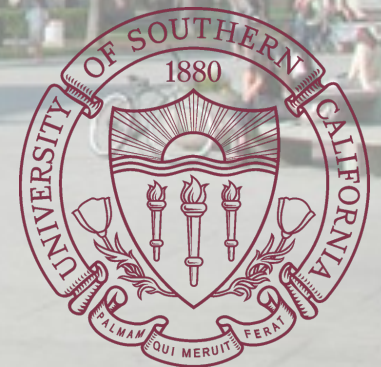


Hydrogen Release from Concentrated Media with Reusable Catalysts

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Project ID ST216



University of Southern California
Los Alamos National Laboratory



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Overview

- **Timeline**

- Project start date: 1 October 2019
(Funds received Feb 2020)
- Project end date: 30 September 2022

- **Budget**

- Total project budget: \$1,250,000
 - Total recipient share: \$250,000
 - Total federal share: \$1,000,000
 - FY19 funds received: \$0
 - FY20 funds planned: \$306,214

- **Barriers**

- Generate H₂ from formic acid
 - Increase reaction scale
 - Target: Continuous flow
 - Demonstrate H₂ throughput
 - Should show scalability to 300 kg/hr in principle
 - Remove CO₂ from output stream
 - ANSI target: 2 ppm
- Apply technology to blended fuels
- Understand molecular mechanism

- **Partners**

- University of Southern California (lead)
- Los Alamos National Laboratory

Relevance

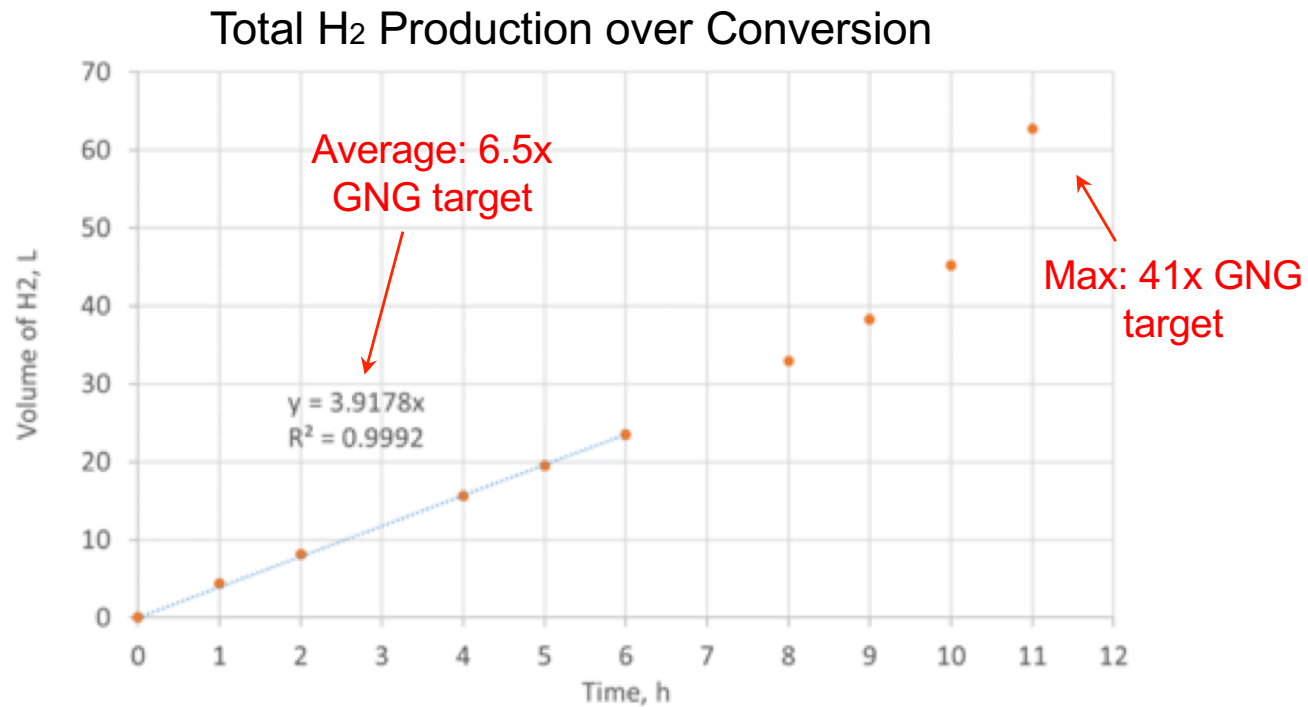
- **Project Objectives:** Demonstrate H₂ evolution from formic acid or a formic acid fuel blend, (2) using a demonstration-scale flow reactor, and (3) use mechanistic studies to optimize catalyst and fuel blend. The project began in February 2020, so we report here the first quarter's progress.
- **Hydrogen Evolution Status and Metrics**
 - Increase reaction scale
Outset: 5 mL batch Current: 100 mL batch Target: Continuous flow
Achieved 20x scaleup in Q1 of the project
 - Demonstrate H₂ throughput
Outset: 1.3 L/hr Current: 25 L/hr Target: scalable to 300 kg/hr
Achieved 20x flow increase in Q1 of the project, demonstrating linear scalability
 - Remove CO₂ from output stream (beginning in BP2)
Outset: 50% BP2 target: 400 ppm BP3 target: 2 ppm
- **Demonstration Reactor** design and construction are being led by the LANL team; work will begin summer 2020.
- **Mechanistic Studies** are underway between experimental work at USC and theoretical work at LANL.

While we can hit DOE targets with formic acid alone, mechanistic work can enable us to push beyond what's possible with formic acid by blending in other H₂ carriers

Approach

- **Research Strategy**
 - Scale and analyze the Williams Ir₂H₃ formic acid H₂ release system
 - Demonstrate the Ir₂H₃ system in a flow reactor; hit H₂ evolution metrics
 - Use mechanistic data on Ir₂H₃ system to enable blended fuels
 - Screen alternative catalysts to enable blended fuels or mixed catalyst systems
- **First GNG** (Feb 2021): Demonstrate generation of 600 mL H₂/hr with commensurate rate of 925 μL/hr or formic acid consumption and minimally 3.5 wt% H₂ release from the formic acid using < 250 ppm catalyst loading. Show a calculation of how this prototype-scale reactor can scale to the DOE target of 300 kg H₂/hr.
 - *We have exceeded this goal by a factor of 41x in flow rate at 4 wt% H₂ loading.*
 - *At our present peak flow rate, a batch reactor of 13,500 L (13.5 m³) volume should peak at the DOE target of 300 kg/min H₂ flow rate using 50 ppm catalyst loading at 100 °C.*
 - Hydrogen flow rate is a function of reaction conversion in batch (details follow), so we plan to show a demonstration scale flow reaction before submitting our procedure to PNNL for external validation in fall 2020.
- **Mechanistic Studies** are underway. These help us refine our blended fuels and mixed catalyst strategies. After exceeding our BP1 GNG point, we focused on rapid progress in this area (details follow). *We're doing this to enable a formic acid-methanol fuel blend, which will enable a big step up in H₂ density and flow rate.*

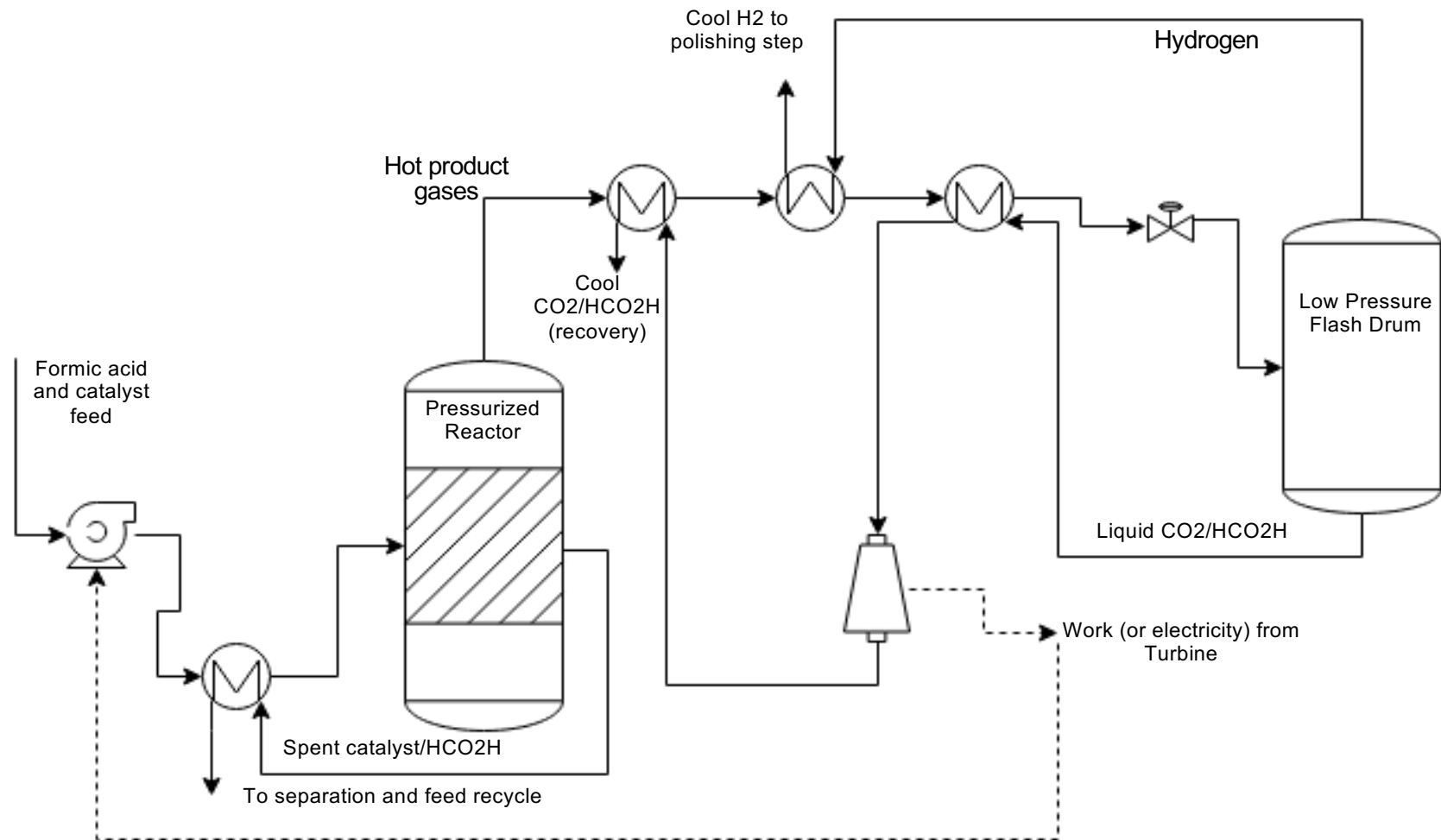
Accomplishment: Hydrogen Evolution



- **Hydrogen Evolution Metrics** for the reaction scaled to 100 mL are a function of reaction conversion. This is because the catalyst concentration increases (as does rate) as the solvent/fuel disappears into the gas phase.
 - **Average H₂ flow** at early conversion is **6.5x target** for our BP1 GNG
 - **Maximum H₂ flow** at late conversion is **> 40x target** for our BP1 GNG
- We will design a system to flow formic acid into this reactor and drive it at sustained late-conversion conditions to show sustainability high H₂ flow rate, then export this procedure for verification at PNNL (Tom Autry, Sam Johnson).

We can hit or BP1 GNG and have room to improve performance before reporting

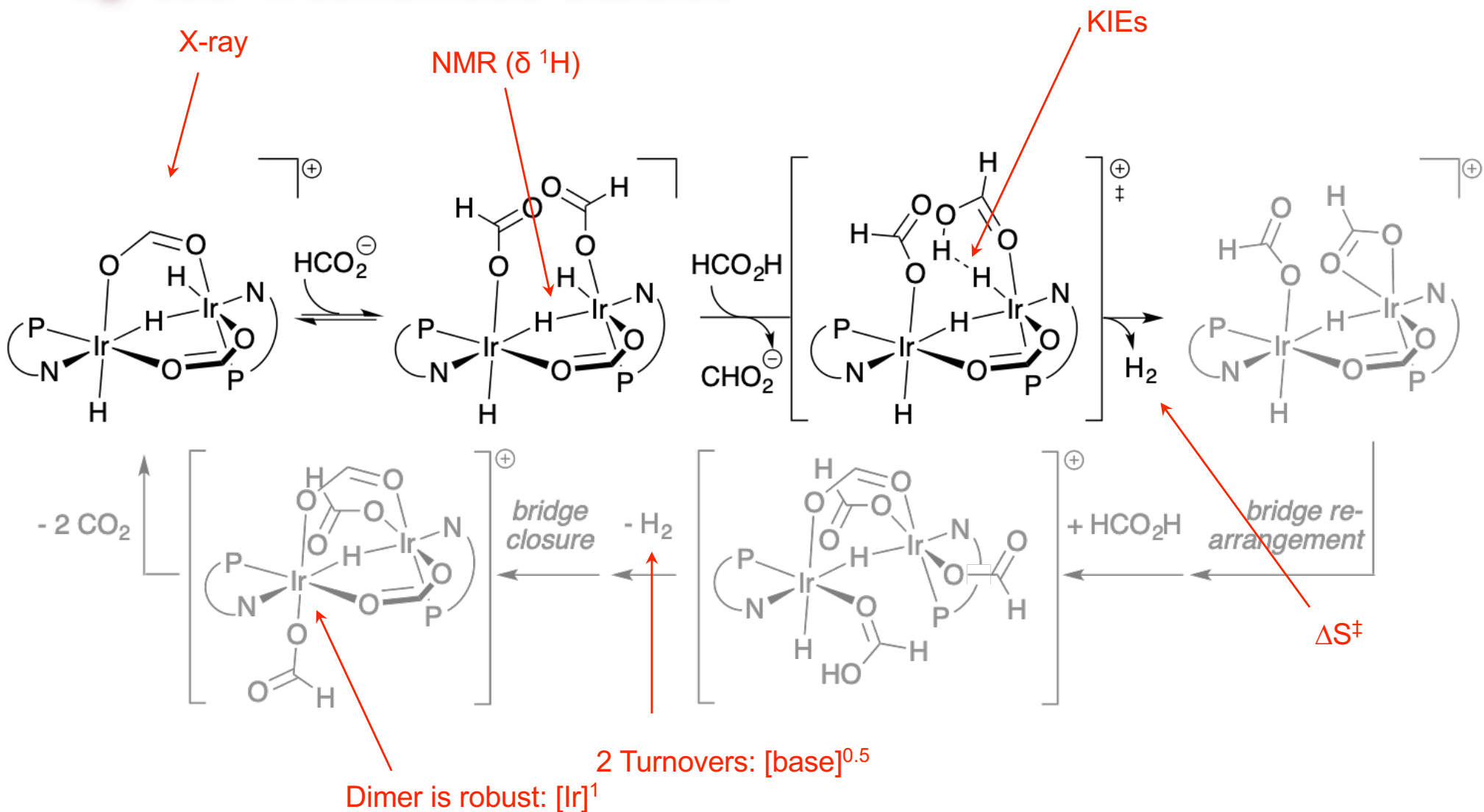
Progress: Demonstration Reactor



- **Demonstration Reactor** design and construction are being led by the LANL team; work will begin summer 2020. The current design layout is above.

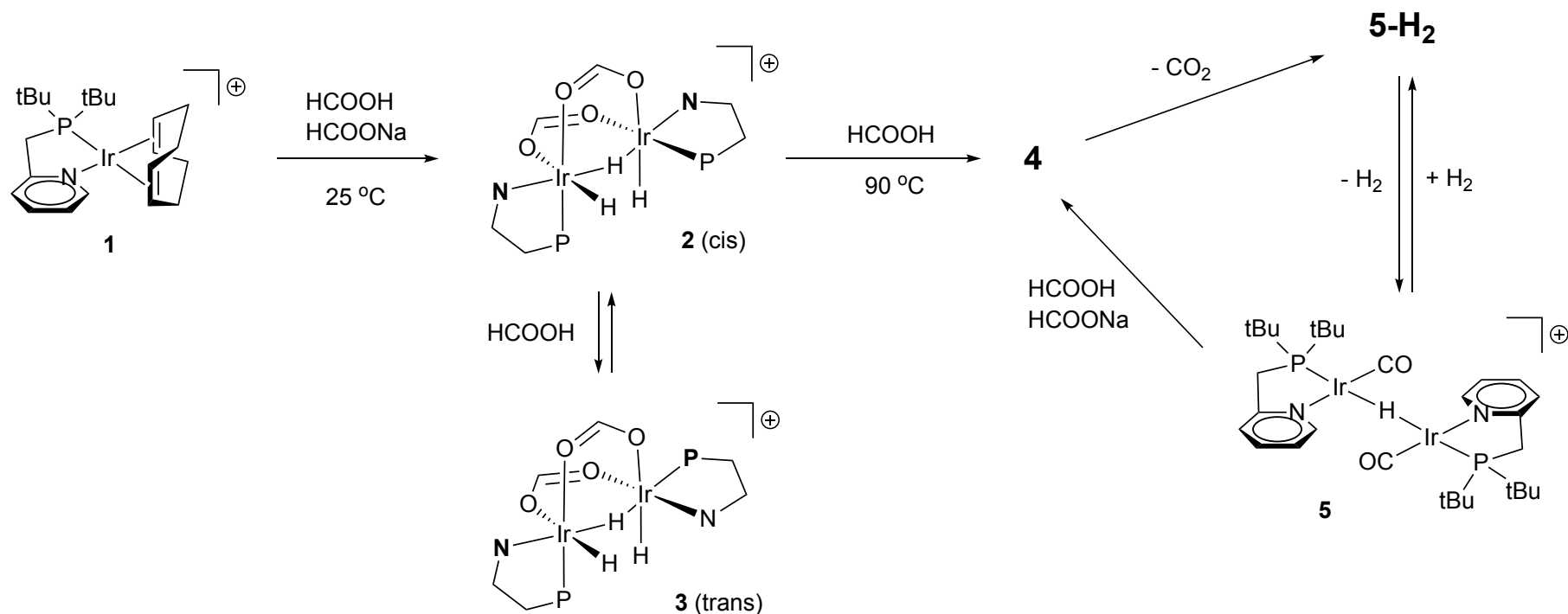
Although delayed by COVID, we've already started design work scheduled for this summer

Progress: Mechanistic Studies



- **Starting Point:** The original report of the Williams Ir_2H_3 included a mechanistic proposal that accounted for experimental data available at the time.

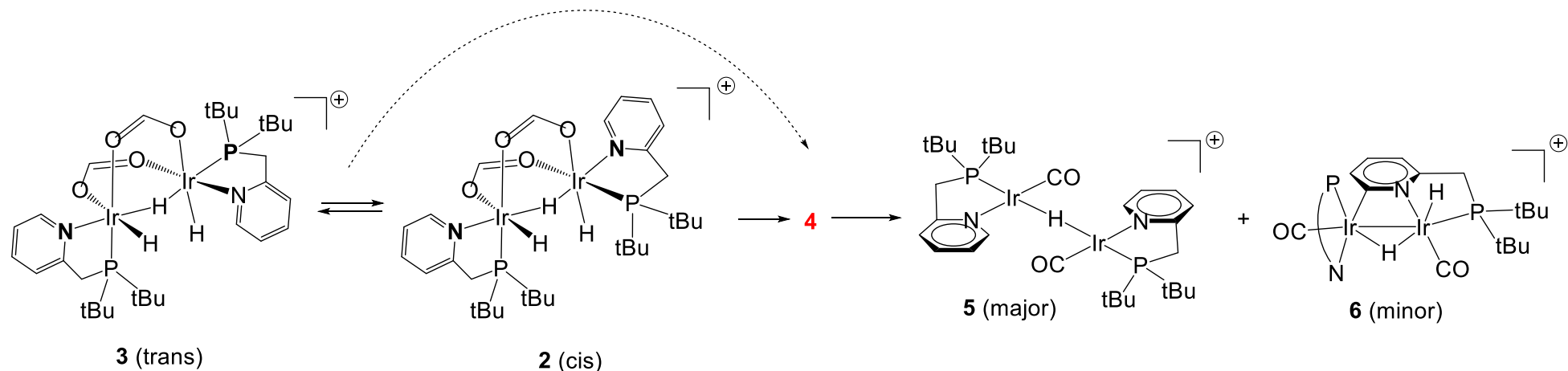
Progress: Mechanistic Studies



- **Synthetic Studies** at USC (Valeriy Cherepakhin) have enabled important revisions to the original proposal, including a **structural re-assignment of compound 3**.

Understanding the active catalyst helps us make the move to blended fuels

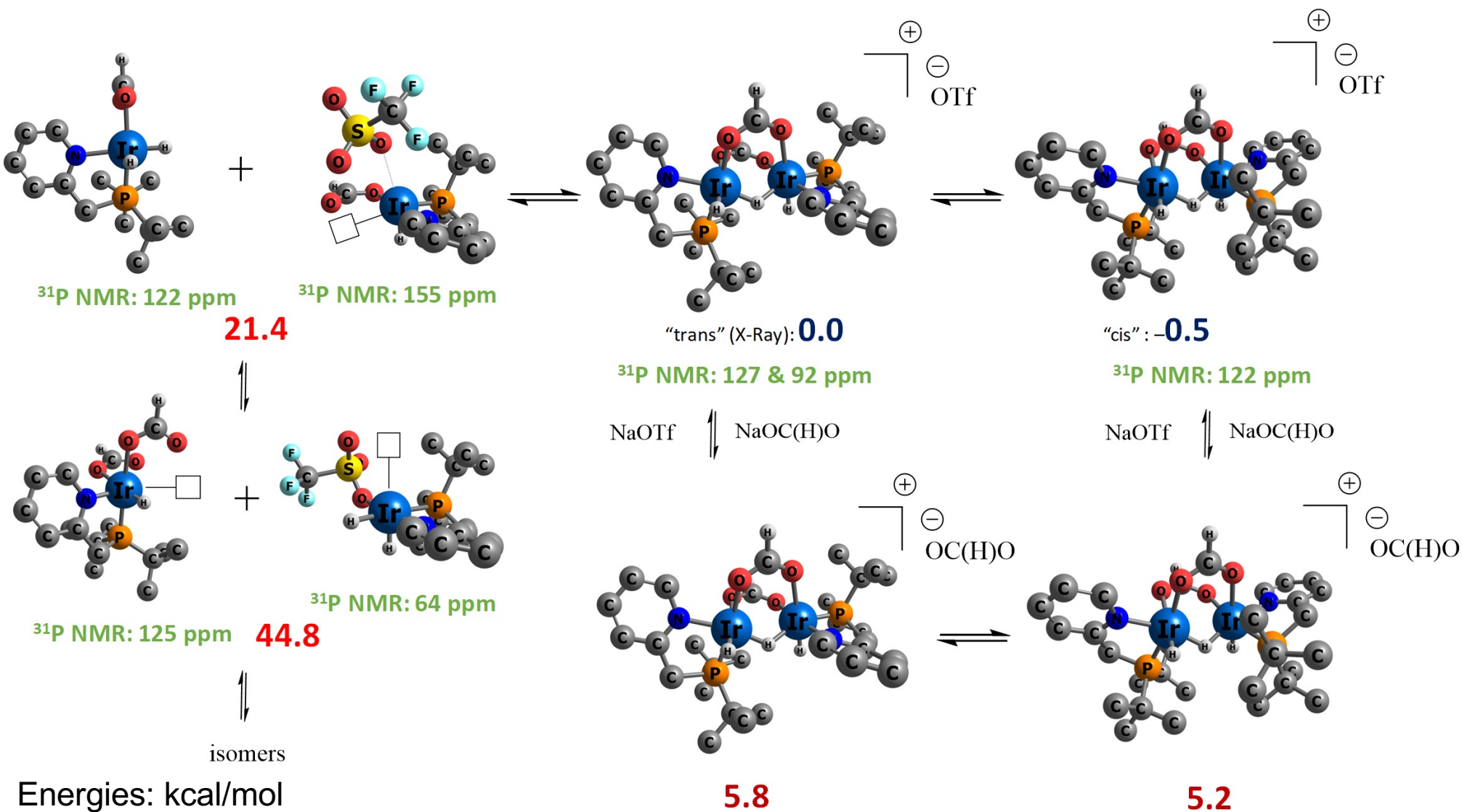
Progress: Mechanistic Studies



- **Synthetic Studies** (Valeriy Cherepakhin, Nick Alfonso) have also re-framed our understanding of the active catalyst. We now know that **carbonylation of iridium from formic acid is essential to the mechanism**.
- Compound **5** appears to be our resting state, while **2** and **3** appear not to be fully initiated. The active catalyst, possibly species **4**, remains elusive.
- We previously believed that **2** and **3** were on-cycle, but we now know that they must be heated $> 90\text{ }^{\circ}\text{C}$ to make **5**, which will catalyze H_2 evolution at temperatures $< 90\text{ }^{\circ}\text{C}$.

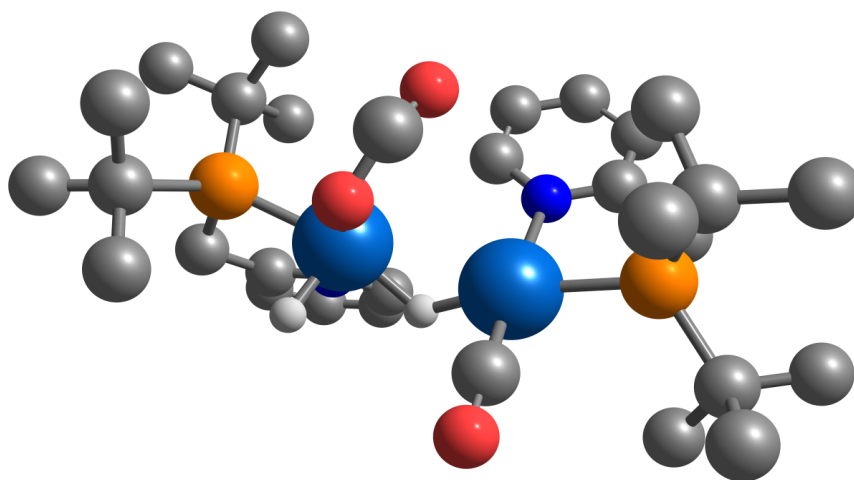
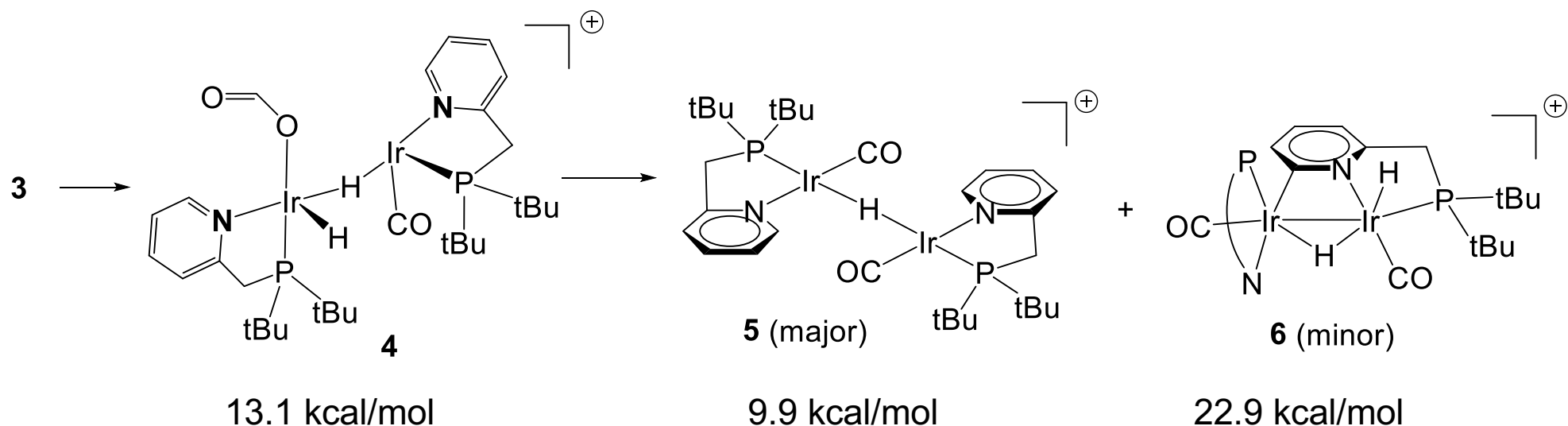
Understanding this carbonylation re-frames our thinking on how the reaction works and enables us to think rationally about our next steps toward blended fuels and mixed catalysts

Progress: Mechanistic Studies



- Computational Studies** at Los Alamos (Pavel Dub) have supported some revisions to the proposed mechanism while refuting others: **catalyst isomerization is facile, cleavage is unreasonable**. This supports our synthetic studies on catalyst initiation and refutes a hypothesis of a free radical mechanism initiated by Ir(II). We were concerned about the latter causing serious purity problems in our product stream.

Progress: Mechanistic Studies



- **Computational Studies** at Los Alamos (Pavel Dub) have supported some revisions to the proposed mechanism while refuting others: **energetics of catalyst carbonylation account for observation of temperature of catalyst initiation v temperature of catalysis.**

Accomplishments and Progress

- **No Prior AMR** is available for this project whereas it has only been funded for one quarter.

Collaboration and Coordination

- **Core Project Team** meetings occur bi-weekly among all USC and Los Alamos investigators. The videoconference modality has enabled this to continue through the COVID lockdown.



- **HyMARC Collaboration** meetings occur monthly by videoconference between the USC group (Williams) and our HyMARC contact at PNNL (Autry, Johnson). This enables the seed project team to remain connected to directions in HyMARC and plan for technology validation and transfer.



Remaining Challenges and Barriers

- **Transition to flow reactor conditions**
 - An initial model will be made by slowly injecting fuel into a batch reactor and observing catalyst performance.
 - The COVID lockdown has delayed progress, particularly in the demonstration reactor. The former model will be needed to model hydrogen evolution outcomes as the demonstration reactor is being built.
- **The reaction mechanism remains elusive**
 - The COVID lockdown has enabled us time to develop foundational knowledge on reaction mechanism, which has revealed a deep challenge.
 - Preliminary experiments show that blended fuels will not be possible in a single reactor with the Ir_2H_3 catalyst. This increases the importance of catalyst screening, which is currently delayed by the lockdown.
- **Timeline** is compressed, because of our first 12 months, 4.5 were lost to problems in the contracting process and 3 will be lost to COVID: we're left *with only 4.5 months in our first budget period*. While we will hit our GNG metric for BP 1, we might not be able to get external validation on these data because of time and travel restrictions.

Proposed Future Work

- **Demonstrate formic acid dehydrogenation under flow conditions**
 - Immediately upon gaining access to our labs, we will quantify H₂ evolution from a batch reactor in which we add formic acid continuously. This will enable us to **show whether our peak H₂ evolution rate regime can be sustained over time** and complete the data we need to export our system for external validation at PNNL.
 - We will **construct our demonstration reactor**. Because our most relevant use cases exploit formic acid's ability to generate high H₂ pressure quickly, we are designing around a high-pressure apparatus which has added cost and time. Despite this and COVID delays, we still hope to have this in the first BP.
- **Link empirical kinetic modeling with de novo mechanistic work**
 - Kinetic data from batch reactions have enabled us to construct a preliminary **model of the number of intermediates in our mechanism** and their kinetic relationships. Once returned to the lab, we will collect sufficient data to ground this model and quantify the rates of our elementary steps.
 - Synthetic and computational experiments are both indicating the same number of intermediates in the cycle as we deduce from our kinetics. We will now link structural data from synthetic/computational work to our kinetics work to **develop a structural picture of our catalytic mechanism**. This will enable us to know what intermediates are candidates to enable methanol or mixed fuel utilization.
- **Find catalysts for dehydrogenation of mixed fuel feedstocks**
 - Once back to lab, we will initiate screening of LANL and USC-LHI catalysts for methanol dehydrogenation. This will show us **what catalyst combinations will be our best candidates to realize H₂ release from blended fuels**.

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- **Licensing strategies** are developing. The PI is discussing technology transfer options with two California startup companies, OCOchem and Catapower.



- The technology and project remain very early phase, so it is not timely to move these relationships toward investment at this point.
- No new patents have been filed since work began in February.

Mandatory Summary Slide

- **Hydrogen Evolution Demonstrated to Date Exceeds BP1 GNG Target**
 - We have exceeded our GNG goal by a factor of 41x in H₂ flow rate.
 - We have demonstrated linear scalability of our batch process, which shows us that we can predict H₂ flow based on flow reactor feeding rate, temperature, and catalyst loading.
 - At our present peak flow rate, a batch reactor of 13.5 m³ volume should peak at the DOE target of 300 L/min H₂ flow rate using 50 ppm catalyst loading at 100 °C.
 - Hydrogen flow rate is a function of reaction conversion in batch (details follow), so we plan to show a demonstration scale flow reaction before submitting our procedure to PNNL for external validation in fall 2020.
- **Mechanistic Studies Reveal important Pivots in our Thinking**
 - As we uncover the mechanism of our reaction and test blended fuel conditions, we find a more complicated and limited landscape than we anticipated.
 - Blended formic acid/methanol-based fuels are incompatible with the present catalyst and reactor design. Catalyst screening will focus on breaking this impasse, but the unanticipated success of scaling the formic acid system enables us to hit our GNG targets without relying on a methanol co-fuel.
 - Our mechanistic work is showing us the path to achieve a blended fuel or mixed catalyst system, which will enable improved H₂ generation metrics.
- **Reactor Construction** is delayed by COVID-19, but design is underway.