of compounds. In oxidative addition, a substrate such as $X-X$ adds to a metal complex in a manner where the $X-X$ bond is cleaved and two $M-X$ bonds are formed. We will examine the reactivity of $M^{II}(isq)_2$ with halogen and peroxide molecules to develop an understanding of the energetic relationship between redox reactivity, $X-X$ bond cleavage, and

M–X bond formation. Preliminary results have shown that the oxidative addition of X_2 (Fig.3) has been carried out for $M=Ni$. The oxidation of the complex from $Ni^{II}[L^{ISQ}]_2$ to $Ni^{II}[L^{IQ}]_2X_2$ suggests that the electrons contributing to the reactivity come from the ligands. We plan to extend our studies to the palladium and platinum complexes to determine when and if metal oxidation-state changes play a role in reactivity. If we can harness both metal- and ligand-based redox states it may be possible to realize a 6-electron series by accessing a $[Pt^{IV}X_2(iq)_2]^{2+}$ species.

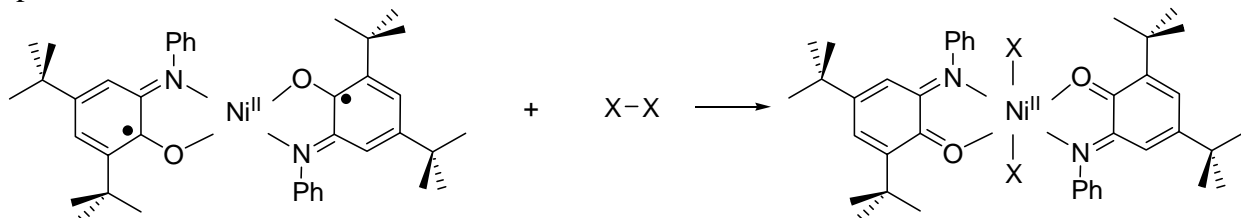


Figure 3. Oxidative addition of the Ni complex. $X=Cl, Br$.

Another key aspect of this research will be to examine the reactivity of the $M^{II}(isq)_2$ platform with protic reagents, $H-X$ ($X = Cl, Br, I$). Here the potential exists to observe oxidative addition of two equivalents of $H-X$ to $M^{II}(isq)_2$ with concomitant reductive elimination of H_2 as depicted in Figure 4. We expect that the propensity of the complex to promote H_2 formation will be related to the polarization of the $M-H$ bond resulting from the first addition of $H-X$ to $M^{II}(isq)_2$. Uneven electron sharing in the $H-X$ bond facilitates the attack of M on the $H-X$ substrate and subsequent addition of $H-X$ to the metal complex.

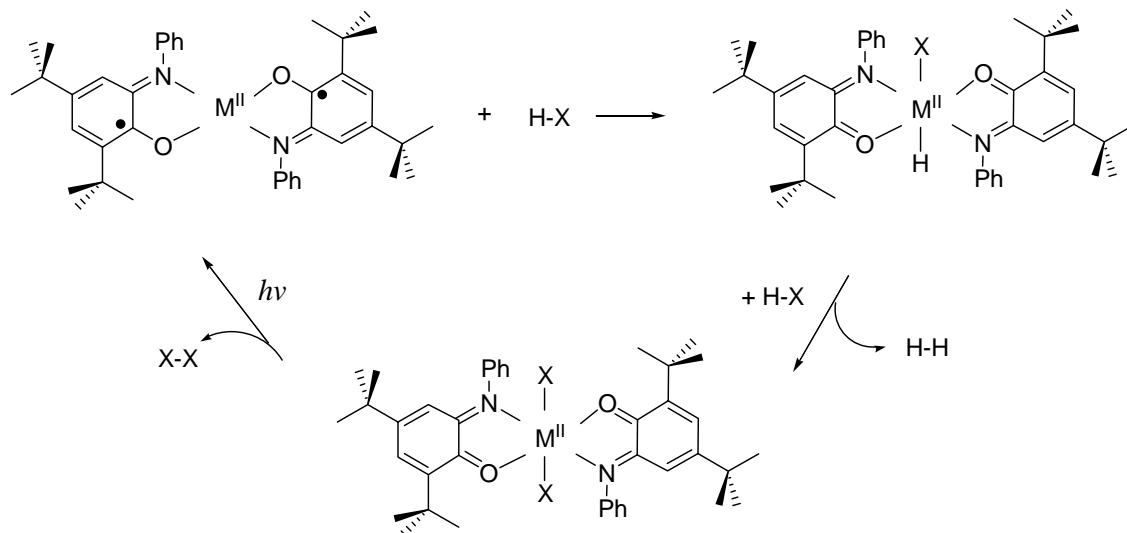


Figure 4. Catalytic cycle for the oxidative addition of $2H-X$ to the complex, followed by the reductive elimination of H_2 . $X=Cl, Br, I$.

To better understand the reactivity of the $M^{II}(isq)_2$ family of complexes and to gauge their effectiveness for harnessing solar energy we must develop a detailed understanding of electronic structure. We will approach this problem from experimental and theoretical angles. Absorption spectroscopy will be used as an experimental probe of the electronic structure of the $M^{II}(isq)_2$

complexes as well as their oxidative addition products $M^{II}X_2(iq)_2$, $M^{IV}X_2(isq)_2$, and $[Pt^{IV}X_2(iq)_2]^{2+}$. Computational chemistry will be used to interpret the experimental results by providing models of the molecular orbital structure and charge distribution for the family of molecules.

Conclusion

In a limited time of less than a century, our world will no longer be able to rely on fossil fuels as an energy source and must quickly find, develop, and utilize alternative energy sources. The proposed chemistry and all results generated would contribute an understanding to the newly developing science behind solar energy conversion. Crucial technological advances needed to sustain current and future energy demands via solar energy can only begin to develop as soon as the groundwork for such science is founded and the chemistry behind it understood.

SURP Timeline

- Weeks 1-3: Synthesis and characterization of metal complexes $M^{II}(isq)_2$ ($M = Ni, Pd, Pt$) via 1H NMR spectroscopy and X-ray crystallography.
- Weeks 4-6: Oxidative addition of X_2 to $M^{II}(isq)_2$ for $M = Ni, Pd, Pt$ and subsequent characterization. Oxidative addition of $H-X$ to $M^{II}(isq)_2$ and characterization of adducts.
- Weeks 6-8: Substitution reactions. Attempts to reductively eliminate H_2 and various O-O substrates.
- Weeks 8-10: UV/Vis spectroscopic studies of complexes. Investigation of charge transfer within metal complex.

References

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