Homogeneous Tridentate Ruthenium Based Hydrogenation Catalysts for the Deoxygenation of Biomass Derived Substrates in Aqueous Acidic Media

by

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ABSTRACT

HOMOGENEOUS TRIDENTATE RUTHENIUM BASED HYDROGENATION CATALYSTS FOR THE DEOXYGENATION OF BIOMASS DERIVED SUBSTRATES IN AQUEOUS ACIDIC MEDIA

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Project I: [Ru(OH)$_3$(4′-phenyl-2,2′:6′:2″-terpyridine)](OTf)$_2$ as a Homogeneous Hydrogenation Catalyst for Biomass Derived Substrates.

The complex [Ru(OH)$_3$(4′-phenyl-2,2′:6′:2″-terpyridine)](OTf)$_2$ has been shown to be an active ionic hydrogenation catalyst for selected carbonyls, diols and glycerol by the Schlaf group. It was postulated to also be active for other biomass derived substrates such as levulinic acid (LA), furfural and 5-hydroxymethyl furfural (HMF). Synthesis of the complex was optimized and full characterization carried out by $^1$H/$^{13}$C –NMR. The complex was tested against LA in aqueous sulfolane medium and the furfural/HMF model system 2,5-hexanedione in water. Activity of the complex was compared to the analogous metal-ligand bifunctional (MLB) system described in Project II. The complex exhibited good thermal stability up to 200 °C in 90/10 wt% sulfolane/water mixtures and was capable of hydrogenation of LA to $\gamma$-valerolactone in 95% yield. Addition of protic acids to the reaction mixture and increasing proportions of water decreased the activity of the complex towards the hydrogenation of LA.

Project II: [Ru(OH)$_3$(di(picolyl)amine)](OTf)$_2$ as an acid-, water- stable, metal-ligand bifunctional deoxygenation catalyst.

The complex [Ru(OH)$_3$(di(picolyl)amine)](OTf)$_2$ was postulated to be an active MLB ionic hydrogenation catalyst under acidic aqueous conditions. Using the substantially labile
[Ru(DMF)₆](OTF)₃ ruthenium complex as the precursor, the desired complex was prepared in-situ by coordination of the DPA ligand and concomitant reduction of Ru³⁺ to Ru²⁺. The complex was characterized by $^1$H/$^{13}$C-NMR and tested for the hydrogenation of LA, 2,5-hexanediione, furfural and HMF under acidic aqueous conditions. The complex exhibited thermal stability up to 150 °C and was active for the hydrogenation of carbonyls, as demonstrated by the conversion of 2,5-hexanediione to 2,5-hexanediol in 94% yield in water. Addition of H₃PO₄ as an acid co-catalyst resulted in nearly complete conversion to dimethyltetrahydrofuran (DMTHF) but further deoxygenation could not be achieved. Direct comparison of [Ru(OH₂)₃(di(picolyl)amine)](OTf)₂ and [Ru(OH₂)₃(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)₂ under identical conditions against LA and 2,5-hexanediione demonstrated that the [Ru(OH₂)₃(di(picolyl)amine)](OTf)₂ catalyst is more active than the [Ru(OH₂)₃(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)₂ complex in all cases, suggesting that the di(picolyl)amine complex operates through a MLB ionic hydrogenation mechanism.
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LIST OF ABBREVIATIONS

AE    Autoclave Engineers
ABE   Acetone-butanol-ethanol
acac  acetylacetone
amt.  amount
APD-H aqueous-phase deoxygenation/hydrogenation
APR   aqueous-phase reforming
bipy  2,2′-bipyridine
b.p.  boiling point
br    broad
Bu    n-butyl
r-Bu  tert-butyl
cal   calorie (4.184 J)
calc. calculated
cat.  catalyst
cm    centimetre
conc. concentrated
conv. conversion
cp    cyclopentadienyl, C₅H₅−
cp*  pentamethylcyclopentadienyithion, C₅Me₅⁻
d  doublet (NMR)
dabipy  6,6’-diamino-2,2’-bipyridine
daphen  2,9-diamino-1,10-phenanthroline
dec.  decomposed (m.p.)
dd  doublet of doublets (NMR)
dil.  dilute
DMS  dimethylsulfone
dmso  dimethyl sulfoxide
DMTHF  2,5-dimethyltetrahydrofuran
DPA  di(picolyl)amine
EA  elemental analysis
eq., equiv.  equivalents
ESI  electrospray ionization
Et  ethyl
FID  flame ionization detector
FTS  Fischer-Tropsch synthesis
GC  gas chromatography
GC-MS  gas chromatography-mass spectrosocpy
xx
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>GVL</td>
<td>γ-valerolactone</td>
</tr>
<tr>
<td>HMF</td>
<td>5-hydroxymethylfurfural</td>
</tr>
<tr>
<td>HOTf</td>
<td>trifluoromethanesulfonic acid, triflic acid</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>IR</td>
<td>infrared (spectroscopy)</td>
</tr>
<tr>
<td>ISTD</td>
<td>internal standard</td>
</tr>
<tr>
<td>LA</td>
<td>levulinic acid</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos National Laboratory</td>
</tr>
<tr>
<td>lbs</td>
<td>pounds</td>
</tr>
<tr>
<td>liq/liq</td>
<td>Liquid/liquid extractor</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (NMR)</td>
</tr>
<tr>
<td>M</td>
<td>mole/litre</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption ionization</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>m/e</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>MLB</td>
<td>metal-ligand bifunctionality</td>
</tr>
<tr>
<td>mM</td>
<td>millimole/litre</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>MMt</td>
<td>million metric tonnes</td>
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</table>
mol  mole(s)
m.p.  melting point
MS   mass spectroscopy
MTHF methyltetrahydrofuran
MW   molecular weight
NMR  nuclear magnetic resonance (spectroscopy)
OMe  methoxy
OTf  trifluoromethanesulfonate, triflate, CF$_3$SO$_3^-$
PA   pentanoic acid
PDO  propanediol
Ph   phenyl
phen 1,10-phenanthroline
Ph-trpy 4′-phenyl-2,2′:6′,2″-terpyridine
ppm  parts per million
PPT  poly(propylene) terephthalate
Pr   $n$-propyl
Psi  pounds per square inch
s    singlet (NMR)
t    triplet (NMR)

xxii
td \hspace{2em} \text{triplet of doublets (NMR)}

terpy \hspace{2em} 2,2':6',2''-\text{terpyridine}

triphos \hspace{2em} \text{bis(2-diphenylphosphinoethyl)phenylphosphine}

THF \hspace{2em} \text{tetrahydrofuran}

TOF \hspace{2em} \text{turnover frequency}

TON \hspace{2em} \text{turnover number}

TPPTS \hspace{2em} \text{sodium triphenylphosphine trisulfonate}

Ts, tosyl \hspace{2em} (p-toluenesulfonyl)

TS \hspace{2em} \text{transition state}

\( \mu \text{L} \) \hspace{2em} \text{microlitre}

UV \hspace{2em} \text{ultraviolet (spectroscopy)}

v/v \hspace{2em} \text{volume/volume}

WGSR \hspace{2em} \text{water-gas shift reaction}

wt\% \hspace{2em} \text{weight percent}
1 Introduction

1.1 Motivation

For over one hundred and fifty years a large body of knowledge has been developed on the refining, processing and transformation of crude oil into useful petrochemicals such as fuels, polymers, and fine or specialty chemicals. Although the use of crude oil as a precursor to a plethora of useful materials has been exceedingly profitable to present, its components are characterized by a lack of oxygen and nitrogen containing functional groups, and are therefore underfunctionalized. To circumvent the lack of reactivity displayed in the alkane and arene crude oil components many processes have been developed to activate the carbon-carbon or carbon-hydrogen bonds by converting alkenes, arenes and alkanes into aldehydes, ketones, alcohols, carboxylic acids, nitriles, phenols or other reactive compounds. Often such processes involve the use of heterogeneous or homogenous catalysts and are highly specialized and optimized for use on a technical scale to effect amination, oxidation, hydration, hydroformylation, hydrocyanation and dehydrogenation to name but a few examples.\(^1,2\)

However, the use of fossil petroleum is putting an increasing burden on the natural environment. Furthermore, it is a finite feedstock, and therefore not sustainable indefinitely. A possibly feasible alternative is the shift to renewable carbon sources for the production of petrochemical feedstocks. An exceedingly abundant carbon source lies within the sugar monomers of lignocellulosic biomass, the material which comprises the cell wall of plant organisms. It is undoubtedly the most abundant source of carbon on the planet; with annual planetary production estimated at over 200 billion tonnes. The particular attraction of biomass is not only that it is exceptionally cheap, but it is carbon-neutral, meaning that the production of the
biomass itself helps to consume carbon dioxide. The challenge in using biomass based feedstocks lies in addressing the overfunctionalization of the lignocellulosic biomass. Biomass is comprised mainly of three components; cellulose, hemicellulose and lignin. Each component is characterized by having a large number of hydroxyl functions and iterative dehydration, hydrogenation and hydrogenolysis reactions will be required before the components begin to resemble existing petro-chemical feedstocks. Significantly less research and development has focused on this area compared to the use of crude oil as a precursor.

Figure 1.1: Potential routes for carbon-based feedstocks.

1.2 Lignocellulose

Of the three main components of lignocellulose; cellulose, hemicellulose and lignin, 75-90 wt.% are polymeric sugars while the remainder is lignin in the form of aromatic macromolecule composed of irregular arrays of propyl-catechol units derived from coumaryl and syringyl alcohols. The main component, cellulose, is comprised mostly of glucose monomers bound by
β-1,4-glycosidic linkages which can – in principle – be hydrolyzed to produce dimers, trimers and tetramers. These components can be further hydrolyzed to the monomer glucose. Hemicellulose is similar in structure although the sugar monomers with which it is constructed are mainly the two C₅ sugars xylose and arabinose in varying proportion depending on plant species, as well as galactose, glucose and mannose, three C₆ sugars. Hemicellulose accounts for 20-40 wt. % of biomass. Hydrolyzing hemicellulose is substantially more facile due to the amorphous structure caused by the five bound sugars whereas cellulose has a distinct crystalline structure due to regular inter-strand hydrogen bonding of glucose monomers.

Figure 1.2: Structure and polymeric components of lignocellulosic biomass.⁶

The conversion of lignocellulosic biomass to platform feedstocks can be achieved through several methods: pyrolysis, gasification, hydrolysis and refining.⁷⁻¹⁰ Pyrolysis of biomass is the rapid heating of biomass at temperatures in excess of 500 °C in anaerobic
conditions to form bio-oil. Further heating of biomass beyond 800 °C results in gasification to synthesis gas (Syngas), CO\(_{(g)}\) and H\(_{2(g)}\), an extremely useful intermediate.\(^7\) The proportions of CO\(_{(g)}\) and H\(_{2(g)}\) produced can be controlled by the water gas shift reaction (WGSR), a reaction between CO\(_{(g)}\) and H\(_2\)O to form CO\(_2(g)\) and H\(_2(g)\), catalyzed by iron and chromium-oxide.\(^{11}\) The combination of gasification, WGSR and Fischer-Tropsch synthesis (FTS) can therefore be used to produce hydrocarbons and methanol from biomass (Figure 1.3).\(^{12}\)

\[
\begin{align*}
\text{Biomass} & \xrightarrow{\Delta} \text{CO} + \text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \xrightarrow{[\text{Fe} / \text{CrO cat.}]} \text{CO}_2 + \text{H}_2 \quad \text{WGSR} \\
\text{CO} + 2 \text{H}_2\text{O} & \xrightarrow{[\text{Cu} / \text{ZnO cat.}]} \text{CH}_3\text{OH} \\
n\text{CO} + (n + m/2) \text{H}_2 & \xrightarrow{[\text{Fe cat.}]} \text{C}_n\text{H}_m + n\text{H}_2\text{O} \quad \text{FTS}
\end{align*}
\]

**Figure 1.3:** Conversion of biomass by gasification to hydrocarbons via WGSR and FTS.

Several problems arise when these methods are employed including thermal efficiencies, which are typically less than 60%, even with the use of integrated thermal recovery, and a wide product distribution, especially for Fischer-Tropsch. The production of many varying carbon chain lengths means that further refining is required to suit the needs of conventional diesel or aviation fuel which requires only a narrow range of carbon chain lengths. Furthermore, catalytic processes using synthesis gas require that the gas is purified to remove all traces of sulfur and ammonia to avoid poisoning the catalyst, meaning the syn-gas must be further treated.\(^{13}\) Consequently current methods for biomass conversion have dismal carbon atom efficiencies where with only about one out of five biomass derived carbon atoms being retained in a viable fuel product, not including the amount of carbon based feedstock required to heat the gasifiers and produce electricity for the plant to operate.
Hydrolysis of biomass refers to the acidic or basic breakdown of polysaccharides in aqueous conditions to generate sugar monomers.\(^8\) Further dehydration and hydration reactions can lead to various platform molecules; species which are the most promising sugar derived molecules for the production of carbon based polymers, such as levulinic acid, furfural, 5-hydroxymethylfurfural (HMF) and sugar polyalcohols.

In recent years methods for the hydrolysis of sugar polymers to monomer constituents has become increasingly efficient. Glucose, xylose and HMF can be obtained from hydrolysis in ionic liquids under relatively mild conditions (\(\leq 140\,^\circ\text{C}, 1\,\text{atm.}\)).\(^{14,15}\) Ionic liquids provide a homogeneous medium for the hydrolysis of cellulose and hemicellulose to reducing sugars and can be further converted to furfural and HMF through the use of an aldose-ketose isomerization catalyst such as CrCl\(_2\).\(^{14}\) Once hydrolysis to C5/C6 units is achieved, further deoxygenation can proceed through the acid-catalyzed dehydration followed by hydrogenation of the resulting unsaturated bonds. The net effect is the removal of oxygen from the substrate (Figure 1.4). When this reaction motif is applied iteratively to hemicellulose (Scheme 1.1) and cellulose (Scheme 1.2) a large variety of value added chemicals can be produced including alkenes, alkanes and primary alcohols.

![Figure 1.4: Strategy for the deoxygenation of sugar polyalcohols.](image)

\(\text{Net reaction: } -n\,\text{H}_2\text{O} + n\,\text{H}_2(\text{g}) = -n\,\text{O}\)
Scheme 1.1: Potential pathways for the deoxygenation of hemi-cellulose derived platform chemicals.

Scheme 1.2: Potential pathways for the deoxygenation of cellulose derived platform chemicals.
Despite the great breadth of research on the catalytic hydrogenation/hydrogenolysis of various substrates, only recently has this knowledge begun to be applied to the conversion of biomass. The primary goal of our research is to develop a catalytic system which can selectively deoxygenate biomass-derived substrates. This thesis investigates the deoxygenation of levulinic acid and 2,5-hexanedione (a model system for furfural and HMF) with two rationally designed homogeneous ruthenium based complexes.

1.3 Hydrogenation/Hydrogenolysis of Biomass Derived Substrates

In 2002 a comprehensive review was undertaken by the U.S. Department of Energy to identify the top value added chemicals achievable from biomass derivation. They began from 300 potential candidate platform chemicals. The criteria for selection were the overall feedstock cost, processing costs, current market prices and volumes and their relevance to biorefinery operations in the future. In two years the list had been reduced tenfold and was further narrowed to a top 12 chemicals.

1.3.1 Levulinic Acid

Levulinic acid (LA) is produced by the acid hydrolysis of lignocellulosic materials into 5-hydroxymethylfurfural (HMF) followed by the thermal deformylation shown in Scheme 1.3. Levulinic acid is currently produced for $0.09 - $0.22 per kg using a patented technology involving HMF as an intermediate. Its availability and reactivity make it an important precursor for polymers and petrochemicals.
Scheme 1.3: Production of levulinic acid from cellulose via the deformylation of HMF.

Once obtained, LA can undergo a series of deoxygenation reactions to value added chemicals such as methyl-tetrahydrofuran (MTHF), a useful fuel additive, or pentanoic acid, a precursor for ethyl-pentanoate, a diesel fuel additive.\textsuperscript{17,18} A conceivable pathway for the selective and complete deoxygenation of LA is presented in Scheme 1.4

Scheme 1.4: Levulinic acid value chain to methyl THF or pentene.
In acidic media levulinic acid undergoes an acid-catalyzed ring closure to \(\gamma\)-angelica lactone which is catalytically hydrogenated to \(\gamma\)-valerolactone (GVL). Further hydrogenolysis ring opens to pentanoic acid.\(^{17,19}\) Pentanoic acid can undergo decarboxylation to butene, which can be oligomerized to higher alkanes or hydrogenated to butane.\(^{20,21}\) It is also possible to proceed from pentanoic acid by hydrogenation to pentanal and pentanol. A final acid-catalyzed dehydration would produce pentene which can phase separate or further hydrogenate to pentane.\(^{22}\) Alternatively the cyclic GVL can undergo iterative metal-catalyzed hydrogenations and acid-catalyzed dehydrations as seen with the polyols to yield methyltetrahydrofuran (MTHF). MTHF can continue through the deoxygenation pathway and reach pentene and pentane or directly be used as an oxygenated fuel or solvent, i.e., a biomass derived THF replacement.\(^{18}\) Pentene and pentane hold high value as feedstocks for PlatFoming (Platinum Reforming) to produce gasoline or elastomers.\(^{23}\)

1.3.2 HMF/Furfural Derived Substrates

One of the challenges associated with the use of biomass as a precursor for petrochemicals is the restriction of available carbon chain lengths. Carbon chain lengths of \(C_8\)-\(C_{15}\) are required for fuel applications while typical carbon chain lengths in biomass range from \(C_3\)-\(C_6\). These light alkenes and alkanes can be produced from sugar-derived polyalcohols through the aqueous-phase dehydration/hydrogenation (APD-H) or aqueous-phase reforming (APR) (Scheme 1.5). Dumesic \textit{et al.} have been able to selectively form blends of light alkanes with the use of Re, Ru, Rh, Ir, Ni, Pd and Pt on silica supports along with a solid acid or mineral acid co-catalyst,\(^{24}\) however longer chain lengths are more desirable. Dumesic has attempted to address this issue with the use of upstream aldol condensations to increase substrate chain length (\(C_7\)-\(C_{15}\)) followed by APD-H as shown in Scheme 1.5.\(^{24}\) The condensation of acetone and HMF
allows for the production of C₉ alkanes while further aldol condensations with HMF increase possible chain lengths to C₁₅. The APD-H process was performed with a metal/acid catalyst in a four-phase reactor system comprised of the aqueous substrate inlet stream (1), a hexadecane alkane inlet stream (2), a H₂ inlet stream (3) and the solid Pt/SiO₂-Al₂O₃ catalyst (4). The production of C₉-C₁₅ alkanes in these conditions leads to a significant buildup of coke in the reactor and degradation of the catalyst under APD-H conditions (20-50% coke formation).²⁴

**Scheme 1.5:** Production of liquid alkanes (C₉-C₁₅) from glucose through APD-H over acid/metal catalysts.²⁴

More recently, Silks and coworkers at a collaborating research group at Los Alamos National Laboratory (LANL) devised a method of extending the chain lengths of furfural and HMF derived substrates to C₈-C₁₅ in good yields and selectivity.²⁵ The novel use of aldol condensation reactions takes relatively inexpensive starting materials and converts them to long chain feedstocks for deoxygenation (Scheme 1.6). Using a metal Zn/Yb proline based catalyst or an organic benzimidazole based catalayst shown in Figure 1.5 a variety of aldol products can be
obtained. Condensing HMF or furfural with ethyl levulinate, produced by esterification of LA, brings substrates into the realm of $C_{10}-C_{12}$. 1,1-Dimethoxy-2-propanone (pyruvaldehyde dimethylacetal) can be obtained from methanol and pyruvaldehyde in good yields, resulting in $C_8-C_9$ when condensed with furfural and HMF respectively. Acetone is a common byproduct of the cumene process and can also be obtained from biomass via the Acetone-butanol-ethanol (ABE) process or by ketonization of acetic acid and is therefore readily available. It allows for the condensation with furfural and HMF into the $C_8-C_9$ range and further condensation of the resulting $\alpha,\beta$-unsaturated ketone with furfural and HMF leads into the $C_{13}-C_{15}$ range quite easily.

**Scheme 1.6**: LANL derived aldol condensation products from; HMF (R= CH$_2$OH), methyl furfural (R= CH$_3$) and furfural (R=H) produced by Silks’ catalysts.
**Figure 1.5:** Catalysts produced by Silks and coworkers for the aldol chain extension of furfural and HMF.

HMF, furfural and their corresponding condensates (as shown above) and hydrogenated alcohols are highly reactive species towards further uncontrollable cross-condensations and polymerizations leading to humins and coking. As some of these substrates are presently only available in limited amounts (research scale) it is therefore useful to first test and develop a suitable cheap and commercially available model substrate system to test the efficacy of newly developed catalytic systems against the same functional groups a homogeneous complex would encounter for the deoxygenation of furfural or HMF without the risk of coking and polymerization. An ideal substrate for this purpose is 2,5-hexanedione which, when subjected to acid-catalyzed dehydration followed by metal-catalyzed hydrogenation pathways described previously, will form many structures analogous or directly equivalent to furfural and HMF. The deoxygenation reaction cascade of 2,5-hexanedione is presented in Scheme 1.7 and begins with either an intramolecular aldol condensation, leading to methyl cyclopentane after hydrogenation, or hydrogenation to 5-hydroxy-2-hexanone which would undergo cyclisation to the hemiacetal. Alternatively 2,5-hexanedione can be hydrogenated with 2 equivalents of $H_2$ to yield 2,5-hexanediol. Further deoxygenation of the hemiacetal leads to 2,5-dimethyltetrahydrofuran (DMTHF). DMTHF is very stable to both hydrolysis and hydrogenolysis and the equilibrium between DMTHF and 2,5-hexanediol lies heavily towards DMTHF and requiring temperatures ~
250 °C to obtain the ring opened product. Once the DMTHF is reopened it can undergo further dehydration/hydrogenation reactions to hexane/hexane.

The overall goal with respect to 2,5-hexanedione is to design a catalytic system capable of complete deoxygenation to alkenes/alkanes, which could then be applied to furfural and HMF systems.

Scheme 1.7: Potential deoxygenation pathways of model substrate 2,5-hexanedione.
1.4 Homogeneous Deoxygenation of Biomass

As mentioned previously, the challenge in using biomass-derived materials as precursors to petrochemicals is the relatively high oxygen content with respect to petroleum. Instead of introducing functionality through such processes as oxidation, hydrocyanation, hydroformylation, etc., the selective removal of alcohols and carbonyls is required. The sheer number of oxygen containing functional groups make typical existing methods for deoxygenation non-viable. Heterogeneous catalyst systems typically succumb to coking and caramelization in polar aqueous conditions when applied to biomass substrates, especially sugars, and thus require very costly catalyst recycling. The deoxygenation of carbonyls and alcohols to alkanes has certainly been possible for some time by Wolf-Kishner and Clemmensen reductions or the Barton-McCombie mechanism. These reactions are not feasible for the deoxygenation of biomass due to the stoichiometric use of toxic/expensive reagents and their inability to deal with substrates containing many functional groups. Typically biomass derived substrates contain a functionality on every carbon (sugar polyols/glycerol) or a variety of different oxygen functions on a portion of carbons (LA/HMF). Remarkably, the deoxygenation of biomass derived substrates, as presented in the previous section, only involves the use of only four fundamental reactions shown in Figure 1.6. The common trait shared by reactions 1,2 and 3 in the series is that the first step is the acid catalyzed dehydration of a hydroxyl group followed by metal catalyzed hydrogenation. In the case of reaction 1, vicinal diols, the secondary alcohol will always dehydrate first to form the thermodynamically more favoured secondary carbocation. Keto-enol tautomerization then yields a carbonyl which can be catalytically hydrogenated to the alcohol. The logical progression after no vicinal diols remain is reaction 2 where dehydration yields an alkene which is hydrogenated to the alkane. Both reactions 1 and 2 have been
successfully been demonstrated using model substrates with both heterogeneous and homogeneous systems.\textsuperscript{34-36} Reactions 3a and 3b are quite common when forming the furano and pyrano (5- and 6-membered) oxacycles. Kinetically the direct hydrogenolysis of the oxacycle is difficult although thermodynamically feasible (3a). More likely is the rehydration equilibria of the oxacycle forming the diol (3b) which allows for deoxygenation through reactions 1 and 2. Reaction 4 demonstrates the hydrogenolysis of an ester into the alcohol and aldehyde components which can also proceed through reactions 1 and 2. Examples have recently been reported in literature.\textsuperscript{37,38}

1.4.1 Known Homogeneous Systems for the Deoxygenation of Biomass: Levulinic Acid

Relatively little work has been carried out on the homogeneous deoxygenation of substrates other than glycerol, and direct conversion of LA to deoxygenated products by a homogeneous system is rare. Heterogeneous systems typically approach the challenge of LA deoxygenation in two steps; the (almost trivial) conversion of LA to GVL,\textsuperscript{39} followed by the much more challenging conversion of GVL to 2-methyltetrahydrofuran (2-MTHF) or pentanoic acid. Braca and coworkers were able to successfully convert LA to GVL in high yields employing iodocarbonyl ruthenium or ruthenium triphenylphosine complexes.\textsuperscript{40,41} Other systems based on water soluble ruthenium sodium triphenylphosphine trisulfonate (TPPTS),\textsuperscript{42} and iridium PNP pincer ligands\textsuperscript{43} have been capable of performing the transformation of LA to GVL in aqueous media with extremely high TON. However, until recently no efficient process for the conversion of LA directly into 2-MTHF by a homogeneous system existed. Horvath employed a Ru(acac)$_3$/NH$_4$PF$_6$/PBu$_3$ catalytic system in a high pressure NMR experiment and showed quantitative conversion of LA to 2-MTHF after 10 hours at 200 °C with 1200 psi of external H$_2$ pressure.\textsuperscript{44,45} Building on these results, Klankermayer and Leitner have developed a similar
homogeneous system based on the Ru(acac)$_3$, 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) ligand and NH$_4$PF$_6$ in an ionic liquid shown in Figure 1.7.

1) Dehydration of vic-diols and hydrogenation of the resulting C=O double bond:

\[
\begin{align*}
\text{HOH} & \quad [\text{H}^+] \quad -\text{H}_2\text{O} \\
\text{R} & \quad \text{R'} \\
\text{OH} & \quad \text{R} & \quad \text{R'} \\
\text{OH} & \quad \text{R} & \quad \text{R'} \\
\rightarrow & \quad \text{R} & \quad \text{R'} \\
\end{align*}
\]

R = alkyl, hydroxy alkyl; R' = H, alkyl, hydroxy alkyl

2) Dehydration of alcohols and hydrogenation of the resulting C=C double bond:

\[
\begin{align*}
\text{HOH} & \quad [\text{H}^+] \quad -\text{H}_2\text{O} \\
\text{R} & \quad \text{R'} \\
\text{OH} & \quad \text{R} & \quad \text{R'} \\
\text{OH} & \quad \text{R} & \quad \text{R'} \\
\rightarrow & \quad \text{R} & \quad \text{R'} \\
\end{align*}
\]

3) Condensation of alcohols to oxacycles and hydrogenolysis of the resulting ether:

a) Direct Hydrogenolysis (thermodynamically possible but kinetically difficult)

\[
\begin{align*}
\text{R} & \quad \text{RR'} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
(\text{CHX})_n & \quad (\text{CHX})_n & \quad (\text{CHX})_n \\
\rightarrow & \quad \text{R} & \quad \text{RR'} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
(\text{CHX})_n & \quad (\text{CHX})_n & \quad (\text{CHX})_n \\
\end{align*}
\]

X = H, OH, alkyl, aryl; n = 2,3,4

b) Easier: Rehydration, Loss of Water, Hydrogenation

\[
\begin{align*}
\text{R} & \quad \text{RR'} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
(\text{CHX})_n & \quad (\text{CHX})_n & \quad (\text{CHX})_n \\
\rightarrow & \quad \text{R} & \quad \text{RR'} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
(\text{CHX})_n & \quad (\text{CHX})_n & \quad (\text{CHX})_n \\
\end{align*}
\]

Reactions 1 or 2

4) Ester Hydrogenolysis

\[
\begin{align*}
\text{R} & \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{O} & \quad \text{O} \quad \text{O} \\
\rightarrow & \quad \text{R} & \quad \text{OH} \quad \text{OH} \\
\text{O} & \quad \text{O} \quad \text{O} \\
\rightarrow & \quad \text{R} & \quad \text{OH} \quad \text{OH} \\
\end{align*}
\]

Reactions 1 or 2

**Figure 1.6:** Fundamental reaction pathways for the deoxygenation of biomass.
The active species is generated in situ through the coordination of the triphos ligand which hydrogenates LA to the 1,4-pentanediol species. The NH₄PF₆ additive and the ionic liquid 1-butyl-2-(4-sulfobutyl)imidazolium-p-toluenesulfonate catalyze the cyclisation of the 1,4-pentanediol to the desired product 2-MTHF. The ionic liquid was necessary to stabilize the reactive intermediate and maximize 2-MTHF yields at 92% with little GVL or 1,4-pentanediol side products. To date this system remains the most successful and highest yielding homogeneous process for the conversion of LA to 2-MTHF.

![Figure 1.7](image)

**Figure 1.7:** Klankermayer and Leitner system for the homogeneous hydrogenation of Levulinic acid to 2-methyltetrahydrofuran.

Currently the conversion of LA to pentanoic acid by a homogeneous system remains elusive. Homogeneous systems for the hydrogenation of LA have only yielded trace amount of pentanoic acid as a byproduct. The usefulness of pentanoic acid as an intermediate to pentene/pentane makes the ring opening of GVL to pentanoic acid (Scheme 1.4) by hydrogenolysis a desirable target. The development of an acid-/water- stable homogeneous system capable of this transformation would be extremely alluring.
1.4.2 Rational Design of a Homogeneous Deoxygenation Catalyst

Based on the reaction cascades for the deoxygenation of LA, HMF, furfural and 2,5-hexanediol, and the necessary reactions in Figure 1.6, a set of four main criteria emerge which set the stage for the design of a homogeneous catalyst capable of biomass deoxygenation devised by the Schlaf group.\(^1\)

The first is the use of an electron poor transition metal capable of heterolytic hydrogen gas activation into a proton and a metal hydride. The proton generated has a $K_a$ up to 40 orders of magnitude lower than free dihydrogen ($pK_a(H_2) > 35$) when bound to a coordinatively unsaturated electron poor metal.\(^{47}\) This proton can be abstracted from the complex by a basic species present (counter-ion, solvent, water, or ligand) and delivered to the substrate to generate an electrophilic. Subsequent hydride transfer results in the net transfer of hydrogen across an unsaturation by a ionic mechanism (Figure 1.8).\(^{48}\) Ionic hydrogenolysis of ethers and esters is in principle possible by a similar mechanism. The basic oxygen of the substrate becomes protonated, generating an electrophilic oxonium cation. Nucleophilic attack of the hydride results in carbon-oxygen bond cleavage and net hydrogenolysis.

Another consideration is that all the reactions outlined in Figure 1.6 intrinsically produce water, and therefore the catalyst must be compatible with acidic aqueous media. The catalyst must also not be deactivated by the formation of inert metal-oxygen bonds. As with the early transition metals, up to group VII, the formation of oxo or alkoxide complexes results in loss of activity.\(^{49,50}\)

Additionally any ligands used to stabilize the metal must be able to tolerate the acidic aqueous conditions generated during the deoxygenation process. They must also be capable of
surviving the strongly reducing conditions of H\textsubscript{2} pressure and high temperatures required for biomass deoxygenation. For this reason robust ligands with nitrogen donor atoms are used (multidentate pyridyl based ligands).

![Diagram illustrating Heterolytic Activation of H\textsubscript{2} and Ionic Hydrogenation](image)

**Figure 1.8:** Heterolytic activation of H\textsubscript{2} for the hydrogenation of olefins and hydrogenolysis of ethers and esters.

Finally, any acids or counter ions used in the complex for the catalyzed dehydration must be non-coordinating and hydrolysis stable at high temperatures. Often triflic acid is an ideal choice for its low pK\textsubscript{a} (-15),\textsuperscript{51} high thermal stability and availability as a counter ion for the metal complex. Solvents used for the deoxygenation should be (relatively) non-toxic, high boiling and non-coordinating. Water is an ideal choice but alternatively sulfolane (b.p. 285 °C, LD\textsubscript{50} ≈ 2g/kg) is commercially available, acid resistant and capable of dissolving the polar substrates, catalysts and water.

If all the above criteria are met, vision of the Schlaf group as outlined in Figure 1.9, is to develop a homogeneous, acid-/water-stable procatalyst which could be placed in aqueous
solution with a sugar/sugar derived substrate and subjected to strongly reducing conditions (high temperature, \( \text{H}_2 \)) pressure). As mentioned earlier, deoxygenation proceeds by the iterative removal of \( \text{H}_2\text{O} \) and input of \( \text{H}_2 \), resulting in a net removal of an oxygen atom per iterative cycle. As the oxygen is removed from the substrate, a more non-polar product is generated which would phase-separate from the aqueous mixture. This phase separation allows for decanting of the product phase and easy isolation as well as facile catalyst recovery through distillation of excess water from the aqueous solution. More substrate can then be introduced into the catalytic solution and the process repeated for as long as the catalyst remains active.

1.4.3 Metal-Ligand Bifunctional Catalysis

As mentioned in the previous section, ionic activation of dihydrogen generates a metal-hydride and acidic proton (Figure 1.8). The basis for metal-ligand bifunctionality (MLB) is that the protic acceptor present in the system is on the ligand, i.e., the ligand serves as a proton-shuttle. The earliest example of such a system was demonstrated by Shvo and coworkers in 1985, who performed the hydrogenation of alkenes, alkynes, ketones, aldehydes and anthracene using a cyclopentadienyl (Cp) ruthenium dimer.\(^{52,53}\) The complex dissociates upon heating into the catalytically active species and a ruthenium cyclopentadienone complex which is coordinatively unsaturated (Figure 1.10). Mechanistic studies by Casey\(^{54}\) and Comas-Vives\(^{55}\) established that the hydrogen transfer occurs concertedly wherein the hydride is transferred from the metal and the proton is transferred from the hydroxycyclopentadienyl ligand with no coordination of ligand. This confirmed the Shvo catalyst to be the first MLB hydrogenation catalyst.
Figure 1.9: Generic example of a proposed catalytic deoxygenation reaction setup; substrate (sorbitol) is hydrogenated in a sulfolane/water mixture with the presence of acid. The non-polar products separate from the mixture into a hydrocarbon phase and aqueous phase which are easily separable.
Figure 1.10: General mechanism for the hydrogenation of aldehydes and ketones by the Shvo catalyst.

Noyori and coworkers developed the first asymmetric system which operated through an outer-sphere mechanism.\(^{56}\) For his work with asymmetric catalytic hydrogenations, Noyori was awarded the 2001 Nobel Prize and is considered a leader in this field. The ruthenium based catalyst employs a \(\eta^6\)-arene ligand and an N-sulfonylated ethylenediamine or \(\beta\)-amino alcohol as the ligand containing a proton (Figure 1.11). The complex operates through a transfer hydrogenation mechanism, meaning that it does not perform the ionic activation of hydrogen gas, but requires a secondary alcohol as a hydrogen donor (typically also playing the role of solvent).\(^{56,57}\) Noyori had chosen the \(\eta^6\)-arene ruthenium system in order to create an octahedral coordination environment with three \(\text{fac}\) unsaturated sites.\(^{58}\) The presence of free sites \(\text{fac}\) to other functions in the complex allowing for the hydride to be in close proximity of the protic site, is a requirement for MLB. The analogous non-bifunctional systems show turnover frequencies
approximately 200 times less than the systems with a bifunctional auxiliary ligand for the hydrogenation of acetophenone, confirming the effectiveness of the MLB mechanism.\(^{57}\)

\[
\text{TS 1}
\]

\[
\text{TS 2}
\]

**Figure 1.11:** Proposed mechanism of transfer hydrogenation of carbonyls using Noyori’s metal-ligand bifunctional catalyst and *iso*-propanol as hydrogen source and reaction media.

The increased activity of the MLB mechanism is a result of the ability of the complex to hydrogenate the carbonyl without coordination of the substrate. The hydride and the proton are delivered concertedly from the amine and metal-hydride in a pericyclic 6-membered transition state (TS2 in Figure 1.11) instead of substrate insertion to the metal-hydride. Employing a MLB mechanism for industrial use could be extremely beneficial, giving the ability to increase TON and TOF and thus enhance economic viability. However, the Noyori systems are not well suited
for the conversion of biomass since they are sensitive to acidic conditions and high temperatures, both of which are required for biomass deoxygenation.

As already discussed above the heterolytic activation of hydrogen gas by a transition metal has been shown to require the presence of an external base which can abstract the proton from activated dihydrogen.\textsuperscript{59-62} In many cases MLB could be introduced into a metal complex through the addition of pendant groups capable of some basicity but which do not interfere with or participate in, metal-ligand binding. This would result in an intramolecular means of heterolytic H\textsubscript{2} cleavage and could, in theory, be applied to many existing heterolytic H\textsubscript{2} activation catalysts. This concept was explored by Crabtree who inserted a -NH\textsubscript{2} pendant amine onto the 2-position of a cyclometalated 7,8-benzoquinolate (bq-NH\textsubscript{2}) ligand.\textsuperscript{63} The bq-NH\textsubscript{2} ligand was chosen for its rigidity and inability for the pendant amine to bind the iridium due to the required bite angle, as well as the basicity of the amine and hydrogen bonding capabilities.\textsuperscript{63} It was shown by NMR that the aqua complex [IrH(bq-NH\textsubscript{2})(OH\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2}][BF\textsubscript{4}] reacts with H\textsubscript{2} in a heterolytic activation mechanism resulting in two hydride signals at $\delta$ = -23.2 and -25.7 ppm with protonation of the amine appearing as a broad signal at $\delta$ = 3.8 ppm.\textsuperscript{63} The binding of H\textsubscript{2} to the complex was demonstrated to be reversible, indicated by reformation of the aqua complex upon the removal of H\textsubscript{2} atmosphere suggesting the complexes activity as a MLB catalyst.
Figure 1.12: Intramolecular reversible activation of H₂ by pendant amine in Crabtree’s Ir complex.

1.4.4 Previous Homogeneous Systems Investigated by the Schlaf Group

Based on the set of criteria discussed earlier, the Schlaf group has designed, characterized and tested a series of ruthenium based complexes for the ionic hydrogenation of biomass. Although a widely successful catalyst has not yet been developed, through logical progression, large advances have been made with regards to designing a homogeneous catalyst which can withstand aqueous acidic media at elevated temperatures. The evolution of the homogeneous complexes designed by the Schlaf group are shown in Figure 1.13 and each has improved upon the previous generation.
Figure 1.13: Catalytic systems designed and tested by the Schlaf group.

The first complex tested [A] was synthesized by Lau and demonstrated to be an active homogeneous hydrogenation catalyst.\textsuperscript{64,65} The postulated active species has a free coordination site formed by the dissociation of water, followed by $\eta^2$ coordination of H\textsubscript{2} to form $[\textit{cis-Ru}(6,6'$-Cl\textsubscript{2}-2,2'-bipyridine)\textsubscript{2}($\eta^2$-H\textsubscript{2})(H\textsubscript{2}O)](OTf)\textsubscript{2}\textsuperscript{2+}. An acidic proton is generated and abstracted by H\textsubscript{2}O or OTf$^-$ forming hydronium/triflic acid and $[\textit{cis-Ru}(6,6'$-Cl\textsubscript{2}-2,2'-bipyridine)\textsubscript{2}(H)(H\textsubscript{2}O)](OTf)$. The complex should be stable in acidic aqueous media given the presence of aquo ligands and therefore meets the criteria set out by the Schlaf group and was selected as a starting point for the development of a homogeneous system for biomass deoxygenation. Xie demonstrated that [A]
was capable of converting terminal diols into the primary alcohol. C_{3-6} n-alcohols were obtained in yields ranging from 20-65% but no activity was observed for the conversion of glycerol. This was attributed to the low thermal stability of the complex above 150 °C, which as mentioned previously is the minimum temperature required to breach the activation barrier for acid assisted dehydration. The next step in the development of a suitable complex was to enhance thermal stability.

As a means of increasing the thermal stability range one bipyridyl ligand was exchanged for an η\textsuperscript{6}-arene ligand. The hypothesis was that by switching the bipyridyl for something more electron rich, the complex would be less susceptible to reduction to Ru\textsuperscript{0} under strongly reducing conditions. The chlorides were also removed from the remaining bipyridyl ligand as to not sterically crowd the active site, yielding [B]. Fukuzumi and co-workers had already demonstrated the success of [B] in the case where X=H as a homogeneous ketone and CO\textsubscript{2} hydrogenation catalyst. In an attempt to introduce MLB into the complex, Dykeman and Luska modified [B] with amino groups on the ortho positions of the bipyridine/phenanthroline ligand in a manner akin to the Noyori and Crabtree systems. As shown in Figure 1.14 it was postulated that the introduction of pendant amines allows for intramolecular heterolytic H\textsubscript{2} cleavage, resulting in a MLB mechanism capable of concerted hydrogenation.

The catalysts developed by Dykeman and Luska hydrogenated 1,2-hexanediol to 1-hexanol in good yield and selectivity, at a temperature range of 110-125 °C. Despite this success, several problems existed for these complexes. When temperatures above 150 °C were explored, the complexes lost the arene ligand and suffered decomposition, making them unsuitable for glycerol deoxygenation. Also, the introduction of amine functions to the chelating ligands did not result in improved activity as expected. X-ray structures revealed that the amino
groups were likely too far from the coordinated hydride position to deliver hydrogen to the substrates effectively.\textsuperscript{67} \textsuperscript{1}H-NMR experiments and UV/VIS experiments indicated that protonation of the amine groups would require an acid with pK\textsubscript{a} < -2, a significant problem since the strongest acid present in solution would be hydronium with a pK\textsubscript{a} of -1.74.\textsuperscript{72} Due to solvent leveling and the requirement to be in aqueous media, complex [B] was therefore not capable of a MLB mechanism.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure114.png}
\caption{Postulated catalytic cycle for ionic hydrogenation by metal-ligand bifunctionality by [B].}
\end{figure}
To overcome the difficulties of thermal stability and loss of the arene ligand, two possible routes were pursued. The first was the introduction of an anionic pentamethylcyclopentadienyl (η⁵-C₅Me₅, Cp⁺) ligand which, being more donating, would bind much stronger to the metal centre and not be at risk of dissociation. Furthermore ruthenium complexes with Cp⁺ ligands can exhibit increased thermal stability. This led to the design and synthesis of system [C] by Thibault. The second route to thermal stability was to increase the denticity of the chelating ligand. By moving from a bidentate ligand to a tridentate ligand the number of donating pyridyl groups increases and results in a system with a high complex formation constant and enhanced stability by the chelate effect. The 4′-phenyl-2,2′:6′,2″-terpyridine (ph-trpy) ligand was chosen, leading to system [D] developed by Thibault and Taher.

The two Ru(Cp⁺) complexes explored were based on the 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) ligands. Unfortunately the complexes employing the analogous ligands with pendant –NH₂ groups could not be synthesized, likely due to the steric encumbrance of the Cp⁺ methyl groups and the amine groups preventing chelation. The two complexes did in fact demonstrate enhanced stability, and survived at temperatures of 225 °C with no observable decomposition. The complexes were able to hydrogenate ketones, terminal diols as well as convert glycerol to 1-propanol with approximately 20% conversion, however no 1,3-propanediol was observed. Also there was no observable difference in activity was observed between the bipy and phen complexes, indicating little involvement of ligand rigidity.

The tridentate complex [D] was tested for the deoxygenation of glycerol. Reactions with glycerol were carried out in a sulfolane solution with varying proportions of water (10-50% v/v) and trifluoromethanesulfonic acid at 200 °C. The singly deoxygenated products, 1,3-propanediol or 1,2-propanediol, were not observed at any time during the reactions, however,
samples taken 2 hours into the reactions showed presence of the doubly deoxygenated product 1-propanol. Yields of 1-propanol ranged from 2-14% and in many cases quantitative GC analysis showed that the mass balance for the conversion of glycerol was deficient. Only by gas-phase GC-MS was it shown that a significant amount of propane was produced during the reactions. After a 24 hour reaction time, no glycerol remained which indicates the ability of the [D] complex to convert glycerol to the completely deoxygenated product propane.76 The thermal stability of the complex above 200 °C indicated the success of the multidentate ligand approach and demonstrated that the largest barrier for polyalcohol deoxygenation is the first dehydration reaction. After initial acid catalyzed dehydration (requiring temperatures >150 °C), under strongly reducing conditions, the complete deoxygenation is thermodynamically downhill (Figure 1.15).76

![Reaction cascade for the deoxygenation of glycerol by [D].](image)

Building on the Ru(Cp’) complexes developed by Thibault, Di Mondo attempted to introduce the capability for MLB by modifying the chelating ligands with amino functions and removing steric inhibition from the complex by using a cyclopentadienyl (Cp) ligand resulting in system [E].74,78 The complexes were stable to 175 °C and were capable of quantitative ketone
and aldehyde hydrogenation to the corresponding alcohols. In all cases TON for system [E] where X= NH$_2$ were greater, demonstrating increased activity. It follows that the enhanced activity is a direct result of the preference for the complex to proceed through a MLB ionic hydrogenation mechanism (Figure 1.16).$^{78}$ $^1$H-NMR experiments confirmed the pK$_a$ of the pendant amines at 0.46, a suitable basicity for the protonation of the amine by H$_3$O$^+$ (pK$_a$= -1.74).$^{72}$ Overall complex [E] was demonstrated as being the first ruthenium based MLB catalyst to operate through a non-coordinated amine.

**Figure 1.16:** Ionic hydrogenation mechanism of 3-pentanone by [E] where X=NH$_2$.$^{78}$

The next step in the evolution of catalysts in the Schlaf group is to further explore the tridentate system [D] as well as combine its thermal stability characteristics whilst introducing a basic function capable of participating in MLB.

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1.5 Overview of Research Projects

1.5.1 Project I: \([\text{Ru(OH}_2\text{)}_3(4\text{'-phenyl-2,2':6',2''-terpyridine})\text{](OTf)}_2\) as a Homogeneous Hydrogenation Catalyst for Biomass Derived Substrates

![Diagram of the complex](image)

**Figure 1.17:** \([\text{Ru(OH}_2\text{)}_3(4\text{'-phenyl-2,2':6',2''-terpyridine})\text{](OTf)}_2\) as a procatalyst for the selective deoxygenation of biomass derived substrates.

The \([\text{Ru(OH}_2\text{)}_3(4\text{'-phenyl-2,2':6',2''-terpyridine})\text{](OTf)}_2\) complex previously synthesized by Thibault (Figure 1.17) has been tested for the conversion of the 1,2-hexanediol model system and glycerol as mentioned previously\(^{76,77}\). Its thermal stability and activity towards deoxygenation make it an excellent candidate for the testing against other biomass derived substrates of higher chain lengths (C\(_5\)-C\(_6\)). We hypothesized that the complex should also be active for the hydrogenation of carbonyls to alcohols, alcohols to alkenes/alkanes and be capable of hydrogenolysis of furan/tetrahydrofuran rings systems. The complex was tested against levulinic acid (LA), a valuable platform biomass derived feedstock, and furfural and 5-hydroxymethyl furfural (HMF). At temperatures in excess of 200 °C it is expected that pentene and pentane could be observe from the total deoxygenation of LA and furfural, or hexene and hexane from the total deoxygenation of HMF.
1.5.2 Project II: [Ru(OH$_2$)$_3$(di(picolyl)amine)](OTf)$_2$ as an acid-, water- stable, metal-ligand bifunctional deoxygenation catalyst

![Chemical Structure](image)

**Figure 1.18:** [Ru(OH$_2$)$_3$(di(picolyl)amine)](OTf)$_2$ as a procatalyst for the selective deoxygenation of biomass derived substrates.

Combining the tridentate chelation motif of the temperature stable Ph-terpy complex with the MLB capabilities of an amine functionality has led to the development of the di(picolyl)amine (DPA) system (Figure 1.18). In comparison to previous systems developed by the Schlaf group, this system has a tridentate chelating ligand which is electron rich and is postulated to provide thermal stability of the complex above 150°C. Additionally the ligand contains a basic amine functionality which can participate in proton abstraction from activated dihydrogen without hindering the active site, as seen with Dykeman and Luska systems. The DPA system was synthesized and tested against a model system 2,5-hexanedione and furfural and 5-hydroxymethyl furfural (HMF) and its activity was compared to the analogous non MLB system, Ph-terpy. We postulate that the DPA based system will show considerable thermal stability as well as enhanced activity towards the deoxygenation of biomass derived substrates.
2 Results and Discussion- Project I

2.1 Synthesis and Characterization of \([\text{Ru(OH}_2]_3(4'-\text{phenyl}-2,2':6',2''-\text{terpyridine})][\text{OTf}_2\]

2.1.1 Synthesis of 4'-phenyl-2,2':6',2''-terpyridine

The synthesis of 4'-phenyl-2,2':6',2''-terpyridine was achieved through a previously reported solvent-less procedure developed by Cave and Raston (Scheme 2.1).\textsuperscript{70} The ligand was obtained in 2 steps, the first being the condensation between benzaldehyde and 2 equivalents of 2-acetylpyridine with excess potassium hydroxide ground together to form a tan solid which was recrystallized from ethanol to yield [1] as a white crystalline solid. The desired ligand [2] is obtained from [1] by a double condensation reaction with ammonium acetate in refluxing acetic acid. The result is the ring closed product which undergoes auto-oxidation to form the aromatic pyridine ring.

\[\begin{align*}
\text{O} + 2 \text{N} & \xrightarrow{\text{KOH}} \text{N} \quad \text{O} \\
[1] & \xrightarrow{1) \text{NH}_4\text{OAc, AcOH}} \text{O} \quad \text{N} \\
[1] & \xrightarrow{2) \text{H}_2\text{O}} \text{N} \quad \text{N} \\
\end{align*}\]

Scheme 2.1: Synthesis of 4'-phenyl-2,2':6',2''-terpyridine.

It should be noted that likely due to the formation of a side product of unknown composition the product appears orange but \textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectra do not indicate the presence of any impurities. The orange contaminant can be removed by dissolving the product in acetone and performing a filtration through a short (10 cm) column of basic alumina (Brockman
activity 1). The desired ligand [2] can then be obtained in 67% percent yield after all purification steps.

2.1.2 Synthesis of $[\text{Ru(OH}_2\text{)}_3(4′-\text{phenyl-2,2′:6′,2′′-terpyridine})\text{]}\text{(OTf)}_2$

Once the purified ligand was obtained synthesis of [4] was achieved by a protocol previously reported by the Schlaf group which is outlined in Scheme 2.2. $\text{RuCl}_3$ was dissolved in ethanol with ph-trpy and refluxed for 12 hours. Due to the lack of solubility of [3] in ethanol a red-brown suspension is formed which can then be filtered resulting in high yields of [3] as a red-brown powder. Metathesis of the chloro ligands was achieved using AgOTf in degassed water at 50 °C for one hour resulting in a green solution of $[\text{Ru(OH}_2\text{)}_3(\text{Ph-trpy})]^{3+}$, which was then reduced with zinc dust yielding a purple solution of [4]. The solvent was then removed in vacuo and [4] was obtained as a purple powder. ZnOTf was formed as a side product of the reduction step but its presence is undesirable for catalysis due to the potential for Lewis acid activity. Separation of the desired complex and ZnOTf was achieved by dissolving the complex in 2-propanol, performing a filtration through Celite® to remove the insoluble ZnOTf, followed by removal of the solvent by rotary evaporation. The complex [4] is relatively air stable, although it is best kept under argon atmosphere to prevent oxidation over long periods.
Scheme 2.2: Synthesis of [Ru(OH)$_2$]<sub>3</sub>(Ph-trpy)](OTf)$_2$ complex.

### 2.2 Catalytic Hydrogenations by [Ru(OH)$_2$]<sub>3</sub>(4'-phenyl-2,2':6',2''-terpyridine)](OTf)$_2$

Expanding on the success of the [Ru(OH)$_2$]<sub>3</sub>(4'-phenyl-2,2':6',2''-terpyridine)](OTf)$_2$ complex as a catalyst for the total deoxygenation of glycerol to propane in sulfolane and aqueous media as previously reported by the Schlaf group, levulinic acid was chosen as an industrially relevant precursor for C5 alkenes and alkanes. The following section presents the investigation of using the [Ru(OH)$_2$]<sub>3</sub>(4'-phenyl-2,2':6',2''-terpyridine)](OTf)$_2$ as a homogeneous hydrogenation catalyst for the deoxygenation of levulinic acid as a function of temperature, solvent polarity, and acidity. Furthermore, as a step towards the deoxygenation of furfural, the activity of the [Ru(OH)$_2$]<sub>3</sub>(4'-phenyl-2,2':6',2''-terpyridine)](OTf)$_2$ system on the 2,5-hexanedione model system in aqueous conditions as a function of temperature was investigated.
2.2.1 Temperature series: Deoxygenation of levulinic acid by [Ru(OH)_3(4’-phenyl-2,2’:6’,2’”-terpyridine)](OTf)_2

Hydrogenations of levulinic acid were performed in a medium of 90% sulfolane 10% water at temperatures of 150-250 °C with no additional acid present in solution. The results of the study are outlined in Scheme 2.3, Figure 2.1 and Table 2.1.

Scheme 2.3: Reaction conditions employed in temperature series for the hydrogenation of levulinic acid employing the [Ru(OH)_3(4’-phenyl-2,2’:6’,2’”-terpyridine)](OTf)_2 catalyst.

Table 2.1: Deoxygenation of levulinic acid in 9:1 sulfolane: water catalyzed by [Ru(OH)_3(4’-phenyl-2,2’:6’,2’”-terpyridine)](OTf)_2 as a function of temperature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>H_2(g) uptake (psi)^a</th>
<th>Levulinic Acid (% recovery)^b</th>
<th>γ-valerolactone (% yield)^b</th>
<th>Polymerization products (% yield)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>76</td>
<td>70</td>
<td>18</td>
<td>12</td>
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<td>4</td>
<td>250</td>
<td>121</td>
<td>21</td>
<td>54</td>
<td>25</td>
</tr>
</tbody>
</table>

Reaction conditions: levulinic acid [1000 mmol L^{-1}], 800 psi H_2(g), dimethylsulfone (ISTD) [100 mmol L^{-1}], by [Ru(OH)_3(4’-phenyl-2,2’:6’,2’”-terpyridine)](OTf)_2 [10 mmol L^{-1} = 0.1 mol% w.r.t substrate], time = 16hrs, Nominal reactor volume 50 mL, solution volume 25 mL. ^a Observed pressure drop in reactor (cold). ^b By quantitative GC against internal standard dimethylsulfone. ^c Yield by mass-balance.
Figure 2.1: Hydrogenation of 1000mmol L⁻¹ Levulinic Acid with 0.1mol % [Ru(OH)₃(Ph-trpy)](OTf)₂ from 150-200 °C at 800 psi H₂ for 16 hrs in a 9:1 Sulfolane: H₂O Solution.

As shown earlier in Scheme 1.4 the first step in the deoxygenation of LA is the catalytic hydrogenation of the carbonyl group, after which cyclization to GVL occurs. It is evident that the [Ru(OH)₃(Ph-trpy)](OTf)₂ complex does not exhibit significant activity towards the carbonyl at 150 °C, only converting 30% LA into 18% GVL and losing 12% of substrate to condensation reactions and polymerization. Optimal activity of the complex was seen at 200 °C where nearly complete conversion to GVL was observed with no accumulation of polymerization products and the complex does not decompose until the temperature exceeds 250 °C. Solid condensation products can be avoided by prevention of the formation of γ-angelica lactone by rapid hydrogenation of the carbonyl. After the alcohol is generated, acid catalyzed dehydration yields GVL. As the temperature was increased past 200 °C activity of the complex begins to decline
with a decreasing conversion of levulinic acid to 80% at 225 and 250 °C. The only noticeable difference between reactions at 225 and 250 °C is an increased accumulation of solid resin in the bottom of the reactor body. Further reactions could be carried out at 200 °C for optimal conversion and in order to prevent the formation of solid products. Although GVL is a value added chemical produced from LA, the goal of the investigation was further deoxygenation for the production of pentene or pentane. It was therefore necessary to find a set of reaction conditions in which the GVL ring could be opened and further hydrogenation could proceed.

2.2.2 Acid series: Deoxygenation of levulinic acid by [Ru(OH)$_2$(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)$_2$ with the addition of trifluoromethane sulfonic acid

GVL is an extremely stable five membered ring system, the opening of which is not trivial and requires the simultaneous occurrence of ring opening acid catalyzed hydrations and dehydrations (Scheme 2.4) or a direct (and even more challenging and therefore unlikely) ester hydrogenolysis.

![Scheme 2.4: Ring opening and deoxygenation pathway of GVL to pentanoic acid, methyl THF and pentene.](image-url)
To achieve this, a strong, protic, hydrolysis-stable non-oxidizing acid was added to the reaction mixture and the reaction carried out under the optimal temperature conditions determined in the previous section (200 °C). Triflic acid is an ideal choice due to its stability, strength and role as the non-coordinating counter ion in the ruthenium catalyst.

Hydrogenations were performed in a medium of 90% sulfolane 10% water at 200 °C with the addition of various quantities of TfOH at 800 psi H₂ (g) for 16 hours. The results of the study are outlined in Scheme 2.5, Figure 2.2 and Table 2.2.

Scheme 2.5: Reaction conditions employed in acid series for the hydrogenation of levulinic acid under acidic conditions employing the [Ru(OH₂)₃(4'-phenyl-2,2':6',2''-terpyridine)](OTf)₂ catalyst.

Table 2.2: Deoxygenation of levulinic acid in 9:1 sulfolane: water at 200 °C catalyzed by [Ru(OH₂)₃(4'-phenyl-2,2':6',2''-terpyridine)](OTf)₂ as a function of acid concentration.

<table>
<thead>
<tr>
<th>Entry</th>
<th>TfOH (mol % w.r.t. substrate)</th>
<th>H₂(g) uptake (psi)ᵃ</th>
<th>Levulinic Acid (% recovery)ᵇ</th>
<th>γ-valerolactone (% yield)ᵇ</th>
<th>Polymerization products (% yield)ᶜ</th>
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</tr>
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<td>4</td>
<td>2.4</td>
<td>92</td>
<td>30</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

Reaction conditions: levulinic acid (1000 mmol L⁻¹), 800 psi H₂(g), dimethylsulfone (ISTD) (100 mmol L⁻¹), by [Ru(OH₂)₃(4'-phenyl-2,2':6',2''-terpyridine)](OTf)₂ [10 mmol L⁻¹ = 0.1 mol% w.r.t. substrate], T= 200 °C, time = 16 hrs, Nominal reactor volume 50 mL, solution volume 25 mL. ᵃObserved pressure drop in reactor (cold). ᵇBy quantitative GC against internal standard dimethylsulfone. ᶜYield by mass-balance.
Figure 2.2: Hydrogenation of 1000mmolL⁻¹ levulinic acid with 0.1mol % \([\text{Ru(OH}_2)_3(\text{Ph-trpy})](\text{OTf})_2\) at 200 °C and 800 psi H₂ for 16 hrs in a 9:1 Sulfolane: H₂O Solution with addition of 0.8-2.4 mol % (w.r.t. [Ru]) TfOH.

The addition of triflic acid for the hydrogenation of LA actually decreased the effectiveness of the catalyst marked by significant loss of conversion and a drastic increase in polymerization products at higher acid concentrations. The results signify that addition of triflic acid does not enhance the deoxygenation of GVL through ring opening followed by acid catalyzed dehydration and prevents the hydrogenation of the carbonyl of LA resulting in less conversion to GVL. At lower acid concentrations some conversion to GVL occurs but the complex is severely inhibited, possibly due to ligand protonation, or inhibition of ionic hydrogen activation by excess acid. At higher acid concentrations polymerization is greatly increased resulting in more than one third of substrate converted to solids. This suggests that the first step in the hydrogenation of LA is the formation of 4-hydroxyl-valeric acid (4-HVA) which then
undergoes a ring closure to GVL, however, with acid present the ring closure is inhibited and polymerization occurs, likely due to enhance esterification of 4-HVA shown below (Scheme 2.6). Alternatively the addition of acid shifts the keto-enol tautomeration equilibrium of levulinic acid resulting in more γ-angelicalactone and therefore more polymerization products. Solid products are obviously highly undesirable as precursors for petrochemicals and thus the addition of TfOH acid should be avoided for the conversion of levulinic acid by [Ru(OH$_2$)$_3$(Ph-trpy)](OTf)$_2$.

![Scheme 2.6: Proposed esterification mechanism of 4-HVA under acidic aqueous conditions.](image)

2.2.3 Solvent series: Deoxygenation of levulinic acid by [Ru(OH)$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)$_2$ with changing solvent polarity

In an attempt to prevent the formation of polymerization products while also enabling reductive cleavage of the GVL ring, by either hydrolysis/dehydration/hydrogenation or hydrogenolysis, catalyst performance was monitored as a function of solvent polarity. Solvent polarity would be increased by introducing a greater proportion of water into the solvent medium, ranging from 10% H$_2$O by mass to 100%. The rationale behind this investigation was to force the GVL-4-HVA equilibrium in favour of 4-HVA (top left of Scheme 2.4) and prevent
cyclisation of the substrate as well as polymer condensation reactions (Scheme 2.6). This would lead to production of pentanoic acid which through further hydrogenation would yield pentanal, pentanol and finally pentene, which by di- or trimerization could be used as gasoline and JET-A precursor.

Aside from the effects of solvent polarity on the substrate and the various (de)hydration equilibria, it was hypothesized that increasing the amount of water present could enhance catalytic activity by supplying a greater number of the basic groups (in this case oxygen in water) necessary for abstracting acidic protons from activated dihydrogen bound in an $\eta^2$ fashion to the ruthenium complex while forming hydronium as the strongest solvent-leveled acid in the system. Hydrogenations were thus performed in a medium varying from 90% sulfolane/10% water, 50/50 sulfolane to water and 100 % water at 200 °C and 800 psi H$_2$ (g) for 16 hours. The results of the study are outlined in Scheme 2.7, Figure 2.3 and Table 2.3.

\[ \text{Scheme 2.7: Reaction conditions employed in the solvent series for the hydrogenation of levulinic acid employing the [Ru(OH)$_2$]$_2$(4′-phenyl-2,2′:6′,2′′-terpyridine)](OTf)$_2$ catalyst.} \]
Table 2.3: Deoxygenation of levulinic acid at 200 °C catalyzed by [Ru(OH)$_2$(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)$_2$ as a function of solvent polarity.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent (% H$_2$O in Sulfolane)</th>
<th>H$_2$g uptake (psi)$^a$</th>
<th>Levulinic Acid (% recovery)$^b$</th>
<th>γ-valerolactone (% yield)$^b$</th>
<th>Polymerization products (% yield)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>151</td>
<td>5</td>
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<tr>
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<tr>
<td>3</td>
<td>100</td>
<td>96</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

Reaction conditions: levulinic acid [1000 mmol L$^{-1}$], 800 psi H$_2$(g), dimethylsulfone (ISTD) [100 mmol L$^{-1}$], by [Ru(OH)$_2$(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)$_2$ [10 mmol L$^{-1}$] = 0.1 mol% w.r.t substrate, T= 200 °C, time = 16hrs. Nominal reactor volume 50 mL, solution volume 25 mL. $^a$ Observed pressure drop in reactor (cold). $^b$ By quantitative GC against internal standard dimethylsulfone. $^c$ Yield by mass-balance.

The result clearly show that the activity of the complex is inhibited by the addition H$_2$O and is worst at a 50/50 water/sulfolane solvent composition converting less than half the LA. Only 50% conversion was observed in completely aqueous conditions and no polymerization occurred. Although the presence of more water seems to play some role in the prevention of polymerization, the loss of activity is severe. This could either be the consequence of a lower solubility of dihydrogen gas in the reaction mixture at higher water contents, or represent a deactivation of the complex due to the competitive binding of water versus H$_2$ (g) to the ruthenium centre (Figure 2.4). As mentioned previously the binding energy of a dihydrogen molecule to Ru$^{2+}$ is approximately 20 kcalmol$^{-1}$, and any labile ligands on the ruthenium must be less than or equal to that binding energy in order to expose free coordination sites. If in aqueous environments the equilibrium for the dissociation of H$_2$O from the complex lies too far to the left, then the aqua ligands will be incapable of dissociation and a decrease in catalyst activity will be observed.
Figure 2.3: Hydrogenation of \(1000\,\text{mmolL}^{-1}\) levulinic acid with 0.1mol \% \([\text{Ru(OH}_2\text{)}_3(\text{Ph-trpy})](\text{OTf})_2\) at \(200\,\text{\circ C}\) and 800 psi \(\text{H}_2\) for 16 hrs in varying Sulfolane: \(\text{H}_2\text{O}\) Solutions.

![Chart showing percent conversion of Levulinic Acid](image)

Figure 2.4: Competitive water and \(\eta^2\) bonding and activation of dihydrogen to \([\text{Ru(OH}_2\text{)}_3(\text{Ph-trpy})](\text{OTf})_2\)

The \([\text{Ru(OH}_2\text{)}_3(\text{Ph-trpy})](\text{OTf})_2\) complex has shown promising activity towards the conversion of glycerol to propane\(^{26}\) and demonstrated in this investigation its proficiency in hydrogenating carbonyl functions, shown by nearly complete conversion of levulinic acid to
GVL at 200 °C in a 10% water in sulfolane solvent medium. The catalyst is however not able to hydrogenolyze the stable five-membered lactone ring beyond GVL, a reaction which has been performed with high efficiency, e.g., by using Ru/C since the early 1950’s.\textsuperscript{83} It was therefore necessary to investigate the possibility using of an analogous system with enhanced catalytic activity, but with similar thermal stability ranges. Using the criteria outlined previously for the rational design of deoxygenation catalysts by the Schlaf group and hypothesizing that an enhanced catalyst activity may result by employing a ligand capable of enabling a metal-ligand bifunctional mechanism, in which a basic functionality built into the ligand backbone acts as a proton shuttle, the \([\text{Ru(OH}_2)_3(\text{DPA})]\)(OTf)\textsubscript{2} complex was envisioned as an acid-, water- and temperature stable ionic hydrogenation catalyst.

2.3 Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk-line techniques or in a MBraun glove box. All NMR spectra were obtained on 300 MHz, 400 MHz, or 600 MHz spectrometers and calibrated to the residual protonated solvent signal.

GC analyses were performed on a Varian 3800 using a 30 m Rtx-1701 (14% cyanopropylphenyl/ 86% dimethyl polysiloxane) column or a 30 m Stabilwax-DA (acid-deactivated polyethylene glycol) column. Quantification was carried out using internal standard calibration against 100 mmolL\textsuperscript{-1} dimethyl sulfone in a three level calibration. GC-MS analyses were performed on a Varian Saturn 2000 GC/MS using a 30 m Rtx-1701 (14% cyanopropylphenyl/ 86% dimethyl polysiloxane) column or a 30 m Stabilwax-Da (acid-deactivated polyethylene glycol) column running in CI mode. Headspace gas analyses were carried out on a SRI 8610 micro-GC with a TCD detector against authentic gas samples.
Calibration was performed using 1000 ppm in helium of C$_1$-C$_6$ alkanes and C$_2$-C$_6$ alkenes purchased from GRACE Davison Discovery Sciences.

All reagents and solvents were purchased from readily available commercial sources and used as received unless otherwise specified. Trifluoromethansulfonic (triflic) acid was stored under argon atmosphere in a Rotaflo Schlenk tube sealed with Teflon stopcock.

All hydrogenation experiments employed industrial grade H$_2$ gas (99.995%) and carried out in an Autoclave Engineers (AE) Mini-reactor with a 50 mL 316 stainless steel (316SS) reactor vessel and impeller. Both reactor vessel and impeller were polished thoroughly after every run by lathe at 600 rpm with 3M Abrasive pads and sand blasting respectively.

2.3.1 3-phenyl-1,5-di(pyrid-2-yl)-pentane-1,5-dione [1]

Synthesis of [1] was carried out by the published literature procedure.$^7$ 1.5 g (0.027 mol) KOH was powdered in a mortar and pestle. 1.049 g (9.88 mmol) benzaldehyde was added with 2.477 g (20.40 mmol) 2-acyl pyridine and ground together for 20 min to form a brown-yellow powder. The powder was recrystallized from 90 mL anhydrous ethanol yielding 2.18 g (67%) of [1] as a white crystalline solid. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 3.70 (dq, $J_1$ = 6.9 Hz, $J_2$ = 6.9 Hz, $J_3$ = 17.5 Hz, 4H), 4.16 (p, $J_1$ = 7.1 Hz, 1H), 7.13 (m, 1H), 7.23 (m, 2H), 7.40 (m, 2H), 7.78 (dt, $J_1$ = 1.8 Hz, $J_2$ = 7.8 Hz, 2H), 7.94 (dt, $J_1$ = 5.7 Hz, $J_2$ = 7.7 Hz, 2H), 8.63 (dq, $J_1$ = 0.9 Hz, $J_2$ = 4.8 Hz, 2H). $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 36.30 (CH), 44.29 (CH$_2$), 121.94 (CH), 126.43 (CH), 127.14 (CH), 127.86 (CH), 128.49 (CH), 136.94 (CH), 144.72 (C), 148.94 (CH), 153.57 (C), 200.15 (CO).
2.3.2 4′-phenyl-2,2′:6′,2″-terpyridine [2]

The synthesis of [2] was carried out by literature procedure. 1.534 g (4.64 mmol) of [1] was refluxed in 50 mL anhydrous acetic acid with 1.87 g (24.2 mmol) ammonium acetate under ambient atmosphere for 12 h. The yellow solution changed to orange-red, 200 mL HPLC water was added and an orange crystalline solid precipitated, crude yield 1.020 g (71 %). The orange solid was dissolved in 50 mL of chloroform and passed through 30.0 g basic alumina (Brockman activity 1). The solvent was removed in vacuo on a rotary evaporator to yield 0.96 g (67%) of a white powder. 1H-NMR (400 MHz, CDCl₃): δ= 7.34 (dd, J=4.8, 6.6 Hz, 2H), 7.47 (m, 3H), 7.86 (m, 4H), 8.69 (m, 4H), 8.73 (s, 2H). 13C-NMR (100 MHz, CDCl₃): δ= 118.9 (CH), 121.3 (CH), 123.8 (CH), 127.3 (CH), 128.9 (CH), 136.8 (C), 138.5 (C), 149.1 (CH), 150.3 (C), 155.9 (C), 156.3 (C).

2.3.3 Ru(4′-phenyl-2,2′:6′,2″-terpyridine)Cl₃ [3]

1.315 g (5.39 mmol) of RuCl₃ was refluxed in 250 mL ethanol with 1.839 g (5.94 mmol) of [2] for 16 h under dynamic argon atmosphere. A red-brown precipitate formed which was filtered and washed with 3 (10 mL) portions of diethylether and dried. 1.894 g (64%) yield of a red-brown powder.

2.3.4 [Ru(OH)₃(4′-phenyl-2,2′:6′,2″-terpyridine)][OTf]₂ [4]

2.1929 g (4.24 mmol) of [3] was suspended in 25 mL degassed H₂O. 3.53 (13.7 mmol) AgOTf was dissolved in 10 mL degassed H₂O and added to the solution of [3] by cannula transfer. The solution was heated to 50 °C and stirred for 1 h until the solution was dark green. The solution was filtered through Celite® and 7.96 (0.106 mol) of Zn dust was added to the filtrate and stirred, the solution immediately turned a deep purple and was stirred 15 min at room temperature. The solution was again filtered through Celite® and the water was removed in
vacuo. The purple powder was stirred in 30 mL n-propanol for 30 min. and filtered through Celite® to remove Zn(OTf)$_2$. The n-propanol was removed by rotary evaporation yielding 1.34 g (60%) of purple crystals. $^1$H-NMR (300 MHz, D$_2$O), \( \delta = 7.38 \) (d, J= 7.2 Hz, 1H), 7.47 (t, J= 7.4 Hz, 2H), 7.65 (t, J= 7.4 Hz, 2H), 7.84 (d, J= 7.5 Hz, 2H), 7.94 (t, J= 7.7 Hz, 2H), 8.32 (d, J= 8.1 Hz, 2H), 8.43 (s, 2H), 9.04 (d, J= 5.1 Hz, 2H). $^{13}$C-NMR (75 MHz, D$_2$O): 118.7 (CH), 119.6 (q, \( J_{CF} = 315 \) Hz, CF$_3$SO$_3^-$), 122.8 (CH), 126.7 (CH), 127.5 (CH), 129.3 (CH), 129.8 (CH), 135.8 (C), 137.8 (CH), 143.2 (C), 153.1 (CH), 160.0 (C), 163.5 (C).

### 2.3.5 Representative hydrogenation of levulinic acid

In a 25.00 mL volumetric flask, 2.903 g (25 mmol) levulinic acid was added with 0.2353 (2.5 mmol) DMS (internal standard), 0.0191 g (0.025 mmol) [Ru(OH)$_2$)$_3$(Ph-trpy)][OTf]$_2$ and filled with 90% sulfolane 10% HPLC grade H$_2$O solution to yield a deep purple solution. This solution was sonicated for 5 min to ensure proper mixing and a 0.5 mL sample was removed for initial GC analysis. The reaction solution was placed in a 316SS Autoclave Engineers (AE) mini-reactor and sealed. The reactor was pressurized three times with 800 psi H$_2$ (g) and vented to purge any oxygen. The reactor was then pressurized to 800 psi and the temperature was allowed to equilibrate. The reactor was then heated to the set reaction temperature (100-250 °C) and the stirrer was set to 500 rpm. After 16 h the heating was removed and the reactor was allowed to cool to room temperature. Head space gas sample was collected for Micro-GC analysis and a 0.5 mL sample was taken for final GC and GC/MS analysis.
3 Results and Discussion: Project II

3.1 Synthesis and Characterization of [Ru(OH$_2$)$_3$(Di(picolyl)amine)](OTf)$_2$

3.1.1 Synthesis of Di(picolyl)amine

Di(picolyl)amine (DPA) can be synthesized according to the literature in good yields by a facile two-step process (Scheme 3.1). Step one of the reaction is the condensation of 2-picolylamine with 2-pyridine aldehyde to give the resulting imine. The imine is then reduced with H$_2$ gas with Pd/C as a catalyst. Purification of the product is achieved by fractional distillation in vacuo.

The ligand exists as a yellow oil and was obtained in yields comparable to reported yields by Gruenwedel before distillation. Distillation of the pure ligand occurs at 171-172 °C/0.1 Torr.

Scheme 3.1: Synthesis of DPA.

3.1.2 Initial Synthetic Routes to Generalized Complex [Ru(L)$_n$(DPA)](X)$_m$

Once the DPA ligand had been obtained the initial synthetic strategy was analogous to that of the [Ru(OH$_2$)$_3$(Ph-trpy)](OTf)$_2$ complex. The expected product is either the meridional or facial bound DPA with labile aquo ligands making up the remainder of the coordination sphere (Scheme 3.2).
Scheme 3.2: Potential synthetic pathway to DPA based ruthenium procatalyst analogous to [Ru(OH)$_2$(Ph-trpy)](OTf)$_2$ synthesis.

The first step was coordination of the DPA ligand in ethanol to produce the deep red [Ru(Cl)$_3$(DPA)] complex, whose identity was confirmed by EA (CHN). Addition of AgOTf to this in solution did result in a colour change, however, after the addition of Zn dust only a black sticky solid could be obtained.

An alternative strategy was to first begin with a ruthenium starting material in the Ru$^{2+}$ oxidation state and then coordinate the ligand followed by sequestering of any chlorides. The material chosen for this was cis/trans(tetrakis acetonitrile) ruthenium dichloride which could be prepared easily according to published literature procedures and then coordinated to DPA by displacing any combination of three ligands.$^{82}$ The proposed synthesis is outlined in Scheme 3.3.
Scheme 3.3: Proposed synthesis of [Ru(MeCN)$_3$(DPA)](OTf)$_2$.

RuCl$_3$ was dissolved in acetonitrile and stirred 3 days with zinc dust. This led to the reduction of the ruthenium by the zinc followed by coordination of four acetonitrile ligands. The tetrakis acetonitrile dichloride species was isolated and refluxed with DPA in acetone to yield the coordinated ruthenium-DPA complex. However, exchange of the chloride ligands/counterions for triflate proved to be challenging and manipulations at room temperature did not yield any solid Ru$^{2+}$ products. Furthermore, attempting the counterion/ligand exchange at higher temperatures yielded only the [Ru(MeCN)$_6$]Cl$_2$ complex. This suggested that either the chloride and/or the acetonitrile ligands were not as labile as suspected and that the latter beyond the immediate synthetic consideration would also not be suitable for catalysis in H$_2$O. Therefore a new ruthenium starting material was required with a more labile coordination sphere, allowing
for both a reliable synthetic route and a resulting pro-catalyst with ligands labile enough to be displaced by hydrogen. This led us to examine $\text{[Ru(DMF)}_6\text{](OTf)}_3$ as an alternative ruthenium platform.

### 3.1.3 Synthesis of $\text{[Ru(DMF)}_6\text{](OTf)}_3$

Synthesis of the platform starting material was performed according to literature procedures described by Judd and Merbach. The two step synthesis, as outlined in Scheme 3.4, begins with reduction of $\text{RuCl}_3$ in DMF/H$_2$(g) with PtO$_2$ as a catalyst, resulting in blue ruthenium chloride clusters in solution. The chlorides are then metathesized from the clusters by AgOTf while heating the solution to 135 °C. The insoluble AgCl produced precipitates from solution leaving DMF as the only coordinating species in solution, giving a deep yellow solution as the complex $\text{[Ru(DMF)}_6\text{](OTf)}_3$ forms.

$$\text{RuCl}_3 \cdot x \text{H}_2\text{O} \xrightarrow{\text{PtO}_2, \text{H}_2, \text{DMF}} \text{"Ru Blue"} \xrightarrow{\text{AgOTf, DMF}} \text{[Ru(DMF)}_6\text{](OTf)}_3$$

**Scheme 3.4:** Synthesis of $\text{[Ru(DMF)}_6\text{](OTf)}_3$

Isolation of the complex from solution is achieved by first filtration of the AgCl through Celite® followed by removal of DMF by rotary evaporation. The concentrated solution can then be added dropwise to Et$_2$O which removes most of the excess DMF and gives a yellow oil. Adding a small portion of anhydrous ethanol to the oil results in precipitation of bright yellow crystals isolated in yields up to 45%.
3.1.4 **In-situ Generation of [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$**

As mentioned previously the [Ru(DMF)$_6$](OTf)$_3$ complex is an ideal platform ruthenium starting material given the labile nature of its coordination sphere in aqueous environments. On the basis of previous results by Sardarian and Douglas, it was hypothesized that introducing the DPA ligand into an aqueous solution containing the [Ru(DMF)$_6$](OTf)$_3$ complex would result in complexation, given the large preference of a chelating tridentate ligand versus three DMF ligands. Adding a stoichiometric quantity of the DPA ligand to a yellow [Ru(DMF)$_6$](OTf)$_3$ solution in water or methanol resulted in a deep red-orange solution after several minutes at room temperature. Bubbles forming in the solution suggested a secondary process generating a gas may be occurring in solution. The same complexation reaction was then performed in D$_2$O, resulting in a slightly darker solution. Upon obtaining a $^1$H-NMR spectrum it was clear that no paramagnetic species were present and signals for free DMF in H$_2$O were evident, indicating that coordination was occurring along with concomitant reduction in solution resulting in the desired complex [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ (Scheme 3.5 and Figure 3.1). The complex in solution is stable indefinitely under atmospheric conditions and retains a deep red colour.

![Scheme 3.5](attachment:image.png)

**Scheme 3.5:** In-situ generation of [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$. 

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Figure 3.1: $^1$H-NMR of the in-situ generation of [Ru(OH)$_3$(DPA)](OTf)$_2$.

The appearance of free DMF and shifting of ligand peaks in the NMR indicates a shedding of the coordination sphere upon addition of the ligand. An additional peak upfield of the free DMF corresponds to the NMe$_2$ group, a decomposition product from DMF (Scheme 3.6). The presence of NMe$_2$ suggests that the reductant in the reaction is free electrons generated by the decomposition of DMF into dimethyl ammonium and formate. The formate then decomposes to CO$_2$ and two electrons reducing the ruthenium to Ru$^{2+}$.

Scheme 3.6: Proposed mechanism for the decomposition of N,N-dimethylformamide in aqueous acidic conditions.
It is clear from Scheme 3.6 that one equivalent of DMF can reduce two equivalents of Ru$^{3+}$, and the driving force of the reaction is the entropic benefit of CO$_2$ release from the solution. Although the use of DMF as a reduction medium is not typical, these observations match those made by Sardarian and Douglas in the synthesis of tris-bipyridine ruthenium by the same pathway.\textsuperscript{84} A similar reaction of DMF on gold nano-particles has also been employed previously by Pastoriza-Santos and Liz-Marzan in 2009.\textsuperscript{85} One major benefit to this method of procatalyst generation is that the transformation from [Ru(DMF)$_6$](OTf)$_3$ to [Ru(OH)$_3$(DPA)](OTf)$_2$ upon addition of the ligand occurs within several minutes, a timescale which can be monitored by NMR. Experiments were then performed in which a solution of ligand was prepared in D$_2$O with an internal DMS standard and $^1$H-NMR spectra were obtained every 5 minutes for 3 hours after addition of [Ru(DMF)$_6$](OTf)$_3$. The goal of these experiments was not only to visibly witness the complex formation, as indicated by the observed colour change and ligand peak shifting in the NMR, but also to possibly gain information about the kinetics of the complex formation as well as the minimum time frame for completion of the complex formation. Shown below is a series of selected spectra from the $^1$H-NMR showing the formation of the complex in D$_2$O over the course of two hours (Figure 3.2).

It is interesting to note that almost instantaneously free DMF peaks are visible and the ligand peaks shift, then gradually more DMF is released into solution but the amounts of dimethyl ammonium are relatively stable. This indicates two things: 1) binding of the ligand to the complex occurs very rapidly, since within the first two minutes no free ligand peaks remain and, 2) reduction of the Ru$^{3+}$ to Ru$^{2+}$ takes place immediately, releasing the decomposition product dimethyl ammonium into solution. Further evidence for the rapid reduction is indicated by the lack of peak broadening one would expect if paramagnetic species were lingering in
solution. Since the appearance of chelated ligand and dimethyl amine were too rapid to obtain kinetic data from the NMR, the appearance of free DMF was chosen versus the internal standard DMS. In order to probe the reaction kinetics, including fractional orders, the integrated rate laws shown below which were used for a graphical analysis (Equation 3.1). Forming plots of $[A]^{(1-n)}$ versus $t$ should yield a linear plot for any reaction of order $n$ where $n$ is between 0 and 2 but not equal to 1.

\[
[A]^{(1-n)} = -kt + [A_o]^{(1-n)}
\]  

\textbf{Equation 3.1}

For the case of $n = 1$ (first order kinetics), the natural logarithm was used (Equation 3.2)
\[ \ln[A] = -kt + \ln[A_o] \quad \text{Equation 3.2} \]

As \( n \) was increased in steps of 0.1, no model of the system demonstrated any linearity, indicating that the formation of the \([\text{Ru(OH}_2\text{)}_3(\text{DPA})](\text{OTf})_2\) complex is not zero, first, second or fractional reaction order but rather some complex mixed order reaction pathway. Since the \([\text{Ru(DMF)}_6](\text{OTf})_3\) complex is stable in aqueous environments without ligand present it can be deduced that the reduction of the ruthenium centre is dependent on the presence of the ligand.

Initial trials to determine the temperature stability of the complex were performed by first generating the complex \textit{in-situ} inside a sealed Teflon screw-top NMR tube under inert atmosphere in D\(_2\)O. The mixture was then heated in an oil bath while periodically observing the \(^1\)H-NMR spectrum at steps of 50 °C starting at 100 °C. At 100 °C the solution remains homogeneous but it is clear from the NMR spectrum that multiple species are being generated in solution, possibly due to \textit{mer-}/\textit{fac-} isomers of the complex being formed as well as any complexes in which DPA is bound in a bidentate fashion(Figure 3.4). At 150 °C the \(^1\)H-NMR spectrum remains unchanged and the solution remained deep red and homogeneous. Increasing the temperature further resulted in a black precipitate in the NMR tube as well as loss of the red colour in solution, indicating decomposition of the complex occurs between 150-200 °C.
Figure 3.3: [DMF] (a), [DMF]$^{0.5}$ (b), ln[DMF] (c), [DMF]$^{1.5}$ (d), and [DMF]$^{-1}$ (e) versus time in seconds for the appearance of free DMF during the formation of [Ru(OD$_2$)$_3$(DPA)](OTf)$_2$ in D$_2$O by integration against internal standard DMS in the $^1$H-NMR (600 MHz) for 3 hours.
**Figure 3.4**: Possible Isomers of \([\text{Ru(OD}_2)_3(\text{DPA})](\text{OTf})_2\) formed in \(\text{D}_2\text{O}\) solution at elevated temperature.

As mentioned earlier, an additional requirement for the catalyst complex is tolerance to low \(pH\), given that the deoxygenation of biomass derived substrates intrinsically generates an acidic aqueous medium as mentioned earlier and may require the addition of excess acid as the dehydration co-catalyst. A sample of the complex was generated *in-situ* in a screw top NMR tube under argon with the addition of 10 equivalents of triflic acid with respect to ruthenium. A noticeable change in chemical shifts was observed in the \(^1\text{H-NMR}\) likely indicating protonation of the ligand. This protonation is not definitive evidence for a MLB mediated by the complex but does suggest that the complex can operate via a MLB ionic hydrogenation mechanism. Upon heating the solution to 100 °C it is clear that the remainder of free DMF in the solution has decomposed and a large singlet is seen corresponding to dimethyl ammonium/dimethylamine. Furthermore two sets of ligand peaks are present in an approximately 1:5 ratio which is likely the unprotonated tridentate species and the protonated bidentate species respectively. Decomposition
of the complex was not observed until heating the solution to 200 °C demonstrating an increase in the stability of the complex at lower pH, a highly beneficial trait for deoxygenation in acidic aqueous environments.

3.2 Catalytic Hydrogenations by [Ru(OH$_2$)$_3$(di(picolyl)amine)](OTf)$_2$

The design of the [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ complex and the [Ru(OH$_2$)$_3$(Ph-trpy)](OTf)$_2$ complex was intended to meet all the criteria set out by the Schlaf group to be an effective deoxygenation catalyst. The differing factor between the two is the placement of the central pyridine from the Ph-trpy ligand in exchange for a secondary amine. This structural difference was postulated to introduce the ability to operate by a MLB mechanism into the complex thus inferring that the [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ would have enhanced activity to the [Ru(OH$_2$)$_3$(Ph-trpy)](OTf)$_2$ complex while demonstrating similar thermal stability. In this fashion the effectiveness of introducing the MLB ability to a complex could be probed effectively by examining the ability of the [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ complex to deoxygenate both 2,5-hexanedione and levulinic acid.

3.2.1 Temperature Series: Deoxygenation of 2,5-hexanedione by

[Ru(OH$_2$)$_3$(di(picolyl)amine)](OTf)$_2$

The initial step in determining the effectiveness of the complex was to assess its temperature stability limits under hydrogen atmosphere in aqueous acidic medium against the model substrates chosen. The temperature series was performed in H$_2$O with 1000 mmol L$^{-1}$ substrate with a 0.1 mol% catalyst load under 800 psi H$_2$(g) (cold). Each experiment was run for 16 hours ranging in temperature from 100-200 °C. The products were analyzed by GC and GC/MS against 100 mmol L$^{-1}$ DMS as an internal standard. The results are summarized below in Scheme 3.7, Figure 3.5 and Table 3.1.
Scheme 3.7: Reaction conditions employed in temperature series for the hydrogenation of 2,5-hexanedione employing the \([\text{Ru(OH}_2]_3(\text{di}(\text{picoly})\text{amine})]\)(OTf)_2\) catalyst.

Table 3.1: Deoxygenation of 2,5-hexanedione in water catalyzed by \([\text{Ru(OH}_2]_3(\text{di}(\text{picoly})\text{amine})]\)(OTf)_2\) as a function of temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>(\text{H}_2) (psi) uptake</th>
<th>2,5-hexanedione (% recovery)(^b)</th>
<th>Hemiacetal (% yield)(^b)</th>
<th>2,5-hexanediol (% yield)(^b)</th>
<th>DMTMF (% yield)(^b)</th>
<th>Self Aldol (% yield)(^b)</th>
<th>MCP (% yield)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>26</td>
<td>96</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>125</td>
<td>92</td>
<td>21</td>
<td>24</td>
<td>51</td>
<td>4</td>
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<td>0</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>349</td>
<td>0</td>
<td>0</td>
<td>94</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>175</td>
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<td>28</td>
<td>16</td>
<td>4</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>177</td>
<td>40</td>
<td>30</td>
<td>27</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Reaction conditions: 2,5-hexanedione [1000 mmol L\(^{-1}\)], 800 psi \(\text{H}_2\)(g), dimethyl sulfone (ISTD) [100 mmol L\(^{-1}\)], by \([\text{Ru(OH}_2]_3(\text{Di}(\text{picoly})\text{amine})]\)(OTf)_2 \(\times\) 10 mmol L\(^{-1}\) = 0.1 mol% w.r.t substrate, time = 16hrs. Nominal reactor volume 50 mL, solution volume 25 mL. \(^a\) Observed pressure drop in reactor (cold). \(^b\) By quantitative GC and GC/MS against internal standard dimethyl sulfone.
Figure 3.5: Hydrogenation of 1000mmolL$^{-1}$ 2,5-hexanediol with 0.1 mol% [Ru(DPA)(OH$_2$)$_3$](OTf)$_2$ from 100-200 °C at 800 psi H$_2$ for 16 hrs.

In concurrence with the $^1$H-NMR temperature study performed on the complex, it is clear that the activity of the catalyst improves with temperature but also that it is no longer stable above 150 °C. This is further supported by the formation of a blue ruthenium coating on the body of the reactor at higher temperatures and loss of homogeneous character. As the temperature increases the yield of 2,5-hexanediol also increases with some formation of dimethyl THF. Beyond 150 °C, where the decomposition of the complex occurs, selectivity and activity of the catalyst decreases and a variety of products are observed, mainly unconverted substrate, unhydrogenated hemiacetal and 2,5-hexanediol, with smaller concentrations of aldol self-condensation products as well as some methyl cyclopentanol and dimethyl THF. Further
increasing the reaction temperature, where only heterogenous behaviour is occurring, only substrate, hemiacetal and 2,5-hexanediol are present with a small amount of dimethyl THF, i.e. after thermal decomposition of the homogeneous catalyst a much lower catalytic activity is observed. It is clear that the optimal temperature for peak activity of the [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ complex is 150 °C, where 100% conversion of substrate is observed yielding 94% of the 2,5-hexanediol and 6% of DMTHF. This is indicative of the active catalyst being highly selective towards carbonyls and hydrogenating both carbonyls of the substrate before: 1) a self aldol condensation can occur prior to the hydrogenation of the first carbonyl, or 2) formation of the hemiacetetal after the first hydrogenation (Scheme 1.7).

A small portion of DMTHF is formed during the reaction likely through the acid catalyzed dehydration of 2,5-hexanediol, forming a stable species which is extremely resistant to hydrolysis and/or hydrogenolysis at temperatures below 250 °C. Beyond the decomposition point of the catalyst selectivity and activity suffer drastically resulting in a wide variety of products generated under heterogeneous conditions. Since heterogeneous behaviour of ruthenium was of little interest in the scope of the project, it was necessary to improve the temperature stability of the complex. This is possible by the addition of TfOH as demonstrated in the $^1$H-NMR study mentioned in the previous section.

3.2.2 Temperature Series with the addition of triflic acid: Deoxygenation of 2,5-hexanediol by [Ru(OH$_2$)$_3$(di(picolyl)amine)](OTf)$_2$

Since the [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ complex demonstrated enhanced stability at lower pH an additional temperature series was performed with the addition of TfOH aiming to increase the range of attainable temperatures. The temperature series was performed in H$_2$O with 1000 mmol L$^{-1}$ substrate with a 0.1 mol% catalyst load and 10 equivalents of TfOH with respect to catalyst
under 800 psi $H_2(g)$ (cold). Each experiment was run for 16 hours at temperatures ranging from 100-175 °C. The products were again analyzed by GC and GC/MS against 100 mmol L$^{-1}$ DMS as an internal standard. The results are summarized below in Scheme 3.8, Figure 3.6 and Table 3.2.

**Scheme 3.8:** Reaction conditions employed in temperature series for the hydrogenation of 2,5-hexanediol employing the $[\text{Ru(OH}_2]^3\text{(Di(picolyl)amine)}](\text{OTf})_2$ catalyst with the addition of 1.0 mol % TfOH.

**Table 3.2:** Deoxygenation of 2,5-hexanediol in water catalyzed by $[\text{Ru(OH}_2]^3\text{(di(picolyl)amine)}](\text{OTf})_2$ as a function of temperature with the addition of TfOH

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>$H_2$ (g) uptake (psi)$^a$</th>
<th>2,5-hexanediol (% recovery)$^b$</th>
<th>Hemiacetal (% yield)$^b$</th>
<th>2,5-hexanediol (% yield)$^b$</th>
<th>DMTHF (% yield)$^b$</th>
<th>Self Aldol (% yield)$^b$</th>
<th>MCP (% yield)$^b$</th>
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</tr>
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<td>20</td>
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</table>

Reaction conditions: 2,5-hexanediol [1000 mmol L$^{-1}$], 800 psi $H_2(g)$, dimethylsulfone (ISTD) [100 mmol L$^{-1}$], $[\text{Ru(OH}_2]^3\text{(Di(picolyl)amine)}](\text{OTf})_2$ [10 mmol L$^{-1}$= 0.1 mol% w.r.t substrate], TfOH [100 mmol L$^{-1}$ = 1.0 mol % w.r.t. substrate], time = 16hrs, Nominal reactor volume 50 mL, solution volume 25 mL. $^a$Observed pressure drop in reactor (cold). $^b$ By quantitative GC and GC/MS against internal standard dimethylsulfone.
Figure 3.6: Hydrogenation of $1000\text{mmolL}^{-1}$ 2,5-hexanedione with 0.1 mol% \([\text{Ru(DPA)}(\text{OH}_2)_3](\text{OTf})_2\) and 10 eq. TfOH (w.r.t. Ru) from 100-150 °C at 800 psi $H_2$ (g) for 16 hrs.

Although the $[\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2$ complex did exhibit increased stability with the addition of a protic acid, the activity of the complex suffered greatly. At 150 °C only 21% conversion of 2,5-hexanedione was observed, a trend which was surprising given the expected enhancement of acid catalyzed dehydration of the substrate with additional TfOH present. Further increasing the temperature increased conversion to 52% resulting in a mix of products composed mainly of cyclized deoxygenation products. Increasing the temperature beyond 175 °C resulted in complete loss of the homogenous complex (marked by the loss of colour in solution and formation of a metallic blue coating in the reactor body) and was therefore not included in the study.
The results suggest that addition of protic acids to the solution decrease the activity of the catalyst. This can be rationalized by examining the mechanism by which a MLB catalyst is expected to undergo heterolytic activation of H₂ gas. As mentioned earlier following η² coordination of H₂ to the ruthenium centre, the pKₐ of H₂ is reduced by many orders of magnitude as a result of pi back-donation from the ruthenium. The overall result is the generation of hydronium H₃O⁺ in aqueous medium and a metal-bound hydride where the proton can be abstracted from the complex by a base. In the case of a MLB catalyst the role of the base is performed by a basic group on the ligand; in this case the central amine of the DPA ligand. The DPA ligand can abstract a proton from the complex through the lone pair on the amine formerly involved in a dative bond to the ruthenium. A complex equilibrium is then possible between the DPA ligand and the ruthenium where equivalents of H₂ can be exchanged from the complex to the substrate concertedly (Scheme 3.9).

**Scheme 3.9:** Proposed H₂ exchange equilibrium between ruthenium and MLB ligand DPA.

Postulating that the active species is one in which the amine nitrogen is coordinated to the Ruthenium, the activity of the system is then hindered by the fact that the equilibrium shown in Scheme 3.9 lies heavily to the left with the addition of strong protic acid. The ratio of DMTTHF to hexanediol suggests that the addition of acid did in fact favour the acid catalyzed dehydration of the diol and the hemiacetal however significant concentrations of the hemiacetal suggest that the complex was not active enough to hydrogenate the 2,5- dihydrofuran generated by the acid
catalyzed dehydration of the hemiacetal (Scheme 1.7). Building on this information it was clear that an acid catalyst was necessary and would benefit the conversion of the substrate but a non-protic acid would be required to circumvent hindrance of the complex MLB mechanism. The next stage was to investigate acids whose function would be to directly affect the substrate while minimizing interaction with the ruthenium complex, potentially a Lewis acid or an acid known to form esters with alcohols such as H₃PO₄ or B(OH)₃.

3.2.3 Acid Series: Deoxygenation of 2,5-hexanediol

Based on the criteria discussed in the previous section it was necessary to investigate the potential for acid activation of the substrate without protonating the DPA ligand. Two possible approaches were outlined: 1) the use of a water-soluble non-protic Lewis acid (Scheme 3.10) or 2) the use of a mineral acid capable of forming ester linkages with alcohols such as H₃PO₄ or B(OH)₃ (Scheme 3.11).

The ideal choice for a Lewis acid in aqueous conditions was La(OTf)₃, a commonly available water soluble Lewis acid capable of catalyzing many organic transformations. The intended effect of the La(OTf)₃ would be to polarize and thus activate the carbon-oxygen double bond by forming an adduct with the available oxygen lone pairs. This would generate an electrophilic carbon accepting a hydride delivered form the catalyst along with a proton to the oxygen in a concerted manner resulting in hydrogenation of the carbonyl to an alcohol. Additionally formation of the adduct could prevent ring closure of 2,5-hexanediol to DMTHF, or alternatively activate the DMTHF ring to hydrogenolyze to 2-hexanol.
Scheme 3.10: Proposed mechanism for Lewis acid (LA) activation of 2,5-hexanedione in aqueous medium.

As an alternative to bond activation by a Lewis acid an attempt was made using H$_3$PO$_4$ and B(OH)$_3$, two common water soluble mineral acids. The rationale behind the use of such acids was to deoxygenate 2,5-hexanediol through activation of the carbon-oxygen bond in a manner similar to ATP bond cleavage using phosphate ester hydrolysis (Scheme 3.11). Once 2,5-hexanediol is produced H$_3$PO$_4$ could in principle form a dioxaphosphorinane ring through a double condensation mechanism. The formation of a phosphodiester bond effectively polarizes the oxygen-carbon bond, making it more susceptible to ionic hydrogenation. An analogous mechanism can be envisioned for the behavior of boric acid under identical conditions.

Scheme 3.11: Proposed activation of 2,5-hexanedione through the formation of phosphate-ester linkages.

Investigations with the various acids mentioned earlier were performed at 150°C in H$_2$O with 1000 mmol L$^{-1}$ substrate with a 0.1 mol % catalyst load and 10 mol % of each acid with
respect to substrate under 800 psi H$_2$(g) (cold). Each experiment was run for 16 hours and the products were analyzed by GC and GC/MS against 100 mmolL$^{-1}$ DMS as an internal standard as before. The results are summarized below in Scheme 3.12, Figure 3.7 and Table 3.3.

Scheme 3.12: Reaction conditions employed in acid series for the hydrogenation of 2,5-hexanodione employing the [Ru(OH)$_2$)$_3$(di(picolyl)amine)](OTf)$_2$ catalyst at 150$^\circ$C with the addition of La(OTf)$_3$, H$_3$PO$_4$ and B(OH)$_3$.

Table 3.3: Deoxygenation of 2,5-hexanodione in water catalyzed by [Ru(OH)$_2$)$_3$(Di(picolyl)amine)](OTf)$_2$ as a function of acid co-catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid</th>
<th>H$_2$(g) uptake (psi)$^a$</th>
<th>2,5-hexanodione (% recovery)$^b$</th>
<th>Hemiacetal (% yield)$^b$</th>
<th>2,5-hexanediol (% yield)$^b$</th>
<th>DMTHF (% yield)$^b$</th>
<th>Self Aldol (% yield)$^b$</th>
<th>MCP (% yield)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>349</td>
<td>0</td>
<td>0</td>
<td>94</td>
<td>6</td>
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<td>0</td>
</tr>
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<td>2</td>
<td>TiOH</td>
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<td>79</td>
<td>9</td>
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<td>265</td>
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<td>9</td>
<td>38</td>
<td>2</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>H$_3$PO$_4$</td>
<td>368</td>
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<td>0</td>
<td>0</td>
<td>98</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>La(OTf)$_3$</td>
<td>362</td>
<td>0</td>
<td>0</td>
<td>92</td>
<td>8</td>
<td>0</td>
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</tr>
</tbody>
</table>

Reaction conditions: 2,5-hexanodione [1000 mmol L$^{-1}$], 800 psi H$_2$(g), dimethylsulfone (ISTD) [100 mmol L$^{-1}$], [Ru(OH)$_2$)$_3$(di(picolyl)amine)](OTf)$_2$ [10 mmolL$^{-1}$= 0.1 mol% w.r.t substrate], TiOH [10 mmolL$^{-1}$ = 1.0 mol % w.r.t. substrate], B(OH)$_3$/H$_3$PO$_4$/La(OTf)$_3$ [100 mmolL$^{-1}$= 10.0 mol% w.r.t. substrate], time = 16hrs. Nominal reactor volume 50 mL, solution volume 25 mL. $^a$ Observed pressure drop in reactor (cold). $^b$ By quantitative GC and GC/MS against internal standard dimethylsulfone.
Figure 3.7: Hydrogenation of 1000mmolL\(^{-1}\) 2,5-hexanedione with 0.1mol % Ru(DPA)(OH\(_2\))\(_3\)(OTf\(_2\)) and various acids at 150 °C at 800 psi H\(_2\) for 16 hrs.

The use of La(OTf)\(_3\) as a Lewis acid co-catalyst did not inhibit the activity of the [Ru(OH\(_2\))(DPA)](OTf)\(_2\) complex, as anticipated, but neither did it enhance the deoxygenation beyond 2,5-hexanediol. Overall the addition of La(OTf)\(_3\) had few observable effects with respect to activity of the complex and conversion of 2,5-hexanediione. It is possible that La(OTf)\(_3\) enhanced the rate of hydrogenation of 2,5-hexanedione to 2,5-hexanediol which could be determined by a time dependent hydrogenation experiment in which reaction progress is monitored hourly until completion. Since the completely deoxygenated products were of primary interest in this study, these experiments were not performed and enhancement of carbonyl
hydrogenation by La(OTf)$_3$ should be considered as a possible avenue of investigation in the future.

Addition of boric acid resulted in significant loss of activity and selectivity of the complex. Conversion of 2,5-hexanediol fell to 92% with 37% of the substrate lost due to polymerization in the reactor. Only 38% converted to hexanediol with the remainder of products being composed of the incompletely hydrogenated hemiacetal and aldol products with only small amounts of DMTHF detected. In addition to the polymerization of the substrate in the reactor, there was a noticeable disappearance of the complex from the liquid reaction mixture, marked by a clear colourless solution following the reaction. The overall difficulty with the use of boric acid is its characteristics as a polymer cross-linking agent.\(^8\) Polymerization in the reactor was likely due to borate cross-linkages formed between 2,5-hexanediol monomers (Scheme 3.13). As 2,5-hexanediol is generated in solution it can form condensation products with boric acid leading to the formation of a branched hexanediol-borate species insoluble in water which precipitates out of the mixture. This demonstrates that indeed borate-ester linkages were being formed but the carbon-oxygen bond had not been polarized to a great enough degree to undergo hydrogenolysis by the complex. In addition, it is conceivable that the boric acid irreversibly reacted with the N-H function on the DPA ligand, resulting in a carbon-carbon isoelectronic boron-nitrogen bond, which also accounts for the decreased catalytic activity observed with this acid.
**Scheme 3.13:** Formation of borate cross-links between 2,5-hexanediol and boric acid.

The most interesting results were obtained with the addition of H$_3$PO$_4$. Upon completion, two clear phases were visible in the reactor; an orange aqueous phase and a colourless organic phase. Both phases were analyzed by GC and GC/MS and the gas headspace of the reactor was also sampled by micro-GC. Due to partitioning of the internal standard between organic and aqueous phases, quantification of the products was performed by using absolute peak areas directly from the FID detector against the peak area for the initial solution of 2,5-hexanediol. The aqueous phase contained approximately 250 mmol L$^{-1}$ DMTHF and no other species aside from DMS. The organic phase was composed almost entirely of DMTHF, with a small quantity of methylcyclopentanol. Based on the lack of colour in the organic phase it is evident that the complex, preferring the aqueous medium, hydrogenated 2,5-hexanediol to 2,5-hexandiol and with the aid of H$_3$PO$_4$ generated substantial amounts of DMTHF. DMTHF is sparingly miscible...
with H₂O and therefore phase separated, resulting in easy separation of organic products and aqueous catalyst solution, making for facile recovery of product and catalyst recycling.

The nearly quantitative formation of DMTHF was not the intended goal of the addition of H₃PO₄ but can be explained when examining the possible equilibria present under acidic aqueous conditions (Scheme 3.14). Upon the formation of 2,5-hexanediol, H₃PO₄ can undergo a condensation reaction to form a phosphate ester linkage after which ring closure condensation of the secondary alcohol to form 2,5-dimethyl-2-dihydrofuran is possible.

Scheme 3.14: Proposed mechanism for the formation of DMTHF from 2,5-hexanediol catalyzed by H₃PO₄ and [Ru(OH₂)₃(DPA)](OTf)₂.

The dihydrofuran species then undergoes catalytic hydrogenation to form DMTHF. At the conditions outlined in this section (150 °C, 800 psi H₂ (g)) further deoxygenation of DMTHF cannot occur and thus exists as the major product. Although hexane could not be generated from 2,5-hexanediol, the results presented demonstrate that the [Ru(OH₂)₃(DPA)](OTf)₂ system with H₃PO₄ as an acid co-catalyst could potentially hydrogenate a more relevant substrate, such as furfural, to methyl THF. Such a transformation would be extremely beneficial and generate a value added chemical from furfural.
3.3 Experimental

All manipulations were performed under argon atmosphere using standard Schlenk-line techniques or in a MBraun glove box. All NMR spectra were obtained on 300 MHz, 400 MHz, or 600 MHz spectrometers and calibrated to the residual protonated solvent signal.

GC analyses were performed on a Varian 3800 using a 30 m Rtx-1701 (14% cyanopropylphenyl/ 86% dimethyl polysiloxane) column or a 30 m Stabilwax-DA (acid-deactivated polyethylene glycol) column. Quantification was carried out using internal standard calibration against 100 mmol L\(^{-1}\) dimethyl sulfone in a three level calibration. GC-MS analyses were performed on a Varian Saturn 2000 GC/MS using a 30 m Rtx-1701 (14% cyanopropylphenyl/ 86% dimethyl polysiloxane) column or a 30 m Stabilwax-Da (acid-deactivated polyethylene glycol) column running in CI mode. Headspace gas analyses were carried out on a SRI 8610 micro-GC with a TCD detector against authentic gas samples. Calibration was performed using 1000 ppm of C\(_1\)-C\(_6\) alkanes and C\(_2\)-C\(_6\) alkenes in helium purchased from GRACE Davison Discovery Sciences.

All reagents and solvents were purchased from readily available commercial sources and used as received unless otherwise specified. Trifluoromethansulfonic acid was stored under argon atmosphere in a Rotaflo Schlenk tube sealed with Teflon stopcock.

All hydrogenation experiments employed industrial grade H\(_2\) gas (99.995 %) and run on an Autoclave Engineers (AE) Mini-reactor with a 50 mL 316 stainless steel (316SS) reactor vessel and impellor. Both reactor vessel and impellor were polished thoroughly after every run by lathe at 600 rpm with 3M Abrasive pads and Sand blasting respectively.
3.3.1 Di(picolyl)amine [5] 

Pyridine carboxaldehyde (9.051 g, 84.6 mmol) was dissolved in 20 mL methanol and stirred. Picolyl amine (9.133 g, 84.6 mol) was added dropwise. The solution changed to red immediately and was stirred for an additional 30 min. The solution was diluted with 100 mL of methanol, 0.5049 g Pd/C was added and H₂(g) was bubbled through solution via a balloon. The solution was hydrogenated for 4 h changing the balloon 3 times. The resulting yellow solution was filtered through Celite® and the solvent removed by rotary evaporation, crude yield 16.267 g. The crude product was distilled in vacuo at 172 °C/0.1 Torr. Obtained 8.1176 g (48%) yellow oil. ¹H-NMR (300 MHz, D₂O): δ = 3.52 (s, 2H), 7.027 (t, J= 3.9 Hz, 1H), 7.066 (d, J= 5.9 Hz, 1H), 7.501 (dt, J₁= 1.3 Hz, J₂= 5.8 Hz, 1H), 8.129 (d, J= 3.2 Hz, 1H).

3.3.2 Ru(di(picolyl)amine)Cl₃ [6]

1.655 g (8.30 mmol) di(picolyl)amine was added to a solution of 2.005 g (8.22 mmol) RuCl₃ in 500 mL anhydrous ethanol and stirred for 24 h. The brown mixture was refluxed for 6 hours until purple-red. The solution was cooled to 0°C and filtered yielding 3.428 g (74%) of a brown-red powder.

3.3.3 Ru(MeCN)₄Cl₂ [7]

2.524 g (12.2 mmol) RuCl₃ was added to 95 mL acetonitrile. Brown solution was stirred 10 min before the addition of 1.772 g (27.1 mmol) Zn dust. The brown solution was stirred three days, during which time the solution changed from brown to yellow and finally light green. Filtration through Celite® gave a yellow solution from which the solvent was removed by rotary evaporation yielding 2.311 g (54%) yellow powder.
3.3.4 [Ru(MeCN)$_3$(di(picolyl)amine)]Cl$_2$ [8]

0.1021 g (0.304 mmol) of [7] were dissolved in 9.0 mL acetone. 0.0632 g (0.317 mmol) of [5] were added and the mixture refluxed for 12 h, during which time the solution turned red. An orange-yellow precipitate formed upon cooling to 0 °C, which was filtered and washed with 3 portions (10 mL) diethylether. 0.0980 g (65%) of [8] was obtained as an orange powder.

3.3.5 [Ru(DMF)$_6$](OTf)$_3$ [9]

[9] was prepared according to the literature procedure. 1.030 g (3.94 mmol) RuCl$_3$ was ground to a fine dust in a mortar and pestle and dissolved in 80 mL DMF and stirred 24 h. The solution was then filtered and 0.005 g (0.027 mmol) Pt black was added. The solution was saturated with H$_2$ (g) for 4 h until deep blue. 4.337 g (16.88 mmol) of AgOTf were added and the reaction mixture refluxed at 140 °C for 1 h until the solution was clear yellow. Cooled to room temperature then filtered through Celite®. The solvent was then reduced by rotary evaporation to 25 mL. The 25 mL of solution were added dropwise to 500 mL of stirring diethylether and the mixture was cooled to 0°C. The excess ether was decanted from the solution leaving a thick yellow oil. 5 mL anhydrous ethanol was added to the oil causing immediate precipitate of yellow crystals. Solution was cooled and filtered to obtain a bright yellow powder. Recrystallized from 30 mL of hot ethanol to yield 1.7488 g (45%) of a yellow crystalline solid.

3.3.6 [Ru(OH)$_2$)$_3$(di(picolyl)amine)](OTf)$_2$ [10]

0.1105 g (0.112 mmol) of [9] was dissolved in 2.0 mL of HPLC-grade H$_2$O. 0.0229 g (0.115 mmol) of di(picolyl)amine was dissolved separately in 1.0 mL of HPLC-grade H$_2$O. The di(picolyl)amine solution was then added slowly to the [Ru(DMF)$_6$](OTf)$_3$ solution and the mixture stirred. A colour change from yellow to deep red was observed after 5 min. $^1$H-NMR (300 MHz, D$_2$O): δ= 4.369 (s, 2H), 7.383 (dt, J$_1$= 2.4 Hz, J$_2$= 6.3 Hz, 1H), 7.416 (d, J= 7.8 Hz,
1H), 7.826 (t, J= 6.6 Hz, 1H), 8.488 (d, J= 4.2 Hz, 1H). $^{13}$C-NMR (75 MHz, D$_2$O): δ= 50.74 (CH$_2$), 124.29 (CH), 124.61 (CH), 138.91 (CH), 149.04 (CH), 150.10 (CH). m/z 149.49 [C$_{12}$H$_{11}$N$_3$Ru]$^{2+}$

3.3.7 Representative procedure for the hydrogenation of 2,5-hexanedione

0.0246 g (0.025 mmol) [Ru(DMF)$_6$(OTf)$_3$] was dissolved in 1.0 mL HPLC-grade H$_2$O and mixed with 0.000495 g (0.025 mmol) di(picolyl)amine and stirred for 3 h. In a 25.00 mL volumetric flask, 2.853 g (25 mmol) 2,5-hexanedione was added with 0.2353 (2.5 mmol) DMS (internal standard), premade catalyst solution and filled with HPLC-grade H$_2$O to yield a red solution. The solution was sonicated for 5 min to ensure proper mixing and a 0.5 mL sample was removed for initial GC analysis. The reaction solution was placed in a 316SS Autoclave Engineers (AE) mini-reactor and sealed. The reactor was pressurized three times with 800 psi H$_2$ (g) and vented to purge any oxygen. The reactor was then pressurized to 800 psi and the temperature was allowed to equilibrate. The reactor was then heated to the set reaction temperature (100-250 °C) and the stirrer was set to 500 rpm. After 16 h the heating was removed and the reactor was allowed to cool to room temperature. Head space gas sample was collected for Micro-GC analysis and a 0.5 mL sample was taken for final GC and GC/MS analysis.
4 Comparitive Study of \([\text{Ru(OH}_2\text{)}_3(4\text{'-phenyl-2,2':6',2''-terpyridine})](\text{OTf})_2\)

and of \([\text{Ru(OH}_2\text{)}_3(\text{Di(picolyl)amine})](\text{OTf})_2\)

Direct evidence for metal-ligand bifunctionality (MLB) for a catalytic species is challenging to obtain and therefore MLB hydrogenation mechanisms are usually demonstrated through inference. This is generally achieved by comparing two analogous systems under near identical conditions where one system contains the possibility of proceeding through a MLB hydrogenation mechanism and complex activity is then compared.\(^{57,89,90}\) The same approach has been followed in this section where the \([\text{Ru(OH}_2\text{)}_3(\text{ph-trpy})](\text{OTf})_2\) and \([\text{Ru(OH}_2\text{)}_3(\text{DPA})](\text{OTf})_2\) complexes, discussed earlier, were compared for the substrates 2,5-hexanodione, levulinic acid and furfural under similar reaction conditions. It was hypothesized that conversions for the MLB mechanism would be enhanced for each substrate.

Each set of reactions was performed under static hydrogen pressure of 800 psi H\(_2\) (g) in water at 150 °C for 16 hours with identical concentrations of substrate and catalyst. The relative catalytic activities can be compared post-run by observing total conversion of substrate and yield of respective products. For a MLB mechanism it is expected that conversions will generally be closer to complete and that greater yields of higher order deoxygenated products will be observed. Previous complexes in the Schlaf group used pendant amine functions to introduce MLB, if successful and a MLB mechanism is observed enhance activity is seen as with the \([\text{Ru(η}_5\text{-C}_5\text{H}_5)(\text{dabipy})]\_2(\text{OTf})_2\) system investigated by Di Mondo.\(^{91}\) If unsuccessful the pendant amines add steric bulk near the ruthenium active site and activity of the complexes decrease, as observed with systems described by Dykeman and Luska.\(^{67}\) This complication is circumvented in the \([\text{Ru(OH}_2\text{)}_3(\text{DPA})](\text{OTf})_2\) system by avoiding the use of pendant amines in the ligand and instead introducing functionality directly into the donor atoms of the ligand.
4.1 Levulinic Acid

Hydrogenations of levulinic acid were performed under 800 psi (cold) static hydrogen pressure in water at 150°C for 16 hours with 1000 mmol L⁻¹ levulinic acid and 0.1 mol% catalyst load with 100 mmol L⁻¹ DMS as an internal standard. The results of the investigation are summarized below in Scheme 4.1 and Table 4.1.

**Scheme 4.1:** Reaction conditions employed for the hydrogenation of levulinic acid employing the [Ru(OH)₃(4'-phenyl-2,2':6',2''-terpyridine)](OTf)₂ and [Ru(OH)₃(di(picolyl)amine)](OTf)₂ catalyst.

![Scheme 4.1](image-url)
Table 4.1: Percent yield of products formed from hydrogenation of levulinic acid by [Ru(OH)$_2$](Ph-trpy)](OTf)$_2$ and [Ru(OH)$_2$(DPA)](OTf)$_2$

<table>
<thead>
<tr>
<th>Species Present Post Reaction</th>
<th>% yield</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td><strong>Solids</strong></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

4.2 2,5-Hexanedione

4.2.1 Hydrogenations without the addition of acid

Hydrogenations of 2,5-hexanedione were performed under 800 psi (cold) static hydrogen pressure in water at 150 °C for 16 hours with 1000 mmol L$^{-1}$ 2,5-hexanedione and 0.1 mol% catalyst load with 100 mmol L$^{-1}$ DMS as an internal standard. The results of the investigation are summarized below in Scheme 4.2 and Table 4.2.
Scheme 4.2: Reaction conditions employed for the hydrogenation of 2,5-hexanedione employing the [Ru(OH$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpyridine))(OTf)$_2$ and [Ru(OH$_2$)$_3$(di(picolyl)amine))(OTf)$_2$ catalyst.

Table 4.2: Percent yield of products formed from hydrogenation of 2,5-hexanedione by[Ru(OH$_2$)$_3$(ph-trpy))(OTf)$_2$ and [Ru(OH$_2$)$_3$(DPA))(OTf)$_2$
4.2.2 Hydrogenations with the addition of H$_3$PO$_4$

Since optimal results with [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ for the deoxygenation of 2,5-hexanedione were observed with the addition of H$_3$PO$_4$, a comparative reaction was done employing [Ru(OH$_2$)$_3$(ph-trpy)](OTf)$_2$. Hydrogenations of 2,5-hexanedione with 10 % H$_3$PO$_4$ (w.r.t. substrate) were performed under 800 psi (cold) static hydrogen pressure in water at 150 °C for 16 hours with 1000 mmol L$^{-1}$ 2,5-hexanedione and 0.1 mol% catalyst load with 100 mmol L$^{-1}$ DMS as an internal standard. The results of the investigation are summarized below in Scheme 4.3 and Table 4.3.

Scheme 4.3: Reaction conditions employed for the hydrogenation of 2,5-hexanedione employing the [Ru(OH$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpyridine)](OTf)$_2$ and [Ru(OH$_2$)$_3$(Di(picolyl)amine)](OTf)$_2$ catalyst in the presence of H$_3$PO$_4$. 

![Scheme 4.3](image-url)
Table 4.3: Percent yield of products formed from hydrogenation of 2,5-hexanediode by [Ru(OH)₂(ph-trpy)](OTf)₂ and [Ru(OH)₂(DPA)](OTf)₂ in the presence of H₃PO₄.

<table>
<thead>
<tr>
<th>Species Present</th>
<th>Post Reaction</th>
<th>% yield</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-NRuIIOH₂OH₂₂⁺(OTf⁻)₂</td>
<td>Ph</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>OH</td>
<td>-OH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OOH</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Furfural

In an attempt to test both complexes against a more industrially relevant substrate, several hydrogenations with furfural were attempted in acidic aqueous medium. Based on the activity exhibited by each complex it was postulated that furfural could be hydrogenated to methyl THF (Scheme 4.4)
Scheme 4.4: Hydrogenation pathway of furfural to methyl THF.

Hydrogenations of furfural were performed at 150 °C under static 800 psi (cold) of hydrogen pressure with 500 mmol L\(^{-1}\) furfural and 0.1 mol% catalyst load in H\(_2\)O for 16 hours. Unfortunately only complete solidification of the substrate was observed in all cases forming an extremely hard resin in the reactor. GC and GC/MS analysis of the reaction solutions, against an internal standard of 100 mmol L\(^{-1}\) DMS, showed only trace amounts of any hydrogenated products or furfural.

The clear challenge with furfural and hydroxy-methyl furfural (HMF) is the intrinsic reactivity of the substrate caused by the highly reactive aldehyde function. It was observed that 500 mmol L\(^{-1}\) samples of furfural in H\(_2\)O left at room temperature contained thick precipitate after only 24 hours and contained only trace amounts of furfural after one week.

In an attempt to avoid the reactivity of the aldehyde function of furfural, the hydrogenated product furfuryl alcohol was used as a model substrate under identical conditions.
Complete loss of substrate was observed after 16 hours and a significant amount of solid resin was present in the reactor, demonstrating that both furfural and furfuryl alcohol are too intrinsically reactive towards self-condensation to be used as a substrate in acidic aqueous media.

4.4 Summary of the Comparative Study of $[\text{Ru(OH}_2)_3(4\text{'-phenyl-2,2’:6,2''-terpyridine})](\text{OTf})_2$ and of $[\text{Ru(OH}_2)_3(\text{di(picolyl)amine})](\text{OTf})_2$

It is evident from the data presented in the previous sections that the more active complex at the conditions presented is the $[\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2$ complex. In all cases the conversions of substrates at 150 °C were significantly greater and often close to complete conversion. This suggests that the $[\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2$ complex is indeed capable of proceeding by a MLB ionic hydrogenation mechanism through the central amine function as discussed previously and shown in Scheme 3.9.

Although the $[\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2$ complex demonstrated higher activity towards the hydrogenation of levulinic acid than the $[\text{Ru(OH}_2)_3(\text{ph-trpy})](\text{OTf})_2$ complex, no hydrogenation beyond GVL was observed and conversion was still incomplete. Further optimization would be required to maximize yields of GVL, however this reaction is not as interesting as it has been extensively studied and optimized with heterogeneous systems and further deoxygenation products are the intended goal.\(^{39,42,44,45,80,92-97}\)

As expected based on the results for levulinic acid, activity of $[\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2$ for 2,5-hexanediol was also significantly better than $[\text{Ru(OH}_2)_3(\text{ph-trpy})](\text{OTf})_2$. Conversions were quantitative with high selectivity for 2,5-hexanediol at 150 °C. The $[\text{Ru(OH}_2)_3(\text{ph-trpy})](\text{OTf})_2$ complex gave only 71% conversion with low selectivity, resulting in more mono-hydrogenated products (hemiacetal) and overall poorer activity. Addition of H\(_3\)PO\(_4\) to the
solution boosts the activity of MLB mechanism, resulting in large quantities of DMTHF but significantly hindered the performance of the [Ru(OH₂)₃(ph-trpy)](OTf)₂ complex at this temperature, almost completely deactivating the complex. Similar results were observed for the addition of triflic acid (TfOH) to the reaction solution (see earlier discussion), which suggests that at low pH, it becomes more challenging to remove the acidic proton from activated H₂ without an intramolecular base.

It should be noted that the [Ru(OH₂)₃(ph-trpy)](OTf)₂ complex is capable of temperature stability beyond 150 °C and actually exhibits best performance between 200 and 250 °C (see earlier discussion). However the [Ru(OH₂)₃(DPA)](OTf)₂ complex is only stable below 175 °C in aqueous media and therefore, for the purposes of this investigation, comparison of the two complexes had to be carried out at 150 °C to preserve identical reaction conditions even though greater conversions could be obtained for each substrate with the [Ru(OH₂)₃(Ph-trpy)](OTf)₂ complex at higher temperatures.
5 Control Experiments

In order to verify that the activity observed in the previous sections were a result of the reported complexes and not any other species present during the reactions, a complete series of control experiments had to be performed with all substrates. Each set of controls was run at nearly identical conditions, but with the absence of any catalysts. The following sections outline the result of each set of controls for both \([\text{Ru(OH}_2\text{)(ph-trpy)}]^{2+}(\text{OTf})_2\) and \([\text{Ru(OH}_2\text{)}_3(\text{DPA})]^{2+}(\text{OTf})_2\).

5.1 Activity of the 316 SS Reactor Body in Acidic Aqueous Media

Previous research in the Schlaf group led to the discovery that the 316 SS reactor body exhibits some catalytic hydrogenation activity under acidic aqueous conditions. In light of this, it was imperative to test all substrates under identical conditions with the absence of any ruthenium complexes as a means of measuring the background hydrogenation activity of the reactor body. The following sections describe the activity of 316 SS as a catalytic hydrogenation catalyst under acidic aqueous conditions.

5.1.1 Levulinic Acid

As a heterogeneous catalyst, powdered 316 stainless steel is capable of full conversion of levulinic acid into pentene at low pH in water. It was then expected that the reactor body, composed of 316 SS, would contribute some background activity which would need to be accounted for in order to properly assess the relative effectiveness of the complexes discussed.

The first control set was a temperature study of 1000 mmol L\(^{-1}\) substrate in 10 % water in sulfolane solution under 800 psi of static H\(_2\) (g) pressure (cold) for 16 hours, to match conditions used in the levulinic acid temperature study. The products were analyzed by GC.
against 100 mmol L\(^{-1}\) of DMS as an internal standard. The results are outlined in Scheme 5.1 and Figure 5.1.

\[
\text{O} \quad \text{O} \quad \text{OH} \quad \text{100 mM dimethyl sulfone, 10\% H}_2\text{O, 90\% Sulfolane} \quad \text{800 psi H}_2(\text{g}), 16 \text{ hrs} \quad T= 200-250 \, ^\circ\text{C}
\]

Scheme 5.1: Reaction conditions employed in the control temperature series for the hydrogenation of levulinic acid.

![Scheme 5.1: Reaction conditions employed in the control temperature series for the hydrogenation of levulinic acid.](image)

Figure 5.1: Control reaction with 1000mmol L\(^{-1}\) Levulinic Acid with at 200 and 250 °C and 800 psi H\(_2\) for 16 hrs in 9:1 Sulfolane: H\(_2\)O Solution.

The second control set was performed at 200 °C (optimal [Ru(OH\(_2\))\(_3\)(ph-trpy)](OTf)\(_2\) operating conditions, see earlier discussion) with the addition of varying concentrations of triflic
acid (TfOH). The control set employed 1000 mmol L\(^{-1}\) substrate in 10 % water in sulfolane solution under 800 psi of static H\(_2\) (g) pressure (cold) for 16 hours, to match conditions used in the levulinic trifloic acid study. The products were analysed by GC against 100 mmol L\(^{-1}\) of DMS as an internal standard. The results are outlined in Scheme 5.2 and Figure 5.2.

Scheme 5.2: Reaction conditions employed in the control acid series for the hydrogenation of levulinic acid.

The final set of control experiments were performed at 200 °C in a solvent environment with varying proportions of water from 10-100% H\(_2\)O. The set of control reactions employed 1000 mmol L\(^{-1}\) substrate under 800 psi of static H\(_2\) (g) pressure (cold) for 16 hours, to match conditions used in the levulinic acid solvent investigation. The products were analyzed by GC against 100 mmol L\(^{-1}\) of DMS, as an internal standard. The results are outlined in Scheme 5.3 and Figure 5.3.
Figure 5.2: Control reaction with 1000 mmol L\(^{-1}\) Levulinic Acid with at 200 °C and 800 psi \(\text{H}_2\) for 16 hrs in 9:1 Sulfolane: \(\text{H}_2\text{O}\) solution as a function of TfOH concentration.

Scheme 5.3: Reaction conditions employed in the control solvent series for the hydrogenation of levulinic acid.
Figure 5.3: Control reaction with 1000mmolL⁻¹ Levulinic Acid with at 200 °C and 800 psi H₂ for 16 as a function of solvent composition.

The result of the control experiments demonstrate that the reactor body does hold some intrinsic activity towards the hydrogenation of levulinic acid, albeit the activity is quite low. It is evident that in the absence of catalyst levulinic acid would prefer to form more condensation products which precipitate from solution as solids, an effect which is greatly exaggerated with increase in temperature (Figure 5.4). The addition of TfOH to the solution served only to increase the degree of condensation/polymerization occurring in solution and did not enhance the conversion to GVL greatly in 90% sulfolane solution. As expected the activity of the reactor body did increase when the percentage of H₂O in the solvent medium was increased and the condensation products were heavily reduced.
Figure 5.4: Proposed reaction pathways of levulinic acid in the absence of catalyst.

Upon examining all control reactions for levulinic acid it is clear that the majority of activity seen when investigating the efficacy of each complex was indeed a result of the catalyst. It also demonstrates that the complexes are active enough to hydrogenate levulinic acid to GVL before the formation of condensation products.

5.1.2 2,5-Hexanedione

Conversion of levulinic acid to GVL requires first the hydrogenation of the carbonyl of levulinic acid. It follows that the 316 SS would be capable of hydrogenating the carbonyl(s) of 2,5-hexanedione. This section provides a detailed investigation of the behavior of 2,5-hexanedione with 316 SS reactor body under acidic aqueous conditions.

The first set of control experiments was a temperature ramp study using 1000 mmol L\(^{-1}\) substrate in water under 800 psi of static \(\text{H}_2\) (g) pressure (cold) for 16 hours, to match conditions used in the previous temperature study from 100- 175 °C. The products were
analyzed by GC against 100 mmol L$^{-1}$ of DMS as an internal standard. The results are outlined in Scheme 5.4 and Figure 5.5.

**Scheme 5.4:** Reaction conditions employed in the control temperature series for the hydrogenation of 2,5-hexanedione.

**Figure 5.5:** Control reaction with 1000mmolL$^{-1}$ 2,5-hexanedione in H$_2$O at 800 psi H$_2$ for 16 hrs as a Function of Temperature. (Note the expanded scale of the Y-axis).

Further controls reactions were performed with the addition of TfOH (10 mmolL$^{-1}$) to the reaction solutions ranging in temperature from 100-200 °C and maintaining all other reaction parameters the same. The results are shown below in Scheme 5.5 and Figure 5.6.
**Scheme 5.5:** Reaction conditions employed in the control temperature series for the hydrogenation of 2,5-hexanediol with TfOH.

**Figure 5.6:** Control of 1000 mmol L\(^{-1}\) 2,5-hexanediol in H\(_2\)O at 800 psi H\(_2\) for 16 hrs as a Function of Temperature with 10 mmol L\(^{-1}\) Triflic Acid. (Note the expanded scale of the Y-axis).

Finally the effect of adding B(OH)\(_3\), H\(_3\)PO\(_4\) and La(OTf)\(_3\) had to be tested with the 316 SS to observe the background activity. A 1000 mM solution of substrate was run at 150 °C in H\(_2\)O under 800 psi of static H\(_2\) (g) pressure (cold) for 16 hours. Results were analyzed by GC.
and GC/MS against DMS as an internal standard and are summarized below in Scheme 5.6 and Figure 5.7.

![Scheme 5.6: Reaction conditions employed in the control acid series for the hydrogenation of 2,5-hexanedione.](image)

**Scheme 5.6:** Reaction conditions employed in the control acid series for the hydrogenation of 2,5-hexanedione.

**Figure 5.7:** Control reaction of 1000 mmol L\(^{-1}\) 2,5-hexanedione at 150 °C in H\(_2\)O at 800 psi H\(_2\) for 16 hrs as a Function of Acid Co-catalyst.

As expected the reactor body did also show some slight activity towards the hydrogenation of 2,5-hexanedione. As temperature was increased conversion to the
monohydrogenated and dehydrogenated species also increased but did not exceed 6% conversion of substrate even at 175 °C and no DMTHF was observed (Figure 5.5). Upon the addition of TfOH, the activity of the steel at lower temperatures decreased but beyond 150 °C formation of DMTHF occurred with yields as high as 2% at 200 °C. Adding acid co-catalysts simply caused the formation of solid products in the reactor with very little hydrogenated products.

Overall the control experiments demonstrate that the background activity of the reactor body under the conditions employed is negligible compared to the activity of the complexes discussed. Most of the activity observed in the earlier sections is the result of the addition of ruthenium species into the reaction medium, which in the case of the in-situ generation of [Ru(OH$_2$)$_3$(DPA)](OTf)$_2$ could be activity of the ruthenium precursor, [Ru(DMF)$_6$](OTf)$_3$, which will be discussed in the following section.

### 5.2 Activity of [Ru(DMF)$_6$](OTf)$_3$ in Acidic Aqueous Media

One major complication with the in-situ generation of the catalyst is the potential for activity resulting from the ruthenium source used, in this case [Ru(DMF)$_6$](OTf)$_3$. This can often be avoided by using a slight excess of ligand, to ensure that all the [Ru(DMF)$_6$](OTf)$_3$ is complexed and will not be present in solution. However, the ligand could dissociate resulting in decomposition of the complex, but at the same time, a false positive could be observed due to the activity of the precursor or its decomposition into a solid or even nano-particle structured heterogeneous catalyst. The following section describes how the [Ru(DMF)$_6$](OTf)$_3$ platform starting material behaves under the catalytic conditions presented in the previous sections.
5.2.1 2,5-Hexanedione

For each study performed for the [Ru(OH)\(_2\)(DPA)](OTf)\(_2\) complex, an analogous study had to be performed with the absence ligand present. The goal was to confirm formation of the complex if the results of the control experiments were significantly different than those employing [Ru(OH)\(_2\)(DPA)](OTf)\(_2\). A temperature study was performed employing only the [Ru(DMF)\(_6\)](OTf)\(_3\) complex using the identical conditions to those used in the [Ru(OH)\(_2\)(DPA)](OTf)\(_2\)/2,5-hexanadione temperature study (see earlier discussion). It was expected that the temperature stability of the [Ru(DMF)\(_6\)](OTf)\(_3\) complex would be quite low for two reasons: 1) lack of supporting multidentate ligands on the metal greatly reduces thermal stability and 2) weakly coordinating N,N-dimethyl formamide (DMF) has a typical decomposition temperature of 152-154 °C.\(^9\) It was expected that the complex would exhibit some activity at low temperatures (below 150 °C) and decompose above 150 °C.

The temperature series was performed in H\(_2\)O with 1000 mmol L\(^{-1}\) 2,5-hexanadione with a 0.1 mol% catalyst load under 800 psi H\(_2\)(g) static pressure (cold). Each experiment was run for 16 hours ranging in temperature from 100-200 °C. The products were analyzed by GC and GC/MS against 100 mmol L\(^{-1}\) DMS as an internal standard. The results are summarized below in Scheme 5.7 and Figure 5.8.

![Scheme 5.7: Reaction conditions employed in the control temperature series for the hydrogenation of 2,5-hexanadione by [Ru(DMF)\(_6\)](OTf)\(_3\).](image)

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Figure 5.8: Hydrogenation of 1000mmolL$^{-1}$ 2,5-hexanediione with 0.1 mol % \([\text{Ru(DMF)}_6]^{3+}(\text{OTf}_3)\) from 100-200 °C at 800 psi \(\text{H}_2\) for 16 hrs.

Much to the surprise of the author, the \([\text{Ru(DMF)}_6](\text{OTf})_3\) complex was extremely active towards the hydrogenation of carbonyls at temperatures as low as 100 °C. No decomposition of the complex was evident at this temperature and the solution remained homogeneous. At 150 °C the reaction solution was completely clear with some black Ru$^0$ precipitate, and a lustrous deep-blue coating on the inner wall of the reactor body. The decomposition of the complex leads to aggregates of Ru$^0$ and a heterogeneous mechanism dominates the hydrogenation producing significant quantities of 2,5-hexanediol with some DMTHF and partially hydrogenated products. In comparison to the behavior of \([\text{Ru(OH}_2)_3(\text{DPA})](\text{OTf})_2\) it is clear that the ligand has a substantial stabilizing effect on the metal affording complex stability to 150 °C. Heating the \([\text{Ru(DMF)}_6](\text{OTf})_3\) complex to 200 °C generated a similar reactor coating but significantly less
activity resulting in only 44% conversion of substrate to a mix of partially hydrogenated products and a small quantity of DMTHF.

Analogous to the reactions with the ligand present, TfOH was added to the [Ru(DMF)₆](OTf)₃ complex solution to examine its activity towards hydrogenation of 2,5-hexanediol. Hydrogenations were performed using 1000 mmol L⁻¹ 2,5-hexanediol, 10 mmol L⁻¹ [Ru(DMF)₆](OTf)₃ and 100 mmol L⁻¹ TfOH in H₂O under 800 psi H₂(g) static pressure (cold) from 100-200 °C for 16 hours. The results were analyzed by GC and GC/MS and are presented below in Scheme 5.8 and Figure 5.9.

Scheme 5.8: Reaction conditions employed in the control temperature series for the hydrogenation of 2,5-hexanediol by [Ru(DMF)₆](OTf)₃ with the addition of TfOH.
Figure 5.9: Hydrogenation of 1000 mmol L$^{-1}$ 2,5-hexanedione with 0.1 mol % $[\text{Ru(DMF)}_6]^{3+}(\text{OTf})_3$ from 100-200 °C at 800 psi H$_2$ for 16 hrs with 1.0 mol % TfOH.

Similar results were observed at 100 °C with and without TfOH, the complex is capable of complete conversion of 2,5-hexanediol to 2,5-hexanediol at temperatures as low as 100 °C. Increasing the temperature once again generated a blue coating on the inner wall of the reactor body and resulted in more condensation products and incomplete conversion of the substrate. Conversion decreased to 65% when increasing the temperature further, possibly due to more rapid decomposition of the complex, however DMTHF was the major product with 3 % of hemiacetal present suggesting the presence of an active species.

It was suspected that the blue reactor coating generated in the previous reactions was itself acting as a heterogeneous hydrogenation catalyst. To test this hypothesis the reactor was
reloaded with 2,5-hexanedione in water without polishing and the reactor was run under identical conditions both with and without the presence of TfOH. Without the addition of acid similar conversion was seen as in the blank hydrogenation with a greater amount of DMTHF in the product distribution. Adding TfOH to the reaction mixture seemed to completely deactivate the coating on the reactor and only trace amounts of hydrogenated products were observed (Figure 5.10).

![Hydrogenation of 2,5-hexanediol by Blue Ruthenium Coating at 200 °C in H₂O at 800 psi H₂ for 16 hrs with and without Triflic Acid](image)

**Figure 5.10:** Hydrogenation of 1000mmol L⁻¹ 2,5-hexanedione by Blue Ruthenium Coating at 200 °C in H₂O at 800 psi H₂ for 16 hrs with and without Triflic Acid.
At temperatures where [Ru(DMF)₆](OTf)₃ undergoes decomposition and forms a Ru⁰ coating more activity is observed than the coating itself. This implies that the decomposition of [Ru(DMF)₆](OTf)₃ generates some Ru⁰ aggregates or nano-particles in solution which act as an active hydrogenation catalyst more so than the coating itself. When removing the reaction solution form the reactor but preserving the reactor coating, the Ru⁰ particles are then removed and activity decreases.

Overall the difference in activity of the control reactions confirmed that the [Ru(OH₂)₃(DPA)](OTf)₂ complex was forming in solution, marked by a 50 °C increase in temperature stability and colour change as well as NMR evidence for its formation (see earlier discussion). Although the complex does exhibit some thermal stability, at mild conditions the [Ru(DMF)₆](OTf)₃ is more active towards the hydrogenation of carbonyls, demonstrated by complete conversion of 2,5-hexanedione to 2,5-hexanediol at 100 °C. Although the activity of the [Ru(OH₂)₃(DPA)](OTf)₂ complex was optimal at 150 °C it was capable of similar conversions and even further deoxygenation to DMTHF with the presence of H₃PO₄.
6 Conclusions and Future Work

The goal of this work was the development of two homogeneous ionic hydrogenation catalysts for the selective deoxygenation of biomass derived substrates. Two procatalysts were prepared; [Ru(OH)\(_2\)(ph-trpy)](OTf)\(_2\) [4] and [Ru(OH)\(_2\)(DPA)](OTf)\(_2\) [10], the former being a tridentate non-metal-ligand bifunctional (MLB) procatalyst and the latter intended to be active in a MLB ionic hydrogenation mechanism. Complex [4] was prepared in good yields while [10] was generated in situ through the use of a labile ruthenium precursor in an auto-reduction method. This method of in-situ procatalyst generation is incredibly versatile and could be used to prepare a wide variety of Ru\(^{2+}\) complexes in aqueous environments. Procatalyst [10] was confirmed to operate by a MLB mechanism through inference by comparing the activities of [4] and [10] under identical conditions against 2,5-hexanedione and levulinic acid. In all cases complex [10] performed with greater activity however at sub-optimal temperatures for the activity of [4] due to rapid decomposition of [10] above 150 °C.

The thermal stability ranges required for complete deoxygenation of C\(_5\) and higher substrates require temperatures in excess of 250 °C in order to hydrogenolyze the furan ring system formed. Although complex [4] was stable at 250 °C, it demonstrated little activity towards ring opening and deoxygenation of THF rings (dimethyl THF and \(\gamma\)-valerolactone). Complex [10] decomposed beyond 150 °C which is less than an ideal temperature for the complete deoxygenation of the substrates examined despite the similarities of donating ligand to [4]. Overall neither complex was well suited for application to these particular substrates.

Future design of complexes for the deoxygenation of biomass-derived substrates must be able to tolerate temperatures above 250 °C in aqueous acidic environments. The design may be improved from those discussed in this work by increasing the denticity of the ligand, moving to
tetradentate species with amine functions for a MLB to exist (Figure 6.1), or replacing ruthenium for iridium to strengthen the ligand-metal bonds thus allowing greater thermal stability with similar hydrogenation activity (Figure 6.2).

**Figure 6.1:** Proposed tetradentate ruthenium species for the deoxygenation of biomass-derived substrates. Complexes arranged in order of ligand rigidity.

Moving from tridentate species to tetradentate species would be expected to improve thermal stability by having a more strongly chelating ligand. Furthermore introducing pendant amines will likely allow the complexes to operate via a MLB hydrogenation mechanisms. Alternatively, as with DPA, the backbone of the ligand can contain amine functions which give increased flexibility to the ligand and allow for a variety of binding motifs.

**Figure 6.2:** Proposed complexes with iridium employing the ph-terpy and DPA ligands for greater thermal stability.

With reference to the Ru\(^{II}/\text{Ir}^{III}\) diagonal relationship iridium should be capable of ionic \(H_2\) activation since \(\text{Ir}^{III}\) is also a d\(^6\) system and thermal stability would be improved because of increased strength in the nitrogen-metal bond when moving down a triad. Starting from \(\text{Ir}^1\)
oxidative addition of $H_2$ (g) can occur resulting in a trans-hydride $\text{Ir}^{III}$ species which would be expected to be highly active towards the hydrogenation of biomass-derived substrates (Figure 6.3). One could also envision the use of tetradentate ligands with iridium to make a highly stable and active hydrogenation catalyst.

*Pro-catalysts; Y = water or other labile ligand*

*Postulated active species to form under $H_2(g)$ pressure.*

**Figure 6.3:** Proposed iridium procatalysts and postulated active species generated form the oxidative addition of $H_2$.

Aside from the activity of the complexes discussed, a major conclusion this work has demonstrated are the challenges with using furfural as a feedstock for biomass-derived deoxygenations. The intrinsic reactivity of furfural, furfuryl alcohol, and 5-hydroxymethyl furfural (HMF) results in extensive condensation and polymerization under high temperature and pressure acidic aqueous conditions and has even been observed at room temperature. Alternative feedstocks are the linear sugar polyalcohols sorbitol and xylitol generated from the
hydrogenation of glucose, obtained from cellulose and xylose, obtained from hemicellulose, respectively. These substrates can undergo iterative steps of acid-catalyzed dehydration followed by metal-catalyzed hydrogenation to result in the completely deoxygenated species pentene/pentane and hexane/hexane (Figure 6.4). While the extremely reactive furan alcohol species may also be present in these sequences, they would only be present in small steady-state concentrations, which we postulate would greatly reduce the cross-condensation reactions to resins observed when they are used as pure substrates.

**Figure 6.4:** Deoxygenation of linear sugar polyalcohols sorbitol and xylitol obtained from (hemi)cellulose.


7 References


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Appendix A: Spectroscopic Data for Selected Compounds Described in Chapter 2
Compound Name: 3-phenyl-1,5-di(pyrid-2-yl) pentane-1,5-dione

MW: 330.10 gmol⁻¹

Appearance:
White crystals

Lit. and/or notebook # and page:
CO-II-54 (best), p. 7

First made on date:
October 13, 2010

Made by: Chris Oswin

\[^{1}\text{H}\]: (300 MHz, CDCl\textsubscript{3}): δ = 3.70 (dq, J\textsubscript{1} = 6.9 Hz, J\textsubscript{2} = 6.9 Hz, J\textsubscript{3} = 17.5 Hz, 4H), 4.16 (p, J = 7.1 Hz, 1H), 7.13 (m, 1H), 7.23 (m, 2H), 7.40 (m, 4H), 7.78 (dt, J\textsubscript{1} = 1.8 Hz, J\textsubscript{2} = 7.8 Hz, 2H), 7.94 (dt, J\textsubscript{1} = 5.7 Hz, J\textsubscript{2} = 7.7 Hz, 2H), 8.63 (dq, J\textsubscript{1} = 0.9 Hz, J\textsubscript{2} = 4.8 Hz, 2H)

\[^{13}\text{C}\]: (75 MHz, CDCl\textsubscript{3}): δ = 36.30 (CH), 44.29 (CH\textsubscript{2}), 121.94 (CH), 126.43 (CH), 127.14 (CH), 127.86 (CH), 128.49 (CH), 136.94 (CH), 144.72 (C), 148.94 (CH), 153.57 (C), 200.15 (CO)
**Compound Name:** 4′-Phenyl-2,2′:6′,2″-terpyridine

**MW:** 309.39 g/mol

**Appearance:**
White powder

**Lit. and/or notebook # and page:**
CO-II-54 (best), p. 7

**First made on date:**
October 13, 2011

**Made by:** Chris Oswin

**Synthesis and Structure:**

1H: (300 MHz, CDCl3): δ = 7.33 (dd, J = 4.8, 6.6 Hz, 2H), 7.47 (m, 3H), 7.86 (m, 4H), 8.69 (m, 4H), 8.73 (s, 2H).

13C: (75 MHz, CDCl3): δ = 118.9 (CH), 121.3 (CH), 123.8 (CH), 127.3 (CH), 128.9 (CH), 129.0 (CH), 136.8 (CH), 138.5 (C), 149.1 (CH), 150.3 (C), 155.9 (C), 156.3 (C).
A3.

[Chemical shift diagram with peaks labeled.

A4.

[Chemical shift diagram with peaks labeled.

120
**Compound Name:** Trichloro(4’-phenyl-2,2’:6’,2”-terpyridine)ruthenium(III)

**MW:** 516.81 gmol\(^{-1}\)

**Appearance:**
Dark red-brown powder

**Lit. and/or notebook # and page:**

CO-II-61 (best) p. 22

**First made on date:**
November 29, 2010

**Made by:**
Chris Oswin
**Compound Name:** Triaqua(4′-phenyl-2,2′:6′,2″-terpyridine)ruthenium(II) triflate

**MW:** 736.60 g mol⁻¹

**Appearance:**
Dark purple powder

**Lit. and/or notebook # and page:**
CO-II-78 (best), p. 52

**First made on date:**
December 13, 2010

**Made by:**
Chris Oswin

**1H:** (300 MHz, D₂O): δ = 7.41 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.67 (t, J = 6.6 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.94 (t, J = 7.7 Hz, 2H), 8.34 (d, J = 8.1 Hz, 2H), 8.45 (s, 2H), 9.06 (d, J = 5.1 Hz, 2H).

**13C:** (75 MHz, D₂O): δ = 118.7 (CH), 119.6 (q, J_{CF} = 315 Hz, CF₃SO₃⁻), 122.8 (CH), 126.7 (CH), 127.5 (CH), 129.3 (CH), 129.8 (CH), 135.8 (C), 137.8 (CH), 143.2 (C), 153.1 (CH), 160.0 (C), 163.5 (C).
Appendix B: Spectroscopic Data for Selected Compounds Described in
Chapter 3
**Compound Name:** 2,2’-dipicolylamine (DPA)

MW: 199.28 gmol\(^1\)

Appearance:
Yellow oil

**Lit. and/or notebook # and page:**
CO-II-99 p.84

**First made on date:**
November 30, 2011

**Made by:**
Chris Oswin

\(^1\)H: (300 MHz, D\(_2\)O): \(\delta = 3.55\) (s, 4H), 7.05 (dt, \(J_1 = 1.1\) Hz, \(J_2 = 3.9\) Hz, 2H), 7.09 (d, \(J = 5.9\) Hz, 2H), 7.53 (dt, \(J_1 = 1.3\) Hz, \(J_2 = 5.8\) Hz, 2H), 8.13 (dq, \(J_1 = 0.9\) Hz, \(J_2 = 5.0\) Hz, 2H).

\(^{13}\)C: (75 MHz, D\(_2\)O): \(\delta = 52.83\) (CH\(_2\)), 122.83 (CH), 123.07 (CH), 137.96 (CH), 148.28 (CH), 157.48 (C)
A7.

A8.
**Compound Name:** Trichloro (Di(picolyl)amine)ruthenium(III)

**MW:** 405.9 gmol$^{-1}$

**Appearance:**
Dark red-brown powder

**Lit. and/or notebook # and page:**
CO-II-61 p.22

**First made on date:**
July 4, 2011

**Made by:**
Chris Oswin

**Synthesis and Structure:**

\[
\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \begin{array}{c}
\text{HN} \\
\text{N} \\
\text{N} \\
\text{Ru} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array} \\
\xrightarrow{1) \text{EtOH, reflux}} \\
\begin{array}{c}
\text{HN} \\
\text{N} \\
\text{N} \\
\text{Ru} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array}
\]

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**Compound Name:** Trans-Tetrakis(acetonitrile)dichlororuthenium(II)  
**MW:** 335.9 gmol\(^{-1}\)

**Appearance:**  
Yellow powder

**Lit. and/or notebook # and page:**  
*Acta Crystallographica Section C* 1996, 52, 1105.  
CO-II-81 p. 57

**First made on date:**  
September 13, 2011

**Made by:**  
Chris Oswin

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**Compound Name:** Tris(acetonitrile)(Di(picolyl)amine)ruthenium(II) dichloride

**MW:** 538.1 g/mol

**Appearance:**
Orange powder

**Lit. and/or notebook # and page:**
CO-II-86 (best) p. 64

**First made on date:**
September 13, 2011

**Made by:**
Chris Oswin

\[ ^1 \text{H}: (400 \text{ MHz, D}_2\text{O}) \delta = 2.05 (s, 3\text{H}), 2.36 (s, 6\text{H}), 3.87 (d, J=16.4\text{ Hz}, 1\text{H}), 4.43 (d, J=16.4 \text{ Hz}, 1\text{H}), 7.36 (m, 2\text{H}), 7.85 (dt, J_1= 1.4 \text{ Hz}, J_2= 7.7\text{Hz}, 2\text{H}), 8.44 (d, J= 5.0 \text{ Hz}, 1\text{H}) \]

**Synthesis and Structure:**

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**Compound Name:** Hexakis(N,N-dimethylformamide)ruthenium(III) triflate

**MW:** 986.94 gmol\(^{-1}\)

**Synthesis and Structure:**

1. \(\text{PtO}_2, \text{H}_2\)
2. 4 eq. \(\text{AgOTf}\)

\[
\text{RuCl}_3 \cdot x \text{H}_2\text{O} \xrightarrow{\text{DMF}} \text{Ru}^{3+}(\text{OTf})_3
\]

**Appearance:**
Yellow crystals

**Lit. and/or notebook # and page:**
CO-III-166(best) p.90

**First made on date:**
January 13, 2012

**Made by:**
Chris Oswin

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**Compound Name:** Tris(aqua)(di(picolyl)amine)ruthenium(II) triflate

**MW:** 653.16 g/mol

**Appearance:** Deep red-brown in aqueous solution

**Synthesis and Structure:**

\[
[Ru^{III}(DMF)_6]^{3+}(OTf)_2 \xrightarrow{MeOH/H_2O} \]

**Lit. and/or notebook # and page:**
CO-III-112 p. 13

**First made on date:**
February 1\(^{st}\) 2012

**Made by:**
Chris Oswin

\[^1H\]: (400 MHz, D\(_2\)O) 2.57 (s, 1H), 2.70 (s, 9H), 2.84 (s, 9H), 4.31 (s, 2H), 7.33 (t, J= 5.2 Hz, 1H), 7.37 (d, J= 8.4 Hz, 1H), 7.77 (m, 4H), 8.44 (d, J= 4.8 Hz, 1H)

\[^{13}C\]: (100 MHz, D\(_2\)O) 31.41 (CH\(_3\)), 36.91 (CH\(_3\)), 50.74 (CH\(_2\)), 124.29 (CH), 124.61 (CH), 138.91 (CH), 149.04 (CH), 150.10 (C), 164.93 (HCO)

\(m/z\) 149.49 [C\(_{12}\) H\(_{11}\) N\(_3\) Ru]\(^{2+}\)