

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Lauren Farrell
FACULTY ADVISOR:	Dr. Seth N. Brown
PROJECT PERIOD:	June 2023 – July 2023
PROJECT TITLE:	Exploring the Reactivity of Nucleophilic Iridium Complex with Electrophilic Carbon Compounds
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETE
Study kinetics of iridium complex with different alkyl halides	Kinetics of butyl chloride, butyl iodide, and butyl bromide studied and compared; appears to follow trends with known alkyl S _N 2 reaction rates.	80%
Study kinetics of iridium complex with different benzyl halides	NMR of benzyl chloride reaction shows the expected S _N 2 reaction product, however rate of reaction does not appear to follow known S _N 2 reaction rates between butyl and benzyl compounds; did not determine rate constants for any of the benzyl halides and have not figured out what is causing this discrepancy.	30%
Study the reactivity of the iridium complex with carbon dioxide	The [CoCp ₂] ⁺ [(Diso) ₂ Ir] ⁻ anion does not readily react with carbon dioxide; did not try using co-activators or heating the reaction yet.	40%
Gain access to the proposed catalytic cycle	Only one step of the proposed cycle has been completed and have not accessed any of the other intermediates.	3%
Successfully make the [(Diso) ₂ Ir] ⁻ anion	Successfully synthesized the anion by the reduction of the neutral with sodium naphthalenide.	100%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium poster presentation, "Exploring the Reactivity of Nucleophilic Iridium Complex with Electrophilic Carbon Compounds", 07/26/23, University of Notre Dame
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	
INTERNAL COLLABORATIONS FOSTERED	
EXTERNAL COLLABORATIONS FOSTERED	
WEBSITE(S) FEATURING RESEARCH PROJECT	

OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

My research experience definitely met my expectations. Everyone in my lab was super helpful and supportive. I was able to learn so much, including numerous lab skills and techniques, but also more about problem solving and how the lab environment works.

FINAL WRITTEN REPORT

One method that could potentially produce fuels from carbon dioxide is anchoring it to a metal, which would allow it to be reduced to methanol or another functional fuel. It has been noted previously that the bis(iminoxolene)iridium complex $[(\text{Diso})_2\text{Ir}]^-$ (Diso = *N*-(2,6-diisopropylphenyl)-3,5-di-*tert*-butyl-*o*-iminobenzoquinone) forms strong bonds with carbon compounds and thus is an interesting complex to consider to hold on to carbon dioxide as it gets reduced to a fuel.

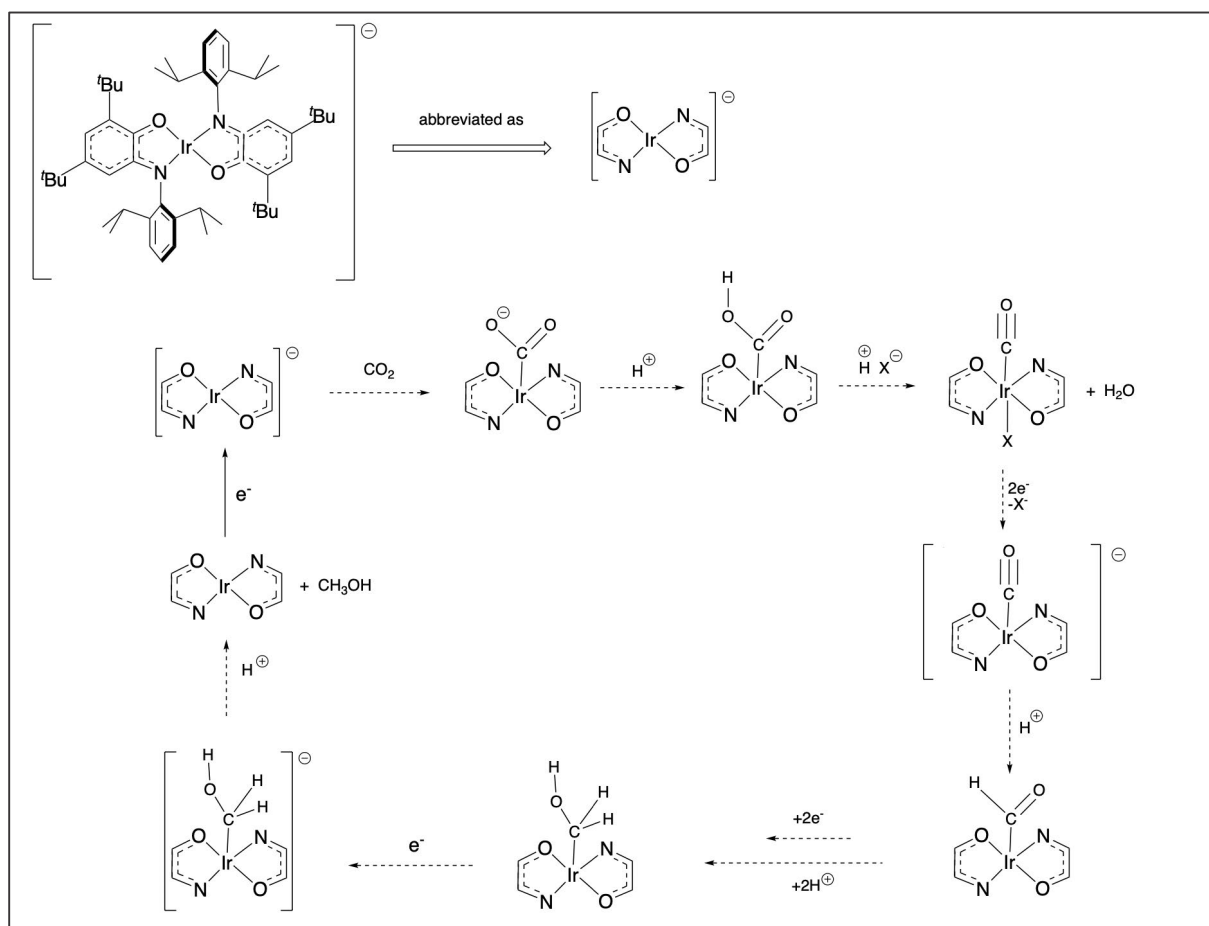


Figure 1. Proposed catalytic cycle with the $(\text{Diso})_2\text{Ir}$ anion holding onto carbon dioxide as it gets reduced to methanol.

In order to be able to actualize this with the bis(iminoxolene) iridium complex, its reactivity with electrophiles needs to be well understood. The iridium complex reacts with alkyl halides and benzyl halides, replacing the halide in a typical S_N2 fashion. It follows the expectations of an S_N2 mechanism in that it reacts the fastest with butyl iodide and slowest with butyl chloride—as the leaving group improves, the rate constant increases.

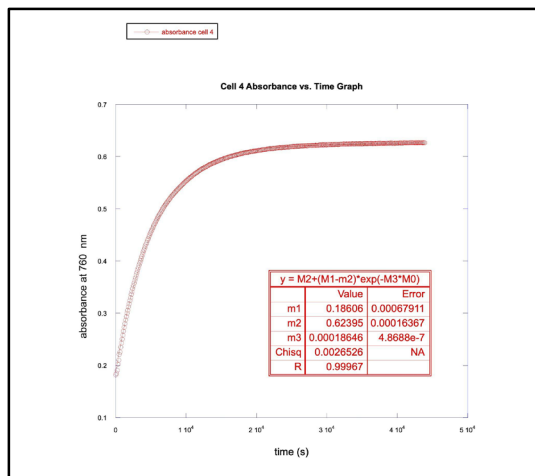


Figure 2. Absorbance versus time graph of the reaction of $\text{Na}[(\text{Diso})_2\text{Ir}]$ with 1-chlorobutane.

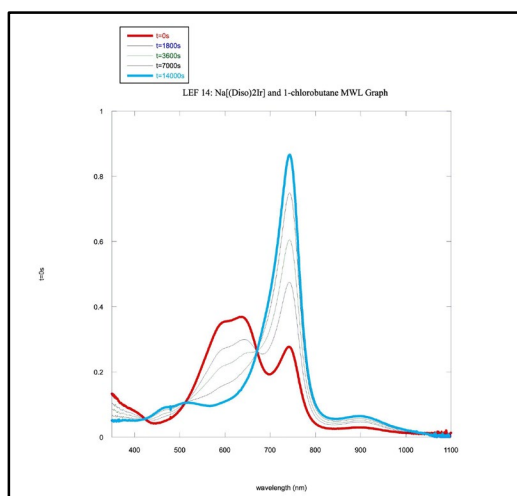


Figure 3. Multi-wavelength graph of the reaction of $\text{Na}[(\text{Diso})_2\text{Ir}]$ with 1-chlorobutane.

	k with $[(\text{Diso})_2\text{Ir}]^-$ ($\text{M}^{-1} \text{s}^{-1}$)	k_{rel}
1-chlorobutane	$2.74(11) \times 10^{-4}$	1
1-bromobutane	$3.9(3) \times 10^{-2}$	140
1-iodobutane	1.85(2)	6800

Table 1. Calculated rate constants for the reaction of $[(\text{Diso})_2\text{Ir}]^-$ with different alkyl halides; kinetic data for butyl iodide and butyl bromide provided by Peter D. Nguyen (Brown lab).

However, it appears that it reacts faster with butyl halides over benzyl halides, which is not observed in typical $\text{S}_{\text{N}}2$ reactions—benzyl halides typically react 10^5 times faster than butyl halides. This difference may be because of a change in mechanism or that the reactivity properties of this particular nucleophile are atypical; further study is required to determine what is causing this discrepancy.

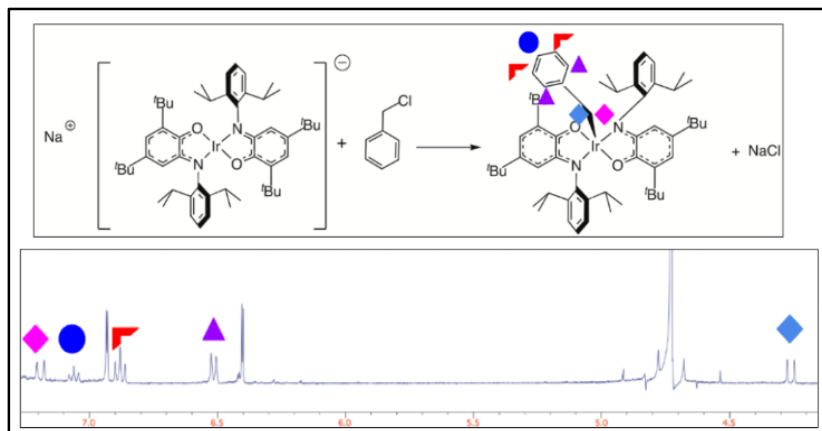


Figure 4. NMR spectra of the product formed by the reaction of $[(\text{Diso})_2\text{Ir}]^-$ with benzyl chloride; taken one week after the addition of benzyl chloride to anion.

	k with $[(\text{Diso})_2\text{Ir}]^-$ ($\text{M}^{-1} \text{s}^{-1}$)	k_{rel}
1-chlorobutane	$2.74(11) \times 10^{-4}$	1
benzyl chloride	$\sim 1 \times 10^{-4}$	~ 0.4

Table 2. Rate constants for the reaction of $[(\text{Diso})_2\text{Ir}]^-$ with 1-chlorobutane and benzyl chloride.

In contrast to alkyl electrophiles, the $[\text{CoCp}_2]^+ [(\text{Diso})_2\text{Ir}]^-$ anion does not react readily with carbon dioxide or carbon disulfide.

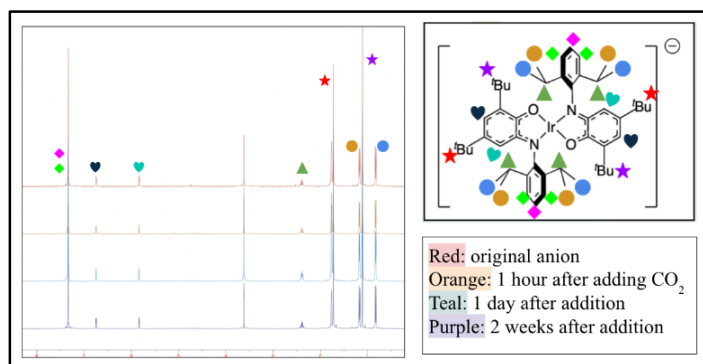


Figure 5. No reaction of the $[\text{CoCp}_2]^+ [(\text{Diso})_2\text{Ir}]^-$ anion with CO_2 after two weeks.

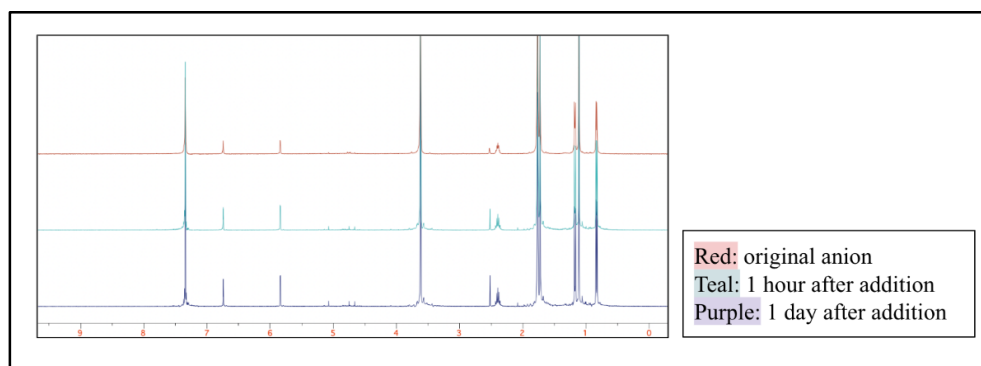


Figure 6. No reaction of the $[\text{CoCp}_2]^+ [(\text{Diso})_2\text{Ir}]^-$ anion with 6 equivalents of CS_2 added.

Future studies include using co-activators to facilitate the interaction of the iridium complex with carbon dioxide and trying to forge iridium-carbon bonds with other oxidation states of carbon.