Design and Development of Ruthenium-Based Catalysts for Enabling Hydrogen Storage

Isabelle Beaudoin
ibeaudoin@smu.edu

Follow this and additional works at: https://scholar.smu.edu/jour

Recommended Citation
Beaudoin, Isabelle (2022) "Design and Development of Ruthenium-Based Catalysts for Enabling Hydrogen Storage," SMU Journal of Undergraduate Research: Vol. 7: Iss. 2, Article 2. DOI: https://doi.org/10.25172/jour.7.2.1
Available at: https://scholar.smu.edu/jour/vol7/iss2/2

This Article is brought to you for free and open access by SMU Scholar. It has been accepted for inclusion in SMU Journal of Undergraduate Research by an authorized administrator of SMU Scholar. For more information, please visit http://digitalrepository.smu.edu.
Design and Development of Ruthenium-Based Catalysts for Enabling Hydrogen Storage

Isabelle Beaudoin
ibeaudoin@smu.edu

Mentor: Dr. Andrew Phillips

ABSTRACT

For past decades, hydrocarbon-based fuels have been the primary source of energy as a necessity for modern machines and automotive vehicles. Despite use in combustion engines and power plants, fossil fuels reserves are unpredictable and the associated CO₂ emissions are now causing terrible effects on the environment and human health. Researchers have realized H₂ as a potentially safe and efficient energy source, with an energy density of 33.3 kWh per kg. Moreover, H₂ is significantly more environmentally friendly as H₂O is the only by-product. Currently, the development of on-board storage technology is progress for use in the transportation industry. The chemical storage of hydrogen, in which H₂ is bound to a carrier molecule, provides a more practical and safer method to store and release immense amounts of H₂. Ammonia Borane (H₃N-BH₃, AB) is a useful material for storing up to 19.6 wt% of and 0.145 kg L⁻¹ of H₂ with the ability to release H₂ under mild ambient conditions through exposure to a suitable catalyst. This project investigates the use of pyrazole-based compounds as ligands for η₆-arene Ru-complexes in order to formulate efficient catalysts for AB dehydrogenation. Pyrazoles are interesting diaza-five member heterocycles and have strong electron-donating properties. Mono- and di-coordinating substituted pyrazole complexes and an unusual Cl-bridging dimeric Ru complex were successfully synthesized and characterized (NMR, ESI-MS and X-ray diffraction crystallography) before undergoing evaluation for AB dehydrogenation studies in a high-pressure stainless steel reactor. The dimeric Ru Cl-bridging catalyst released the largest H₂ equivalent per mol of AB with 1.45 with a total of 7.82 bar of H₂ pressure, proving to be the most successful catalyst in the series. However, from the H₂ release profiles, it appears that catalysts undergo slow transformation where it is possible that the pyrazole ligands are lost. Further mechanistic studies are required to determine the decomposition process.

1. INTRODUCTION

1.1 Current Energy Problem

In the current economy, energy production is focused on carbon-based fuels through reliance on fossil and hydrocarbon fuels.¹⁰ Crude oil fuels are necessary to run combustion engines used in the numerous motor vehicles that exist today. However, the long-term efficiency of these methods can become inadequate due to the unpredictable amount of fossil fuels remaining and the harmful effects of their CO₂ emissions on climate change.⁴ Essentially, natural resources involved in the current production of energy are non-renewable and, as shown by Figure 1, the fuel discovery is predicted to decline sharply and almost completely deplete before 2050.⁶ This, as well as the need to reduce CO₂ emissions and maintenance of increased energy production for a strong economy, has encouraged researchers to explore the use of hydrogen gas as an energy source. H₂ gas can be utilized for transportation, heat generation, and a power source instead of carbon-based fuels.¹⁰ In order for H₂ to take on this role, viable methods of storage must be established.

Figure 1: Oil Discovery and Future Discovery
Reproduced from Crystal O’Connor, based on data from ExxonMobil⁶

1.2 Hydrogen

1.2.1 Production

Hydrogen is the most plentiful and available element on Earth today (0.9 wt%) and is often referred to as an all-purpose energy source, maintaining its content of energy at 120 MJ/kg or 33.3 kWh/kg.²⁴ This element is produced from other hydrogen-containing sources using renewable materials, nuclear power, or fossil fuels.²⁰ First,
H₂ gas can be produced from steam reforming hydrocarbons, typically methane (CH₄). This process does produce carbon dioxide as a by-product, which can be monitored through processes of sequestration, in which CO₂ is captured and stored underground. Secondly, splitting water through numerous different methods can produce hydrogen gas as well. These processes can include electrolysis, photo-electrolysis, high-temperature decomposition and photobiological water separation. Despite its high costs, the electrolysis of water, in which water is split into gaseous hydrogen and oxygen through the use of electricity, the process produces a sufficient amount of hydrogen with 80 to 85% efficiency. Once hydrogen gas is properly produced and stored, it generates power in a device, called a fuel cell, that combines hydrogen and oxygen without undergoing combustion. More specifically, a PEM fuel cell, or Proton Exchange Membrane cell, produces energy by separating the H-H bond of H₂. There are various processes that can produce hydrogen, but the necessary safe and efficient storage of this element currently stands as a major obstacle to a wide-scale deployment.

1.2.2 Storage Methods

In order to use hydrogen energy in vehicles, the situation surrounding on-board storage must be addressed. A hydrogen storage method that is minimal-cost, safe to use, low in weight, and has a high-performance rate currently poses a challenge to obtain. For application on automotive vehicles, gas tanks operating at high temperatures or that employ liquid hydrogen gas cooled to cryogenic temperatures (21.2K) stand as the only viable options. However, these methods expend an immense amount of energy given that approximately 20% of hydrogen’s energy content is required to compress the gas and up to 40% of its energy can be used for it to liquefy. Researchers are beginning to look at methods surrounding solid-state hydrogen gas storage, in which hydrogen is incorporated into solid materials, to examine the chemical mechanisms that promote hydrogen storage and dehydrogenation processes. Materials with the correct absorption and adsorption characteristics are necessary for the storage and release of H₂ in a way that is compact, easily regenerated, and efficient to obtain in large quantities for use in the automotive industry.

1.2.2.1 Liquid H₂ Storage

Numerous methods are used to store hydrogen at appropriate densities. Hydrogen can be cooled to low temperatures (21.2K) to be stored in liquid form. This cryogenic temperature is necessary due to the extremely low boiling point and critical temperature of H₂ (-252°C and -240°C). However, the process of liquefaction consumes significant energy, and represents approximately 30% of the stored chemical energy. Boil-off mechanisms additionally create problems during the cooling process to afford liquid H₂, in which thermal conduction may allow heat to enter the system and thus evaporate the fluid and increase pressure. The increased pressure of the system must then be released around 1 MPa by opening a valve and venting H₂.

1.2.2.2 Compressed Hydrogen Gas Storage

In addition to liquid hydrogen storage, compressed hydrogen gas storage is another operable method. A vessel, particularly a high-pressure tank, holds compressed H₂ gas at pressures now up to 70MPa. However, to reach this high pressure a 110kg tank and results in only a 6% gravimetric storage density. The immense weights of the tanks and small volumes of hydrogen stored cause difficulties for using this method of storage. Compressing gaseous H₂ also expends significant energy just as liquefaction, but only consumes 15% as opposed to 30%. The development of H₂ tank systems, including the cylindrical steel BMW Hydrogen 7 (100kg), Lightweight StorHy (40 kg), and the complex Lightweight 2010 (38kg), have attempted to create storage solutions with less weight for automotive usage, but only carry 10kg of fuel. Contrarily, a complex gasoline tank (10kg) carries 30kg of fuel, exhibiting the low compressibility of H₂ compared to gasoline. Furthermore, compressing 1 kg of hydrogen adiabatically can require up to 5.45 MJ/kg of work and 3.03 MJ/kg for isothermal compression, further showing the obstacle of compressing H₂. Liquid and compressed gas hydrogen storage methods fall under physical-based techniques, as shown by Figure 2.

![Figure 2: Physical vs. Material-based Methods of Hydrogen Storage](image)

Reproduced by the US Department of Energy

1.2.2.3 Material-Based Hydrogen Storage

Likewise, the incorporation of H₂ into a solid-state material is an alternative, material-based method for storage. This approach uses a substance that can reversibly absorb or adsorb hydrogen in atomic (H) or molecular (H₂) form to compress hydrogen chemically or physically. Metal-Organic Frameworks (MOFs) are an example of solid storage materials that contain organically linked metal ions, and are reported to have high gravimetric capacities up to 6.9 wt% at 77K and a hydrogen pressure of 9.0 MPa. However, this particular research focuses on another material-based method, chemical hydrogen storage, in which a carrier molecule is covalently bound to H₂. Chemical H₂ storage is non-reversible, thus requiring an efficient method for regeneration and often involves the use of catalysts. Materials that are used with this type of storage are primarily boron-containing compounds due to the fact that these compounds can obtain high gravimetric and volumetric contents.
storage densities compared to other organic solutions. Ammonia borane, for example, stores 19.6 wt% and 0.145 kg L⁻¹, contributing to its practicality for hydrogen storage.

### 1.2.2.3.1 Metal Hydrides

Metal hydrides, also shown in Figure 1, additionally fall into the category of material-based methods of storing H₂. These compounds are able to maintain higher storage densities than liquid or compressed gas hydrogen storage. With the case of interstitial metal hydrides, molecular H₂ is split and then absorbed into the bulk of the material. Examples of interstitial metal hydrides include LaN₅ and Pd/C, in addition to the intermetallic compounds, TiFe and TiC₁₃₃, and vanadium-based solid alloys. Absorption of H₂ with interstitial metal hydrides generally does not function at suitable temperatures or pressures, and the volumes of hydrogen can be affected by the large amount of metal present. Complex metal hydrides instead store molecular hydrogen as part of the main molecule structure, which can decompose into two products, one of which being H₂. These hydrides compass high storage capacities, such as Mg₂FeH₆ and Al(BH₄)₃ with a volumetric density twice that of liquid hydrogen at 150 kg m⁻³. However, LiBH₄ with a gravimetric H₂ density of 18.36 wt% has the strongest hydrogen content among the metal hydrides as displayed in Table 1. Complex metal hydrides do hold limitations specific to each case, in that air and moisture sensitivity must be considered.

| Borohydrides | Hydrogen content, wt% | Start of decomposition |
|--------------|-----------------------|-----------------------|
| LiBH₄        | 18.5                  | 380                   |
| NaBH₄        | 10.8                  | 400                   |
| KBH₄         | 7.4                   | 500                   |
| Mg(BH₄)₂     | 13.7                  | 260-280               |
| Ca(BH₄)₂     | 9.6                   | 350                   |
| Al(BH₄)₃     | 16.8                  | 20                    |
| Be(BH₄)₂     | 20.7                  | --                    |

Table 1: Select metal hydrides with listed hydrogen content and temperatures of decomposition Reproduced from Atahl Nathanson.

### 1.3 Ammonia Borane

This project focuses on H₂ storage using ammonia borane (herein abbreviated as AB), due to its suitable properties as a chemical hydrogen storing material. AB is widely known to be a useful material for storing H₂ due to a hydrogen-to-mass ratio of up to 19.6%. Compared to other molecules that store significant quantities of H₂, the volume to mass density retention for the release of 3 equivalents of H₂ is one of the highest, as displayed in Figure 3.

\[ \delta \downarrow H - N: \rightarrow B - H_3 \delta^- \]

Figure 4: Dipole movement in AB due to molecule polarity Reproduced from Atahl Nathanson.

### 1.4 Catalysts for AB Dehydrogenation

AB has been studied as a promising hydrogen storage material due to its capacity to release a molecule of H₂ under mild ambient conditions. Equation 1 displays how 3 equivalents of H₂ can be released from AB from undergoing hydrolysis by reacting with H₂O, and this process can be accelerated by the presence of a catalyst.

\[ \text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2 \]

Equation 1: Hydrolysis in which AB is Reacted with Water Reproduced from Hai-Long Jiang and Qiang Xu.

In the process of AB dehydrogenation, transition metal catalysts, such as multiplex systems of iron, iridium, molybdenum, nickel, rhodium, palladium, and ruthenium are viable and often used for the process of releasing H₂. This occurs by establishing a chemical bond with either or both the BH₃ or NH₃ groups. Suitable catalysts with electrophilic metal sites and nucleophilic sites in proximity have the capacity to simultaneously activate both the B–H and N–H bond at the same time. Although catalysts...
promote the dehydrogenation of AB, their complexes can either release one equivalent of H$_2$ gas at a fast rate, or two to three equivalents are a much slower rate. Catalysts shown in this Figure 5 have the capability to release over 2.5 equivalents of H$_2$\textsuperscript{13} Ruthenium-centered catalysts, as utilized in this project, show high productivity for the release of hydrogen, and are capable of borazine dehydrogenation, thus exhibiting among the highest H$_2$ productivity reported to date for AB dehydrogenation.\textsuperscript{13} With an appropriate catalyst, ammonia borane has the potential to release three equivalents of H$_2$.

Through the utilization of transition metal catalysts, one method to dehydrogenate AB efficiently is to employ a metal-halide catalyst. The cation of the metal in the metal halide initiates the dehydrocoupling of AB and retains the B-N unit during dehydrogenation.\textsuperscript{7} FeCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$ are examples of commonly used metal-halide catalysts.\textsuperscript{7} Single site catalysts are also applied for the hydrogenation and dehydrogenation of AB, where an M-H bond is formed through the reaction of hydrogen and a center metal atom. Various complexes involved in this single site mechanism, shown in Figure 6, can be used for AB where a proton and hydride are shifted from substrate to metal.\textsuperscript{6} Examples of these catalysts include the nickel complex reported by Baker et. al and the iridium POCOP catalyst by Goldberg et. al, an extremely efficient catalyst that releases one hydrogen equivalent per 14 minutes.\textsuperscript{6} Although regeneration is possible under immense pressure, these catalysts can be deactivated through the interaction of the metal and borane.

Another category of catalysts is the metal-ligand bifunctional catalysts where simultaneous interaction of metal and ligand takes place. A Ru-BINAP complex was modified in 1995 by Noyori, where hydrogenation involved the metal and the nitrogen group.\textsuperscript{6} Variations of Noyori’s catalysts, as well as complexes with osmium, iridium, and iron, have exhibited bifunctional hydrogenation catalysis and thus increased hydrogen release rates.\textsuperscript{6} Lastly, complexes involving ruthenium have become customary for the process of catalysis. AB dehydrogenation has shown to be very successful through the usage of platnoid elements and thus ruthenium.\textsuperscript{6} Various researchers employed ruthenium-based catalysts and their modifications due to desirable properties, such as compatibility with different solvents, water stability, and lack of hindrance by functional groups.\textsuperscript{6} Therefore, a bifunctional ruthenium catalyst complex for AB dehydrogenation is implemented in this research.

Withal, the dehydrogenation of AB and N,N-dimethylamine borane (abbreviated as DMAB) in this research is carried out by homogenous transition metal catalysis, or the non-hydrolytic release of hydrogen. This process maintains high selectivity in reactions between substrate and catalyst, in which transition metal catalyst systems are of particular focus. These systems of homogenous catalyzed dehydrogenation are applied to amine borane substrates due to their appropriate properties as chemical hydrogen storage materials. In order to examine the controlled, efficient release of hydrogen from these amine boranes, the ruthenium-complex B-Diketiminato (n$_6$-arene) –Ru(II) is specifically used.\textsuperscript{11} This molecule is particularly utilized considering ruthenium-based catalysts are well-established in their ability to interact with dihydrogen, and many past dehydrocoupling reactions of AB and BN substrates have used these catalysts.\textsuperscript{11} The ruthenium compound, under mild conditions, has the capability to cleave H$_2$ in a heterolytic manner through the usage of a metal-ligand complex, or essentially a catalyst.\textsuperscript{11}
Efficient and plentiful $\text{H}_2$ generation and applied on a larger scale to mobile devices. an efficient means of energy can be obtained for power promotion of dehydrogenation from hydrogen storage materials, renewable source of power. The potential to improve quality of life through a practical, efficient catalyst to dehydrogenate AB can be determined. Compared for the ability to release hydrogen, and the most harmful $\text{CO}_2$ emissions causing climate change. Ultimately, exploring $\text{H}_2$ storage technologies and releasing agents have the potential to improve quality of life through a practical, renewable source of power.

2. SYNTHESIS AND CHARACTERIZATION OF RUTHENIUM CATALYST COMPLEXES

2.1 Introduction to ruthenium complex synthesis

This particular area of the research examines the reaction between an arene-Ru dimeric complex $\left[\eta^6$-$\text{C}_6\text{H}_6\right]\text{RuCl}_2$ and a pyrazole ligand. These 5-member rings exhibit high reactivity, containing 6 electrons and two N that reduce the electron density from the nearby carbons, which is of particular interest for use in catalyst formation. Figure 8 displays the pyrazoles utilized in this project and their numerous substitution patterns and substituent groups, including methyl, trifluoromethyl, and phenyl. The activating and deactivating nature of these substituents is observed for their effect on the binding capacity of the pyrazole. Through these reactions, the goal is to successfully react the ruthenium dimer with a series of these pyrazole-based ligands, in order to form a complex that combines both the arene-Ru fragment with one, two, or three attached ligands. The electron-dense N atoms of the ring are intended to react with the central metal, Ru, of the dimer. Various methods, including the solvents, counter-ions, and experimental conditions, were applied to improve this synthesis. The resulting Ru complexes are then evaluated as suitable catalysts for AB dehydrogenation and tested in a high-pressure reactor. The reactor shows how rapidly the increase of pressure attributed to the release of $\text{H}_2$ from AB. In this way, the different ruthenium catalysts can be compared for the ability to release hydrogen, and the most efficient catalyst to dehydrogenate AB can be determined.

2.2 Mono-Substituted Catalysts

2.2.1 $\left[\eta^6$-$\text{C}_6\text{H}_6\right]\text{RuCl}_2(\text{Me}_2\text{HPz})$}

Results

Synthesis of this product was performed with a refluxing method that heated and mixed the Ru-dimer with 4 equivalents of the ligand, 3,5-dimethylpyrazole, in acetone solvent (bp 56°C). Through this procedure, the dimer was split and yielded a mono-substituted product, $\left[\eta^6$-$\text{C}_6\text{H}_6\right]\text{RuCl}_2(\text{Me}_2\text{HPz})$, where a singular ligand attached to the central Ru atom. However, the experiment intended for the yield of a di-substituted catalyst where two pyrazole ligands successfully bond to the central metal atom. The production of a mono-coordinated product can be related to the requirement of excess ligand in the reaction in order for two to attach properly. The lack of a counter-ion also helps initiate the cleavage of the Ru-Cl bonds in the dimer complex for the pyrazole ligands to bond to Ru. In the product obtained, only one of the Ru-Cl bonds of each Ru in the starting dimer was broken and thus leaving room for one 3,5-dimethylpyrazole.

Characterization

Three separate characterization tests were carried out to determine if the complex was successfully made. 1mg of the solid product was dissolved in a small vial with methanol for ESI electrospray ionization analysis, and approximately 15mg was dissolved in CDCl$_3$ for $^1$H NMR analysis. A small amount of the solid was additionally dissolved in dichloromethane and left under the fume hood to evaporate and yield crystals for suitable structure determination by x-ray crystallography. The $^1$H NMR of the product was the first test of characterization and exhibited the correct proton signals corresponding to a successful synthesis of the product. The specific peaks are shown below. However, these results would appear the same regardless of whether one or two ligands were attached to the Ru center due to the fact that both are equivalent and would hence show the same number of NMR signals. Therefore, the ESI-MS was then taken to determine the mass of the product and indicate if one or two pyrazole ligands bonded to the Ru center.

$^1$H NMR (25°C, 300 MHz, CDCl$_3$) δ ppm: 11.14 (s, 1H), 5.98 (s, 1H), 5.75 (s, 6H), 2.51 (s, 3H), 2.23 (s, 3H).

$^1$C NMR (25°C, 400 MHz, CDCl$_3$) δ ppm: 153.1, 141.3, 107.7, 84.0, 15.2, 10.9.

The ESI-MS for this product is displayed in Figure 10 in the third spectra. A relatively strong peak is prominent at 311.0m/z, which is significantly less than the intended 407.1m/z if two ligands had attached to Ru, as in the first spectra. The mass of the 3,5-dimethylpyrazole ligand is 96.13g/mol, which is almost the exact difference of these two masses. Hence, the product displays the correct mass characteristic of a mono-substituted pyrazole complex with 2 Ru-Cl bonds present.
The X-ray crystallography results also confirmed the successful synthesis of the mono-substituted product. Figure 11 shows the crystal structure of \( [(\eta^6-C_6H_6)RuCl_2(Me_2HPz)] \). It is clear that one 3,5-dimethylpyrazole (purple) is attached to the central Ru (dark green), that is also bonded to 2 chloride atoms (light green) and an arene group. No counter-ion was observed.

Characterization

The \(^1\)H NMR displays the correct peaks for the product to be present. This procedure was also preferred under conditions that intended for two pyrazole ligands to be attached, which would again show equivalent peaks in the NMR spectra.

\(^1\)H NMR (25°C, 500 MHz CDCl3) δ ppm: 11.75 (s, 1H) 7.97 (t, \( J = 2.1 \) Hz, 1H) 7.50-7.46 (m, 2H, phenyl) 7.44-7.35 (m, 3H, phenyl) 6.64 (t, 2.3 Hz, 1H), 5.80 (s, 6H, C6H6).

\(^13\)C NMR (25°C, 400 MHz, CDCl3) δ ppm: 144.1, 129.6, 129.2, 125.8, 122.0, 105.0, 84.1.

The ESI-MS spectra exhibit the most prominent peak at 358.1 m/z. This is consistent with a mono product and indicates that only one of the 3-phenyl-1H-pyrazole ligands is attached to the Ru central atom. Again, this Ru(II) complex with two M-Cl bonds should have no counter-ion. ESI additionally shows a species with one less Cl at 323.0 m/z, indicating that Ru-Cl bonds can be broken easily.

Results

The same procedure as 2.2.1 was done with the ligand 3-phenyl-1H-pyrazole implemented instead, which is a bulkier ligand than the methyl version. The results indicate that this ligand behaved in the same manner as the 3,5-dimethylpyrazole in that only one attached on to Ru and thus producing a mono-substituted product, \( [(\eta^6-C_6H_6)RuCl_2(Me_2HPz)] \), instead of the expected di-substituted product. As in the previous reaction, only one Ru-Cl bond in the dimer was cleaved and one pyrazole ligand was attached.

2.3 Di-Substituted Catalyst

2.3.1 \( [(\eta^6-C_6H_6)RuCl(Me_2HPz)_2] \)

Results

The procedure of 2.2.1-2.2.2 was used under the same conditions by employing the ligand 3,4-dimethyl-1H-pyrazole and yielded the di-substituted product instead. This ligand is very similar to 3,5-dimethylpyrazole that was previously used to synthesize the mono-coordinated \( [(\eta^6-C_6H_6)RuCl_2(Me_2HPz)] \) and differs only in that the second \( CH_3 \) group is placed on a different core carbon of the pyrazole ligand. These results are extremely interesting because the Ru dimer was able to successfully split and two equivalents of the ligand attached to the Ru center, cleaving the two bridging Ru-Cl bonds of the complex. \( CH_3 \) is an electron-donating group and thus an activating group that
stimulates the reactivity of the pyrazole. Although the previous reaction featured a ligand with the same substituents, the arrangements of the CH$_3$ groups should have an effect on the pyrazoles’ ability to coordinate. The ligand used in this reaction, 3,4-dimethyl-1H-pyrazole, has CH$_3$ groups that are closer together and are both adjacent to the N coordination site. This can be why two ligands rather than one were present in the product. In addition, there is a presence of a counter-ion, Cl$^-$, that balances the positive charge of the synthesized di-substituted complex.

Characterization

The $^1$H NMR correctly characterized the protons, as shown by the results below. The proton on the central carbon of the pyrazole and the proton attached to the N were more deshielded in this product and displayed peaks that were thus further deshielded. This can be attributed to the placement of the CH$_3$ groups, which are closer to the electronegative N.

$^1$H NMR (25°C, 400 MHz, CDCl$_3$) δ ppm: 13.87 (s, 1H, NH), 7.61 (s, 2H, CH), 5.89 (s, 6H C$_6$H$_6$), 2.30 (s, 6H, 2xCH$_3$), 1.86 (s, 6H, 2xCH$_3$).

$^{13}$C NMR (25°C, 400 MHz, CDCl$_3$) δ ppm: 142.5 (s, CH), 141.9 (s, CH$_3$C=CH), 114.1 (s, CH$_3$C=CN), 85.8 (s, C$_6$H$_6$), 9.2 (s, 2xCH$_3$), 7.9 (s, 2xCH$_3$).

For the predicted product, in which the ruthenium dimer was split and two pyrazole ligands successfully attached to each Ru, the molecular weight is predicted to be 407.1 g/mol. The resulting ESI-MS spectra showed a peak at 407.1 m/z, exhibiting that the product features the correct number of ligands. There is also a peak at 311.0 m/z which is consistent with the previously synthesized mono-product, indicating the loss of one pyrazole ligand. However, it is possible that this ion fragment was generated during the ESI-MS process.

Results

The synthesis of a di-substituted Ru complex with the 3-phenyl-1H-pyrazole ligand, as intended in the synthesis of the mono-substituted [(η$^6$-C$_6$H$_6$)RuCl(PhHP$_z$)$_2$] in 2.2.2, was attempted using a different procedure. However, a tri-substituted complex was obtained instead. Although this complex is not eligible for dehydrogenation in the AB reactor due to steric hindrance, it is particularly interesting how three ligands were able to successfully attach to the center Ru. This procedure called for an excess of ligand to be reacted with the Ru dimer along with the use of a counter-ion, NaBPh$_4$, which appears to have cleaved all M-Cl bonds. Two equivalents of BPh$_4^-$ balance the +2 charge of complex due to the absence of Cl$^-$. The $^1$H NMR (25°C, 300 MHz, CDCl$_3$) δ ppm: 11.30 (s, 2H), 7.59-7.48 (m, 8H Ar counter-ion) 7.46 (d, J=2.0 Hz, 1H), 7.44-7.34 (m, aromatic), 7.31 (d, J=1.9 Hz, 2H), 7.29-7.18 (m, counter-ion), 7.08 (t, J=7.3 Hz, 8H counter-ion), 6.94 (t, J=7.1 Hz, 7H counter-ion), 6.58 (d, J=1.9 Hz, 1H), 6.53 (d, J=1.9 Hz, 2H), 5.22 (s, 6H).

$^{13}$C NMR (25°C, 400 MHz, CDCl$_3$) δ ppm: 148.0, 146.5, 146.0, 136.4, 134.3, 130.0, 129.3, 129.0, 128.3, 127.3, 125.9, 125.9, 125.9, 125.9, 125.7, 122.2, 105.9, 86.7, 85.6, 85.3.

A small amount of the solid was prepared to produce crystals suitable for x-ray crystallography. Figure 18 displays the structure of [(η$^6$-C$_6$H$_6$)Ru(PhHP$_z$)$_3$]BPh$_4$. It appears that three 3-phenyl-1H-pyrazole ligands are...
connected to the central ruthenium atom. The arrangement of the ligands can be due to the deprotonation of the nitrogen of one of the pyrazoles, shown by the ligand protruding up in the crystal structure. It is possible that this causes hydrogen bonding between the two pyrazole ligands and pulls them into the formation seen below. This experiment added an extra equivalent of ligand, as well as the strong counter-ion, NaBPh$_4$ to cleave the chlorides. It is possible that the NaBPh$_4$ cleaved all the Ru-Cl bonds and a third pyrazole ligand was able to attach to the Ru center.

Figure 18: Solid-State Structure for [(η⁶-C₆H₆)Ru(PhHP₂)₃]BPh₄. Counter-ion was omitted for clarity.

The ESI-MS results did not show a peak at the predicted mass of the tri-substituted product, 611.0 m/z, but a small peak at 502.9 m/z is shown in Figure 19, which is very close to the mass of the di-substituted derivative, 503.1 m/z. However, that could mean that this particular fragment of the product is sensitive to ESI-MS conditions or is not present in a large abundance. There is a possibility that the complex is unstable and may have lost a ligand when tested in the ESI-MS, giving the peak shown below.

Figure 19: ESI-MS of [(η⁶-C₆H₆)Ru(PhHP₂)₃]BPh₄

2.5 Bridged Ruthenium Dimers

2.5.1 Cl-Bridged Ru Dimeric Catalyst

This complex was synthesized using a previous procedure with the counter-ion NaBPh$_4$ and a solvent mixture of ethanol and dichloromethane. However, a different Ru dimer starting material was implemented, the Ru p-cymene Dimer, which is more soluble in polar organic solvents. This dimer was reacted with an excess of ligand 3-trifluoromethylpyrazole and NaBPh$_4$. the Na$^+$ cleaved the outside Ru-Cl bonds, keeping the dimer intact and yielding bonds between the Ru atoms and nitrogen center of the pyrazole. Through the reaction, one of the nitrogens was deprotonated which enabled its connection to Ru while the other nitrogen attached to the other Ru atom of the dimer, producing a pyrazole ligand bridging dimeric complex.

Characterization

$^1$H NMR (25°C, 400 MHz, CDC13) δ ppm: 7.74 (d, J=2.0 Hz, 1H), 7.47-7.39 (m, 6H), 7.02 (t, J= 7.4 Hz, 6H), 6.89 (t, 7.2 Hz, 3H), 6.69 (d, J= 2.3 Hz, 1H), 5.49 (d, J= 5.7 Hz, 1H), 5.35 (d, J= 5.9 Hz, 1H), 5.09 (d, J=6.3 Hz, 1H), 4.85 (d, J=6.2 Hz, 1H), 2.63 (sept, J= 6.9 Hz, 1H), 2.51 (sept, J= 6.9 Hz 1H), 1.93 (s, 1H CH3), 1.83 (s, 1H CH3), 1.14 (d, J= 6.9 Hz, 3H), 1.08 (d, J= 6.9 Hz, 3H).

$^{13}$C NMR (25°C, 400 MHz, CDC13) δ ppm: 164.9, 164.4, 163.9, 163.4, 144.0, 130.3, 136.3, 128.3, [125. 8, 125.7, 125.7, 125.7 (q)] 121.8, 109.3, 103.8, 102.2, 98.0, 96.5, 82.6, 81.5, 30.9, 30.9, 22.0, 18.4, 18.4.

$^{19}$F NMR δ ppm: 57.67 (s).

In Figure 21, the ESI-MS shows a strong peak at 676.5 m/z. The extremely high molecular mass can be attributed to the fact that the p-cymene Ru dimer did not split and the product still maintains two ruthenium centers. However, $^{19}$F NMR shows that fluorine is additionally in the contained product, indicating that the ligand is present in the obtained complex. The H of one nitrogen was cleaved by the counter ion, NaBPh$_4$, instead of the chlorides, which hindered the complex from splitting and placed a negative charge on that nitrogen of the ligand. This allowed the ligand to bond to the central ruthenium atoms, creating a dimer, bridged by a pyrazole ligand. The chemical formula of this dimer, C$_{24}$H$_{30}$N$_2$F$_3$Ru$_2$Cl$_2$, would give a mass of 676 m/z, directly paralleling the results from the product’s ESI-MS. Additionally, the isotropic pattern of the ESI-MS peak itself indicates the presence of two Ru centers.
2.5.2 Dimethoxy-Bridged Ru Dimer

This experiment was performed to afford a dimer that was bridged by the 3,5-dimethylpyrazole ligand. The ligand was first stirred in the solvent methanol and K"tBuO" was used to deprotonate the nitrogen in the pyrazole before exposure to the Ru-dimer and counter-ion NaBPh₄. Deprotonating the N allows for both nitrogens of the pyrazole to react with the Ru atoms while the NaBPh₄ cleaves the two outside Ru-Cl bonds. The ESI-MS in Figure 23 displays a peak at 517.0 m/z, meaning that the product is slightly off from the assumed structure (524.9 m/z). By analyzing different product possibilities and the molecular mass, it was determined that the ligand was able to successfully form a bridge in the dimer, but the \(-\text{OCH}_3\) of the methanol solvent replaced the chlorides. It can be inferred that the Ru-Cl bonds were extremely unstable and the \(-\text{OCH}_3\) groups were instead implemented from the methanol solvent. Although this complex was not used or measured for AB dehydrogenation, it gives insight into the structural tendencies of Ru dimers in that the chloride bond is extremely weak and can be easily detached.

To prevent this substitution, the same procedure was performed in a different solvent, dichloromethane, which cannot form this bridge. Figure 24 exhibits peaks at 516.2 m/z and 516.9 m/z from a second run, which is extremely close to that of the previous reaction and implies that the same product was synthesized. Methanol was used to dissolve the complex for mass spectroscopy testing, possibly allowing for the cleavage of Cl\(^-\) and replacement by \(-\text{OCH}_3\). This implies that the complex is sensitive to methanol because it reacts as soon it comes in contact with this solvent.

Characterization

The \(^1\text{H NMR}\) of this product is particularly interesting because different isomers are present. It can be predicted that there are two isomers because there are four sets of arene peaks with two at the same intensity between 6.03 ppm and 5.76 ppm, meaning that there are four different positions of the Ru-attached \(\eta^6\)-C\(_6\)H\(_6\).

\(^1\text{H NMR (25°C, 400 MHz, DMSO)}\delta \text{ ppm: 7.24-7.12 (m, Ar counter-ion 8H), 6.92 (t, J=7.3 Hz, 8H, Ar counter-ion), 6.79 (t, J=7.0 Hz, 4H, Ar counter-ion), 6.47 (s, CH, 1H),}\)
6.37 (s, CH, 1H), 6.03 (s, 6H, C\textsubscript{6}H\textsubscript{6}), 5.97(s, 6H, C\textsubscript{6}H\textsubscript{6}), 5.88(s, 6H, C\textsubscript{6}H\textsubscript{6}), 5.78(s, 6H, C\textsubscript{6}H\textsubscript{6}), 2.60-2.31 (m, 12H, CH\textsubscript{3}).

\textsuperscript{13}C NMR (25°C, 400 MHz, DMSO) \( \delta \text{ ppm: } 164.5, 164.0, 163.5, 163.0, 154.1, 153.4, 150.6, 136.0, 135.9, 125.7, 125.7, 121.9, 91.1, 88.9, 88.1, 84.9, 83.7, 83.4, 80.1, 80.0, 71.2, 17.4, 17.1, 16.2.

3. **Dehydrogenation of AB in High-Pressure Reactor**

A mono-substituted, di-substituted, and dimeric synthesized complex were used as catalysts for the dehydrogenation of AB in a high-pressure reactor to compare the effects and efficiency of the different substituted complexes. The device measures the release of H\textsubscript{2} from AB through the increase in pressure over the timespan of 24 hours when the catalyst is reacted. Figure 25 exhibits the reaction equation for AB catalyzed dehydrogenation.

\[ \text{NH}_3\text{BH}_3 \xrightarrow{\text{Catalyst}} (\text{NH}_2\text{BH}_2)_n \]

Figure 25: AB catalytic dehydrogenation reaction

3.1 **Mono-Substituted Catalyst:** \([\eta^6\text{-C}_6H_6]\text{RuCl}_2(\text{PhHPz})]\)

The procedure consists of 0.0315g of the mono-substituted catalyst, \([\eta^6\text{-C}_6H_6]\text{RuCl}_2(\text{PhHPz})]\), was used. Figure 26 exhibits the results after the catalyst reacted with 0.500g of AB for approximately 24 hours. The solvent diglyme was used due to catalyst solubility. This catalyst released a maximum of 1.31 equivalents of H\textsubscript{2} per mol of AB at a total pressure of 7.23 bar. The pattern of H\textsubscript{2} release appears to be gradual with no initial sharp increase. This exhibits that this catalyst cannot rapidly dehydrogenate AB and implies that it is not very efficient. The catalyst is mono-substituted with only one pyrazole ligand, making it easier to disassemble and lose this ligand through the reaction process. This can be the reason why this complex reacted at a slower rate.

Figure 26: Equivalents of H\textsubscript{2} released from AB monitored over time at 42°C using mono-substituted catalyst, \([\eta^6\text{-C}_6H_6]\text{RuCl}_2(\text{PhHPz})]\).

3.2 **Di-Substituted Catalyst**

For this test, 0.0277g of the di-substituted catalyst was used to dehydrogenate AB and Figure 27 displays the results after reaction for 24 hours at 42°C. The di-substituted catalyst released a maximum of 1.37 equivalents of H\textsubscript{2} per single mol of AB with a total pressure of 7.58 bar. The initial increase in H\textsubscript{2} release was faster than the previously used mono-substituted catalyst, making it more efficient. However, at 0.6 H\textsubscript{2} equivalents, the complex appears to gradually slow its dehydrogenation ability, which can also indicate that the complex is disassembling and the pyrazole ligands are detaching. If this is the case, the Ru-pyrazole bond may be unstable or extremely weak.

Figure 27: Amount of H\textsubscript{2} released from AB monitored over time at 42°C using di-substituted catalyst, \([\eta^6\text{-C}_6H_6]\text{RuCl}(\text{Me}_2\text{HPz})]\).

3.3 **Dimeric Catalyst**

For the last test, 0.0797g of the dimeric catalyst was used to dehydrogenate AB and Figure 28 displays the results after reaction for 24 hours at 42°C. The chloride-bridged Ru dimeric catalyst released a maximum of 1.46 equivalents of H\textsubscript{2} per single mol of AB at a total pressure of 7.82 bar. This catalyst appears to have a sharp increase in its release of H\textsubscript{2} from AB initially, giving the notion that it has a fast-acting nature. However, around 0.8 H\textsubscript{2} equivalents it appears to rapidly slow in its AB dehydrogenation and continues to slow in increase. This suggests that the complex decomposed in the high-pressure reactor due to instability or issues surrounding the attachment of the ligand.

Figure 28: Amount of H\textsubscript{2} released from AB monitored over time at 42°C using dimeric catalyst, \([\eta^6\text{-C}_6H_6]\text{RuCl}(\text{Me}_2\text{HPz})_2]\).
Figure 28: Amount of H₂ released from AB monitored overtime at 42°C using Cl-bridged Ru dimer catalyst, [C₂H₅Nₛ₅F₃R₆RuCl₂]  

4. MATERIALS AND METHODS  
**Materials 4.1-4.3:** 3-mouth 250mL round-bottom flask, reflux condenser, dry syn, hot plate/stirrer, stirring barglass stopper, rubber stopper, needle, single mouth 250mL round-bottom flask, vacuum-connecting glassware, filter.  
**Materials 4.4-4.5:** two 50mL schlenk tubes, stirrer, stirring bar, needle, in-line trap, tube connector, vacuum-connecting glassware, single mouth 250mL round-bottom flask, filter.  
**Materials 4.6:** two 50mL schlenk tubes, stirrer, stirring bar, vacuum-connecting glassware, single mouth 250mL round-bottom flask, filter.  
**Materials 4.7:** 50mL schlink tube, syringe, needle, stainless-steel high-pressure reactor setup (Figure 29).  

**Characterization Instruments 4.1:** ¹H NMR (25°C, 300 MHz, CDCl₃), ¹³C NMR (25°C, 400 MHz, CDCl₃), ESI-MS (in methanol), X-ray crystallography.  
**Characterization Instruments 4.2:** ¹H NMR (25°C, 500 MHz, CDCl₃), ¹³C NMR (25°C, 400 MHz, CDCl₃), ESI-MS (in methanol).  
**Characterization Instruments 4.3:** ¹H NMR (25°C, 400 MHz, CDCl₃), ¹³C NMR (25°C, 400 MHz, CDCl₃), ESI-MS (in methanol), X-ray crystallography.  
**Characterization Instruments 4.4:** ¹H NMR (25°C, 300 MHz, CDCl₃), ¹³C NMR (25°C, 400 MHz, CDCl₃), ESI-MS (in methanol), X-ray crystallography.  
**Characterization Instruments 4.5:** ¹H NMR (25°C, 400 MHz, CDCl₃), ¹³C NMR (25°C, 400 MHz, CDCl₃), ¹⁹F NMR, ESI-MS (in methanol).  
**Characterization Instruments 4.6:** ¹H NMR (25°C, 400 MHz, DMSO), ¹³C NMR (25°C, 400 MHz, DMSO), ESI-MS (in methanol).  

4.1 Synthesis of [(η⁶-C₆H₆)RuCl₂(Me₂HP₂)]  
The reaction apparatus was assembled, using a 3-mouth 250 mL round-bottom flask with a reflux condenser attached to the middle opening. A glass and rubber stopper were placed on the other openings. The system was flushed with vacuum and nitrogen gas before a mixture of [(η⁶-C₆H₆)RuCl₂] and 3,5-dimethylpyrazole was added. Approximately 100mL of extra dry acetone was further degassed with nitrogen gas in a 100mL schlenk tube before being transferred to the mixture in the round-bottom flask by needle. The reaction was set to reflux at 60°C for 4 hours. The red/brown solution was then cooled and filtered into another 250mL round-bottom flask that was capped and put in the freezer overnight. It remained a red/orange color by the next day and a small amount of precipitate was present, which was filtered for a second time and collected.  

4.2 Synthesis of [(η⁶-C₆H₆)RuCl₂(PhHP₂)]  
The procedure of 4.1 was followed in this experiment. Approximately 100mL of dry acetone was added to a mixture of [(η⁶-C₆H₆)RuCl₂] and four equivalents of 3-phenyl-1H-pyrazole. After refluxing overnight and then filtering, an orange solid was recovered.

| [[(η⁶-C₆H₆)RuCl₂] (product)] | 3-phenylpyrazole | [(η⁶-C₆H₆)RuCl₂(PhHP₂)] (product) |
|-------------------------------|-----------------|-----------------------------------|
| Mols                           | 0.0005mols      | 0.0005mol                          |
| Grams                         | 0.250g          | 0.250g                             |
| Molecular Weight              | 499.8g/mol      | 499.8g/mol                         |

Percent yield: 70%  

4.3 Synthesis of [(η⁶-C₆H₆)RuCl(Me₂HP₂)]  
The procedure of 4.1 was followed and used the exact amounts of each chemical, implementing a similar ligand, 3,4-dimethyl-1H-pyrazole. After the solution was left in the freezer overnight, a yellow precipitate formed at the bottom of the flask by the next day. The solution continued to be filtered for a second time and the yellow solid precipitate was collected.

| [(η⁶-C₆H₆)RuCl₂] (product) | 3,4-dimethyl-1H-pyrazole | [(η⁶-C₆H₆)RuCl(Me₂HP₂)] (product) |
|----------------------------|--------------------------|----------------------------------|
| Mols                       | 0.0005mols               | 0.0005mol                         |
| Grams                      | 0.250g                   | 0.250g                            |
| Molecular Weight           | 499.8g/mol               | 499.8g/mol                        |

Percent yield: 53%  

4.4 Synthesis of Tri-Substituted Ru Complex  
Two, preheated 50mL schlenk tubes were flushed with vacuum/nitrogen gas 3 times. In one, [(η⁶-C₆H₆)RuCl₂], 3-phenyl-1H-pyrazole, and NaB₆Ph₄ were added. In the other, 3mL of ethanol and 5mL of dichloromethane were added and degassed with nitrogen flow for approximately 10mins. The solvents were transferred by needle to the other schlenk tube with the solids. The orange/brown solution was left to stir overnight, where the substance turned a dark green color. The solvents were reduced down using an in-line trap with liquid nitrogen, and the resulting solution was washed with pentane to be filtered, yielding a green/yellow solid.

| [(η⁶-C₆H₆)RuCl₂] (product) | 3-phenylpyrazole | NaB₆Ph₄ | [(η⁶-C₆H₆)RuCl(PhHP₄)] (product) |
|----------------------------|-----------------|--------|----------------------------------|
| Mols                       | 0.0005mols      | 0.0005mol | 0.0005mol                         |
| Grams                      | 0.100g          | 0.200g   | 0.362g                            |
| Molecular Weight           | 499.8g/mol      | 144.17g/mol | 499.8g/mol                        |

Percent yield: 26%  

4.5 Synthesis of Cl-Bridged Ru Dimeric Catalyst  
The procedure of 4.4 was followed and substituted a different ruthenium complex, the p-cymene chloro-dimer, in which the arene groups have a methyl and isopropyl group attached. 0.183g (0.0003mols) of this dimer reacted with the
3- trifluoromethylpyrazole (0.204g, 0.0015mols) and NaBPh₄ (0.205g, 0.0006mols) in 3mL of ethanol and 5mL of dichloromethane. The reaction yielded an orange solid product (0.1854g).

| p-cymene dichlor-dimer | 3-trifluoromethylpyrazole | NaBPh₄ | Ci-Bridged Ru Dimer Catalyst (product) |
|-------------------------|---------------------------|--------|---------------------------------------|
| Mols                    | 0.0002mols                | 0.0015mols | 0.0000mols                             |
| Grams                   | 0.184g                    | 0.204g  | 0.205g                                |
| Molar Weight            | 611.0 g/mol               | 136.08 g/mol | 341.7 g/mol                            |
|                         |                           | 476 g/mol | obtained                              |

Percent yield: 62%

4.6 Synthesis of Dimethoxy-Bridged Ru Dimer

A 50mL schlenk tube was flushed with vacuum/nitrogen gas before adding 3,5-dimethylpyrazole, K'tBuO⁻, and 20mL of dry methanol. This mixture stirred for one hour to deprotonate the nitrogen of the pyrazole ligand. NaBPh₄ and [η⁶-C₆H₆]RuCl₂ were added and the reaction was left to stir overnight. The solution was then filtered to collect an orange solid product. This procedure was repeated for a second time in dichloromethane solvent instead of methanol. Results were the same.

Percent yield: 76%

4.7 Ammonia Borane Reactor Procedure

Under a fume hood, AB was transferred to a preheated 50mL schlenk tube and dissolved in 5mL of diglyme. 0.5mol% of the catalyst was measured in a glass insert. This insert was then transferred to the reactor, where the system was heated to an internal temperature of 42°C. When this temperature was reached, the AB and diglyme solution was taken up and transferred by syringe to the Parr pressure reactor. The reactor runs for approximately 24 hours and measures the increase in pressure which directly corresponds to the amount of H₂ released from AB.

Figure 29: Experimental setup for measuring catalytic dehydrogenation of AB in stainless-steel Parr Reactor

5. Conclusion and Future Work

Various experiments were carried out to test the binding affinity of pyrazole ligands to an arene-Ru dimer complex in order to successfully create catalysts for the dehydrogenation of AB. Reactions involving pyrazole with CF₃ substituents were particularly difficult when forming the desired products due to their electron-withdrawing nature. However, an unusual chloride-bridged Ru dimer was formed and placed in a high-pressure reactor to measure the rate of dehydrogenation from AB. This dimeric catalyst released the largest equivalent of H₂ from AB (1.5 equivalents), thus establishing it as the most efficient catalyst synthesized in this project. The stability of the catalyst stands as a concern due to its rapid decrease in H₂ release after approximately 4 hours. The release is initially very fast, but this slowing can be attributed to the decomposition of the catalyst in that the pyrazole ligand could be detached from the Ru center. The lifetime of this catalyst appears to be unpredictable and studies surrounding the stabilization of the dimer catalyst can be carried out in the future. The use of chelating pyrazole ligands may be necessary in order to stabilize this complex, in that multiple sites of attachment may be necessary. This is also known as a bi-dentate and can increase the efficiency of this catalyst by enabling it to stay intact in the high-pressure reactor. The dimeric catalyst contained two nitrogen sites that were attached to the Ru centers and may have increased its H₂ releasing efficiency compared to the other catalysts. Further research is needed to solidify these claims and improve the performance of this catalyst for possible application to larger-scale devices in the future.

6. Acknowledgements

I am grateful to Arcadia University for providing the opportunity to participate in this program. I would also like to thank Dr. Andrew Phillips for the privilege of working in his lab, in addition to Francesca Giulia Nucca and Gearóid Manning for helping me obtain the skills and techniques to complete this project.
7. References

[1] Broom, Darren P. Hydrogen Storage Materials: the Characterisation of Their Storage Properties. Springer, 2011.

[2] Godula-Jopek, Agata, et al. Hydrogen Storage Technologies New Materials, Transport, and Infrastructure. Wiley-VCH, 2012.

[3] “Hydrogen Storage.” Energy.gov, Department of Energy, www.energy.gov/eere/fuelcells/hydrogen-storage.

[4] Jiang, Hai-Long, and Qiang Xu. “Catalytic Hydrolysis of Ammonia Borane for Chemical Hydrogen Storage.” Catalysis Today, Elsevier, 27 Oct. 2010, www.sciencedirect.com/science/article/pii/S0920586110005699.

[5] Nathanson, Atahl. Ammonia Borane Composites for Solid State Hydrogen Storage and Calcium-Ammonia Solutions in Graphite. University College London. Degree of Engineering Doctorate thesis. http://discovery.ucl.ac.uk/1456361/2/Atahl%20Nathanson%20Thesis%20Ammonia%20borane%20composites%20for%20solid%20state%20hydrogen%20storage%20and%20calcium-ammonia%20solutions%20in%20graphite.pdf.

[6] O’Connor, Crystal. Ru(II) and Os(II) Complexes Bearing Acetylacetonato, B-Ketoiminato and B-Diketiminato Ligands Towards the Efficient Dehydrogenation of Amine-Boranes. 2015. University College Dublin, PhD dissertation.

[7] Pai, Sung Jin, and Sang Soo Han. “SE2 Reaction in Noncarbon System: Metal-Halide Catalysis for Dehydrogenation of Ammonia Borane.” PNAS, National Academy of Sciences, 26 Dec. 2017, www.pnas.org/content/114/52/13625.abstract.

[8] Parafiniuk, Monika, and Mariusz Pawel Mitoraj. “Origin of Binding of Ammonia–Borane to Transition-Metal-Based Catalysts: An Insight from the Charge and Energy Decomposition Method ETS-NOCV.” Organometallics, vol. 32, no. 15, 2013, pp. 4103–4113, doi:10.1021/om400235e.

[9] Roberts, David. “This Company May Have Solved One of the Hardest Problems in Clean Energy.” Vox, Vox, 16 Feb. 2018, www.vox.com/energy-and-environment/2018/2/16/16926950/hydrogen-fuel-technology-economy-hytech-storage.

[10] Sarthaeva, A., et al. “Hydrogen Nexus in a Sustainable Energy Future.” Energy & Environmental Science, The Royal Society of Chemistry, 2 July 2008, pubs.rsc.org/en/content/articlelanding/2008/EE/B810104N#!divAbstract.

[11] Schreiber, Dominique F., et al. “Application of β-Diketiminato Arene-Substituted Ru(II) Complexes in Highly Efficient H2 Dehydrocoupling of Amine Boranes.” ACS Catalysis, vol. 2, no. 12, 2012, pp. 2505–2511, doi:10.1021/cs300499d.

[12] Yang, J. B., et al. “Structural Evolution of Ammonia Borane for Hydrogen Storage.” Structural Evolution of Ammonia Borane for Hydrogen Storage: Applied Physics Letters: Vol 92, No 9, Applied Physics Letters, 7 Mar. 2008, aip.scitation.org/doi/full/10.1063/1.2889535.

[13] Zhang, Xingyue, et al. “Dehydrogenation of Ammonia Borane through the Third Equivalent of Hydrogen.” Dalton Transactions, The Royal Society of Chemistry, 23 Mar. 2016, pubs.rsc.org/en/content/articlelanding/2016/dt/c6dt00604c#!divAbstract.

[14] Züttel, Andreas. “Hydrogen Storage Methods.” SpringerLink, Springer-Verlag, 17 Mar. 2004, link.springer.com/article/10.1007%2Fs00114-004-0516-x#citeas.