

Iridium Complexes of Quinone-Based Phosphine Ligands

Sachin S. Thackeray, Miles Wilklow-Marnell

Abstract

This project was focused on the synthesis of iridium complexes containing Quinone-based phosphine ligands under dry and inert conditions. Iridium complexes with pincer-type ligands have been shown to serve as efficient catalysts in alkane dehydrogenation. However, to regenerate these compounds to their original states and maintain catalytic activity, a sacrificial hydrogen acceptor must be used which is costly and creates unnecessary by-products. Quinones may serve as a counter-balance to this inefficiency by acting as a catalytic hydrogen acceptor. Quinones may rapidly transition between their dehydrogenated and hydrogenated states through electron/proton transfers which may be driven electrochemically. The initial aim of this research was to produce iridium complexes bonded to a Quinone base in a pincer/tridentate framework. Two Quinone-based phosphine ligands (PCAQ and POAQ) were synthesized prior to being reacted with iridium-based catalysts. Synthesis reactions between Quinone-based ligands and iridium-based catalysts yielded a compound, which upon further investigation using ^{31}P -NMR and ^1H -NMR spectroscopy revealed a bidentate complex which was stabilized with a CO molecule. Further work is needed to characterize the compounds using X-ray crystallography and to compare the complexes to other iridium catalysts in efficiency of catalytic reactions.

Keywords: biology, chemistry, organometallic chemistry, iridium, metal complexes, air-free chemistry, inorganic chemistry, transition metals, catalytic reactions, Quinones

Introduction

The dehydrogenation of alkanes is a process that results in an alkene by the removal of two hydrogen atoms. This forms a double bond, making the product much more versatile synthetically, and is of great importance to industrial/pharmaceutical chemistry¹. Iridium-pincer complexes are complexes that contain a ligand bound to an iridium atom in a tridentate framework. These complexes are known to be catalysts for dehydrogenation reactions of alkanes, but pose a challenge in that they are highly selective and require a sacrificial hydrogen acceptor for the pincer complex to return to its original state after dehydrogenation of the alkane. This is due to the highly endothermic nature of dehydrogenation without acceptors. This process creates a 1:1 stoichiometric waste product making the catalyst unproductive. **Figure 1** shows the catalytic dehydrogenation of alkanes using a general pincer-iridium complex with *tert*-butylethylene as hydrogen acceptor.

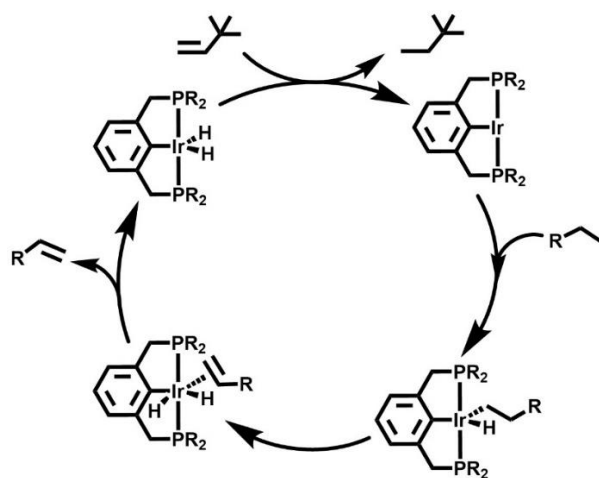


Figure 1. Catalytic cycle of alkane dehydrogenation with a pincer iridium complex

¹ Geldmacher, Yvonne, Melanie Oleszak, and William S. Sheldrick. 2012. "Rhodium(III) and Iridium(III) Complexes as Anticancer Agents." *Inorganica Chimica Acta* 393: 84–102. doi:10.1016/j.ica.2012.06.046.

Quinones are a class of organic compounds commonly found in biological systems. Quinones act as natural catalysts that easily hydrogenate and dehydrogenate to alternate between their two states by the exchange of 2 electrons and 2 protons, which is utilized in biological energy transport systems. This property may possibly be used to improve the efficiency of a pincer complex's dehydrogenation process by acting as a catalytic hydrogen acceptor. **Figure 2** shows the electron/proton exchange between benzoquinone (dehydrogenated) and hydroquinone (hydrogenated) which are the simplest Quinone structures.

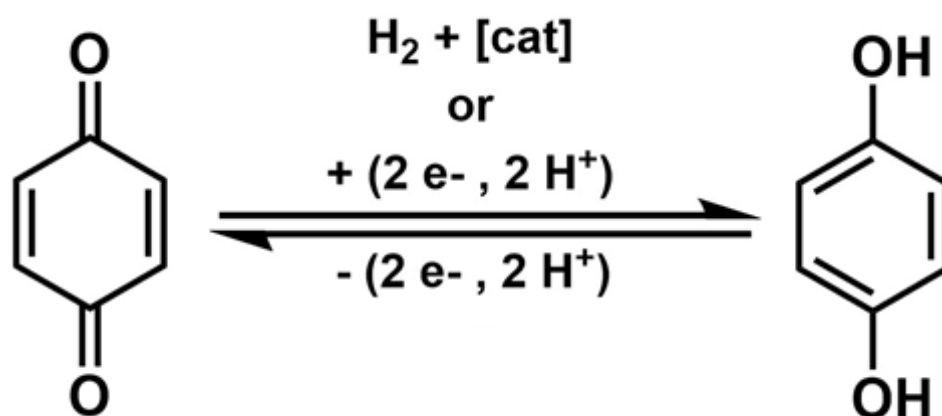


Figure 2. Transition of Quinone to hydroquinone with an exchange of protons and electrons.

Previous work by Dr. Wilklow-Marnell² on the uses of pincer-iridium complexes for alcohol dehydrogenation using the addition of extraneous Quinones showed that this system could undergo two cycles of alcohol dehydrogenation driven

²Wilklow-Marnell, Miles, William W. Brennessel, and William D. Jones. 2018. "Reactivity of iPrPCPIrH₄ with Para-BenzoQuinones." *Polyhedron* 143: 209–214. doi:10.1016/j.poly.2017.10.026.

electrochemically. This poor performance can be partially attributed to the inhibitory nature of the catalyst by strong Quinone coordination.

It was theorized that inclusion of a Quinone moiety into the ligand itself could minimize or prevent this inhibition, while possibly maintaining the catalytic activity of both the iridium and Quinone portions. Towards this end, the phosphine ligands “PCAQ” (Figure 3) and “POAQ” (Figure 4) were synthesized from commercially available materials as shown in Figure 5. The expectation was to then metallate these phosphine ligands by reacting them with an iridium catalyst, $[\text{Ir}(\text{COD})\text{Cl}]_2$ (Figure 6) and toluene to create a metallation product (Figure 7) with the process being described in Figure 8. The key difference being in the presence of a C or O in the “arm” of the compound. This difference is two-fold. First, carbon is larger than oxygen which allows phosphorous to be closer to the iridium for the molecule with the PCAQ ligand which allows for different characteristics for the iridium complex. Second, oxygen being more electronegative than carbon results in different binding properties for these compounds.

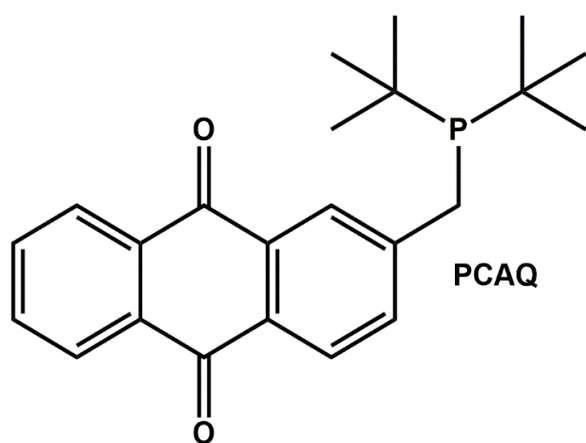


Figure 3. Diagram of a PCAQ molecule

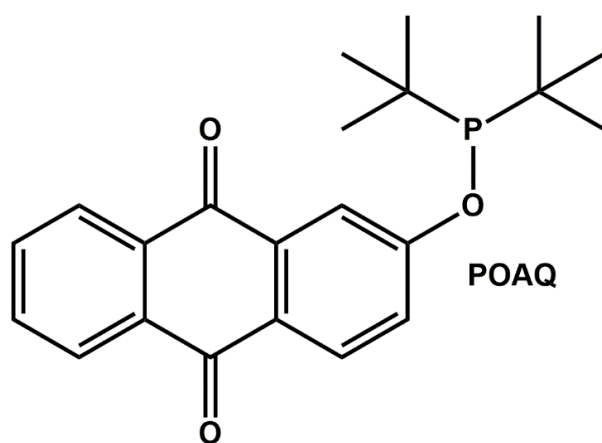


Figure 4. Diagram of a POAQ molecule

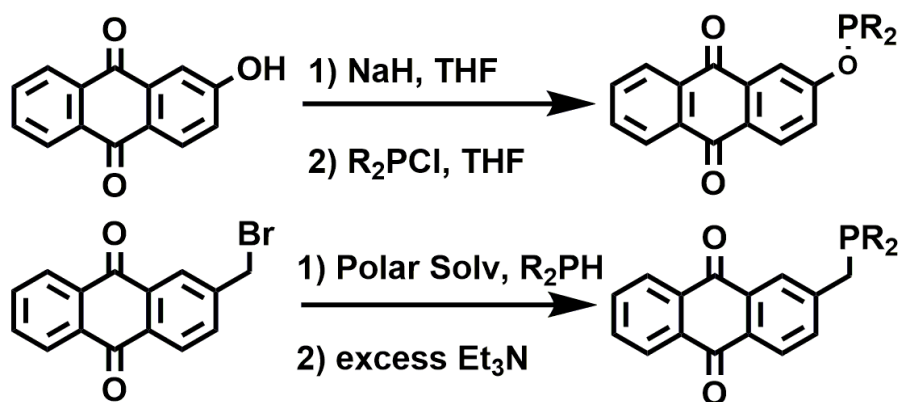


Figure 5. The generalized reactions to produce POAQ (top) and PCAQ (bottom).

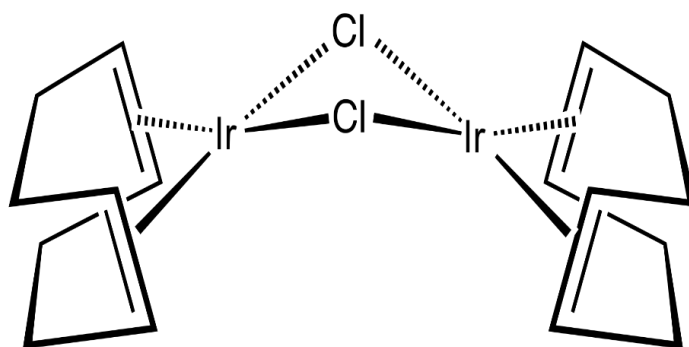
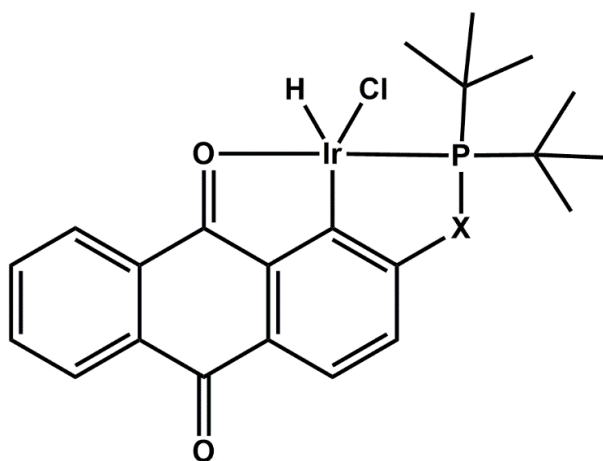


Figure 6. Diagram of a [Ir(COD)Cl]₂ molecule: an iridium precursor



Intended PXAQ IrMetallation Product

Figure 7. Expected tridentate pincer iridium complex with a possible C or O at the site of the "X" on the arm based on starting ligand.

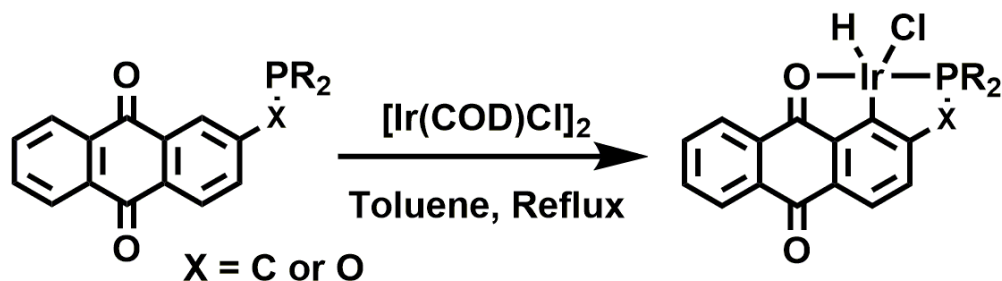


Figure 8. Reaction of phosphine ligands with iridium catalysts and toluene to create a metallation product.

In theory, if a Quinone were incorporated into the ligand of a pincer iridium complex, it could be equipped for efficient dehydrogenation capabilities without the necessity of a sacrificial acceptor providing a greater atom economy than a standard iridium pincer complex. As envisioned, the iridium could remove H_2 from the substrate, which could then be passed to the Quinone portion of the molecule, and the active catalyst regenerated by electrochemical oxidation of the Quinone. Furthermore, the electrochemically removed electron/proton may be recombined to generate H_2 gas, a valuable resource. Multiple mechanisms are possible for creating H_2 gas with one such mechanism shown in [Figure 9](#). In this mechanism, the iridium oscillates between a +1 oxidation state and a +3 oxidation state as it undergoes the alkane dehydrogenation. This is analogous to the alkane dehydrogenation for PCP-Ir complexes. Furthermore, this binding motif is expected to be successful because of previous results³ with a very similar POCO-type pincer iridium complex, as shown in [Figure 10](#).

³ Wilklow-Marnell, Miles, and William W. Brennessel. 2019. "A POCO Type Pincer Complex of Iridium: Synthesis, Characterization, and Catalysis." *Polyhedron* 160: 83–91. doi:10.1016/j.poly.2018.12.001

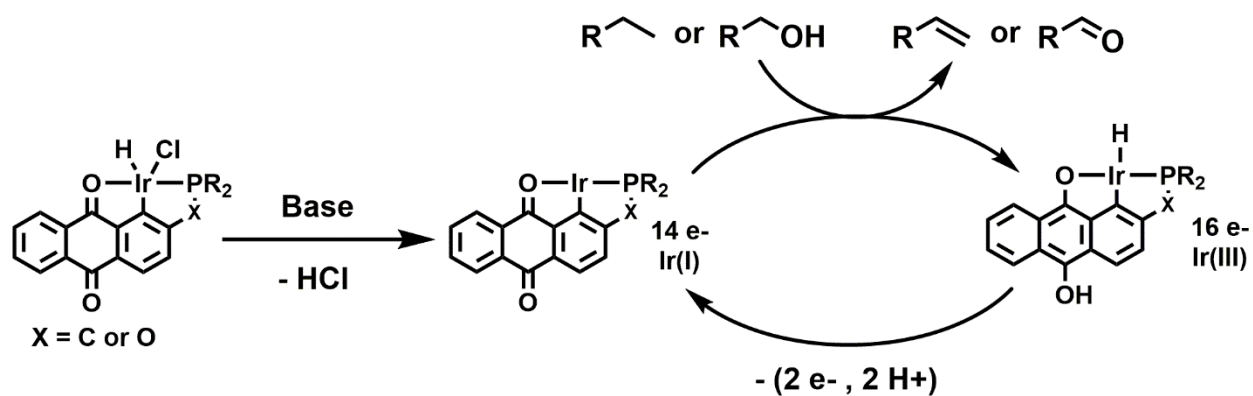


Figure 9. Schematic showing the formation of a pincer iridium complex capable of dehydrogenating alkanes into alkenes with Quinones as a co-catalytic hydrogen acceptor.

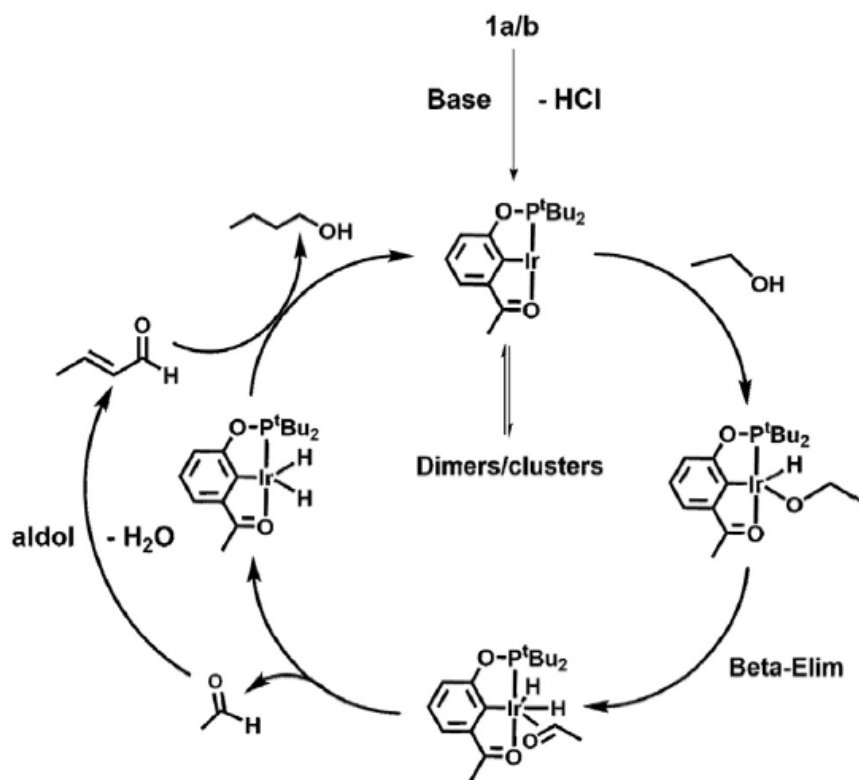
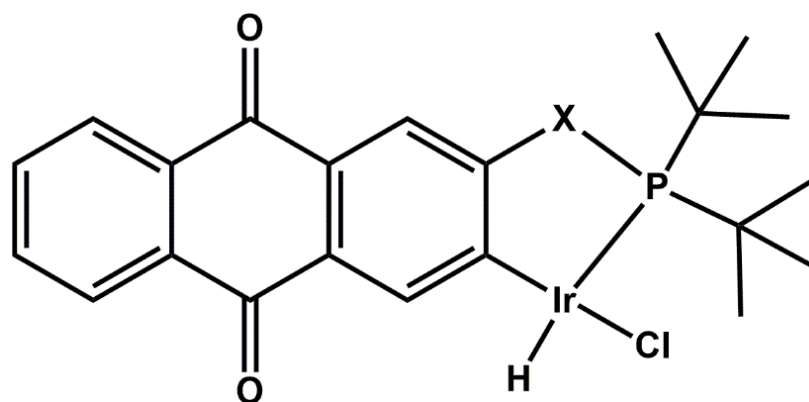


Figure 10. POCO complex undergoing hydrogenation reaction from iridium catalysis

The initial plan was to create a tridentate complex with iridium as shown in **Figure 7**, but later characterization revealed the product to be a bidentate complex, as proposed in **Figure 11**. The bidentate complexes formed were found to be fluxional and conformationally unstable in solution and addition of CO was found to stabilize the compounds providing cleaner NMR characterization.



Room Temperature Metallation Product

Figure 11. Hypothesized structure of the generalized bidentate structure synthesized with the reaction between $[\text{Ir}(\text{COD})\text{Cl}]_2$ and PCOQ/PCAQ.

Experimental

Synthesizing metal complexes using PCAQ with toluene and heat

Under inert conditions within a glovebox, 100 mg of PCAQ were reacted with a stoichiometric equivalent of 0.910 grams of Bis(1,5-cyclooctadiene)diiridium(I) dichloride $[\text{Ir}(\text{COD})\text{Cl}_2]$ with approximately 19 mL of toluene. The resulting solution was refluxed in a condenser flask. This condenser flask had an inlet for argon gas and an outlet for gas to an oil bubbler. After two days of boiling, the resulting solution

consisted of a dark brown-red liquid with orange solid precipitation at the bottom. After measuring the container, it was found to contain 0.6777 grams of solid after vacuuming away volatiles.

A small sample of the solution was taken and added to a J-young NMR tube after which the tube was brought to the Schlenk line and CDCl_3 was vacuum transferred into the tube for a ^{31}P and ^1H NMR spectroscopy.

Synthesizing metal complexes using PCAQ with tetrahydrofuran (THF)

Under inert conditions within a glovebox, 0.016 g of PCAQ and 0.016 g of $[\text{Ir}(\text{COD})\text{Cl}]_2$ were dissolved. Then, 0.75 mL of THF were added to this mixture of PCAQ and $[\text{Ir}(\text{COD})\text{Cl}]_2$ and the solution was transferred to a J-young NMR tube for further characterization.

A larger scale reaction was conducted later with 100.0 mg of PCAQ and 100.0 mg of $[\text{Ir}(\text{COD})\text{Cl}]_2$. Then, 0.75 mL of THF was added until the PCAQ and $[\text{Ir}(\text{COD})\text{Cl}]_2$ were dissolved and the solution was left to be stirred for the entirety of the day. The next day, the solution was removed from the glovebox to be brought to the Schlenk line where it was attached to the vacuum line and stirred with a flask of lukewarm water under the flask to promote the evaporation of THF into the vacuum line. After the vacuum gauge dropped to 50 mTorr and the pressure was maintained consistently, the water was replaced with a warmer flask of water to evaporate any remnants of cyclooctadiene (COD). New THF was added to the solution using vacuum transfer techniques and solution was brought to the glovebox and had CHCl_3 added

to it after the THF was pumped out using a vacuum. Green crystals were noted and additional CHCl_3 was added which created more crystals which were characterized with NMR.

Synthesizing metal complexes using POAQ with tetrahydrofuran (THF)

Under inert conditions within a glovebox, 0.105 grams of POAQ were mixed in with THF until full dissolution. Similarly, 0.105 grams of $[\text{Ir}(\text{COD})\text{Cl}]_2$ were mixed in with THF until full dissolution. The two solutions were mixed together to create a dark red/maroon transparent liquid. The solution changed from the dark liquid to a dull orange-brown liquid within minutes with precipitates in the solution. The POAQ solution was filtered and resulted in a golden solid on the top of the micro filter and the bottom of the filter contained a dark red liquid similar to the initial condition of the solution. NMR spectroscopy was performed to characterize the solids and liquids from the solution. The THF was pumped out from the yellow precipitate and CDCl_3 was added by vacuum transfer. One atmosphere carbon monoxide (CO) was added to the NMR tube and the resultant solution was characterized with a ^{31}P -NMR and a ^1H -NMR. After adding CO to the NMR tube, there was a notable color change with the solution going from orange to light yellow.

On a larger scale, the remaining POAQ ligand was used (0.1635 grams) with a stoichiometric equivalent of 0.1579 grams of $[\text{Ir}(\text{COD})\text{Cl}]_2$ both being independently dissolved in THF prior to being dissolved together in solution. Precipitation of brown solids was noted as in previous reaction and a filtration of the solution was done to the solids and liquids. THF and COD were pumped out from the solution and the

solution was transferred into a round-bottom flask. The POAQ solid filtrate was dissolved with CHCl_3 and was filtered through a glass wool filter to remove waste product from the solution. One atmosphere CO was added in the container for further ^{31}P -NMR and ^1H -NMR characterization. The POAQ liquid was brought to the glovebox for transfer into a larger container for further addition of CO into container.

Results and Discussion

The experiment was set out to synthesize a pincer iridium complex with the expectation of a tridentate iridium framework as a product as shown in [Figure 6](#). However, upon further examination of the ^{31}P -NMR and ^1H -NMR from the reaction of $[\text{Ir}(\text{COD})\text{Cl}]_2$ and POAQ and PCAQ ligands, a bidentate complex is likely the result. The NMR spectra showed unclear peaks or peak broadening which remained until CO was added to the solution. The bidentate complex formed have 4 out of the 6 possible coordination site occupied. A complex with iridium in +3 oxidization state is most stable in a square pyramidal or octahedral geometry with 5 or 6 occupied sites, respectively. In order to attain this state, it is believed that the bidentate complexes participate in rapid equilibrium reactions between itself (dimerization), clusters (oligomers), and/or the solvent. This rapid changing of the complex results in the aforementioned peak broadening. Furthermore, it is also possible that the complex is paramagnetic in the geometry it has as a bidentate molecule before the addition of the CO. This was further established by the emergent stability of the compound after the addition of the CO to the NMR sample. Two NMR samples were taken of the Ir+POAQ exposed to 1 atmosphere of CO and dissolved in CDCl_3 . The first ^{31}P -NMR

sample (Figure 13) shows two major peaks close to one another at approximately 165 and 170 ppm with the peak at 165 ppm being greater in amplitude than the peak at 170 ppm. The second ^{31}P -NMR sample (Figure 14) taken 3 hours after the first shows the same two peaks, but with the 170 ppm peak being greater than the one at 165 ppm. It is hypothesized that these peaks are the result of two isomers of the proposed metallated bidentate product with the difference having to do with the arrangement of the atoms bound to the iridium. The changes between the two NMR solutions point to one isomer transforming into the other due to thermodynamic favorability of the isomer indicated at 170 ppm. This explanation is further evidenced by looking at the ^1H -NMR of these samples (Figure 14) which show two relevant peaks at approximately -8.5 ppm and -16 ppm which represents the Ir-H bond. On the first NMR, the more prominent isomer (at -8.5 ppm) has its proton less magnetically shielded. This paradigm changes for the second ^1H -NMR which points to the more prominent isomer having its proton be more magnetically shielded. These changes can be explained by understanding the properties of the molecule trans to the proton in question and its effects on the proton. The more deshielded environment of the more prominent proton on the first NMR may be due to the π basic ligand, Cl, which donates electron density to the Ir from the proton thus pushing it farther away from the iridium and deshielding it in the process. The second NMR presents with the more prominent isomer being trans to a CO atom which is a π acidic ligand and withdraws electron density from the Ir to the proton and in the process pulling it closer to the adjacent iridium atom and shielding it. Analogous transformations were

observed in the NMR spectra of PCAQIr treated with 1 atmospheric CO. Also, previously grown crystals were obtained from a single sample of PCAQIr + 1 atmosphere CO that confirmed a bidentate structure by X-ray crystallography, as shown in **Figure 16**. The mother liquor of this sample provided the same $^{31}\text{P}/^1\text{H}$ signals as seen by the samples worked on in this project.

In conclusion, two Quinone-bearing phosphine ligands were synthesized and metallated using iridium cyclooctadiene. Attempts to form pincer complexes were inconclusive, but bidentate iridium complexes were formed readily at room temperature. Stable octahedral complexes were later obtained by the addition of one atmosphere of CO in the solution and complete characterization of these resultant reactions via X-ray crystallography is forthcoming.

Further research can be conducted in the future on replicating the reactions on a larger scale and crystallizing to obtain samples for X-ray crystallography characterization, as well as comparing the reaction rates of these iridium complexes with Quinone-based phosphine ligands to other iridium complexes such as the Crabtree's catalyst or PCPIr⁴, POCOIr⁵. Furthermore, research can also be conducted in following up with the tridentate framework of the iridium complexes by using different reaction conditions and characterizing the resulting compounds.

⁴ Wilklow-Marnell, Miles, William W. Brennessel, and William D. Jones. 2018. "Reactivity of iPrPCPIrH₄ with Para-BenzoQuinones." *Polyhedron*143: 209–214. doi:10.1016/j.poly.2017.10.026.

⁵ Wilklow-Marnell, Miles, and William W. Brennessel. 2019. "A POCO Type Pincer Complex of Iridium: Synthesis, Characterization, and Catalysis." *Polyhedron*160: 83–91. doi:10.1016/j.poly.2018.12.001

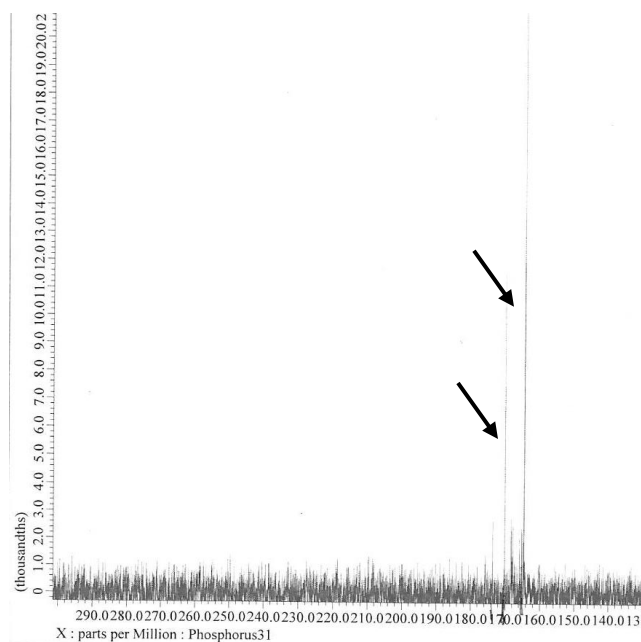


Figure 13. ^{31}P -NMR of the POAQ reaction with the $[\text{Ir}(\text{COD})\text{Cl}]_2$ after addition of CO in CDCl_3 with arrows indicating prominent peaks.

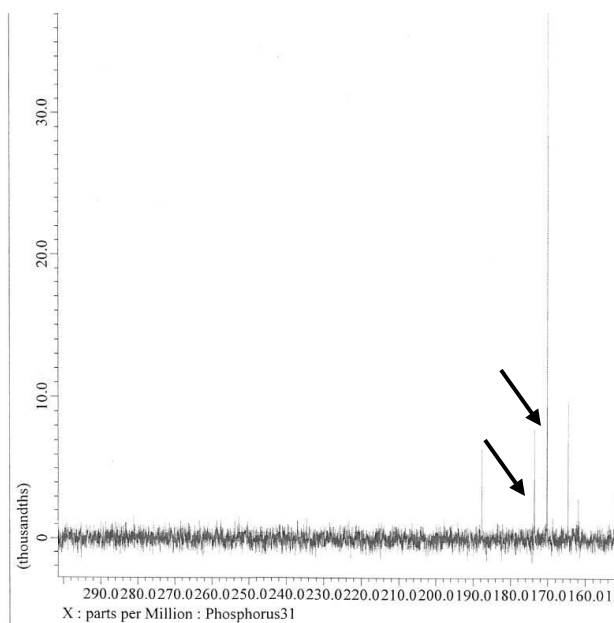


Figure 14. ^{31}P -NMR of the POAQ reaction with the $[\text{Ir}(\text{COD})\text{Cl}]_2$ after addition of CO in CDCl_3 after waiting a few hours with arrows indicating prominent peaks.

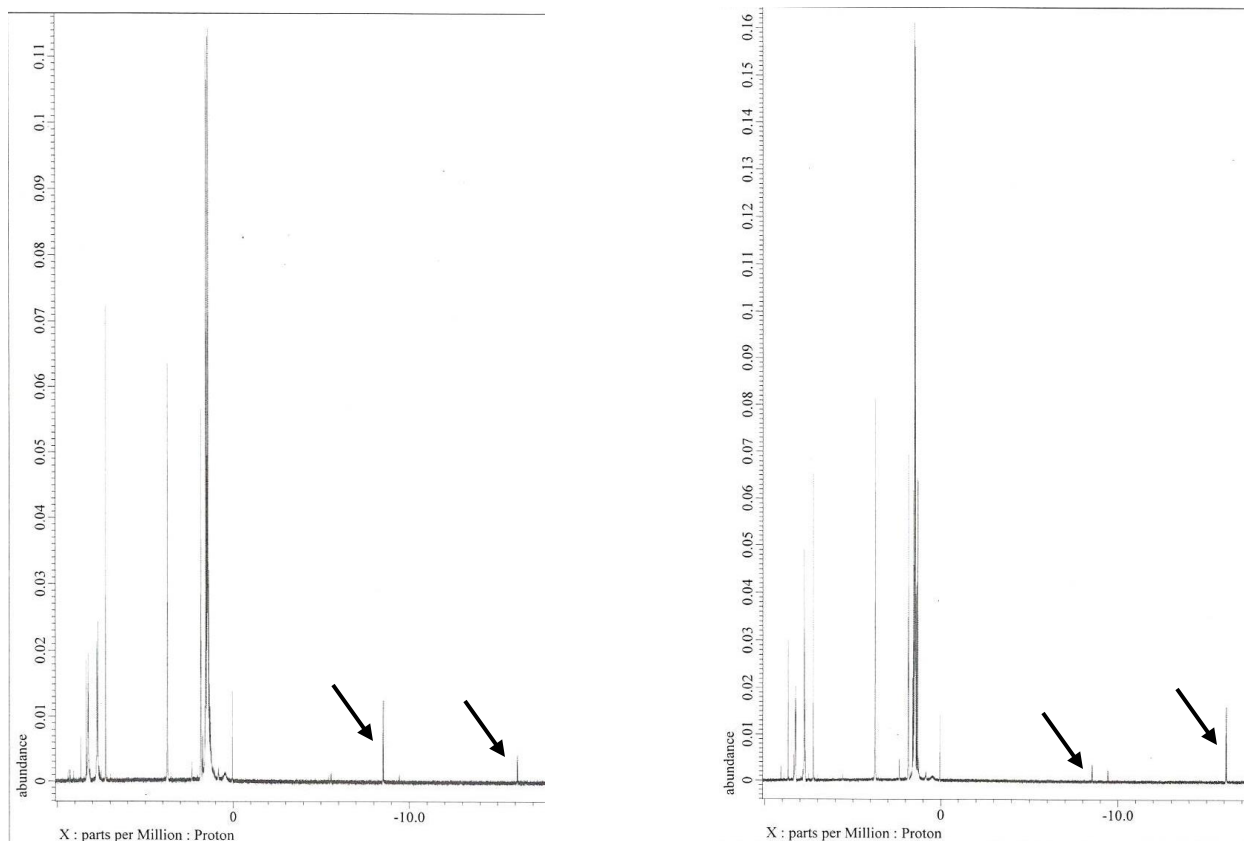


Figure 15. Comparison of the ^1H -NMR of the PCOQ iridium complex over time with arrows indicating change of peaks.

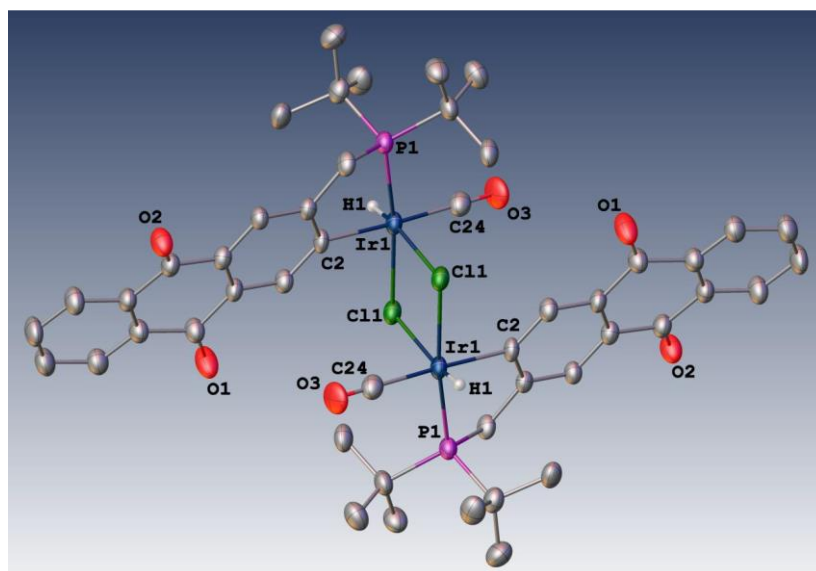


Figure 16. X-ray crystallography of a bidentate iridium structure- $^t\text{BuPCAQIrHClCO}$