

## **Dihydrogen Heterolysis and Hydride Transfer utilizing an Iridium Catalyst**

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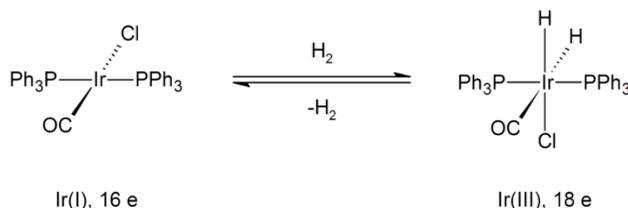
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### **Abstract**

Hydride transfer is an efficient means of reducing oxidized matter for a variety of purposes, and iridium is a popular metal center when homogeneous methods are used. Hydrogen gas is the most used method of obtaining a hydride. The goal of this study is to computationally analyze an iridium catalyst's potential to obtain and transfer a hydride. In particular, an Iridium (III) catalyst containing a picolinamide bidentate ligand as well as a cyclopentadienyl half sandwich. In aqueous solution the catalyst can reduce carbon dioxide to formic acid. Energy and geometry calculations of a published study utilize the density functional theory method m06, and however this study will process the data differently, use the basis set cc-pvdz for all atoms except iridium which will utilize LANL2DZ's effective core potential, and the solvent model will utilize a different permittivity. The data is qualitatively similar, with the largest deviation likely caused by the values of the relative permittivity, of which this study does not acknowledge the ionic strength of the solution. Nonetheless, the data was used to compare point modifications on the catalysts picolinamide ligand to the molecular geometry and energetics of the chemical environment. From these energy and geometry calculations the catalytic efficiency and dynamics of the catalyst can be inferred. It was found that the point modifications decrease catalytic efficiency probably because they disrupt the conjugation and  $e^-$  inductive effects. The vinyl functional group maintains the symmetry of the p orbitals however the lack of an oxygen causes its energy to increase relative to the control, but this intermediate is still downhill from the subsequent step. We can infer that means maintaining the resonance stability of the picolinamide is more important for the structure of the intermediate than just the presence of the strongly electronegative oxygen. The second pattern is found in the optimizations after [Ir-H<sub>2</sub>O] where the catalyst has a greater number of  $\sigma$ -bonds. While the Ir has more electron density around it the hydroxyl point modification is lower in energy than the vinyl, but only slightly (<2 kcal/mol).

## Introduction

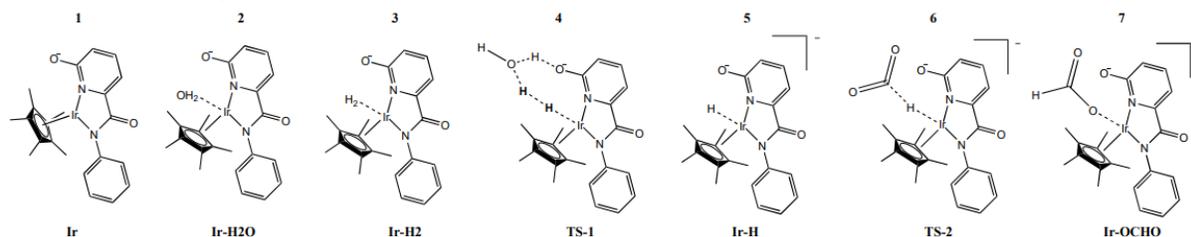
In the 1970's R. Schrock, and J. Osborn discovered useful ionic rhodium complexes for heterolysis of  $H_2$  and subsequent hydrogenation of olefins.<sup>1</sup> Around the same time, R. Crabtree discovered highly catalytic iridium hydride complexes (Figure 1) for similar purposes.<sup>2</sup> Since these discoveries, catalysts utilizing rhodium, iridium, and other rare earth metal catalysts have been found for enantioselective hydrogenation, polymerization, and hydride transfer.<sup>3</sup>



**Figure 1:** Crabtree discovered many catalysts capable of reducing olefins in the 70's. This was done by providing the catalyst in a solvent, usually ethanol, acetone, or THF, with  $H_2$  which would form a metal dihydrido complex. The reaction would begin with oxidative addition (forward) and a subsequent step through an inner sphere mechanism where a ligand would dissociate to allow the olefin to coordinate with the metal center, and then accept the hydrogens.<sup>2</sup>

Iridium organometallic catalysts are often successful in forming a hydride comparative to the other metals in its group. In a computational study of catalysts of group 6 transition metals (Co, Rh, and Ir) it was found that Iridium's experimentally high TOF can be attributed to its superior d-orbital back-donation characteristics which reduces the significant energy barrier required by heterolytic cleavage of  $H_2$ .<sup>4</sup> These Iridium (III) hydride catalysts featuring amides and cyclopentadienyl ligands are capable of amination of ketones as well.<sup>5</sup>

Another study of this same catalyst is shown to have an experimental TOF of  $198 \text{ h}^{-1}$  when reducing  $CO_2$  to formic acid. This rate is achieved by only water, dihydrogen, carbon dioxide, potassium formate and the catalyst at pH 8.8.<sup>6</sup> It was found that the rate determining step was dihydrogen heterolysis, though hydride transfer to carbon dioxide had a similar energy barrier.<sup>7</sup> The nearby hydroxyl group of the pyridone allows for an outer sphere intermolecular interaction to reduce the energy barrier of heterolysis of hydrogen.<sup>7</sup> Himeda proposed this catalyst is for hydrogen storage, as the catalyst will hydrogenate  $CO_2$  or dehydrogenate formic acid dependent on pH.<sup>6</sup> This allows for a safer alternative to  $H_2$  transportation.



**Figure 2:** Relevant molecular interactions in the catalytic pathway of carbon dioxide reduction at near ambient conditions. Formic acid oxidation occurs by a different pathway at a pH of 3.3.<sup>7</sup>

Brookhaven National Labs is researching a means of reducing the energy barrier of the rate determining step, heterolytic cleavage of dihydrogen. It is speculated there is a possible low energy transition state that does not require a water molecule; however, it is thermodynamically unfavorable with the current form of the catalyst.<sup>7</sup>

This study reproduces the calculations (Figure 2) of the catalyst with the highest TOF used in the Brookhaven Lab studies with different basis sets, and solvent model. Slight alterations to the carbonyl on the backbone of the picolinamide ligand are made to probe the functionality of the catalyst's amide ligand. The amide is a strong  $\pi$  donor involved in providing electron density required by the  $18 e^-$  valency of Ir (III).

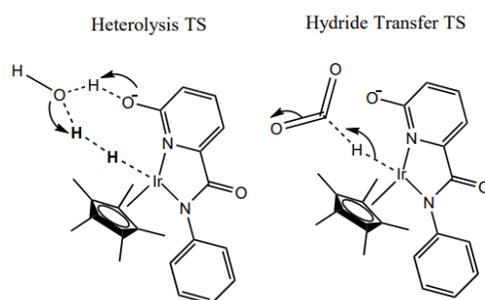
## Experimental

Minnesota functional m06 was used as the level of theory. LANL2DZ basis sets were applied to the iridium atom as its large quantity of chemically inert electrons can be replaced with the pseudopotentials of ECP. The basis set used for all other atoms is cc-pVDZ. Vibrational frequencies were derived from the same level of theory to verify the minimum and transition structure geometries. Frequencies below  $50 \text{ cm}^{-1}$  were replaced with a value of  $50 \text{ cm}^{-1}$  as a correction to better represent an anharmonic oscillator. A temperature of 298.15 K was used to include

thermodynamics. Solvation Model Based on Density was used with a dielectric constant like that of water at pH 7.0. A loose convergence threshold was used.

## Background

The catalytic cycle of proton coupled electron donation to reduce CO<sub>2</sub> has two transition states.<sup>4,7</sup> The first is the H<sub>2</sub> heterolysis and the second is hydride transfer (Figure 3). There are many ways by which the transition state can occur for both states, however previous studies indicate that a H<sub>2</sub>O assisted heterolytic pathway is the lowest energy and most likely.<sup>4,7</sup> Likewise, it was found carbonate and H<sub>2</sub>O do not significantly reduce the energy barrier for hydride transfer.<sup>7</sup> Interestingly Nijamudheen reported a thermodynamically unfavorable yet desirable pathway to hydrogen heterolysis, it involves dihydrogen heterolysis assisted by the outer sphere alkoxide which removes the need for a docked H<sub>2</sub>O molecule to assist in catalysis. The energy required to deprotonate at the alkoxide results in a less energetically favorable pathway.<sup>7</sup>



**Figure 3:** Structures of two rate determining steps in the catalytic cycle of the reduction of CO<sub>2</sub> to formate. Heterolysis TS (TS-1) Involves the formation of a hydride sigma bonded to the Ir, while a proton solvates into solution. Hydride Transfer (TS-2) Involves the encounter of a CO<sub>2</sub> molecule to the hydride, and electron transfer to the carbon.

## Results & Discussion

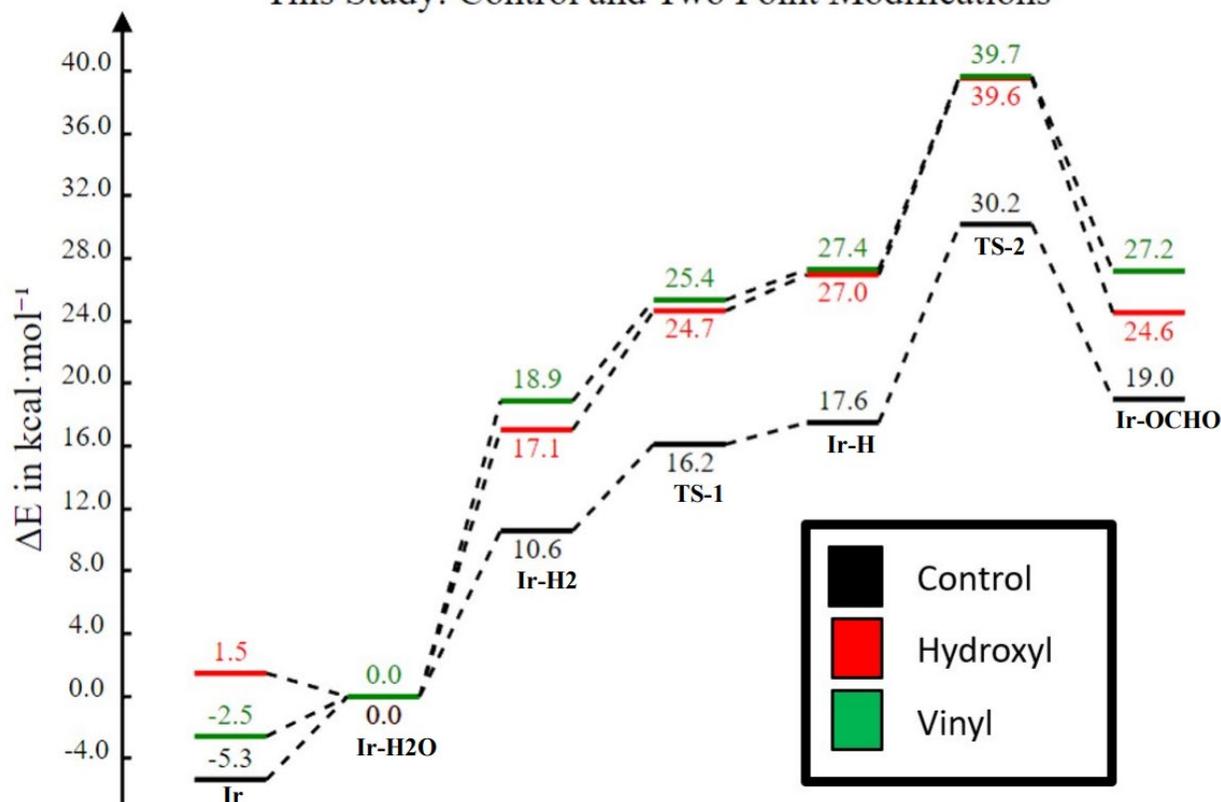
This study probes the amide to better understand the electronic effects it has on catalyst function. Point modifications are made to the oxygen atom on the amide. Notable features provided by an amide is a  $\pi$  system with higher electron induction on the oxygen, and the ability for the oxygen to hydrogen bond with the solution.

Replacing the carbonyl group with a hydroxyl and a hydrogen provides similar atoms to the original molecule, though the geometry and the presence of pi bonded orbitals changes by breaking the  $\pi$  system of the amide. The phenyl group provides a possible  $\pi$  system for the lone pair on the nitrogen to interact with, however it is significantly less favorable than that of the amide. This will draw a comparison between an amides  $\pi$  effects to a phenyl ring conjugated with the nitrogen.

Replacing the carbonyl group with the sp<sup>2</sup> hybridized methylene results in the e<sup>-</sup> induction by oxygen being replaced with one of a lesser magnitude while maintaining conjugation. The optimized structures maintain a three membered  $\pi$  system, however the carbon does not provide strong electron induction or hydrogen bonding with the solvent.

It was found that both modifications led to very similar energetic barriers. Both increased the energy of each optimization, especially the hydride transfer transition state.

## This Study: Control and Two Point Modifications



**Figure 4:** Energy diagram of three pathways beginning with the Ir, un-ligated catalyst. If a correction of 14 kcal/mol is applied to optimizations after TS-1 the data is qualitatively the same as previous studies calculated at a pH of 8.3. R represents the position of point modification. Red: Hydroxyl substitution. Blue: Carbon substitution. Black: Control, no substitution.

### Energetics:

The absolute free energy of a solvated proton in aqueous solution is -265.9 kcal/mol, though other studies obtained results differing by about 5%.<sup>7</sup> The energetically favorable process of proton solvation in aqueous solution is included in this correction. It can be applied to the states after TS-1 as the proton is considered to solvate.

The data deviates from publication<sup>7,8</sup> by 14 kcal/mol in correlation with the negative charge on the affected optimizations [Ir-H], [TS-2] and [Ir-OCHO]. This indicated an error in the methodology when representing charged species and could be a result of the differing solvent model. Relative permittivity is an important value in the calculation of the Solvation Model Based on Density and is affected by temperature and ionic strength, of which this study utilizes pure H<sub>2</sub>O rather than the experimental 2M potassium carbonate in aqueous solution. Nonetheless there are two patterns to recognize from the data.

Firstly, the first intermediate [Ir] where the  $\pi$  effects from the picolinamide are strongly interacting with the Ir. This is a result of the optimization having only a 16e<sup>-</sup> from  $\sigma$ -bonds, rather than the optimal 18e<sup>-</sup> valency. The Ir center is therefore interacting strongly with the lone pair of the amide functional group. The hydroxyl group breaks  $\pi$  conjugation and appears to affect the energy most. The vinyl functional group maintains the symmetry of the p orbitals however the lack of an oxygen causes its energy to increase relative to the control.

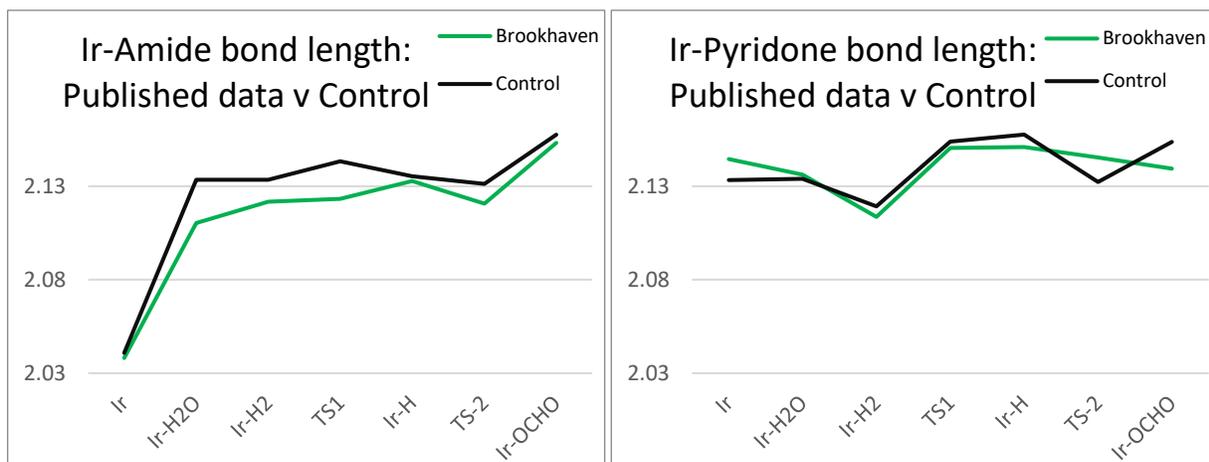
Secondly the optimizations after [Ir-H<sub>2</sub>O] where the catalyst has a greater number of  $\sigma$ -bonds and formally has an 18 e<sup>-</sup> valency. There is a correlation, when Ir has more electron density around it the hydroxyl point modification is lower in energy than the vinyl. This could indicate that electron induction is important when molecules from solution coordinate to the catalyst.

The vinyl functional group maintains the symmetry of the p orbitals however the lack of an oxygen causes its energy to increase relative to the control, but this intermediate is still downhill from the subsequent step. We can infer that means maintaining the resonance stability of the picolinamide is more important for the structure of the intermediate

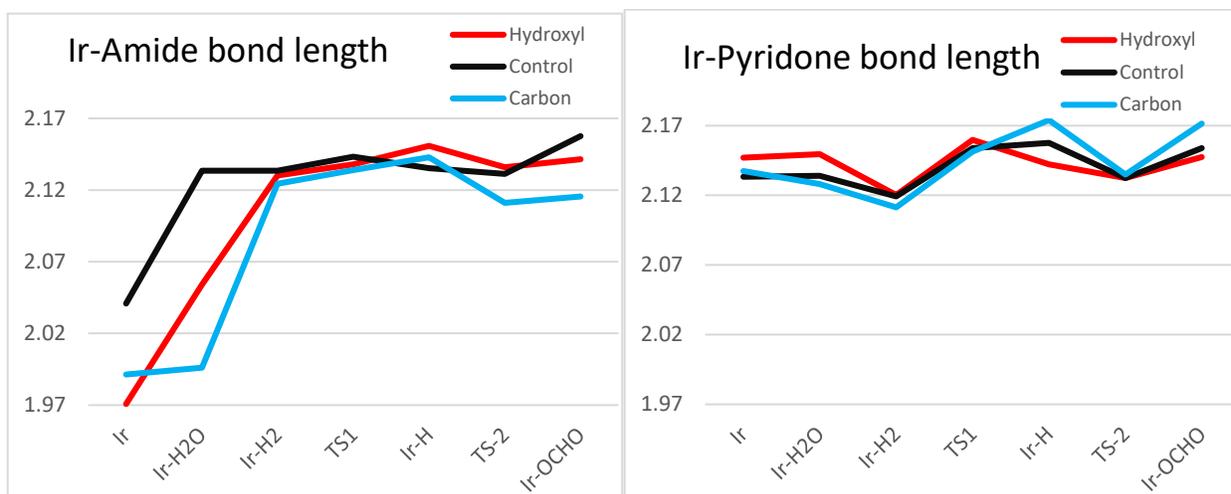
than just the presence of the strongly electronegative oxygen. The second pattern is found in the optimizations after [Ir-H<sub>2</sub>O] where the catalyst has a greater number of  $\sigma$ -bonds. While the Ir has more electron density around it the hydroxyl point modification is lower in energy than the vinyl, but only slightly (<2 kcal/mol)

#### Bond Lengths:

Metal complex bond lengths were observed to extrapolate bonding patterns between the iridium and its ligands. Sigma ( $\sigma$ ) bonding, and pi ( $\pi$ ) effects are prevalent interactions within the organometallic complex. Depending on the presence of ligands the amide functional group will vary in its  $\pi$  effects.



**Graph 1 and 2:** Comparison of nitrogenous ligands. The amide shows a greater magnitude of change that occurs depending on what is ligated to the iridium. The pyridone ligand shows greater consistency in its bond length, which indicates there could be greater consistency with its  $\pi$  donation.



**Graph 3 and 4:** Comparisons of control and point modification bond lengths. The amide shows significant differences to the point modifications likely due to changes in the ligands  $\pi$  donation.

The iridium-amide bond length goes through the largest magnitude of change. It is shortest when there are no ligands other than the picolinamide and cyclopentadienyl. One explanation is the  $\pi$ -base effects become greater as the amide donates electrons to satisfy the 18  $e^-$  valency of the iridium center when no other species are available. When the iridium is coordinated with solvent molecules the  $e^-$  density provided by the amide is reduced and the bond length increases dramatically.

The point modifications result in similar bond length patterns when compared to each other. With respect to the amide ligand on optimizations of [Ir]; when the bond length is shorter, the optimization is higher in energy. The differences can likely be attributed to strong  $e^-$  donation by the nitrogen of the functional group. This occurs when the Ir<sup>3+</sup> is electron deficient and not meeting its 18  $e^-$  valency.

In the case of the carbonous substitution it is possible that weaker  $e^-$  induction on the  $\pi$  system results in the bond length being shorter. In the case of the hydroxyl substituted catalyst, the restriction on  $\pi$  system conjugation results in a similar outcome in that it results in an even higher electron density on the nitrogen than the vinyl substitution. Too great of an  $e^-$  density, and therefore a shorter bond length, appears to correlate to a less stable complex.

Both point modifications effect the energetics, a clear comparison can be seen in relation with [Ir] optimizations, where the  $\pi$  effects of the picolinamide are interacting strongest with the metal center. The shorter the bond length between the nitrogen and Ir, the higher in energy, the hydroxyl substitution being highest. This could be a result of stronger  $\pi$  interactions caused by changes in electron density on the nitrogen.

## **Conclusion**

Overall, the point modifications do not create favorable conditions for the catalysis of dihydrogen heterolysis and carbon dioxide reduction. This can be attributed to the changes in  $\pi$  conjugation and the inductive character of the oxygen. Affecting electronic qualities of ligands dramatically changes energetics of a catalytic pathway, in this case the energy barrier increased due to disruptions in the  $\pi$  system and a lower electron induction effect. Both effect the energetics and bond lengths of the active and inactive catalyst. A conjugated  $\pi$  system is favorable for the lowest energy geometry of the catalyst [Ir] with one unoccupied  $\sigma$ -bond. Electron induction by the oxygen on the amide ligand appears to be important to the geometries with fully occupied  $\sigma$ -bonds. Further  $e^-$  population analysis through visualization or natural bond orbital analysis will provide insight as to how the catalyst functions. Other point modifications can be made to better understand the effects of electronegativity and  $\pi$  conjugation such as replacing the oxygen with sulfur or nitrogen to represent different electronegativities and effects on the  $\pi$ -system.

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