

IV.E.2 Development of a Practical Hydrogen Storage System Based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst

Craig Jensen¹ (Primary Contact), Daniel Brayton¹, and Scott Jorgensen²

¹Hawaii Hydrogen Carriers, LLC
531 Cooke Street
Honolulu, HI 96813
Phone: (808) 339-1333
Email: hhcllc@hotmail.com

DOE Managers

Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov
Katie Randolph
Phone: (720) 356-1759
Email: Katie.Randolph@go.doe.gov

Subcontractor:

²General Motors Technical Center, Warren, MI

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Objectives

The objective of this project is to optimize a hydrogen storage media based on a liquid organic hydrogen carrier (LOC) and design a commercially viable hydrogen delivery system based on this LOC media. The project consists of two parts: Part 1 (conducted at Hawaii Hydrogen Carriers, LLC has the objective to develop an optimized catalyst/organic carrier combination; and Part 2 (conducted at General Motor Research Center) has the objective of designing a space, mass and energy efficient tank and reactor system to house the carrier and release hydrogen.

Fiscal Year (FY) 2013 Objectives

- Identify an LOC that undergoes pincer complex catalyzed, selective dehydrogenation at higher rates and with higher hydrogen cycling capacity than methylperhydroindole.
- Determine if the activity of economically viable, low (100 ppm) PCP pincer catalyst loadings are adequate to meet the demands of an automotive fuel cell.
- Initiate long-term, scale-up, dehydrogenation/rehydrogenation cycling studies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (H) Balance-of-Plant (BOP) Components
- (J) Thermal management
- (Q) Regeneration Processes

Technical Targets

1. Identification of a low-cost LOC that, in the presence of low loading of a homogeneous pincer catalyst, will release >7 wt% H₂ at sufficiently high rates and low temperatures in a practical, onboard dehydrogenation reactor to meet the demands of an onboard fuel cell.
2. Identification of a LOC/pincer catalyst combination of sufficiently high hydrogen cycling capacity that rapidly dehydrogenates without also undergoing LOC degradation upon cycling.
3. Utilization of the advantages of the liquid hydrogen storage medium to eliminate thermal management problems associated with solid-state hydrogen absorbing materials.
4. Design of a space-, mass- and energy-efficient tank and reactor system to house the LOC and facilitate hydrogen release that can be easily interfaced with a fuel cell.

FY 2013 Accomplishments

- Identification of a higher performance LOC, butylperhydropyridine (BHP) that undergoes pincer complex catalyzed dehydrogenation at practical rates at 140°C.
- Demonstration of the dehydrogenation of LOCs at practical rates at low, economically viable, 100-ppm catalyst loadings.
- Demonstration that the reversible dehydrogenation of both BHP and methylperhydroindole, (MHI) can be subjected to at least 25 cycles of dehydrogenation and rehydrogenation with virtually no degradation of the

LOC or the phosphorus-carbon-phosphorus (PCP) pincer catalyst.

- Determination that while a double helical reactor would provide a significant saving of space, it would not improve heating efficiency and would be prohibitively costly.



INTRODUCTION

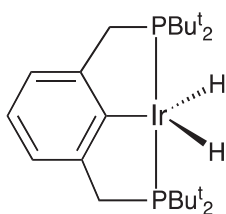
For decades, hydrogen has been targeted as the utopian fuel of the future on account of its abundance and environmental friendliness. However, a major difficulty in the utilization of hydrogen as a fuel for vehicles is the problem of onboard storage because hydrogen is problematic to store at high density. While this is a major problem for vehicles, it is also a significant problem for portable power as it adds to both the cost and inconvenience of frequent delivery and change-over of hydrogen supply for all fuel cell applications. Thus a high density, high stability method for storing hydrogen is essential to the implementation of fuel cells in all but a few niche applications. Another major concern about hydrogen is putting an infrastructure in place. While this could be done for any form of hydrogen carrier, the barrier to implementing an LOC would be significantly lower than others because it is a similar type of chemical to the current distribution system. The tanks, piping and refinery systems used to make and deliver gasoline are appropriate for LOCs. In addition to the easy adaption to existing infrastructure, LOCs have many other enormous practical advantages. Cheap, abundant LOCs can reversibly release 7-8 wt% hydrogen. They can be economically manufactured in the massive quantities required to meet the anticipated demand and would eliminate the thermal management problems commonly associated with the systems based on solid-state hydrogen absorbing materials. The technology has the potential to exceed the performance of carbon-emitting technologies such as direct methanol fuel cell. We have recently discovered catalysts that enable this technology that has remained a tantalizing but impractical possibility over the last 60 years. This project targets the development of a commercially viable LOC-based hydrogen

storage and delivery system. The project consists of two parts: 1) development of an optimized catalyst/carrier combination; and 2) the design of a space, mass, energy efficient tank and reactor system to house the carrier and release the hydrogen.

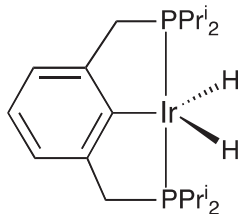
Although promising hydrogen cycling performances have been demonstrated, these previous LOC studies utilized very high loadings of heterogeneous and precious metal catalysts in order to achieve acceptable dehydrogenation kinetics at temperatures that are near the operating temperatures of proton exchange membrane (PEM) fuel cells ($\leq 150^\circ\text{C}$). The high cost of the massive quantities of precious metals precludes the commercialization of these systems.

In order to overcome the barrier to practicality that is imposed by the heterogeneous catalysts, we have developed alternative homogeneous catalysts. Homogeneous catalytic systems typically operate at significantly lower temperatures and show much greater product specificity than their heterogeneous counterparts. In 1997, we discovered that the “pincer” complex, $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}^t\text{Bu}_2\}_2$ (1), catalyzes the dehydrogenation of cycloalkanes to arenes. This was the first report of a homogeneous catalyst for this reaction. The unique reactivity of this especially robust and active catalyst can be ascribed to the tridentate “PCP pincer” ligands which contain two coordinating, neutral phosphorus centers as well as an anionic, coordinating carbon site. It has been found that electronic environment of the catalytic metal center of the pincer complex is highly sensitive to minor changes in the PCP pincer ligand. Following our report that 1 catalyzes the dehydrogenation of aliphatic groups, the related PCP pincer complexes, $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}^i\text{Pr}_2\}_2$ (2) and $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OP}^t\text{Bu}_2)_2\}$ (3) were shown to have incremental improvement in catalytic efficiency. It is now well established that dihydro PCP pincer iridium complexes can selectively dehydrogenate aliphatic groups under much milder conditions than those required for the corresponding heterogeneous catalysts, such as platinum on alumina without harm to other functional groups of an organic molecule.

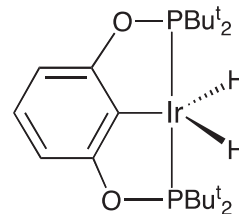
More recently, we found 1 and the related complexes, 2 and 3, to be highly active catalysts for the dehydrogenation of amines, ethylperhydrocarbazole (EHC) and other heterocyclic LOCs.



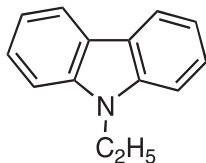
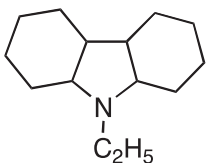
$\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}^t\text{Bu}_2\}_2$ (1)



$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^i\text{Pr}_2)_2\}$ (2)



$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OP}^t\text{Bu}_2)_2\}$ (3)



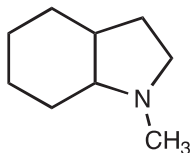
N-ethylperhydroethylcarbazole (EHC) N-ethylcarbazole (EC)

Recently, we synthesized the novel AsCAs pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t_2)\}$ (4), and found it to be a highly active dehydrogenation catalyst for LOCs. At 150°C, 4 catalyzes the dehydrogenation of EHC at rates that are nearly double those achieved with 3. Furthermore, it exhibited acceptable activity at 125°C, a temperature at which the PCP catalysts are completely inactive.

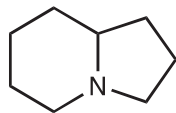
APPROACH

Clearly, our studies of the LOC/pincer catalyst systems have demonstrated the potential of these systems to serve as the basis of a practical hydrogen storage system. However, further studies must be conducted to find the system and conditions that gives the best combination of high cycling capacity, rapid dehydrogenation kinetics, and lack of LOC degradation upon cycling. In order to accomplish this we are conducting the following four tasks:

Task 1.1 Isothermal kinetic studies of the pincer complex catalyzed dehydrogenation of the candidate LOCs, N-EHC, N-MHI, perhydro-indolizidine (HIZ), and aminomethylcyclohexane.



perhydro-methylindole



perhydro-indolizidine (HIZ)

Task 1.2 In cases where incomplete dehydrogenation of the LOC is observed, studies of the dehydrogenation reaction in the presence of a hydrogen acceptor (transfer dehydrogenation) are being carried out to determine if the reaction is limited by kinetic or thermodynamic constraints.

Task 1.3 Studies to determine if the formation of unwanted side products that arise in some LOC systems can be controlled by the addition of additives.

Task 1.4 Cycling studies to determination if LOC/catalyst combinations that have acceptable dehydrogenation kinetics and capacity will undergo cycling without degradation of LOC and/or catalyst.

Additionally, the practical advance of LOC systems also requires the design of a deployable reactor to house the

LOC and facilitate the hydrogen release that can be easily interfaced with a fuel cell. The U.S. DRIVE Hydrogen Storage Tech Team and the reviewers at the Annual Merit Review concluded that much of the value of the engineering portion of the project had already been harvested by the general case analysis. Both sets of reviewers advised us that the engineering portion of the project should be curtailed and that a significantly increased portion of the remaining resources should be used to try to identify an LOC with higher practically available hydrogen. During the past year have taken heed of this advice and reduced the scope of our engineering efforts as detailed in the following.

2.1 Model Development The sub-task is divided into four parts. The first part is to devise a notional model of the entire system. In Part 2, one or more reactor model(s) are developed in detail using COMSOL. As the model or models are completed, they are validated in Part 3 to be certain the fluid mechanics, heat transfer, and reaction proceed as would be expected based on the standard engineering concepts. Part 4 entails a basic estimate of the cost of the system.

2.2 Function Evaluation Our experience indicates that the system function and cost is often fixed by the full flow condition. To ensure efficient use of resources, we will evaluate this functionality first. Once the reactor “runs” at the full-flow condition it will be evaluated at idle. Once these extremes have been evaluated, the mid-speed/mid-load condition will be evaluated and finally transient performance is then evaluated.

2.3 System Optimization This task is centered on improving the storage materials. Based on what we have learned about the system function, we will look for both reactor and BOP aspects where cost-effective change is possible. However, we are focusing on aspects of the LOC enable that can lead to significant improvements in the overall system.

2.4 Final Simulations Steady-state and transient simulations are being carried out.

RESULTS

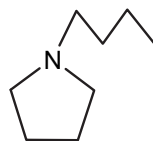
Catalyst and LOC Optimization

Task 1.1 Isothermal Kinetic Studies

During the past year, we obtained improved kinetic data that allowed us to derive more reliable values for the activation energies (MHI, 132 kJ/mol; EHC 107 kJ/mol) and frequency factors (MHI, $7.23 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, EHC $4.53 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$). We also determined that contrary to the indications of preliminary studies we reported last year, higher initial rates of LOC dehydrogenation are achieved with the AsCAs pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t_2)\}$. However, the AsCAs pincer complex has much lower thermal stability than the PCP and begins to undergo significant decomposition

within a few hours at the temperatures required for the dehydrogenation reaction.

We have previously determined that the iridium PCP pincer catalyst, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t\text{)}_2\}$ catalyzes the dehydrogenation of the nitrogen-containing 5-membered ring of MHI and EHC at rates that are adequate for PEM fuel cell applications in the 150-200°C temperature range. These findings led us to explore the dehydrogenation of butyl perhydropyridine (BHP).



Butyl perhydropyridine (BHP)

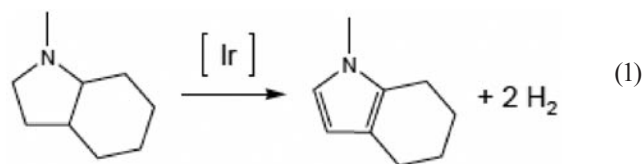
During the past year, we found that the 5-member ring of BHP undergoes dehydrogenation at significantly higher rates than that of MHI. For example, virtually quantitative dehydrogenation was found to occur at 140°C in 18 h. Although isothermal kinetic studies of BHP indicate the activation energy for the dehydrogenation of BHP (166 kJ/mol) is actually higher than for MHI, the frequency factor is 4 orders of magnitude higher ($2.17 \times 10^{14} \text{ M}^{-1}\text{s}^{-1}$). Thus the higher rates of dehydrogenation are apparently due to BHP having much less steric constraint than MHI in accessing the metal center of the pincer catalyst.

The FY 2012 Annual Merit Review reviewers were concerned that the PCP pincer catalyst is based on a precious metal and therefore might be prohibitively expensive for utilization in a commercially affordable hydrogen storage system. The high cost of iridium is indeed a very significant consideration. According to our calculations, the cost of the catalyst would be acceptable only if extremely low catalyst loadings were able to effect the dehydrogenation LOCs at rates that could meet the operational demands of an onboard PEM fuel cell. According to our calculations, an acceptable cost of \$5/liter would allow a catalyst loading of only 100 ppm as opposed to the much higher, 1 mol% catalyst concentrations that were used in our previous studies. We have found that acceptable rates of dehydrogenation can be achieved the low, 100-ppm catalyst concentrations. These finding suggest the iridium-based catalyst could indeed be economically viable.

Surprisingly, we found that the pincer complex exhibits higher catalytic activities at the lower level loadings (rate constants of 1.37×10^{-3} and $2.75 \times 10^{-4} \text{ s}^{-1}$ for BHP and MHI respectively). We believe this is an experimental artifact due to the deposition of significant amounts of catalyst on the walls of our reactors when they are loaded with 1 mol% catalyst solutions. Therefore, we feel that the kinetic values obtained at the 100-ppm catalyst loadings are the more accurate than those based on the 1 mol% solutions.

Task 1.2 Differentiation of Thermodynamic vs. Kinetic Limitations

We have previously determined that, as seen in Equation 1, the iridium PCP pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t\text{)}_2\}$ efficiently catalyzes the dehydrogenation of the nitrogen-containing 5-membered ring of MHI but exhibits only modest activity with the 6-membered ring. This was also found to be the case for HIZ and EHC. In order to differentiate whether this due a high kinetic barrier to the dehydrogenation of the 6-member rings, or high C-H bond strengths in the saturated 6-membered rings, and thus unfavorable free energies of dehydrogenation in the



160-200°C temperature range, we carried out studies of the dehydrogenation of MHI and EHC in the presence of the hydrogen acceptor, t-butylethylene. In all cases, gas chromatograph-mass spectrometry (GCMS) analysis of the product mixture contained less than 5% conversion to the fully dehydrogenated products, N-methylindole and N-ethylcarbazole while the partially dehydrogenated products, N-methyl-tetrahydroindolizidine and N-ethyloctahydrocarbazole were obtained in >95% yield. Thus the more favorable thermodynamics of the transfer dehydrogenation reactions did not result in the production of the fully dehydrogenated products. We conclude that resistance to the dehydrogenation of the 6-membered rings is due to kinetic constraints.

Task 1.3 Additive Intervention of Side Reactions

Work on this task was completed last year.

Task 1.4 Cycling Studies

During the past year, we constructed and tested two reactors for our scale-up cycling studies. Initial cycling experiments were run with the homogenous PCP pincer complex serving as both the dehydrogenation and re-hydrogenation catalyst. MHI was dehydrogenated and re-hydrogenated 10 times and GCMS and nuclear magnetic resonance (NMR) analysis was carried out after each half cycle. No traces of LOC or catalyst decomposition products were detected. However, only 89% re-hydrogenation was achieved in these experiments. In order to achieve 100% re-hydrogenation, second set of cycling studies have been initiated in which 100 ppm of Pd on carbon black was included with the solution of pincer complex and LOC. Studies are currently being carried out on both MHI and BHP. To date, 25 cycles of dehydrogenation and re-hydrogen have been performed. GCMS and NMR analysis confirmed that there has been virtually no degradation of the LOC or

catalyst during 1 million catalytic turnovers that the pincer catalyst has performed to date.

Reactor Design and Modeling Tasks

As mentioned before, the engineering portion of the project was curtailed in accordance with the recommendation of two sets of project reviewers.

Task 2.1 Model Development Our previous modeling studies have shown that helical reactors reduce heat loss in the system and that the mass and volume of the reactor can be significantly reduced by use of micro-channel heat exchangers. During the past year we have designed a double helical reactor that would provide a further significant saving of space.

Task 2.2 Function Evaluation While the double helical reactor provides a significant savings of space. It does not improve the heating efficiency and is prohibitively costly.

Task 2.3 System Optimization Modeling studies show that heat transfer is most effective in a helical reactor. Better heat transfer allows a short, easy to package reactor that reduces heat loss.

Task 2.4 Final Simulations Simulations have been carried out using the rate constants and activation energies that were determined in our isothermal kinetic studies. These studies indicate that if the dehydrogenation kinetics could be improved by a factor of 10, hydrogen could be evolved from a helical reactor containing 100 L of BHP at a rate adequate to meet the requirements of an onboard automotive PEM fuel cell.

CONCLUSIONS

Our previous studies have shown that the PCP pincer complexes effectively catalyze the rapid dehydrogenation of saturated 5-membered, nitrogen-containing rings. During the past year we have determined that higher initial rates of LOC dehydrogenation are obtained with the AsCAs pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OAsBu}^t)_2\}$. However, the AsCAs pincer complex has much low thermal stability than the PCP and begins to undergo significant decomposition within a few hours at the temperatures required for the dehydrogenation reaction. During the past year, we have also found that BHP undergoes quantitative dehydrogenation at 140°C in 18 h. This is significantly lower than the 160 and 180°C temperatures that we previously found to be required to achieve the same rates for MHI and EHC, respectively. Thus the best LOC/catalyst combination that identified in our studies is BHP/ $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(OPBu}^t)_2\}$.

We have found that acceptable rates of LOC dehydrogenation can be achieved at 200°C in the presence of only 100 ppm of the pincer catalyst. This translates to an

acceptable catalyst cost of ~\$5/L. Thus, effective loadings of the iridium-containing catalyst would not be cost prohibitive for an onboard, LOC-based hydrogen storage system. We have also carried out scale-up cycling studies with both MHI and BHP solutions containing low concentrations of the pincer catalyst. To date, 25 cycles of dehydrogenation and re-hydrogen have been carried out. GCMS and NMR analysis has verified that virtually no degradation of the LOC or catalyst occurred during the 1 million catalytic turnovers that the pincer catalyst has performed to date. This finding also indicates the PCP pincer catalyst could be in a practical LOC-based hydrogen storage system.

Our previous modeling studies have shown that helical reactors reduce heat loss in the system and that the mass and volume of the reactor can be significantly reduced by use of micro-channel heat exchangers. During the past year we have found that while a double helical reactor provides a significant saving of space, it does not improve the heating efficiency and is prohibitively costly.

FUTURE DIRECTIONS

LOC Screening and Evaluation

We plan to extend our scale-up, long-term cycling studies of BHP and MHI to 100 cycles of dehydrogenation/re-hydrogenation.

Reactor Design

We plan to carry out a final simulation modeling of our best helical reactor design using the final higher rate constants that were derived from our studies of solutions of BHP and MHI containing low concentrations of the PCP pincer catalysts. The results of the modeling study will be evaluated in order to determine if the operation of the system with our best combination of LOC and pincer catalyst is practically viable.

FY 2013 PRESENTATIONS

1. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, and S. Orimo, Materials for Hydrogen Storage – Future Perspectives, Kirkenes, Norway, 06/20/12.
2. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, and S. Orimo, International Symposium on Metal-Hydrogen Systems; Kyoto, Japan, 10/06/12.
3. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, M. Chong, J. Wang and S. Orimo, 7th EMPA Hydrogen and Energy Symposium, St. Gallen, Switzerland 01/22/13.