STUDY OF HOMOGENEOUS AND HETEROGENIZED RUTHENIUM / TIN HETEROBIMETALLIC COMPLEXES: SYNTHESIS, ELECTROCHEMISTRY AND CATALYTIC PROPERTIES

By

COREY R. ANTHONY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2006
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by

Corey R. Anthony
This dissertation is dedicated to my grandfather, Leonard Legister,
You may be gone POPPA but you will never be forgotten.
ACKNOWLEDGMENTS

I would like to first thank God because with him all things are possible.

I would now like to acknowledge the strong women who have had a positive impact in my life. First and foremost I thank my mother, a remarkable single parent who made countless sacrifices in raising three children. To her I owe my strong work ethic, drive for education and will always love unconditionally. I want to also acknowledge my lovely wife for all her love, support and patience which kept me focused during many endless nights of research. To her I owe a tremendous debt of gratitude for being my rock these last two years. I also wish to thank my sisters Charmaine and Cheryl and my cousin Heather for always being there and making this PhD dream of mine a reality.

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

STUDY OF HOMOGENEOUS AND HETEROGENIZED RUTHENIUM / TIN HETEROBIMETALLIC COMPLEXES: SYNTHESIS, ELECTROCHEMISTRY AND CATALYTIC PROPERTIES

By

Corey R. Anthony

May 2006

Chair: Dr. Lisa McElwee-White
Major Department: Chemistry

This dissertation describes the synthesis, electrochemistry and catalytic properties of a series of Ru/Sn complexes. A single oxidation wave, attributed to the Ru(II/III) couple was observed in the cyclic voltammograms of the Ru/Sn complexes. The electrocatalytic properties of these complexes were investigated during the electrooxidation of methanol. The oxidation products observed are dimethoxymethane (DMM) and methyl formate (MF). The formation of DMM is favored when the catalysis is performed with the Ru/Sn complexes. The selectivity of the catalysts can be tuned by varying the anodic potential. The highest current efficiency (92.4 %) and selectivity (100 %) were obtained from the electrooxidation of methanol with CpRu(TPPMS)$_2$(SnCl$_3$) (23). Chemically modified electrodes were also prepared by attaching Ru/Sn complexes to the electrode surface. The electrochemical properties and stability of these heterogenized complexes were studied using cyclic voltammetry.
A novel Ru/Hg complex $\text{CpRu(PPh}_3\text{)}(\mu-\text{Cl})(\mu-\text{dppm})\text{HgCl}_2$ (16) was synthesized and characterized. X-ray crystallography revealed a unique chloride and dppm linker in 16, the first time a Ru/Hg complex was isolated with these bridging moieties.
CHAPTER 1
LITERATURE REVIEW

Oxidation of Organic Molecules

In inorganic chemistry, oxidation is clearly defined as the loss of an electron by an atom, molecule or ion accompanied with an increase in the formal oxidation state. For organic chemists the concepts of oxidation states and electron transfer are less easily applied, hence the definition of oxidation differs slightly from inorganic to organic chemistry. Organic chemists have defined the oxidation of an organic molecule as either 1) the loss of hydrogen or 2) the replacement of hydrogen with a more electronegative atom such as oxygen or a halogen.

The oxidation of organic molecules has a long history\(^1\) stemming to the 1780’s and Lavoisier’s explanation of combustion. Observations in the 19\(^{th}\) century linked the deterioration of many organic materials such as rubber and natural oils to the adsorption of dioxygen. The control of oxidation is desirable not only for inhibiting the degradation of commercially important materials such as plastics, gasoline, and rubbers but also for promoting the selective oxidation of hydrocarbon feedstocks such as olefins, alkanes and aromatic hydrocarbons.

The first observation of a catalyzed oxidation reaction is attributed to Davy who showed in 1820 that ethanol is oxidized to acetic acid (Eq. 1.1) in the presence of platinum. Since then the scope of the catalyzed oxidation reaction of organic molecules has grown tremendously, becoming basic to organic chemistry and the petrochemical
industry. Catalytic oxidation of ethylene to acetaldehyde (Eq. 1.2, Wacker process) was the first industrial scale reaction that used an organopalladium catalyst. The catalytic oxidation of organic molecules is now widely used in the synthesis of fine chemicals. These reactions are now well understood and can be utilized in synthesizing a wide array of functional groups (Scheme 1-1).²

\[
\begin{align*}
CH_2\equiv CH_2 + H_2O \xrightarrow{[\text{PdCl}_4]^{2-}, \text{CuCl}_2} CH_3CHO \\
\end{align*}
\]

(1.2)

Scheme 1-1. Adapted from reference 2.

**Oxidation of Alcohols**

The selective oxidation of alcohols to the corresponding aldehyde, ketone or carboxylic acid is of significance not only to fundamental research but also for commercial manufacturing processes. Traditionally the oxidation of alcohols is performed with high oxidation state metal reagents such as chromium (VI), Mn (VI) and ruthenium (VIII). These methods have been reviewed extensively²³ and will not be covered within this dissertation. Another area of emphasis is the use of transition metal catalysts along with a chemical co-oxidant such as oxygen⁴⁴⁹, peroxide⁷⁸¹⁰ or an amine
The above transformations have also been extensively studied and are beyond the scope of this review. One area which has recently received significant interest from the scientific community is the electrochemical oxidation of alcohols. The literature on electrochemical oxidation of alcohols can be roughly grouped into two sets: heterogeneous\textsuperscript{13,14} (fuel cell) and homogeneous studies.

**Electrochemical Oxidation of Methanol in Fuel Cells**

Fuel cells have been postulated as the power generation system of the immediate future, poised to replace not only internal combustion engines\textsuperscript{15,16} but also advanced alkali\textsuperscript{16,17} batteries. Due to their simplicity, high energy efficiency and low pollution, direct methanol fuel cells (DMFCs) are especially suited for use in portable electronic devices.\textsuperscript{16,17} In DMFCs aqueous methanol is electrochemically oxidized at the anode (Eq. 1.3) to CO\textsubscript{2}

\[
\text{Anodic Reaction: } \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \quad (1.3)
\]

while oxygen is reduced at the cathode (Eq. 1.4) to form water.

\[
\text{Cathodic Reaction: } \frac{3}{2} \text{O}_2 + 6 \text{H}^+ + 6\text{e}^- \rightarrow 3 \text{H}_2\text{O} \quad (1.4)
\]

When combined, the two half reactions result in an electromotive force of 1.18 V for the overall reaction (Eq. 1.5).

\[
\text{Overall Reaction: } \frac{3}{2} \text{O}_2 + \text{CH}_3\text{OH} \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta E = 1.18 \text{ V} \quad (1.5)
\]

The mechanism for this oxidation has been reviewed\textsuperscript{18,19} extensively and can be summarized in two key steps:

- Physisorption and dehydrogenation of methanol on the electrode surface
- Formation of CO\textsubscript{2} from adsorbed carbonaceous intermediates
Very few electrode materials are capable of performing both reactions, and of these only platinum and platinum based electrodes have displayed any encouraging activity and stability in an acidic medium.

**Mechanism**

The surface catalyzed electrooxidation of methanol has been studied exhaustively,\textsuperscript{18,20-22} and because of this the reaction mechanism is now well understood. The mechanism was elucidated using a variety of electrochemical and spectroscopic methods. These methods include cyclic voltammetry, steady-state galvanostatic polarizations, chronoamperometry, mass spectrometry, FTIR, XAS, etc.\textsuperscript{23-25} *In-situ* spectroscopic experiments were very instrumental in examining adsorbed species and for identifying intermediates formed during the reaction. By combining the results of cyclic voltammetry, *in-situ* ellipsometry, XAS, and *in-situ* FTIR experiments, the reaction steps below were proposed. The reaction is thought to initially proceed through a series of dehydrogenation steps to adsorbed CO (Eq 1.6 - 1.9).\textsuperscript{18,20-22} Adsorbed CO is a widely accepted intermediate of methanol oxidation, and its presence has been observed with the aid of various in-situ infrared spectroscopy techniques.\textsuperscript{26-28} CO and other carbonaceous intermediates can then be oxidized to carbon dioxide and desorbed from the electrode surface by reacting with adsorbed water (Eq 1.10 - 1.12).

The electrochemical oxidation of methanol on Pt is a complicated reaction involving several steps; chemisorption of methanol and water, dehydrogenation of methanol, interaction between adsorbed CO and OH species and the formation of
At potentials below 0.7 V (the potential region of interest) the rate determining step (RDS) on Pt anodes was shown to be the dissociative chemisorption of water (Eq 1.10).

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{Pt} (s) & \rightarrow \text{Pt-CH}_2\text{OH} + \text{H}^+ + \text{e}^- & (1.6) \\
\text{Pt-CH}_2\text{OH} + \text{Pt} (s) & \rightarrow \text{Pt}_2\text{-CHOH} + \text{H}^+ + \text{e}^- & (1.7) \\
\text{Pt}_2\text{-CHOH} + \text{Pt} (s) & \rightarrow \text{Pt}_3\text{-CHO} + \text{H}^+ + \text{e}^- & (1.8) \\
\text{Pt}_3\text{-CHO} & \rightarrow \text{Pt-CO} + 2\text{Pt} (s) + \text{H}^+ + \text{e}^- & (1.9) \\
\text{H}_2\text{O} + \text{Pt} (s) & \rightarrow \text{Pt-OH} + \text{H}^+ + \text{e}^- & (1.10) \\
\text{Pt-CO} + \text{Pt-OH} & \rightarrow \text{Pt-COOH} & (1.11a) \\
\text{Pt-CO} + \text{H}_2\text{O} & \rightarrow \text{Pt-COOH} + \text{H}^+ + \text{e}^- & (1.11b) \\
\text{Pt-COOH} & \rightarrow \text{Pt} (s) + \text{CO}_2 + \text{H}^+ + \text{e}^- & (1.12)
\end{align*}
\]

Presently DMFCs are faced with a few challenging problems, foremost of which is that the overall reaction is very slow. The electrochemical oxidation of methanol (Eq. 1.5), though thermodynamically favored, is a kinetically sluggish reaction even at high catalyst loading. On the other hand, the electrooxidation of hydrogen (a thermodynamically similar reaction) is very fast at low catalyst loading. The formation of stable intermediates (Eq. 1.6 - 1.9)\textsuperscript{29,30} is responsible for the poor kinetics of the methanol oxidation reaction. Adsorbed CO in particular is strongly bound to the surface of Pt requiring a high overpotential (approximately 0.5 V vs NHE) in order to obtain a reasonable current density. Based on these studies it is now accepted that an active surface for methanol electrooxidation must:

- “Activate” water at low potentials
- Be labile to CO chemisorption
- Catalyze the oxidation of CO to CO\textsubscript{2}
**Binary Electrocatalysts**

Although there has been moderate success with Pt anodes,\textsuperscript{31-33} the rapid poisoning of the surface with CO has made these electrodes inadequate for use in DMFCs. This decision led to an intensive search for other materials that can improve the performance of the Pt anode during the methanol oxidation process. Several methods have been investigated for promoting the formation of CO\textsubscript{2} (Eq. 1.10 - 1.12). One method involves alloying Pt with a second metal, to accelerate the RDS. Since the dissociative chemisorption of water (Eq. 1.10) is the RDS, Pt was alloyed with oxophilic metals in order to increase the reaction rate. Alloys of Pt and an oxophilic metal have been investigated as electrocatalysts for over 40 years. Beneficial effects have been observed for Pt/Sn,\textsuperscript{34,35} Pt/Ir,\textsuperscript{36} Pt/W\textsuperscript{37-40} and Pt/Ru\textsuperscript{28,41-44} electrodes. Studies of Pt alloyed with such metals shows that Ru has by far the largest catalytic effect\textsuperscript{18} (Figure 1-1).

![Polarization data for Pt/M alloys at 60 °C in 2.5 M H\textsubscript{2}SO\textsubscript{4} / 1 M CH\textsubscript{3}OH. Adapted from reference 18.](image)

**Figure 1-1.** Polarization data for Pt/M alloys at 60 °C in 2.5 M H\textsubscript{2}SO\textsubscript{4} / 1 M CH\textsubscript{3}OH. Adapted from reference 18.
Pt/Ru binary anodes

Considerable effort has been expended to clarify the role of Ru in Pt/Ru binary electrodes. Of the mechanisms proposed, the bifunctional theory has gained general acceptance.\textsuperscript{44-46} According to this mechanism, the Pt sites are responsible for the chemisorption and dehydrogenation of methanol, while the Ru sites are responsible for water activation (Eq. 1.13 - 1.14). This is supported by the fact that the discharging of water on Ru occurs at 0.2 V, while the chemisorption of methanol on Pt is favored over Ru.

\begin{equation}
\text{H}_2\text{O} + \text{Ru (s)} \rightarrow \text{Ru-OH} + \text{H}^+ + \text{1e}^- \quad (1.13)
\end{equation}

\begin{equation}
\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt (s)} + \text{Ru (s)} + \text{CO}_2 + \text{H}^+ + \text{1e}^- \quad (1.14)
\end{equation}

In-situ CO stripping voltammetry was used to evaluate the active surface area, intrinsic catalytic effect and the surface composition of the anode. An anodic shift of the peak potential was observed for the CO stripping voltammograms of the Pt/Ru electrodes. This shift combined with the improved catalytic activity provides clear evidence that on Pt/Ru binary electrodes CO removal is the RDS. The optimal Pt:Ru ratio is still being aggressively investigated, and remains a source of some controversy. At high temperatures (90 – 130 °C) and on a carbon support it has been shown that the optimal Ru content is 50 mole \%.\textsuperscript{47} It is thought that at 50 % coverage the intrinsic rate constant is maximized.

The alloying of Pt with non-noble metals, most notably Re\textsuperscript{48} and Mo, has been reported to result in a strong enhancement of the methanol oxidation reaction. The effectiveness of binary electrodes, especially Pt/Ru, has resulted in the recent investigation of ternary Pt/Ru/Sn,\textsuperscript{49} Pt/Ru/Mo\textsuperscript{49} and Pt/Ru/W\textsuperscript{49,50} as well as quaternary systems Pt/Ru/Os/Ir,\textsuperscript{41,51,52} Pt/Ru/Mo/W\textsuperscript{53} and Pt/Ru/Sn/W.\textsuperscript{54} Only a slight to moderate
improvement in activity was observed for these systems, relative to the Pt/Ru binary electrode.

**Combinatorial Screening**

After thirty years of research, the Pt/Ru (50/50) binary alloy remains one of the more active electrocatalysts for the methanol oxidation reaction. This lack of a breakthrough and the high cost of the precious metals have made electrocatalysts a prime target for combinatorial screening. Combinatorial chemistry and high-throughput screening have revolutionized drug discovery and the pharmaceutical industry. These complementary technologies are now used for the preparation and evaluation of large numbers of formulations. Combinatorial screening of inorganic material has been used for almost thirty years. This method has been instrumental in characterizing new materials and in the development of new catalysts.

Combinatorial searches for electrocatalysts by current voltage methods are extremely cumbersome, especially for large sample sizes. This obstacle was circumvented in 1998 by Mallouk$^{52}$ who monitored the cell reactions via a fluorescence signal. In 1999 Ward$^{55}$ expanded on this method and used an automated multi-electrode array to perform the combinatorial screening. These methods have since been applied by other researchers and have led to ternary and quaternary electrode materials that display greater catalytic activity than Pt/Ru electrodes.

**Reaction Intermediates**

Although the complete oxidation of methanol to carbon dioxide is desired for fuel cell applications, other species are often formed leading to a decrease in the fuel efficiency. Frequently observed by-products of methanol oxidation include formaldehyde (Eq. 1.15)
and formic acid (Eq. 1.16). These products can undergo a condensation reaction to form
dimethoxymethane (DMM) (Eq. 1.17) and methyl formate (MF) (Eq. 1.18).

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{H}_2\text{CO} + 2 \text{H}^+ + 2 \text{e}^- \quad (1.15) \\
\text{H}_2\text{CO} & \rightarrow \text{HCOOH} + 2 \text{H}^+ + 2 \text{e}^- \quad (1.16) \\
\text{H}_2\text{CO} + 2 \text{CH}_3\text{OH} & \rightarrow \text{CH}_2(\text{OCH}_3)_2 + \text{H}_2\text{O} \quad (1.17) \\
\text{HCOOH} + \text{CH}_3\text{OH} & \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O} \quad (1.18)
\end{align*}
\]

The current efficiency and product ratio were shown to be dependent on several variables
such as temperature, anodic potential, mass transport and the catalyst type.\textsuperscript{56,57} For
example when the electrolysis of methanol is performed on a smooth Pt electrode at
ambient temperature the incomplete oxidation products formaldehyde and formic acid are
preferred.\textsuperscript{58} However when a high surface area platinized Pt electrode was used the
complete oxidation to carbon dioxide was favored.\textsuperscript{58} The condensation products DMM
and MF were observed in the anode exhaust of DMFCs operating at high temperatures
and methanol concentration.

**Electrochemical Oxidation of Alcohols by Metal Complexes**

The electrochemical oxidation of alcohols using a catalyst in solution is an example
of an indirect electrochemical process. It is termed indirect because it is the mediator
(metal complex) not the substrate (alcohol) that is oxidized at the electrode surface
(Scheme 1-2). After undergoing this activation the mediator reacts in bulk solution with
the substrate, regenerating the reduced metal complex and forming the oxidized substrate.
There are two means by which the mediator can oxidize the substrate during the homogeneous reaction:

1. “Redox Catalysis”\textsuperscript{59} in which the mediator merely plays the role of an electron carrier (Scheme 1-3), transferring electrons to the substrate via an outer sphere process

\[
\begin{align*}
[M]_{(\text{red})} & \rightarrow [M]_{(\text{ox})} + n \text{e}^- \\
[M]_{(\text{ox})} + \text{Substrate}_{(\text{red})} & \rightarrow [M]_{(\text{red})} + \text{Substrate}_{(\text{ox})} \\
\text{Substrate}_{(\text{ox})} & \rightarrow \text{Product}
\end{align*}
\]

Scheme 1-3.

2. “Chemical Catalysis”\textsuperscript{59} in which the mediator reacts with the substrate to form an adduct (Scheme 1-4) before electron transfer occurs

\[
\begin{align*}
[M]_{(\text{red})} & \rightarrow [M]_{(\text{ox})} + n \text{e}^- \\
[M]_{(\text{ox})} + \text{Substrate}_{(\text{red})} & \rightarrow [M—\text{Substrate}]_{(\text{ox})} \\
[M—\text{Substrate}]_{(\text{ox})} & \rightarrow \text{Product} + [M]_{(\text{red})}
\end{align*}
\]

Scheme 1-4.

In this dissertation only the chemical catalysis (often referred to as electrocatalysis) will be considered.
**Ruthenium Electrocatalysts**

Ruthenium polypyridyl complexes are suited as electrooxidation catalysts due to the high stability and accessibility of multiple oxidation states, tunable redox potentials by varying ligands and the possibility of multiple electron transfers. The electrochemical oxidation of alcohols has been extensively studied with ruthenium polypyridyl catalysts.\(^{60-68}\)

Significant contribution to this area has been made by Meyer, who in 1978 observed the 2e\(^-\) reduction of a Ru complex accompanied by oxidation of triphenylphosphine to triphenylphosphine oxide (Scheme 1-5).\(^{63}\) The pyridine ligand however, is not suited to prolonged use and eventually dissociates, leading to an inactive oxo bridged dimer. The instability of the pyridine ligand was eventually overcome by replacing it and a bipyridine with the terpyridine (trpy) ligand.\(^{65}\) Of all the polypyridyl complexes investigated as electrocatalysts, \([(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}\) has attracted the most interest.

\[
\text{[ (bpy)$_2$pyRu}^{\text{IV}}\text{O }]^{2+} + \text{PPh}_3 \quad \text{fast} \quad \text{[ (bpy)$_2$pyRu}^{\text{II}}(\text{OPPh}_3)]^{2+} \\
\text{[ (bpy)$_2$pyRu}^{\text{II}}(\text{CH}_3\text{CN})]^{2+} \quad \text{slow} \quad \text{CH}_3\text{CN} \quad \text{[ (bpy)$_2$pyRu}^{\text{II}}(\text{CH}_3\text{CN})]^{2+} + \text{O} = \text{PPh}_3
\]

Scheme 1-5. Adapted from reference 63.

The Ru(II) aquo complex can undergo two reversible proton coupled 1 e\(^-\) oxidation steps to generate the versatile oxidant \([(\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}\) (Eq. 1.19 -1.20).

\[
\text{[ (trpy)(bpy)Ru}^{\text{II}}(\text{OH}_2)]^{2+} \quad \text{[ (trpy)(bpy)Ru}^{\text{III}}(\text{OH})]^{2+} + \text{e}^- + \text{H}^+ \quad (1.19)
\]

\[
\text{[ (trpy)(bpy)Ru}^{\text{III}}(\text{OH})]^{2+} \quad \text{[ (trpy)(bpy)Ru}^{\text{IV}}\text{O}]^{2+} + \text{e}^- + \text{H}^+ \quad (1.20)
\]

As an oxidant \([(\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}\) is very versatile and has been used for the electrocatalytic oxidation of alkenes,\(^{69,70}\) ketones,\(^{68-70}\) aldehydes,\(^{68,71}\) sugars\(^{72,73}\) and
DNA. A simplistic view of the catalytic cycle is shown in Scheme 1-6. In this cartoon a potential capable of oxidizing the metal center from Ru(II) to Ru(IV) is applied at the electrode. The Ru complex is first oxidized at the electrode surface before reacting in solution with the substrate regenerating the Ru(II) aquo complex.

Since Meyer’s publication in 1980 on the electrocatalytic properties of $[(\text{trpy})(\text{bpy})\text{Ru}^{IV}(O)]^{2+}$, the catalytic abilities of several other polypyridyl complexes have been reported. An example of this is $[\text{Ru}(4,4'-\text{Me}_2\text{bpy})_2(\text{PPh}_3)(\text{H}_2\text{O})][(\text{ClO}_4)_2]$, an active electrocatalyst that selectively oxidizes primary alcohols to the corresponding aldehyde. Cyclic voltammograms of these solutions exhibit an increase in anodic current when an alcohol is introduced. This increase in current is characteristic of the catalytic electrooxidation of alcohols by $\text{Ru}^{IV}=\text{O}$. Extensive mechanistic studies have been performed on the electrooxidation of aqueous alcoholic solutions with ruthenium complexes. Several mechanisms have since been proposed with each containing a Ru-oxo complex as the catalytically active species. The Ru-oxo bond is either generated \textit{in situ} from water or is present beforehand in the
pre-catalyst. The mechanisms which have been proposed are hydride transfer\textsuperscript{79,80} (Scheme 1-7), oxygen insertion\textsuperscript{81} (Scheme 1-8) and hydrogen atom abstraction\textsuperscript{82} (Scheme 1-9).

\[
\begin{align*}
\text{Ru}^{IV}=O + \text{HC OH} & \rightarrow \text{Ru}^{IV}=O + \text{HC OH} + \text{H}^+ \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{Ru}^{II} \text{OH} & \rightarrow \text{Ru}^{II} \text{OH} + \text{H}^+ + \text{CO H} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{Ru}^{II} \text{OH}_2 & \rightarrow \text{Ru}^{II} \text{OH}_2 + \text{CO} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

Scheme 1-7. Adapted from reference 79.

\[
\begin{align*}
\text{[Ru}^{VI}(\text{trpy})(\text{O})_2(\text{CH}_3\text{CN})\text{]}^{2+} & + \text{PhCH}_2\text{OH} \\
\rightarrow & \text{[Ru}^{VI}(\text{trpy})(\text{O})_2(\text{CH}_3\text{CN})\text{]}^{2+} + \text{PhCH}_2\text{OH} \\
\rightarrow & \text{[Ru}^{IV}(\text{trpy})(\text{O})(\text{CH}_3\text{CN})_2\text{]}^{2+} + \text{PhCH(OH)}_2 \\
\end{align*}
\]

Scheme 1-8 Adapted from reference 81.

\[
\begin{align*}
\text{Ru}^{IV}=O^{2+} + \text{PhCH}_2\text{OH} & \rightarrow \text{Ru}^{II} \text{OH}^{2+} + \text{PhCHOH} \\
\text{rapid} & \rightarrow \text{Ru}^{II} \text{OH}_2^{2+} + \text{PhCHO} \\
\end{align*}
\]

Scheme 1-9 Adapted from reference 82.

**Reactivity of Bimetallic Complexes**

The term “catalysis” was coined by Berzelius in 1836 to describe a new force other than affinity that can drive a reaction to completion. The modern definition of a catalyst is any substance that accelerates the rate of a chemical reaction without being consumed during the reaction. From an economical and environmental standpoint, catalytic
reactions currently dominate the chemical industry. These reactions have a considerable impact on the production of pharmaceuticals, agrochemicals, polymers, fine chemicals, etc. Catalysis offers the possibility of achieving complex synthetic transformations with high efficiency, chemical and stereochemical control while minimizing, if not eliminating, waste products and solvents.

Because of the distinct advantages gained from being able to catalyze chemical reactions, researchers are constantly trying to improve upon the reactivity and selectivity of current catalysts. It is clear that the catalytic reactions that occur in nature are generally far superior to the reactions developed by chemists. The elucidation of many enzymatic processes has revealed the interaction of two or more reactive centers during some of these catalytic transformations. The multifunctional catalysis observed in nature is rarely exploited in synthetic catalysts which chiefly utilize a single reactive site.

In trying to mimic the hydrolytic cleavage of a phosphate ester bond by a metalloenzyme, Reinhoudt developed a calix[4]arene functionalized with two Zn(II) metal centers. Complex 1 catalyzes the cyclization of the RNA model substrate 2-(hydroxypropyl)-p-nitrophenyl phosphate (HPNP, Scheme 1-10) with a 23,000 fold rate increase at pH 7 and 25 °C. The increased activity of 1 was explained via a bifunctional mechanism (Scheme 1-10) in which one zinc center acts as a Lewis acid and activates the phosphate group while the second activates the nucleophilic hydroxyl group.

Bimetallic complexes are now an accepted means to improving the catalytic properties of some mononuclear systems. In recent years heterobimetallic complexes have also received a tremendous amount of attention due to the possibility of exploiting the different reactivities of the metal centers during a chemical reaction. An example
relevant to this dissertation is the Oppenauer-type oxidation of primary and secondary alcohols to the corresponding aldehyde and ketone with complex 2 (Table 1-1). Although the mechanism for this catalytic cycle is not entirely clear, it is apparent that both metal fragments are crucial to the performance of the catalyst. This certainty was based on the two key observations made by Severin:

1. Under similar conditions, Ru and Rh homobimetallic complexes displayed no Oppenauer-type oxidative ability (Table 1-1)

2. Ligand modification to the Ru or Rh fragment affects the activity of the complexes

Another example relevant to this dissertation is the heterobimetallic catalyst \([\text{N}(n\text{-Bu}_4)][\text{M(N)R}_2(\mu\text{-O})_2\text{CrO}_2]\) where M= Ru or Os developed by Shapley. When air is used as the co-oxidant, this complex selectively oxidizes benzylic, primary and secondary alcohols at 60 °C to the corresponding carbonyl compounds. A mechanism based on the experimental results is shown in Scheme 1-11. It was proposed that after coordinating to Os there is a proton transfer to one of the bridging oxo ligands, followed
by β–hydride elimination and formation of the carbonyl compound. After the carbonyl compound dissociates, molecular oxygen is activated by the Os-Cr bond, regenerating the starting metal complex.\textsuperscript{6}

Table 1-1. Catalytic oxidation of 1-phenylethanol. Adapted from reference 90.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{CpRu(PPh}_3\text{)(Cl)(\mu-Cl)(\mu-dppm)PtCl}_2\text{]} \quad (3)</td>
<td>94</td>
</tr>
<tr>
<td>[\text{CpRu(PPh}_3\text{)(Cl)(\mu-Cl)(\mu-dppm)PdCl}_2\text{]} \quad (4)</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>[\text{CpRu(PPh}_3\text{)(Cl)(\mu-Cl)(\mu-dppm)AuCl}\text{]} \quad (5)</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

**Heterobimetallic Electrooxidation Catalysts**

Previous studies in the McElwee-White research group resulted in the synthesis of three heterobimetallic complexes \(\text{CpRu(PPh}_3\text{)(µ-Cl)(µ-dppm)PtCl}_2\text{]} \quad (3), \(\text{CpRu(PPh}_3\text{)(µ-Cl)(µ-dppm)PdCl}_2\text{]} \quad (4) \) and \(\text{CpRu(PPh}_3\text{)(Cl)(µ-dppm)AuCl}\text{]} \quad (5).\textsuperscript{92,93}

Complexes 3 - 5 were prepared by reacting \(\text{CpRu(PPh}_3\text{)(Cl)(\eta^1-dppm)}\text{]} \quad (6) \) with \(\text{Pt(COD)Cl}_2\text{], Pd(COD)Cl}_2\text{] or Au(PPh}_3\text{)Cl}\text{]} \quad (\text{Scheme 1-12}) \) at room temperature. The molecular structures of 3 - 5 were confirmed via X-ray crystallography and NMR.
Scheme 1-11. Adapted from reference 6.

Scheme 1-12.
Cyclic voltammetry (CV) of complexes 3 - 5 was performed in 1,2-dichloroethane (DCE) containing 0.7 M tetrabutyl ammonium trifluoromethane sulfonate (TBAT). All three complexes exhibited three oxidation waves (Table 1-2). The first and third wave are assigned to the Ru(II/III) and Ru(III/IV) couples respectively, while the middle wave is assigned to the redox couple of the second metal.

Table 1-2. Formal potentials for complexes 3, 4, 5 and 7

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Couple</th>
<th>$E_{1/2}$ (V)</th>
<th>Couple</th>
<th>$E_{pa}$ (V)</th>
<th>Couple</th>
<th>$E_{pa}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Pt (3)</td>
<td>Ru$^{II/III}$</td>
<td>1.21</td>
<td>Pt$^{II/IV}$</td>
<td>1.69</td>
<td>Ru$^{III/IV}$</td>
<td>1.91</td>
</tr>
<tr>
<td>Ru/Pd (4)</td>
<td>Ru$^{II/III}$</td>
<td>1.30</td>
<td>Pd$^{II/IV}$</td>
<td>1.49</td>
<td>Ru$^{III/IV}$</td>
<td>1.92</td>
</tr>
<tr>
<td>Ru/Au (5)</td>
<td>Ru$^{II/III}$</td>
<td>0.89</td>
<td>Au$^{I/III}$</td>
<td>1.42</td>
<td>Ru$^{III/IV}$</td>
<td>1.81</td>
</tr>
<tr>
<td>CpRu($\eta^2$-dppm)Cl (7)</td>
<td>Ru$^{II/III}$</td>
<td>0.61</td>
<td></td>
<td>Ru$^{III/IV}$</td>
<td>1.38</td>
<td></td>
</tr>
</tbody>
</table>

a All potentials obtained in 0.7 M TBAT / DCE and reported vs NHE. Adapted from reference 92.

Cyclic voltammetry was also used in screening the electrocatalytic properties of CpRu(PPh$_3$)(µ-Cl)(µ-dppm)PtCl$_2$ (3), CpRu(PPh$_3$)(µ-Cl)(µ-dppm)PdCl$_2$ (4) and CpRu(PPh$_3$)(Cl)(µ-dppm)AuCl (5) towards methanol oxidation. For complex 3, the introduction of methanol (Figure 1-2) results in a significant increase in current that coincides with the Pt(II/IV) redox wave. This increase in current is typical of an electrocatalytic oxidation process, and is also observed at the Pd(II/IV) redox couple of complex 4. In contrast, the catalytic current of the Ru/Au complex does not occur at the Au(I/III) couple but at the Ru(III/IV) couple.

**Product Formation**

As previously described, the surface catalyzed electrooxidation of methanol involves a complicated multistep reaction (Eq. 1.6 – 1.12). When the electrooxidation of methanol is performed with a homogeneous catalyst, the oxidation products are
formaldehyde (Eq 1.15) and formic acid (Eq 1.16). In the presence of excess methanol both formaldehyde and formic acid undergo condensation reactions to form dimethoxymethane (Eq. 1.17) and methyl formate (Eq. 1.18) respectively. It is important to point out that with the excess of methanol present the equilibria for these reactions should favor the formation of DMM and MF. Therefore when observed, DMM is formed from the incomplete $2e^-$ oxidation of methanol. MF is formed from the $4e^-$ oxidation of methanol. Current efficiency was calculated based on the yields of DMM, MF and the total charge passed (Eq 1.21).

\[
\text{Current efficiency} = \left[ \frac{96485 \text{ (C mol}^{-1})}{\text{charge passed (C)}} \right] \left\{ \left[ 2 \times \text{DMM (mol)} \right] + \left[ 4 \times \text{MF (mol)} \right] \right\} \times 100 \% \quad (1.21)
\]
**Bulk Electrolysis of Methanol**

The bulk electrolyses of 3 - 5 and the Ru model compound CpRu(η²-dppm)Cl (7) were performed at 1.7 V, the potential at which the catalytic current begins for complex 3. Oxidation with the Ru/Pd complex 4 was performed between the Pd(II/IV) and Ru(III/IV) waves, while electrolysis with the Ru/Au compound 5 was performed between the Au(I/III) and Ru(III/IV) waves. Oxidation of methanol with the Ru model compound 7 was performed at a potential more positive than the Ru(III/IV) couple.

The organic products of bulk electrolyses of dry methanol were analyzed with a gas chromatograph (GC) and identified as dimethoxymethane and methyl formate. The formation of these products is consistent with the electrooxidation of methanol on Pt/Ru electrodes. A result of this condensation reaction is that water is formed during the electrolysis. Addition of water not only results in an increase in the catalytic currents for compounds 3 - 5 (Figure 1-2) but also favors the formation of methyl formate (Table 1-3).

**Table 1-3. Bulk electrolysis data for the oxidation of methanol by 3 - 7**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dry Current Efficiency ( % )</th>
<th>Dry Product Ratio (DMM / MF)</th>
<th>Wet Current Efficiency ( % )</th>
<th>Wet Product Ratio (DMM / MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>18.6</td>
<td>1.20</td>
<td>19.5</td>
<td>0.41</td>
</tr>
<tr>
<td>4</td>
<td>24.6</td>
<td>0.87</td>
<td>20.6</td>
<td>0.54</td>
</tr>
<tr>
<td>5</td>
<td>25.4</td>
<td>0.46</td>
<td>26.1</td>
<td>0.34</td>
</tr>
<tr>
<td>7</td>
<td>3.2</td>
<td>∞</td>
<td>7.2</td>
<td>0.33</td>
</tr>
</tbody>
</table>

a Electrolyses were performed at 1.7 V vs NHE. b Product ratio and current efficiencies after 130 C of charge passed. Adapted from reference 92.

Current efficiencies for the oxidation of methanol with 3 - 5 and 7 are summarized in Table 1-3. Although the current efficiencies of the heterobimetallic complexes are moderate at best (18 - 26 %), they are still significantly higher than that of the Ru model compound (3 - 7 %). These results indicate that there is a cooperative interaction
between Ru and the second metal center resulting in an enhancement of the catalytic properties of the heterobimetallic complexes relative to their mononuclear components.

Summary

Ruthenium complexes have been studied as alcohol electrooxidation catalysts since the 1970s. Heterobimetallic homogeneous electrocatalysts is a fairly new field, with research being driven by the McElwee-White group. As a result of this research it is evident that the non-Ru metal center of 3 – 5 has a profound effect on the catalytic activity of the heterobimetallic complexes. The remainder of this dissertation will focus on the role of the non-Ru metal center during the electrooxidation of methanol with ruthenium heterobimetallic complexes.
CHAPTER 2
SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF A RUTHENIUM / MERCURY HETEROBIMETALLIC COMPLEX

Introduction

Interest in heterobimetallic complexes has grown significantly in the last twenty years, mainly due to the potential catalytic application of interacting metal centers.94-97 Cooperative interaction between metal centers has been shown to generate catalysts with greater reactivity and selectivity than their mononuclear components.98-100 A similar cooperative effect was observed during the electrooxidation of methanol on Pt/Ru binary anodes. A cooperative effect was also observed during the oxidation of alcohols with Ru/Rh (Table 1-1) and Os/Cr (Scheme 1-11) homogeneous catalysts. Interest in this cooperative effect led to the synthesis, and investigation of the electrocatalytic properties of CpRu(PPh3)(μ-Cl)(μ-dppm)PtCl2 (3), CpRu(PPh3)(μ-Cl)(μ-dppm)PdCl2 (4) and CpRu(PPh3)(μ-dppm)AuCl (5).92,93 Complexes 3 - 5 were used as catalyst during the electrooxidation of methanol and resulted in significantly better current efficiencies (Table 1-2) than the mononuclear model complex CpRu(η2-dppm)Cl.92

The increased activity displayed by complexes 3 - 5 during the methanol oxidation reaction inspired further study and led to the synthesis of 8 – 14. In complexes 8 – 14 the structures of 3 - 5 were altered by varying the ligands.101 The CVs of 8 - 14 (Table 2-1) are similar to those observed for 3 – 5, and the assignment of the redox waves were made from comparison to these complexes. Electronic interaction between the metal centers of complexes 8 - 12 is observed in their CVs. The presence of a bridging halide promotes
Figure 2-1. Structure of compounds 3 - 5 and 8 - 14

this interaction, and the donation of electron density from Ru to Pd or Pt is reflected in the Ru(II/III) oxidation potential. Due to the considerable loss of electron density, the Ru(II/III) oxidation wave for complexes 8 – 12 occurs at a much higher potential than CpRu(PPh₃)(Cl)(η¹-dppm) (Table 2-1). The lack of electronic interaction between the Ru
and Au metal centers can also be observed by examining the CV data (Table 2-1). The Ru(II/III) and Au(I/III) oxidation waves of 13 and 14 are shifted only slightly relative to their monometallic model compounds.

Table 2-1. Formal potentials for complexes 8 - 14

<table>
<thead>
<tr>
<th>Complex</th>
<th>Couple</th>
<th>E_1/2 (V)</th>
<th>Couple</th>
<th>E_{pa} (V)</th>
<th>Couple</th>
<th>E_{pa} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Ru^{II/III}</td>
<td>1.25</td>
<td>Pt^{II/IV}</td>
<td>1.54</td>
<td>Ru^{III/IV}</td>
<td>1.90</td>
</tr>
<tr>
<td>9</td>
<td>Ru^{II/III}</td>
<td>1.10</td>
<td>Pt^{II/IV}</td>
<td>1.49</td>
<td>Ru^{III/IV}</td>
<td>1.98</td>
</tr>
<tr>
<td>10</td>
<td>Ru^{II/III}</td>
<td>1.08</td>
<td>Pt^{II/IV}</td>
<td>1.53</td>
<td>Ru^{III/IV}</td>
<td>1.95</td>
</tr>
<tr>
<td>11</td>
<td>Ru^{II/III}</td>
<td>1.29</td>
<td>Pd^{II/IV}</td>
<td>1.55</td>
<td>Ru^{III/IV}</td>
<td>1.98</td>
</tr>
<tr>
<td>12</td>
<td>Ru^{II/III}</td>
<td>1.10</td>
<td>Pd^{II/IV}</td>
<td>1.50</td>
<td>Ru^{III/IV}</td>
<td>1.95</td>
</tr>
<tr>
<td>13</td>
<td>Ru^{II/III}</td>
<td>0.89</td>
<td>Au^{I/III}</td>
<td>1.54</td>
<td>Ru^{III/IV}</td>
<td>1.80</td>
</tr>
<tr>
<td>14</td>
<td>Ru^{II/III}</td>
<td>0.75</td>
<td>Au^{I/III}</td>
<td>-</td>
<td>Ru^{III/IV}</td>
<td>1.76</td>
</tr>
<tr>
<td>CpRu(PPh_3)(Cl)(η^1-dppm) (6)</td>
<td>Ru^{II/III}</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(PPh_3)_2Cl</td>
<td>Ru^{II/III}</td>
<td>0.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a All potentials obtained in 0.7 M TBAT / DCE and reported vs NHE. Adapted from reference 101.

The electrooxidation of methanol was performed with complexes 8 - 14 at 1.7 V in 0.7 M TBAT / DCE, forming DMM and MF (Table 2-2) as the only oxidation products. By expanding the Ru/M series of complexes, it is apparent that the Ru/Au complexes are less active during this reaction, than the Ru/Pd and Ru/Pt complexes (Table 2-2). In fact the current efficiency of the Ru/Au complexes are more comparable to the Ru model compound CpRu(PPh_3)_2Cl than to the Ru/Pt and Ru/Pd complexes.
**Role of the Non-Ru Metal Center**

From the current efficiencies in Table 2-2 it is evident that the non-Ru metal center is critical to the improved catalytic ability exhibited by the heterobimetallic complexes.

Possible roles of the non-Ru metal include:

- Oxidant
- Activation of the Ru metal center
- Methanol binding site

**Table 2-2. Bulk electrolysis data for the oxidation of methanol by 8 - 14**

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Current Efficiency (%)</th>
<th>Product Ratio (DMM / MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>18.6</td>
<td>1.20</td>
</tr>
<tr>
<td>8</td>
<td>43</td>
<td>0.98</td>
</tr>
<tr>
<td>9</td>
<td>39</td>
<td>1.26</td>
</tr>
<tr>
<td>10</td>
<td>32</td>
<td>3.02</td>
</tr>
<tr>
<td>4b</td>
<td>24.6</td>
<td>0.87</td>
</tr>
<tr>
<td>11</td>
<td>42</td>
<td>0.91</td>
</tr>
<tr>
<td>12</td>
<td>23</td>
<td>2.94</td>
</tr>
<tr>
<td>5b</td>
<td>25.4</td>
<td>0.46</td>
</tr>
<tr>
<td>13</td>
<td>16</td>
<td>2.10</td>
</tr>
<tr>
<td>14</td>
<td>12</td>
<td>2.32</td>
</tr>
<tr>
<td>CpRu(PPh₃)₂Cl</td>
<td>12</td>
<td>2.87</td>
</tr>
<tr>
<td>CpRu(η²-dppm)Cl</td>
<td>3.2</td>
<td>∞</td>
</tr>
</tbody>
</table>

a Electrolyses performed at 1.7 V vs NHE. Product ratio and current efficiencies after 130 C of charge passed. Adapted from reference 92. b Adapted from reference 101.
The oxidation of alcohols by Pt\textsuperscript{102}, Pd\textsuperscript{103-106} and Au\textsuperscript{107} complexes have literature precedent and are still being actively investigated. Recent examples of these transformations with molecular oxygen as the co-oxidant are shown in Schemes 2-1 and 2-2.

Scheme 2-1. Adapted from reference 105

The Pt, Pd or Au center could also activate the Ru by mediating the electron density around it. The mediation of the Ru(II/III) couple of complexes 8 – 12 (Table 2-1) is an example of this. The bridging halide of complexes 8 – 12 facilitates the electronic interaction between Ru and Pt or Pd. As a result of this interaction the Ru metal center of complexes 8 – 12 will be more electrophilic than complex 6. The increased electrophilicity (Lewis acidity) of Ru would then favor the interaction / coordination with the nucleophilic methanol substrate.

The third possibility that exists is a site for methanol binding. In this role the Pt, Pd or Au metal center would bind and activate the methanol before oxidation is performed.
by the Ru metal center. A similar bifunctional mechanism\textsuperscript{44-46} was proposed for the oxidation of methanol by PtRu binary anodes in DMFCs.

The second and third roles are closely related and could possibly be performed by a Lewis acid metal center. To investigate the role of the second metal a Ru/Hg complex similar to the Ru/Pt and Ru/Pd complexes (Figure 2-1) was synthesized. Mercury was selected because it is of moderate Lewis acidity and non-redox active within the potential window used.

**Lewis Acid Catalysts**

Lewis defined an acid in 1923 as an electron pair acceptor while a Lewis base is an electron pair donor. The term “Lewis acid” is now used to differentiate this interaction from the Brønsted-Lowry acid (proton donor). Lewis acid catalyzed reactions have a rich history in organic synthesis and continue to be extensively studied (Figure 2-2).

![Figure 2-2. References to “Lewis acid” in the scientific literature (SciFinder Scholar).](image-url)
Carbon-carbon bond formation via the Friedel-Crafts reaction (Eq. 2.1), Mukaiyama aldol synthesis, the Diels-Alder and ene reactions are classic organic reactions catalyzed by conventional Lewis acids such as AlCl₃, SnCl₄ or TiCl₄.¹⁰⁸ These simple Lewis acids, although very moisture sensitive, are capable of catalyzing a large number of reactions but with limited stereo-, regio- and chemo-selectivity.

\[
\text{H}_3\text{C} \quad \text{CH}_3 \\
\text{CH}_3 + \text{AlCl}_3 \quad \text{CH}_3 \\
\text{H}_3\text{C} + \text{HCl} \\
\text{(2.1)}
\]

In this modern age of organic synthesis, selectivity is as important a factor to the viability of a catalyst, as is its reactivity. Due to continuing research in the field of Lewis acid catalyzed reactions, two key goals have been met.

1 The number of metals widely used in Lewis acid reagents has grown significantly. Currently more than 28 metals are used in Lewis acid catalyzed reactions each with its own attributes. The expansion of the Lewis acid reagents has led to reactivity previously unavailable to conventional Lewis acids (Eq 2.2).¹⁰⁹
Design of novel ligands capable of stabilizing and promoting unique reactivity of Lewis acid metal centers. An example of this is the enantioselective Diels-Alder reaction (Eq. 2.3) reported by Kelly in 1986. In this reaction the C2 symmetric ligand (a derivative of binaphthol) leads to one enantiomer being favored.

\[
\begin{align*}
\text{2 equiv} \quad \text{1)} &\quad \text{BH}_3 \quad \text{2)} \quad \text{AcOH} \\
\end{align*}
\]

With the use of non-traditional Lewis acids and the design of some novel ligands, the limitations of conventional Lewis acids have been to a large part surmounted. It is now possible to do Lewis acid catalyzed reactions under less stringent conditions, with high stereo-, regio- and chemo- selectivity.

**Classification of Lewis Acids**

Even though a large number of metal reagents have been used as Lewis acids during catalytic organic transformations, most of these reagents are chosen only after experimental trial and error. Trial and error is necessary because scientists currently only
have a crude understanding of Lewis acidic character. There have been a few attempts at classifying Lewis acidic reagents. These classifications have been made using one of the following methods:

- Reactivity of a Lewis acid
- NMR data
- Theoretical calculations

In 1972 Olah arranged over 130 Lewis acids based on their activity during a Friedel-Crafts reaction (Scheme 2-3). The Lewis acids were then placed in one of four categories: very active, moderately active, weak or very weak (Scheme 2-3) based on the amount of products formed during the benzylation and subsequent isomerization.

**Lewis Acid Classification**

**Very active:** High conversion, large amount of isomerization products = AlCl₃, GaCl₃, NbCl₅, TaCl₅

**Moderately active:** High conversion, very little isomerization = InCl₃, WCl₆, ReCl₅, SbCl₅

**Weak:** Low yield, no isomerization = SnCl₄, BBr₃, TiCl₄, FeCl₂, PtCl₄

**Very weak:** No products = SbCl₃, BeCl₂, CuCl₂, IrCl₃, HgCl₂, AuCl₃

Scheme 2-3. Adapted from reference 111.

Kobayashi grouped Lewis acids based on the activity and selectivity during the addition reaction of a silyl enolate to an aldehyde and an aldimine (Scheme 2-4). Based on the experimental results the Lewis acids were classified as: active, weak or inactive (Scheme 2-4).
Lewis Acid Classification

**Active:** Yields greater than 40% = AlCl₃, GaCl₃, NbCl₅, TaCl₅

**Weak:** Yields less than 40% = FeCl₂, PtCl₂, RuCl₃, SiCl₄

**Inactive:** No Products = HgCl, HgCl₂, PdCl₂, AuCl

Scheme 2-4. Adapted from reference 112.

**Lewis Acidic Properties of Mercury Complexes**

In both classification schemes by Olah\textsuperscript{111} and Kobayashi\textsuperscript{112} the mercury halides HgCl and HgCl₂ are listed as inactive and therefore are very weak Lewis acids. As with most metal complexes, the Lewis acidity of mercury is greatly affected by the ligands coordinated to it. Experiments designed at tuning the Lewis acidity through ligand variation have been performed with mercury organometallic complexes.\textsuperscript{113-116} The aim of these experiments is to investigate the mechanism by which polyfunctional Lewis acids activate carbonyl groups during organic reactions. It has been proposed that chelation of the carbonyl group by Lewis acids plays an important role in the enhanced catalytic activity. The Lewis acidity of mercury halides can be increased by coordinating with an electron withdrawing ligand (Scheme 2-5).\textsuperscript{113} Complex 15 exhibits strong Lewis acidic character readily forming an adduct with acetone. The bidentate coordination was confirmed with a crystal structure of the solvent adduct.
Scheme 2-5.

The Lewis acidity of the Hg metal center can be increased even more by expanding the fluorinated backbone. This strategy led to the isolation of the trimeric perfluoro-ortho-phenylene mercury complex (Figure 2-3).\textsuperscript{115} This complex has a strong affinity for aromatic compounds and has formed isolable 1:1 adducts with biphenyl, naphthalene, pyrene and triphenylene. The $\pi$ stacking of trimeric perfluoro-ortho-phenylene mercury and aromatic hydrocarbons result in phosphorescence being observed for the aromatic substrate. It is thought that the phosphorescence is due to a heavy atom effect of mercury promoting intersystem spin crossing from the $S_1$ to the $T_1$ state.\textsuperscript{115}

![Structure of trimeric perfluoro-ortho-phenylene mercury](image)

Figure 2-3. Structure of trimeric perfluoro-ortho-phenylene mercury
Chemistry of Mercury

Organometallic chemistry effectively started in 1849 when Frankland observed that metallic zinc reacts with methyl iodide. Frankland later extended this reaction to other metals and prepared several new organometallic compounds, one of which was methylmercuric iodide. During characterization of methylmercuric iodide he recorded the nauseous taste, totally unaware of its extraordinary toxicity. Mercury compounds are extremely toxic and exposure can occur through inhalation, ingestion or dermal absorption. The amount of mercury absorbed by the body is dependent upon the chemical form. Only 0.01 % of elemental mercury is absorbed when ingested but methyl mercury is almost totally absorbed. In the human body mercury accumulates in the liver, kidney, blood and brain. Due to decreased handling of mercury acute health effects such as cardiovascular collapse or kidney failure (both of which are fatal) are not as common today. Chronic health effects include central nervous system effects, kidney damage and birth defects. Genetic damage is also suspected. Due to the high toxicity of mercury it cannot be overstated how important it is to follow proper lab procedures when handling any material containing this element.

Mercury Catalyzed Reactions

There are limited examples in the literature for mercury catalyzed reactions. A recent example of this includes the reaction between alkynes and phosphonic acid monoesters (Eq. 2.4) to yield vinyl phosphonates.\textsuperscript{117}

\[ \text{R}_1\text{C}≡\text{CH} + \text{R}_2\text{P}\text{O}\text{Et} \xrightarrow{10 \text{ mol} \% \text{Hg(OAc)}_2, 2 \text{ mol} \% \text{BF}_3\text{OEt}_2, \text{toluene, } 80^\circ\text{C}} \text{Yields } 50 - 90\% \]

(2.4)
Mercury acetate is essential to the reaction, forming the corresponding Markovnikov adducts in moderate to good yields with high regioselectivity. Little to no vinyl phosphonates were formed when other addition catalysts such as RuCl₃, PdCl₂(Ph₃P)₂ and Pd(Ph₃P)₄ were used.

Another Hg(II) catalyzed reaction is the homogeneous oxidation of methane to methanol (Eq. 2.5 – 2.8).¹¹⁸ This transformation is extremely selective (85 %) with high yields (43 %) in the presence of Hg(II) ions.

\[
\begin{align*}
\text{CH}_4 + 2 \text{H}_2\text{SO}_4 & \xrightarrow{\text{HgSO}_4} \text{CH}_3\text{OSO}_3\text{H} + 2 \text{H}_2\text{O} + \text{SO}_2 & (2.5) \\
\text{CH}_3\text{OSO}_3\text{H} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 & (2.6) \\
\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 & (2.7) \\
\text{CH}_4 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CH}_3\text{OH} & (2.8)
\end{align*}
\]

**Synthesis and Characterization of CpRu(Ph₃)(µ-Cl)(µ-dppm)HgCl₂**

**Attempted Synthesis of CpRu(Ph₃)(µ-Cl)(µ-dppm)HgCl₂ (16)**

Initial attempts at preparing 16 involved reacting CpRu(Ph₃)Cl(η¹-dppm) with HgCl₂. A similar method was used during the synthesis of complexes 3 – 5 (Scheme 1-12) and for the preparation of (CO)₃Ru(µ-Ph₂PCH₂NC₄H₈O)₂HgI₂ (Eq. 2.9).¹¹⁹ Instead of the desired dppm bridged complex the reaction between CpRu(Ph₃)Cl(η¹-dppm) (6) and HgCl₂ led to the formation of [CpRu(Ph₃)(η²-dppm)]⁺ (17) (Eq 2.10) as confirmed by ³¹P{¹H} NMR (Table 2-3). The phosphorus NMR of 17 displayed a triplet at 50.2 ppm for the Ru bound Ph₃ and a doublet at 2.2 ppm for the chelated dppm. ZnCl₂ and CdCl₂ also reacted in a similar manner and an unrefined X-ray crystal structure of the resulting Zn complex can be seen in Figure 2-4.
Figure 2-4. Unrefined crystal structure of \([\text{CpRu(PPh}_3)(\eta^2\text{-dppm})]^+ [\text{ZnCl}_3]^-(17)\).
**Synthesis of CpRu(PPh₃)(μ-Cl)(μ-dppm)HgCl₂ (16)**

An alternative route to 16 was found by first reacting CpRu(PPh₃)Cl(η¹-dppm) (6) with Hg(OAc)₂ followed by acetyl chloride (Eq. 2.11). CpRu(PPh₃)(μ-Cl)(μ-dppm)HgCl₂ is a yellow air and moisture stable solid. Solutions of 16 are also very stable when stored in an inert atmosphere; they however decompose upon prolonged exposure to air. The $^{31}$P{$^1$H} NMR spectrum of complex 16 displays the expected resonances (Table 2-3). The Ru bound phosphorus signals appear as a doublet for PPh₃ at 40.0 ppm ($J_{PP} = 41$ Hz) and a doublet of doublets for dppm at 35.1 ppm ($J_{PP} = 41$ Hz and 11 Hz). The Hg bound phosphorus appears as a doublet at 29.7 ppm ($J_{PP} = 11$ Hz).

![Reaction Scheme](image)

**Synthesis of CpRu(PPh₃)(μ-Cl)(μ-dppm)Hg(OAc)₂ (18)**

The Hg acetate intermediate CpRu(PPh₃)(μ-Cl)(μ-dppm)Hg(OAc)₂ (18) that is formed during the synthesis of 16 (Eq. 2.11), can be isolated cleanly and in high yields if acetyl chloride is not added to the reaction mixture. The stability of complex 18 is very similar to 16, and it is isolated as an air and moisture stable yellow solid with moderate stability in solution. Complex 18 displays the expected $^{31}$P{$^1$H} NMR spectrum, which is analogous to that of compound 16 (Table 2-3). The Ru bound phosphorus signals are shifted downfield relative to the analogous signals in 16, appearing as a doublet for PPh₃ at 41.9 ppm ($J_{PP} = 43$ Hz) and a doublet of doublets for dppm at 36.9 ppm ($J_{PP} = 43$ Hz.)
and 28 Hz). The Hg bound phosphorus signal is shifted upfield relative to 16, appearing as a doublet at 24.1 ppm ($J_{PP} = 28$ Hz).

Table 2-3. Selected NMR data for complexes 16 - 18

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru-PPh$_3$</th>
<th>Ru-dppm</th>
<th>Hg-dppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>39.9 (d, $J_{PP} = 40$ Hz)</td>
<td>35.0 (dd, $J_{PP} = 40$, 10 Hz)</td>
<td>30.1 (d, $J_{PP} = 10$ Hz)</td>
</tr>
<tr>
<td>17</td>
<td>48.0 (t, $J_{PP} = 35$ Hz)</td>
<td>1.9 (d, $J_{PP} = 35$ Hz)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>41.9 (d, $J_{PP} = 43$ Hz)</td>
<td>36.9 (dd, $J_{PP} = 43$, 28 Hz)</td>
<td>24.1 (d, $J_{PP} = 28$ Hz)</td>
</tr>
</tbody>
</table>

Analysis of CpRu(PPh$_3$)(μ-Cl)(μ-dppm)HgCl$_2$ Structure

Selected bond lengths and angles for 16 are shown in Table 2-4; crystallographic data and structure refinement are provided in Table 2-5. In the solid state, the crystal structure of CpRu(PPh$_3$)(μ-Cl)(μ-dppm)HgCl$_2$ contains the complex and two disordered DCE solvent molecules with no unusual contacts between any of these species. Complex 16 (Figure 2-5) contains a bridging chloride and dppm moiety as do the structurally similar CpRu(PPh$_3$)(μ-Cl)(μ-dppm)PtCl$_2$ (3) and CpRu(PPh$_3$)(μ-Cl)(μ-dppm)PdCl$_2$ (4). The metal centers and bridging ligands form a distorted six-membered ring consisting of Ru, Cl$_3$, Hg, P$_1$, C$_6$ and P$_2$.

The Cp ligand is bound to Ru in a $\eta^5$ mode resulting in the typical three legged piano stool conformation about the Ru center. The Ru-Cl bond length of 2.4577(8) Å in 16 is longer than distance of 2.4403(7) Å reported for the Ru-Cl bond in complex 4. The Ru-Cl bond in 16 is comparable to that of complex 5, [2.4598(11) Å] whose chloride is not bridging. The Hg metal center is four coordinate and forms bonds with three chlorides and a phosphorus atom to give the expected tetrahedral geometry. The Hg-Cl$_3$ bond length of 2.7372(8) Å is shorter than the bridging chloride [2.763(9) Å] reported for the Hg dimer [Hg$_2$(Cl)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ in which the Hg centers are also bridged by two dppm ligands. The bridging chloride exerts a strong trans effect on the Hg-Cl$_1$ bond
[2.4901(11) Å] making it much longer than the Hg-Cl2 bond [2.3993(9) Å]. The bond lengths of both terminal chlorides are shorter than the terminal Hg-Cl bonds reported for Rh₂Cp₂(µ-CO)(µ-dppm)(µ-HgCl₂) [2.534(3) Å and 2.581(3) Å] and within the typical range of four coordinate Hg species (2.28 – 2.68 Å).

Figure 2-5. Thermal ellipsoids drawing of the molecular structure of CpRu(PPh₃)(µ-Cl)(µ-dppm)HgCl₂ (16). Thermal ellipsoids are plotted at 50 % probability. Phenyl rings and hydrogen atoms are omitted for clarity.

Table 2-4. Selected bond distances (Å) and angles (deg) for CpRu(PPh₃)(µ-Cl)(µ-dppm)HgCl₂ (16).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-P1</td>
<td>2.4143(8)</td>
</tr>
<tr>
<td>Hg-Cl1</td>
<td>2.4901(11)</td>
</tr>
<tr>
<td>Hg-Cl2</td>
<td>2.3993(9)</td>
</tr>
<tr>
<td>Hg-Cl3</td>
<td>2.7372(8)</td>
</tr>
<tr>
<td>Ru-P2</td>
<td>2.3193(8)</td>
</tr>
<tr>
<td>Ru-P3</td>
<td>2.3387(8)</td>
</tr>
<tr>
<td>Ru-Cl3</td>
<td>2.4577(8)</td>
</tr>
<tr>
<td>Ru-C1</td>
<td>2.217(3)</td>
</tr>
<tr>
<td>Ru-C2</td>
<td>2.230(3)</td>
</tr>
<tr>
<td>Ru-C3</td>
<td>2.232(3)</td>
</tr>
<tr>
<td>Ru-C4</td>
<td>2.186(3)</td>
</tr>
<tr>
<td>Ru-C5</td>
<td>2.178(3)</td>
</tr>
</tbody>
</table>
Table 2-5. Crystal data and structure refinement for
\[ \text{CpRu(PPh}_3\text{)(µ-Cl)(µ-dppm)HgCl}_2 \text{ (16)} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>( \text{C}<em>5\text{H}</em>{50}\text{Cl}_7\text{HgP}_3\text{Ru} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1317.64</td>
</tr>
<tr>
<td>Temperature</td>
<td>193(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{Cc} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>( a = 23.384(2) \text{ Å} )</td>
<td>( a = 90^\circ )</td>
</tr>
<tr>
<td>( b = 11.5264(7) \text{ Å} )</td>
<td>( \beta = 94.875(2)^\circ )</td>
</tr>
<tr>
<td>( c = 19.295(2) \text{ Å} )</td>
<td>( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>5182.2(6)</td>
</tr>
<tr>
<td>Density (calcd) (Mg/m(^3))</td>
<td>1.689</td>
</tr>
<tr>
<td>Absorption coefficient (mm(^{-1}))</td>
<td>3.739</td>
</tr>
<tr>
<td>( F_{000} )</td>
<td>2600</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.27 x 0.23 x 0.20</td>
</tr>
<tr>
<td>( \theta ) range (deg)</td>
<td>1.75 to 27.50</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-30 ≤ h ≤ 29, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>22341</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>11134[R(int) = 0.0160]</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>99.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Analytical</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.5328 and 0.3680</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix least squares on ( F^2 )</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>11134 / 2 / 581</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>1.023</td>
</tr>
<tr>
<td>Final R indices [I &gt;2sigma(I)]</td>
<td>( ^a R1 = 0.0207 )</td>
</tr>
<tr>
<td></td>
<td>( ^b W2 = 0.0523 )</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>( ^a R1 = 0.0211 )</td>
</tr>
<tr>
<td></td>
<td>( ^b W2 = 0.526 )</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>-0.0063(17)</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å(^3))</td>
<td>0.893 and -0.607</td>
</tr>
</tbody>
</table>

\( ^a R1 = \Sigma(\|F_o\| - \|F_c\|) / \Sigma|F_o|, \quad ^b W2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)]^{1/2}, S = [\Sigma[w(Fo^2 - Fc^2)^2] / (n-p)]^{1/2} w = 1/[\sigma^2(Fo^2)+(0.027*p)^2+8.56*p], p = [\max(Fo^2,0)+2*Fc^2]/3 \)

**Cyclic Voltammetry**

The first three ionization potentials for mercury are 10.43, 18.65 and 34.4 eV respectively. The large difference between the second and third ionization potentials is one reason why the formation of Hg(III) species is so difficult if not impossible to attain. There is only one report of a Hg(III) species, a short lived \([\text{Hg(cyclam)}]^3+\) which was electrochemically generated and observed in 1976.\(^{120}\) Unfortunately, this experiment has
never been independently confirmed. Based on this and the absence of any oxidation waves for the model compound HgCl$_2$(PPh$_3$)$_2$ (0 – 2.0 V), it was assumed that Hg(II) is non-redox active within the potential window used for these studies.

During the CV studies of complex 16, three irreversible redox waves at 0.70, 1.02 and 1.50 V were observed (Figure 2-6). Three oxidation waves were unexpected since the only redox active species in the solution is the Ru(II) metal center. During previous studies on complexes 3 – 14 (Table 1-1 and Table 2-1) only two Ru based redox processes, the Ru(II/III) and Ru(III/IV) oxidation waves were observed. Since Hg(II) is not redox active within the potential window used in these experiments there should only be two oxidation processes. With subsequent scans the first and third wave diminish in intensity, until only the second oxidation wave, now shifted to 1.14 V (Figure 2-6) was observed. Analysis of the resulting solution after the CV experiments confirmed that CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ (16) had decomposed during the CV experiments. The decomposition of 16 resulted in the formation of [CpRu(PPh$_3$)(η$_2$-dppm)]$^+$ (17). A comparison of the CVs for [CpRu(PPh$_3$)(η$_2$-dppm)]$^+[PF_6]^{-}$ and 16 after decomposition allowed the assignment of the oxidation wave at 1.14 V (Figure 2-6) to the Ru(II/III) couple of [CpRu(PPh$_3$)(η$_2$-dppm)]$^+$. The first oxidation wave at 0.70 V is much lower than any observed for the halide bridged complexes 8 -12 (Table 2-1). The oxidation wave at 0.70 V is instead closer to the Ru(II/III) couple of CpRu(PPh$_3$)(Cl)(η$^1$-dppm) (6) and CpRu(PPh$_3$)(Cl)(µ-dppb)AuCl (14) (Table 2-1), complexes containing no halide bridge. The stability of 16, in 0.7 M TBAT / DCE was monitored via $^{31}$P{${}^1$H} NMR. Complete decomposition to 17 occurred after only 5 hours, without the passage of any current. A similar result was observed at lower electrolyte concentration
Figure 2-6. Cyclic voltammograms of $16$ under nitrogen in $3.5$ mL of DCE / $0.7$ M TBAT; glassy carbon working electrode; Ag/Ag$^+$ reference electrode; $50$ mV/s scan rate.

(0.1 M TBAT / DCE). The supporting electrolyte was also changed to the weakly coordinating electrolyte tetra-n-butylammonium tetrakis(pentafluorophenyl)borate. Changing the supporting electrolyte had no effect, and CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ ($16$) still decomposed to [CpRu(PPh$_3$)(η$^2$-dppm)]$^+$ ($17$). These results indicate that the decomposition is not only due to the passage of current but also to the interaction of the supporting electrolyte with the complex.

**Summary**

A novel Ru/Hg complex CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ ($16$) was synthesized and characterized. The metal centers are connected with a bridging chloride and dppm
ligands. This is the first reported Ru/Hg complex bridged in this manner. 

CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ is unstable in solutions containing electrolyte, and rapidly decomposes to [CpRu(PPh$_3$)(η$^2$-dppm)]$^+$ (17) during cyclic voltammetry. Due to the instability of 16 during the CV experiments, the electrocatalytic properties of CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ were not studied
CHAPTER 3
THE SELECTIVE PARTIAL ELECTROOXIDATION OF METHANOL TO DIMETHOXYMETHANE WITH RUTHENIUM/TIN HETEROBIMETALLIC COMPLEXES

Introduction

The cooperative interaction between Ru/Pt, Ru/Pd and Ru/Au complexes has been shown to improve the catalytic ability of the heterobimetallic complexes relative to the monometallic components. As mentioned before one possible role of the non-Ru metal center could be as a Lewis acid. To continue the study of this interaction, a series of Ru/Sn complexes was synthesized and characterized.

Chemistry of Tin

As a group 14 element, tin has the ability to form stable and relatively strong bonds with most elements in the periodic table. Except for the bonds formed to the heavier alkali and alkaline earth metals, most of the bonds formed to tin are covalent in character. The first and second ionization potentials for tin are similar to those of elements that readily form divalent cations (Table 3-1). Hence it is not surprising that tin is able to form stable Sn(II) compounds. The more stable oxidation state is Sn(IV), but the energy difference between it and Sn(II) is very small (Eq 3.1). Due to the stability of the two oxidation states, there are extensive and varied chemistries for both states. Kinetically stable trivalent complexes have been isolated but generally Sn(III) is considered unstable and is thought to readily disproportionate.

\[
\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2 \text{e}^- \quad E^0 = 0.1364 \text{ V} \quad (3.1)
\]
### Table 3-1. Selected ionization potentials

<table>
<thead>
<tr>
<th>Element</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>11.260</td>
<td>24.383</td>
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<tr>
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<td>14.632</td>
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<tr>
<td>Mg</td>
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<td>15.035</td>
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<tr>
<td>Ca</td>
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<td>11.871</td>
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<tr>
<td>Mn</td>
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<td>15.640</td>
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</tr>
<tr>
<td>Fe</td>
<td>7.870</td>
<td>16.18</td>
<td></td>
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</tr>
</tbody>
</table>

### Bonding in Heterobimetallic Tin (II) Complexes

Tin is known to form heterobimetallic complexes containing metal-metal bonds to transition metals, lanthanides, actinides and group 12 metals. In bonding to transition metals, stannylenes donate two of the available p electrons to the transition metal. Stannylenes can also act as Lewis acids, forming adducts with both hard and soft Lewis bases. These adducts are better Lewis bases than the stannylenes (e.g., SnCl₃⁻ is a better Lewis base than SnCl₂). There are empty low lying p and d orbitals on tin, which when hybridized are capable of accepting electron density from the transition metal. Due to these factors the bonds between tin and a transition metal contain both σ and π components.

### Synthesis of Ruthenium / Tin (II) Complexes

There are several synthetic routes available for the preparation of M-Sn complexes, such as salt elimination, elimination of small molecules, oxidative addition, insertion of tin (II) and transmetalation. For the group VIII metals (Fe, Ru and Os), the synthesis is often accomplished via the following methods:

Salt elimination:¹²³ \[ \text{Na}_2\text{Ru(CO)}_4 + 2 \text{Ph}_3\text{SnCl} \rightarrow (\text{Ph}_3\text{Sn})_2\text{Ru(CO)}_4 + 2 \text{NaCl} \]  (3.2)

Oxidative addition:¹²⁴ \[ \text{Fe(CO)}_4(\text{PPh}_3) + \text{SnCl}_4 \rightarrow (\text{SnCl}_3)\text{Fe(CO)}_3(\text{PPh}_3)\text{Cl} + \text{CO} \]  (3.3)

Insertion of SnCl₂:¹²⁵ \[ \text{CpRu(PPh}_3)_2\text{Cl} + \text{SnCl}_2 \rightarrow \text{CpRu(PPh}_3)_2(\text{SnCl}_3) \]  (3.4)
Mechanistic information on the formation of M-Sn complexes is limited. The insertion of tin (II) halides however, has been the subject of much discussion. Though not proven conclusively, there is evidence for the mechanism in Scheme 3-1. It has been proposed that the tin (II) halide first coordinates to the halide ligand of the transition metal before rearranging intramolecularly to the three centered intermediate.

![Scheme 3-1](image)

Scheme 3-1. Adapted from reference 126.

Evidence to support this mechanism includes the isolation of a bridging halide complex Ir(µ-Cl)(SnCl2)(CO)(PPh3)2.127 The reaction between CpRu[Ph2PCH(CH3)CH2PPh2]Cl and SnCl2 (Scheme 3-2) also provides evidence for the intramolecular rearrangement, since the reaction proceeds with retention of configuration at Ru.128 The diastereomers formed during the reaction are configurationally stable and therefore do not interconvert as a solid or in solution.

**Heterobimetallic Tin (II) Catalysts**

Stannylene complexes are often utilized as catalysts or co-catalysts due to the two following properties:

1. As a ligand, tin exerts a strong trans effect hence facilitating the establishment of a vacant coordination site on the transition metal.

2. Tin (II) compounds readily undergo oxidative addition and subsequent reductive elimination.

Heterobimetallic tin complexes have been used in hydrogenation,126,129 dehydrogenation,125,126,130-132 Friedel-Crafts alkylation,133 polymerization134,135 and
hydroformylation. Of relevance to this dissertation is the thermal dehydrogenation of methanol by Ru/Sn heterobimetallic catalysts.

Scheme 3-2. Adapted from reference 128.

A series of Ru/Sn heterobimetallic complexes has been investigated as catalysts for the thermal dehydrogenation of methanol. A comparison of [RuCl₂{P(OMe)₃}₄], [RuCl(SnCl₃){P(OMe)₃}₄] and [Ru(SnCl₃)₂{P(OMe)₃}₃] reveals that the SnCl₃⁻ ligand is vital to the catalytic activity. [Ru(SnCl₃)₂{P(OMe)₃}₃] is the only complex that catalyzed the conversion of methanol to acetic acid or methyl acetate (due to the esterification of acetic acid).

The mechanism for the thermal dehydrogenation of methanol has been studied but is not yet fully understood. Carbonylation was ruled out as a possible route to methyl acetate since isotopically labeled ¹³CO was not incorporated into the product. The reaction path in Scheme 3-3 was then suggested based on previously observed
transformations. Dehydrogenation of methanol to formaldehyde is known to occur for Ru complexes.\textsuperscript{140} It has also been reported that H\textsubscript{2}CO can react with metals to give a methyl-formato complex which upon reductive elimination yields methyl formate.\textsuperscript{141} It is then suggested by Shinoda that methyl formate (which is observed in the reaction mixture) is isomerized to acetic acid.\textsuperscript{139} The isomerization is thought to go through a four center interaction (Scheme 3-3) which is favored by the soft and hard nature of Ru(II) and Sn(II) respectively. The methyl migration step is not evident, but would be stabilized.

Scheme 3-3. Adapted from reference 139.
by the resulting acetate bridge. Other evidence to support methyl migration is that ethyl and isopropyl formates also react to form propionic and isobutyric acids (or their esters) respectively.132

The Ru/Sn complexes investigated as catalysts for the dehydrogenation of methanol include CpRuP2X where X = SnF3, SnCl3 and SnBr3 and P2 = PPh3, PPh2Me and dppe.125 These catalysts were very selective during the dehydrogenation of methanol, forming only methyl acetate. For these catalysts Gusevskaya suggested that the Lewis acidic tin halide ligand rendered Ru more electrophilic. The increased electrophilicity of Ru will favor the β–hydride interaction and subsequent elimination (Eq 3.5) proposed as the rate determining step (Scheme 3-3).

\[
\text{Ru} \quad \text{O} \quad \text{SnCl}_3 \quad \text{Cp} \quad \text{Ru} \quad \text{H} \quad \text{SnCl}_3 \quad \text{Cp} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{O} \quad \text{C} \quad \text{H} \quad \text{H} \\
\quad \quad \text{slow} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad

\text{Methanol as a Chemical Feedstock}

Due to the ease of transportation, storage and reactivity, methanol has been utilized as a chemical feedstock in several industrial processes. Examples of these include the carbonylation of methanol to acetic acid, a chemical reagent used in the production of polymers, aspirin and solvents. The Monsanto process,142 commercialized in 1970, is based on the use of homogeneous Rh catalysts, while the Cativa process,143 commercialized in 1996, uses Ir catalysts. Combined, both catalytic cycles account for approximately 80% of the acetic acid produced worldwide.143
Another industrial example is the methanol to olefin or methanol to gasoline process patented in 1975 by Mobil. In this reaction methanol is converted to ethylene (Scheme 3-4) or propylene over solid acid catalysts. The light olefins can then be used to produce longer chain hydrocarbons. Because of increasing demands for light olefins as a chemical feedstock, this reaction continues to be an industrially interesting process.

\[
\text{CH}_3\text{OH} \rightarrow \text{n H}_2\text{O} \rightarrow \text{(CH}_2\text{)}_n \rightarrow \text{gasoline}
\]

Scheme 3-4. Adapted from reference 144.

The selective oxidation of methanol has also been of interest as a route to several important organic chemicals such as formaldehyde,\textsuperscript{145} methyl formate\textsuperscript{146} (MF) and dimethoxymethane\textsuperscript{147-150} (DMM). Due to the low toxicity, good solvent power, amphiphilic nature, low viscosity, low surface tension and high evaporation rate DMM has many industrial applications. DMM is utilized as a solvent in the cosmetic, pharmaceutical and paint industries as well as a chain length regulator during the preparation of ion exchange resins. Another recent application of DMM is that of an additive to diesel fuel.

Current Environmental Protection Agency (EPA) regulations require a 95% reduction in harmful emissions from diesel engines.\textsuperscript{151} When fully implemented in 2010 it is estimated that 2.6 million tons of smog-causing nitrogen oxide (NO\textsubscript{x}) emissions and 110,000 tons of particulate matter (PM) will be reduced each year. It is proposed that these reductions in smog and particulate matter will have a profound effect on our quality of life. An estimated 8,300 premature deaths, 5,500 cases of chronic bronchitis and 17,600 cases of acute bronchitis in children will also be prevented annually. It is also estimated that more than 360,000 asthma attacks and 386,000 cases of respiratory
symptoms in asthmatic children will be avoided every year. In addition, 1.5 million lost work
days, 7,100 hospital visits and 2,400 emergency room visits for asthma will be
prevented.\textsuperscript{151}

\textit{NO\textsubscript{x}} species are generated from nitrogen and oxygen under the high pressure and
temperature conditions in the engine. Diesel PM is a complex aggregate of solid and liquid material, the formation of which is not exactly understood. Currently pre- and post-combustion methods are being examined for reducing \textit{NO\textsubscript{x}} and PM emissions. One pre-combustion method uses reformulated diesel fuels containing oxygen rich additives such as certain alcohols, esters, glycol ethers and carbonates. DMM is one additive that has been investigated and shown to reduce PM and soot emission from diesel engines.

The commercial synthesis of DMM is performed using a two-step process involving oxidation of methanol to formaldehyde followed by the condensation of the methanol/formaldehyde mixtures to yield DMM. Due to increasing demands for DMM the direct conversion of methanol\textsuperscript{147-150} to DMM has been recently investigated as a possible replacement for the two step process. Rhenium oxides\textsuperscript{147,148} and heteropolyacids with Keggin structures\textsuperscript{149,150} have been reported to catalyze the selective oxidation of methanol vapor to DMM, typically at temperatures above 400K. Among these catalysts, SbRe\textsubscript{2}O\textsubscript{6}\textsuperscript{147,148} has the highest selectivity for DMM, converting 6.5 \% of the methanol feed at 573K with a selectivity as high as 92.5 \%.

Electrooxidation of methanol typically yields a complex mixture of products (Scheme 3-5), with the major product and selectivity dependent upon the reaction conditions.\textsuperscript{153-156} Product distributions have been determined in conjunction with studies on direct methanol fuel cells,\textsuperscript{22,30,153,155-160} using Pt black,\textsuperscript{153,157,158} Pt/Ru\textsuperscript{157,158} and
Pt/Nafion (Pt-SPE)\textsuperscript{155,156,159} anodes. The general trend is that the absence of water and lower methanol concentrations favor formaldehyde formation, with yields of DMM rising as the concentration of methanol increases. The presence of water favors formation of MF and/or complete oxidation to CO\textsubscript{2}.

\[
\begin{align*}
\text{CH}_3\text{OH} & \xrightarrow{-2e^-, -2H^+} \text{H}_2\text{CO} \xrightarrow{-2e^-, -2H^+} \text{HCOOH} \xrightarrow{-2e^-, -2H^+} \text{CO}_2 \\
\text{H}_2\text{C(OCH}_3\text{)}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HCOOCH}_3 + \text{H}_2\text{O}
\end{align*}
\]

Scheme 3-5. Adapted from reference 152.

**Electrochemical Synthesis of Organic Molecules**

Electrochemistry is a powerful technique capable of performing versatile and unique organic transformations. During electrochemical reactions, organic substrates can be activated by adding (reducing) or removing (oxidizing) electrons. The result of this process is the generation of radical anions or cations. Since these electrons are generated from the electrode, there is no reagent waste. Because of this electroorganic synthesis is often considered environmentally friendly.

The advantages of this technique are:

- The selectivity of the reaction can be influenced by the applied potential
- Reaction rate is influenced by the current density
- Reaction conditions are typically very mild
- Environmentally friendly, no need for chemical oxidizing or reducing agents

Disadvantages associated with electroorganic synthesis include:

- Special reactors and equipment, fortunately most of these are now commercially available
Electron transfer is a heterogeneous process, therefore electrodes with large surface area must be used so as to accelerate the reaction rate. Recovery of supporting electrolyte is often difficult and can be expensive.

The first notable application of electrochemistry to organic synthesis was reported in 1843 by Kolbe. During this reaction carboxylic acids are decarboxylated to give an acyloxy radical intermediate that rapidly dimerizes to form a hydrocarbon. Yields for Kolbe type electrolysis typically range from 50 – 90 %, remarkably high for a reaction generating an alkyl radical. Since the work of Kolbe was published, research into electrochemical synthetic transformations has been extensively studied. As a result of these studies some interesting reactions have been developed. Selected examples are shown in Eq. 3.6 – 3.9. It should be pointed out that the fluorination and reduction reactions (Eq 3.7 and 3.8) are unique to electrosynthesis.

\[
\begin{align*}
\text{Oxidation:} & \quad \text{H}_2 \quad \text{HO-C-} \quad \text{H}_2 \quad \text{PbO}_2 \text{ anode} \quad \text{H}_2\text{SO}_4, \text{H}_2\text{O} \quad \text{HOOC-C=} \quad \text{COOH} \\
\text{Fluorination:} & \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{SO}_2\text{Cl} \quad \text{HF} \quad \text{Ni anode} \quad \text{CF}_3 \quad \text{CF}_2 \quad \text{SO}_2\text{F} \\
\text{Reduction:} & \quad \text{Cu cathode} \quad \text{H}_2\text{O}, \text{H}_2\text{SO}_4 \quad \text{rearrangement} \quad \text{NH}_2 \quad \text{OH} \\
\text{Hydrogenation:} & \quad \text{Pb cathode} \quad \text{H}_2\text{O}, \text{H}_2\text{SO}_4 \quad \text{NH} 
\end{align*}
\]
Electrosynthesis of organic compounds is not limited to only laboratory scale preparations, but is also widely used for industrial applications. One example is the reduction of acrylonitrile to adiponitrile (Eq. 3.10), a chemical feedstock used in the synthesis of nylon. The actual reaction is very complicated, involving parallel pathways and competing products. The major side reactions can be limited, to yield adiponitrile selectively (90 %).

\[
2 \text{CH}_2=\text{CHCN} + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{NC(CH}_2\text{)}_4\text{CN} + 2 \text{OH}^- \quad (3.10)
\]

Table 3-2. TEMPO mediated electrooxidation of carbohydrates

<table>
<thead>
<tr>
<th>Substrate (^a)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Substrate Image]</td>
<td>![Product Image]</td>
<td>96</td>
</tr>
<tr>
<td>![Substrate Image]</td>
<td>![Product Image]</td>
<td>89</td>
</tr>
<tr>
<td>![Substrate Image]</td>
<td>![Product Image]</td>
<td>63</td>
</tr>
</tbody>
</table>

\(^a\) Electrolyses performed at 0.53 V vs SCE. Adapted from reference 163.
Apart from the direct electrochemical processes described above indirect electrochemical transformations are also used during the synthesis of organic compounds. An example relevant to this dissertation is the selective oxidation of carbohydrates with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (Table 3-2). Secondary hydroxyl groups are in most cases inert during the electrolysis. This selectivity allows the oxidation of carbohydrates to the corresponding carboxylic acids in moderate to excellent yields. The catalytically active species is the nitrosonium ion formed after the one-electron oxidation of TEMPO (Scheme 3-6). The mechanism proposed for the electrooxidation of carbohydrates, is the same mechanism proposed by de Nooy for the oxidation of alcohols under basic conditions. The initial step is the coordination of the alkoxy to the nitroso group. After β-hydride elimination the corresponding aldehyde is formed, the hydrate of which can be further oxidized to the carboxylic acid.
The electrochemical oxidation of organic molecules with TEMPO is of interest for industrial applications because:

1. TEMPO and its derivatives are cheap and easily prepared
2. TEMPO is easily recovered in quantitative yields after oxidation of polysaccharides
3. As an oxidant TEMPO is very selective
4. Reaction work up is easily performed

In 2002 and 2003 the McElwee-White group reported that Ru/Pt, Ru/Pd and Ru/Au heterobimetallic complexes can act as catalysts during the electrochemical oxidation of methanol.\textsuperscript{92,93,101} For these complexes the non-Ru metal center was shown to improve the catalytic properties as compared to the mononuclear model compounds \textit{CpRu(\eta^2\text{-}dppm)Cl} and \textit{CpRu(PPh_3)_2Cl}. Related beneficial effects of a Lewis acidic tin center in a thermal reaction had previously been reported for \textit{CpRu(PPh_3)_2(SnCl_3)} (\textit{20}), which selectively oxidizes methanol to methyl acetate at elevated temperatures.\textsuperscript{125,165}

In order to continue the study of Lewis acidic interactions during the electrochemical oxidation of methanol the catalytic properties of Ru/Sn complexes \textit{19} – \textit{26} (Figure 3-1) were studied. This chapter also describes the selective partial oxidation of methanol to dimethoxymethane using the Ru/Sn complexes \textit{CpRu(PPh_3)_2(SnCl_3)} (\textit{20}), (\textit{Ind})\textit{Ru(PPh_3)_2(SnCl_3)} (\textit{21}) and \textit{CpRu(TPPMS)_2(SnCl_3)} (\textit{23}).

**Synthesis**

**Synthesis of \textit{CpRu(TPPMS)_2Cl} (22)**

The literature procedure for the synthesis of \textit{CpRu(TPPMS)_2Cl}\textsuperscript{166} yielded a complex reaction mixture in which unreacted triphenylphosphine monosulfonate (TPPMS) and TPPMS oxide were the only identifiable compounds. Samples of \textit{22} were instead prepared by an alternate route involving substitution of \textit{PPh}_3 in \textit{CpRu(PPh_3)_2Cl}
(19) with TPPMS (Eq 3.11). The reaction of TPPMS with a slight excess of CpRu(PPh₃)₂Cl was performed in refluxing toluene. Complex 22 was isolated in excellent yields (90 %) as an orange, moderately air stable solid. The ³¹P{¹H} NMR spectrum of CpRu(TPPMS)₂Cl is very similar to that of CpRu(PPh₃)₂Cl, consisting of a singlet at 40 ppm.

**Figure 3-1. Structure of compounds 19 - 26**
Synthesis of CpRu(TPPMS)$_2$(SnCl$_3$) (23)

The Ru/Sn complex CpRu(TPPMS)$_2$(SnCl$_3$) was prepared in an analogous manner to CpRu(PPh$_3$)$_2$(SnCl$_3$)$^{125}$ by reacting 22 with a slight excess of SnCl$_2$ (Eq. 3.12) in ethanol. The insertion of Sn into the Ru-Cl bond is facile and the reaction is complete after one hour. The resulting bright yellow solid is moderately stable in air and in solutions of methanol and acetonitrile, but decomposes rapidly when dissolved in water. As expected from the NMR spectrum of CpRu(PPh$_3$)$_2$(SnCl$_3$),$^{125}$ the $^{31}$P{H} NMR spectrum of CpRu(TPPMS)$_2$(SnCl$_3$) consists of a singlet at 46 ppm with $^2J_{P-Sn} = 422$ Hz.

Before the synthesis of CpRu(TPPMS)$_2$Cl (22) and CpRu(TPPMS)$_2$(SnCl$_3$) (23) all electrochemical experiments in the McElwee-White lab were performed in the...
chlorinated solvents CH₂Cl₂ or DCE. CH₂Cl₂ or DCE had to be used because of the organic nature of the ligands used in complexes 3 – 5 and 8 – 14. These solvents have a low dielectric constant, and therefore a high ohmic resistance. Because of the resistance, a high concentration of supporting electrolyte has to be used in order to get a reasonable conductivity and electron transfer rate. In order to improve the electron transfer properties of the reactions being studied there has been a concerted effort to use more polar solvents such as methanol and water. As a result of this CpRu(TPPMS)₂Cl (22) and CpRu(TPPMS)₂(SnCl₃) (23) have been synthesized. Another reason for performing the electrochemical studies in water is to be able to compare these catalysts to the widely studied [(trpy)(bpy)Ru⁰(OH₂)]²⁺. As mentioned before the aquo ligand plays a crucial role in the catalytic cycle of [(trpy)(bpy)Ru⁰(OH₂)]²⁺, being deprotonated (Eq. 1.19 and 1.20) to form the catalytically active oxidant [(trpy)(bpy)Ru⁴⁺(O)]²⁺.

**Synthesis of CpRu(η²-dppm)(SnCl₃) (24)**

Complex 24 was prepared in an analogous manner to CpRu(η²-dppe)(SnCl₃) in high yields (85 %), by reacting CpRu(η²-dppm)Cl with SnCl₂ (Eq. 3.13). The ³¹P{¹H} NMR spectrum consists of a singlet at 8.3 ppm with tin satellites (²Jₚ-Sn = 385 Hz). This singlet is shifted upfield by approximately 6 ppm relative to CpRu(η²-dppm)Cl. The ¹H NMR spectrum exhibits a shift downfield for the methylene and cyclopentadienyl protons of approximately 0.3 ppm.

![Synthesis reaction](image)
Synthesis of CpRu($\eta^2$-dppp)(SnCl$_3$) (26)

CpRu($\eta^2$-dppp)(SnCl$_3$) (26) was prepared in an analogous manner to CpRu($\eta^2$-dppe)(SnCl$_3$) in high yields (85%), by reacting CpRu($\eta^2$-dppe)Cl with SnCl$_2$ (Eq. 3.14). The $^{31}$P{$^1$H} NMR spectrum consists of a singlet at 33.9 ppm, shifted upfield by approximately 5 ppm relative to CpRu($\eta^2$-dppp)Cl. Complex 26 has a low solubility in the NMR solvents used; because of this no tin satellites were observed. The $^1$H NMR spectrum exhibits a shift downfield of approximately 0.4 ppm for the cyclopentadienyl protons. A similar shift downfield was observed for CpRu($\eta^2$-dppe)(SnCl$_3$) (24).

The Ru/Sn complexes CpRu(PPh$_3$)$_2$(SnCl$_3$) (20), (Ind)Ru(PPh$_3$)$_2$(SnCl$_3$) (21) and CpRu(TPPMS)$_2$(SnCl$_3$) (23) are coordinatively saturated. Before the methanol oxidation reaction can occur, there has to be ligand dissociation and methanol coordination. Phosphine dissociation has been invoked in numerous mechanisms, and it is this reason why phosphine ligands are often used in metal catalysts. Gusevskaya proposed that phosphine dissociation is a key step during the thermal dehydrogenation of methanol with CpRu(PPh$_3$)$_2$(SnCl$_3$) (20). To probe if a vacant coordination site on Ru is needed, a series of Ru/Sn complexes containing the bidentate phosphines dppm, dppe and dppp was synthesized. If phosphine dissociation occurs during the catalysis the chelate effect of the
bidentate phosphines should result in a decrease in the reaction rate of 24 – 26 relative to 20.

NMR Data

$^1$H and $^{31}$P{ $^1$H} NMR spectrosopies were utilized to determine the ligand arrangement about the Ru center. Selected NMR data are presented in Table 3-3. Only one singlet is observed in the $^{31}$P{ $^1$H} NMR spectra of these complexes suggesting that the phosphine ligands are in similar chemical environments. The proton NMR spectra of the complexes exhibit characteristic peaks for the phenyl, indenyl and cyclopentadienyl groups.

The electron density at the Ru metal center can be varied by changing the peripheral ligands. The chemical shifts of the cyclopentadienyl protons were predictable based on the Lewis acidity of the additional ligands. When the Lewis acidity of the ligands is increased, the Ru metal center will become electron poor and the Cp protons will become deshielded. By being deshielded the Cp protons now experience more of the applied magnetic field and shift to a higher frequency. Hence for CpRu(PPh$_3$)$_2$(X) the Cp resonance of X = SnCl$_3$ (4.54 ppm) > Cl (4.10 ppm)

Table 3-3. Selected NMR data for complexes 19 – 26

<table>
<thead>
<tr>
<th>Complex$^a$</th>
<th>Solvent</th>
<th>Cp$^1$H NMR (ppm)</th>
<th>$^{31}$P{ $^1$H} NMR (ppm)</th>
<th>$^2$J$_{P,Sn}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh$_3$)$_2$Cl (19)</td>
<td>CDCl$_3$</td>
<td>4.10</td>
<td>39.9</td>
<td></td>
</tr>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (20)</td>
<td>CDCl$_3$</td>
<td>4.54</td>
<td>45.2</td>
<td>435</td>
</tr>
<tr>
<td>(Ind)Ru(PPh$_3$)$_2$(SnCl$_3$) (21)</td>
<td>CDCl$_3$</td>
<td>48.8</td>
<td>363</td>
<td></td>
</tr>
<tr>
<td>CpRu(TPPMS)$_2$Cl (22)</td>
<td>DMSO-d$_6$</td>
<td>4.07</td>
<td>40.1</td>
<td></td>
</tr>
<tr>
<td>CpRu(TPPMS)$_2$(SnCl$_3$) (23)</td>
<td>CD$_3$OD</td>
<td>4.65</td>
<td>46.0</td>
<td>422</td>
</tr>
<tr>
<td>CpRu($\eta^2$-dppm)(SnCl$_3$) (24)</td>
<td>CDCl$_3$</td>
<td>5.08</td>
<td>8.3</td>
<td>385</td>
</tr>
<tr>
<td>CpRu($\eta^2$-dppm)(SnCl$_3$) (25)</td>
<td>CDCl$_3$</td>
<td>4.89</td>
<td>77.5</td>
<td>397</td>
</tr>
<tr>
<td>CpRu($\eta^2$-dppp)(SnCl$_3$) (26)$^b$</td>
<td>CDCl$_3$</td>
<td>4.84</td>
<td>33.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All NMR data obtained at room temperature. $^b$ Low solubility no $^2$J$_{P,Sn}$ satellites observed.
Cyclic Voltammetry

Since Sn(II) is not redox active within the solvent window of these experiments, it is assumed that any observed redox processes would be due to oxidation of the Ru metal center. Cyclic voltammograms of complexes 19 - 26 in solutions of methanol (0.50 to 1.40 V) or DCE (0.50 to 1.60 V) each display a single oxidation wave in the potential range of the experiments. This oxidation process has previously been assigned for the monometallic complexes CpRu(PPh₃)₂Cl¹⁶⁷ and (Ind)Ru(PPh₃)₂Cl¹⁶⁸ (Table 3-4) as the reversible one-electron oxidation of the Ru metal center. Based on this assignment the oxidation waves observed for complexes 19 - 26 have been assigned to the Ru(II/III) couple.

Table 3-4. Formal potentials of complexes 19 – 26

<table>
<thead>
<tr>
<th>Complexa</th>
<th>E&lt;sub&gt;pa&lt;/sub&gt; (V)</th>
<th>E&lt;sub&gt;1/2&lt;/sub&gt; b (V)</th>
<th>ΔE&lt;sub&gt;p&lt;/sub&gt; (mV)</th>
<th>i&lt;sub&gt;pa&lt;/sub&gt; / i&lt;sub&gt;pc&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh₃)₂Cl (19)</td>
<td>0.87</td>
<td>0.82</td>
<td>90</td>
<td>1.03</td>
</tr>
<tr>
<td>CpRu(PPh₃)₂(SnCl₃) (20)</td>
<td>1.48</td>
<td>1.44</td>
<td>85</td>
<td>0.92</td>
</tr>
<tr>
<td>(Ind)Ru(PPh₃)₂(SnCl₃) (21)</td>
<td>1.39</td>
<td>1.34</td>
<td>106</td>
<td>0.95</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂Cl (22)</td>
<td>0.93</td>
<td>0.89</td>
<td>104</td>
<td>1.06</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂Cl (22)c</td>
<td>0.79</td>
<td>0.73</td>
<td>90</td>
<td>0.94</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂(SnCl₃) (23)</td>
<td>1.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(TPPMS)₂(SnCl₃) (23)c</td>
<td>1.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(η²-dppm)(SnCl₃) (24)d</td>
<td>1.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(η²-dppe)(SnCl₃) (25)d</td>
<td>1.53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(η²-dppp)(SnCl₃) (26)d</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(PPh₃)₂Clf</td>
<td>0.929</td>
<td>0.869</td>
<td>120</td>
<td>1.00</td>
</tr>
<tr>
<td>(Ind)Ru(PPh₃)₂Clf</td>
<td>0.69</td>
<td>0.69</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>

a All potentials obtained in 0.7 M TBAT / DCE unless otherwise specified.
b E<sub>1/2</sub> reported for reversible waves. c Potential obtained in 0.1 M TBAT/MeOH.
d Potential obtained in 0.7 M TBAT/CH₂Cl₂. e Reference 167, potential originally reported vs SCE. f Reference 168, potential originally reported vs SCE.

When analyzed in DCE, the one-electron oxidation of CpRu(PPh₃)₂Cl (Figure 3-2) at 0.82 V and CpRu(TPPMS)₂Cl at 0.89 V are chemically reversible with i<sub>pa</sub> / i<sub>pc</sub> ≈ 1 (Table 3-4). When small amounts of methanol are added to the DCE solutions, no
significant change is observed in the cyclic voltammograms of 19 and 22 at potentials less than 1.60 V.

Figure 3-2. Cyclic voltammograms of 19 under nitrogen in 3.5 mL of DCE / 0.7 M TBAT; glassy carbon working electrode; Ag/Ag+ reference electrode; 50 mV/s scan rate, solutions as specified in figure. Adapted from reference 169.

The CV of CpRu(PPh₃)₂(SnCl₃) (20) in DCE exhibits a reversible Ru(II/III) couple at 1.44 V (Figure 3-3). The Ru(II/III) couple is shifted by approximately 600 mV positive with respect to the corresponding Ru(II/III) wave of CpRu(PPh₃)₂Cl (19). This positive shift is consistent with the electron withdrawing SnCl₃⁻ ligand rendering the Ru in complex 20 electron-poor relative to that of complex 19. Sn(II) is not redox active within the solvent window (-0.50 – 2.5 V vs. NHE) for these experiments. In the presence of methanol, there is a significant increase in the current that coincides with the oxidation of the Ru metal center (Figure 3-3). This effect is indicative of an electrocatalytic oxidation process.
The CV of 21 is very similar to that of complex 20, exhibiting a reversible Ru(II/III) couple in DCE (Table 3-4). The Ru(II/III) couple however, at 1.34 V is 100 mV negative with respect to the analogous Ru(II/III) couple of complex 20. This shifting of the II/III couple\textsuperscript{168} is due to additional electron density associated with the indenyl ligand. The current rise from electrooxidation of methanol by 21 also coincides with its Ru(II/III) redox wave, as evidenced by a increase in the current at 1.34 V in the presence of methanol.

The CV of 23 exhibits a single irreversible wave in DCE at 1.58 V (Table 3-4). This irreversible redox wave has been assigned to the oxidation of the metal center from Ru(II) to Ru(III). The single irreversible Ru(II/III) wave is also observed in methanol at 1.29 V, shifted by approximately 290 mV relative to the redox potential in DCE. Cyclic voltammetry of 23 in DCE exhibits a significant increase in the catalytic current at the
Ru(II/III) wave when methanol is introduced. A similar catalytic effect was observed for 20 and 21.

Methylene chloride solutions of CpRu(\(\eta^2\)-dppm)(SnCl\(_3\)) (24), 
CpRu(\(\eta^2\)-dppe)(SnCl\(_3\)) (25) and CpRu(\(\eta^2\)-dppp)(SnCl\(_3\)) (26) each exhibit a single irreversible oxidation wave at 1.54, 1.53 and 1.52 V respectively. When methanol is introduced the expected catalytic current is observed at the Ru(II/III) oxidation wave. The oxidation waves for 24, 25 and 26 (Table 3-4) are only 20 mV apart. This indicates that the structurally similar complexes also have similar electronic configuration.

Electrochemical Oxidation of Methanol

The cyclic voltammograms of the Ru-SnCl\(_3\) complexes all exhibit a significant current increase in the presence of methanol. As mentioned before, this increase in anodic current in the presence of an alcohol is characteristic of the catalytic electrooxidation of alcohols. The onset of this electrocatalytic current for the heterobimetallic complexes coincides with the oxidation of the metal center from Ru(II) to Ru(III). A similar current increase was observed in the CVs of the dpdm bridged complexes CpRu(PPh\(_3\))(\(\mu\)-Cl)(\(\mu\)-dppm)PtCl\(_2\) (3), CpRu(PPh\(_3\))(\(\mu\)-Cl)(\(\mu\)-dppm)PdCl\(_2\) (4) and CpRu(PPh\(_3\))(Cl)(\(\mu\)-dppm)AuCl (5) when methanol was introduced. For complexes 3 and 4 the increase in the anodic current coincides with the oxidation of the Pt and Pd metal center. For the Ru/Au complex the onset of the catalytic current coincides with the Ru(III/IV) redox wave. In contrast to the CVs for the heterobimetallic complexes above, the CV of the Ru model compound CpRu(PPh\(_3\))\(_2\)Cl (19) (Figure 3-2) exhibits no significant current increase when methanol is introduced.

In order to assess the electrocatalytic ability of the Ru-SnCl\(_3\) complexes, the electrochemical oxidation of methanol was performed at 1.7 V in 0.7 M TBAT / DCE.
(Table 3-5). The anodic potential of 1.7 V was chosen during the catalytic studies of 3, and is the potential at which the catalytic current begins for complex 3. For comparison purposes initial catalytic studies of 19 – 21 and 24 – 26 were performed at 1.7 V. At 1.7 V, the Ru in all complexes studied will be in the +3 oxidation state and within the catalytic current region.

Bulk electrolysis data for the oxidation of methanol with CpRu(PPh₃)₂Cl (19), CpRu(PPh₃)₂(SnCl₃) (20), (Ind)Ru(PPh₃)₂(SnCl₃) (21), CpRu(η²-dppm)(SnCl₃) (22), CpRu(η²-dppe)(SnCl₃) (23) and CpRu(η²-dppp)(SnCl₃) (24) are presented in Table 3-5. Differences between the activities of the complexes can be seen in the turnover numbers, current efficiencies and product ratios. The chelating phosphines significantly inhibited the catalytic activity of the complexes. At an anodic potential of 1.7 V, CpRu(η²-dppm)(SnCl₃) (22), CpRu(η²-dppe)(SnCl₃) (23) and CpRu(η²-dppp)(SnCl₃) (24) exhibited little to no activity for the methanol oxidation reaction. The heterobimetallic complexes 22 – 24 are less active than the Ru model compound CpRu(PPh₃)₂Cl (19). The Ru model compound CpRu(PPh₃)₂Cl was more active, forming significantly more oxidation products. The inactivity of the complexes with bidentate phosphine suggests that a vacant coordination site on the Ru metal center is critical in the oxidation reaction.
Table 3-5. Bulk electrolysis data for the oxidation of methanol by 19 - 21 and 24 - 26

<table>
<thead>
<tr>
<th>Complex</th>
<th>Anodic Potential (V)</th>
<th>TON(^b)</th>
<th>Current Efficiency(^c) (%)</th>
<th>DMM (10(^{-5}) moles)</th>
<th>MF (10(^{-5}) moles)</th>
<th>Product Ratio (DMM/MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh(_3))(_2)Cl (19)</td>
<td>1.70</td>
<td>2.60 ± 0.15</td>
<td>7.3 ± 0.5</td>
<td>6.84 ± 0.34</td>
<td>2.26 ± 0.11</td>
<td>3.0 ± 1.0</td>
</tr>
<tr>
<td>CpRu(PPh(_3))(_2)(SnCl(_3)) (20)</td>
<td>1.70</td>
<td>3.37 ± 0.20</td>
<td>13.1 ± 0.7</td>
<td>8.65 ± 0.43</td>
<td>3.15 ± 0.16</td>
<td>2.7 ± 1.0</td>
</tr>
<tr>
<td>(Ind)Ru(PPh(_3))(_2)(SnCl(_3)) (21)</td>
<td>1.70</td>
<td>4.69 ± 0.28</td>
<td>17.9 ± 1.0</td>
<td>12.1 ± 0.60</td>
<td>4.34 ± 0.22</td>
<td>2.8 ± 1.0</td>
</tr>
<tr>
<td>CpRu((\eta^2)-dppm)(SnCl(_3)) (24)</td>
<td>1.70</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CpRu((\eta^2)-dppe)(SnCl(_3)) (25)</td>
<td>1.70</td>
<td>0.53 ± 0.03</td>
<td>0.78 ± 0.09</td>
<td>1.85 ± 0.09</td>
<td>0</td>
<td>∞</td>
</tr>
<tr>
<td>CpRu((\eta^2)-dppp)(SnCl(_3)) (26)</td>
<td>1.70</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CpRu(PPh(_3))(_2)Cl (19)</td>
<td>1.55</td>
<td>1.00 ± 0.06</td>
<td>5.6 ± 0.2</td>
<td>2.69 ± 0.13</td>
<td>0.81 ± 0.04</td>
<td>3.3 ± 1.0</td>
</tr>
<tr>
<td>CpRu(PPh(_3))(_2)(SnCl(_3)) (20)</td>
<td>1.55</td>
<td>3.00 ± 0.20</td>
<td>18.2 ± 0.5</td>
<td>9.98 ± 0.50</td>
<td>0.52 ± 0.03</td>
<td>19.2 ± 1.1</td>
</tr>
<tr>
<td>(Ind)Ru(PPh(_3))(_2)(SnCl(_3)) (21)</td>
<td>1.55</td>
<td>2.80 ± 0.18</td>
<td>16.3 ± 0.5</td>
<td>9.07 ± 0.45</td>
<td>0.73 ± 0.04</td>
<td>12.4 ± 1.1</td>
</tr>
</tbody>
</table>

\(^a\) All electrolyses performed in 0.7 M TBAT / DCE with 10 mM catalyst, 0.35 M methanol for 5 hours unless otherwise specified.  
\(^b\) Moles of product formed per mole of catalyst.  
\(^c\) Calculated using Eq. 1.21.
For the complexes 19 – 21 with the monodentate phosphines the heterobimetallic complexes are more active toward methanol oxidation. CpRu(PPh3)2(SnCl3) (20) and (Ind)Ru(PPh3)2(SnCl3) (21) form greater quantities of oxidation products than the Ru model compound CpRu(PPh3)2Cl (19). The greater reactivity is also observed in the current efficiency of these complexes during the reaction. The Ru-SnCl3 complexes have a higher current efficiency and therefore convert a larger portion of the charge passed into products.

To probe the effect of the anodic potential on the electrochemical reaction, the oxidation of methanol with CpRu(PPh3)2Cl (19), CpRu(PPh3)2(SnCl3) (20) and (Ind)Ru(PPh3)2(SnCl3) (21) was also investigated at 1.55 V (Table 3-5). At 1.55 V, the Ru metal center in all three catalysts will be in the Ru(III) oxidation state during the catalysis (Table 3-4). As expected, decreasing the anodic potential has a profound effect on the amounts of products and the TON (Table 3-5). Significantly less products are formed at the lower potential when the electrolysis is performed with 19, 20 and 21.

All three complexes CpRu(PPh3)2Cl (19), CpRu(PPh3)2(SnCl3) (20) and (Ind)Ru(PPh3)2(SnCl3) (21) produce more DMM than MF as evidenced by the large product ratios (Table 3-5). Reducing the anodic potential has a significant effect on the selectivity (product ratio) of the reaction when the heterobimetallic complexes are used as catalysts. For CpRu(PPh3)2(SnCl3) (20) the product ratio increases from 2.07 to 19.2 when the potential is decreased from 1.70 to 1.55 V. A similar effect is observed for (Ind)Ru(PPh3)2(SnCl3) (21); when the potential is decreased the product ratio is increased from 2.79 to 12.4. When the Ru model compound is used as the catalyst, the ratio of
DMM:MF is independent of the anodic potential, remaining virtually unchanged when the potential is decreased.

Bulk electrolyses of the sulfonated complexes 22 and 23 were performed in methanol as the solvent. The electrolysis in methanol was also studied at two anodic potentials. Due to the limited anodic range of methanol, the anodic potentials used during these experiments are 1.40 V and 1.25 V. Similar to the catalysis in DCE and CH₂Cl₂, the electrooxidation of neat methanol resulted in the formation of DMM and MF. The same trends observed during the electrooxidation of methanol in DCE are also observed in neat methanol (Table 3-6):

- DMM formation is favored over MF, by both complexes
- The heterobimetallic complex is much more active than the Ru model compound
- When CpRu(TPPMS)₂(SnCl₃) is used as the catalyst, lowering the anodic potential increases the ratio of DMM:MF

When the electrolysis is performed in methanol instead of the less polar DCE or CH₂Cl₂, there is a significant increase in the current efficiency, amounts of products formed and TON (Table 3-6). This increase in catalytic activity has been attributed to the improved

Table 3-6. Bulk electrolysis data for the oxidation of methanol by 22 and 23

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Anodic Potential (V)</th>
<th>TONb</th>
<th>Current Efficiencyc (%)</th>
<th>DMM (10⁻⁵ moles)</th>
<th>MF (10⁻⁵ moles)</th>
<th>Product Ratio (DMM/MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(TPPMS)₂Cl (22)</td>
<td>1.25</td>
<td>13.4 ± 0.9</td>
<td>63.2 ± 2.3</td>
<td>46.9 ± 2.34</td>
<td>0</td>
<td>∞</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂(SnCl₃) (23)</td>
<td>1.25</td>
<td>33.4 ± 2.3</td>
<td>89.4 ± 5.6</td>
<td>117 ± 5.85</td>
<td>0</td>
<td>∞</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂Cl (22)</td>
<td>1.40</td>
<td>15.1 ± 1.0</td>
<td>76.9 ± 2.6</td>
<td>52.1 ± 2.60</td>
<td>0.75 ± 0.04</td>
<td>69.5 ± 1.1</td>
</tr>
<tr>
<td>CpRu(TPPMS)₂(SnCl₃) (23)</td>
<td>1.40</td>
<td>40.0 ± 2.6</td>
<td>90.1 ± 6.7</td>
<td>127 ± 6.35</td>
<td>13.0 ± 0.65</td>
<td>9.8 ± 1.0</td>
</tr>
</tbody>
</table>

a All electrolyses performed in 0.1 M TBAT / MeOH with 10mM catalyst for 5 hours.
b Moles of product formed per mole of catalyst. c Calculated using Eq. 1.21.
electron transfer kinetics and to the higher concentration of substrate. The
electrooxidation of methanol with CpRu(TPPMS)_2Cl (22) and CpRu(TPPMS)_2(SnCl_3) (23) at 1.25 V resulted in the selective formation of DMM.

As mentioned before, the electrochemical oxidation of methanol is a complicated reaction (Scheme 3-5) that often forms multiple stable products (eg. H_2CO, HCOOH, CO, H_2C(OCH_3)_2 and HCOOCH_3). To the best of my knowledge this is the first time that the electrooxidation of methanol resulted in a single oxidation product. When compared to the high temperature synthesis of DMM (Table 3-7), the electrochemical oxidation of methanol is a promising alternative for the synthesis of DMM.

Table 3-7. Selective partial oxidation of methanol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Conditions</th>
<th>DMM Selectivity (%)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_4PVMo_{11}O_{40} / SiO_2(^a)</td>
<td>493 K, 4 kPa CH_3OH, 9 kPa O_2</td>
<td>58.1</td>
<td>68</td>
</tr>
<tr>
<td>SbRe_2O_6(^b)</td>
<td>573 K, MeOH / O_2 = 4.0 / 9.7 (mol %)</td>
<td>92.5</td>
<td>6.5</td>
</tr>
<tr>
<td>CpRu(TPPMS)_2Cl (22)</td>
<td>1.25 V, 0.1 M TBAT / MeOH</td>
<td>100</td>
<td>63.2(^c)</td>
</tr>
<tr>
<td>CpRu(TPPMS)_2(SnCl_3) (23)</td>
<td>1.25 V, 0.1 M TBAT / MeOH</td>
<td>100</td>
<td>89.4(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Reference 150. \(^b\) Reference 148. \(^c\) Current efficiency (Eq. 1.21).

Electrochemical Oxidation of Wet Methanol

The CVs of the heterobimetallic complexes 20 (Figure 3-3), 21 and 23 all display a slight increase in the catalytic current when small amounts of water are added to the reaction mixtures. It should be noted that all of the samples contain some water due to the condensation of methanol with formaldehyde to generate DMM (Scheme 3-5). The effect of additional water on the electrocatalytic reaction was probed by introducing 5 µL of water before starting the electrolysis. In DCE the addition of water has a profound
effect on the selectivity of the reaction. The product ratio for the oxidation of “wet”
methanol is lower than the corresponding electrolysis in “dry” methanol (Table 3-8). The
addition of water therefore favors the formation of MF. A similar effect was previously
described for heterogenous\textsuperscript{148} and similar ruthenium\textsuperscript{92,93} catalysts.

Table 3-8. Bulk electrolysis data for the oxidation of wet methanol by \textbf{20}, \textbf{21} and \textbf{23}

<table>
<thead>
<tr>
<th>Complex\textsuperscript{a}</th>
<th>Anodic Potential (V)</th>
<th>TON\textsuperscript{b}</th>
<th>Current Efficiency\textsuperscript{c} (%)</th>
<th>DMM \textsuperscript{(10^{-5} moles)}</th>
<th>MF \textsuperscript{(10^{-5} moles)}</th>
<th>Product Ratio (DMM / MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CpRu(PPh}<em>{3}\text{)}</em>{2}(\text{SnCl}_{3}) (20)</td>
<td>1.55</td>
<td>2.50 ± 0.14</td>
<td>17.2 ± 0.5</td>
<td>6.45 ± 0.32</td>
<td>2.30 ± 0.11</td>
<td>2.8 ± 1.0</td>
</tr>
<tr>
<td>\text{(Ind)Ru(PPh}<em>{3}\text{)}</em>{2}(\text{SnCl}_{3}) (21)</td>
<td>1.55</td>
<td>2.90 ± 0.16</td>
<td>20.7 ± 0.6</td>
<td>6.67 ± 0.33</td>
<td>3.48 ± 0.17</td>
<td>1.9 ± 1.0</td>
</tr>
<tr>
<td>\text{CpRu(TPPMS)}<em>{2}(\text{SnCl}</em>{3}) (23)\textsuperscript{d}</td>
<td>1.25</td>
<td>15.3 ± 0.9</td>
<td>74.2 ± 3.1</td>
<td>42.1 ± 2.10</td>
<td>11.5 ± 0.57</td>
<td>3.7 ± 1.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All electrolyses performed in 0.7 M TBAT / DCE with 0.35 M methanol and 5.0 μL H\textsubscript{2}O for 5 hours unless otherwise specified. \textsuperscript{b} Moles of product formed per mole of catalyst. \textsuperscript{c} Calculated using Eq. 1.21. \textsuperscript{d} Electrolyses performed in 0.1 M TBAT/MeOH with 5.0 μL H\textsubscript{2}O for 5 hours.

Methyl formate formation is also favored in “wet” vs “dry” methanol when the
electrolysis is performed in methanol with \text{CpRu(TPPMS)}_{2}(\text{SnCl}_{3}) (23). There is
however a significant decrease in the TON and current efficiency of the catalyst
(Table 3-8). During the synthesis of \text{CpRu(TPPMS)}_{2}(\text{SnCl}_{3}), it was observed that this
complex was very unstable in aqueous solutions. The decrease in TON and current
efficiency is probably due to a shorter catalyst lifetime in aqueous solutions. This
premise is supported by \textsuperscript{31}P\textsubscript{\{\textsuperscript{1}H\}} NMR that revealed more TPPMS oxide in the “wet”
solutions than in the “dry” solutions. \text{CpRu(PPh}_{3}\text{)}_{2}(\text{SnCl}_{3}) and \text{(Ind)Ru(PPh}_{3}\text{)}_{2}(\text{SnCl}_{3}) are
also unstable in solutions containing water. The low solubility of water in DCE probably
accounts for why no significant change in the TON and current efficiency of 
CpRu(PPh$_3$)$_2$(SnCl$_3$) and (Ind)Ru(PPh$_3$)$_2$(SnCl$_3$) was observed.

**Electrochemical Oxidation of Dimethoxymethane**

The electrooxidation of DMM was studied in order to test the competency of DMM as an intermediate on the pathway to methyl formate. Control experiments have established that the electrooxidation of DMM in DCE does not proceed in the absence of catalyst at a potential of 1.70 V. The CV of CpRu(PPh$_3$)$_2$(SnCl$_3$) (20) exhibits no catalytic current in the presence of DMM. After 5 hours of electrolysis at 1.7 V complex 20 formed 6.64 x 10$^{-5}$ moles of MF with a current efficiency of 14.3 %. These results indicate that DMM could be an intermediate during the oxidation of methanol to MF.

**Summary**

A series of heterobimetallic complexes containing a Ru-Sn metal bond were synthesized and characterized. The catalytic activity of these complexes was then investigated during the electrochemical oxidation of methanol. The catalytic activity of these complexes is sensitive to the ligands coordinated to ruthenium. Complexes containing a bidentate phosphine (24 – 26), display little to no catalytic activity (at an anodic potential of 1.7 V) during the electrolysis of methanol. This supports the premise that a vacant coordination site on Ru is critical to the electrooxidation reaction.

Complexes containing a monodentate phosphine (19 – 23), catalyze the electrochemical oxidation of methanol to DMM and MF. The Ru/Sn catalysts 20, 21 and 23 favor the formation of DMM; this selectivity can be increased by lowering the anodic potential. The electrooxidation of methanol is more efficient and selective for the TPPMS complexes 22 and 23, which allow the oxidation to be performed in methanol.
The partial oxidation of methanol to DMM was achieved selectively (100%) and efficiently (89.4%) with CpRu(TPPMS)₂(SnCl₃) (23).

The addition of water to the DCE and methanol solutions favors the formation of MF. In methanol, the presence of water increases the decomposition rate of the catalyst. With a shorter catalyst lifetime there is a significant decrease in the current efficiency and amount of products when water is added to the methanol solutions. Due to the low solubility of water in DCE, the catalyst lifetime is not affected by the addition of water to the DCE solutions.
CHAPTER 4
CHEMICALLY MODIFIED ELECTRODES CONTAINING IMMOBILIZED
RUTHENIUM/TIN HETEROBIMETALLIC COMPLEXES

Introduction

Electrochemistry is a powerful and versatile method for the synthesis of organic molecules. Transition metals are often used as catalysts / mediators to increase the reaction rates of these electrochemical reactions. As with most catalytic cycles involving transition metals, for commercial applications there is a desire to recycle the catalyst. One method of achieving this is by attaching the catalyst to the electrode surface. These chemically modified electrodes (CME) have an extensive history, and excellent reviews on their application have been published. In this chapter, electrodes modified with cationic ruthenium complexes will be prepared and studied.

Nafion®

Nafion® is a fluorinated polymer (Figure 4-1) consisting of a fluorocarbon backbone and side chains that terminate in an anionic sulfonate site. In the commercially available membranes, the charge is typically balanced with proton or sodium ions.

\[
\left[ \left( \text{CF}_2\text{CF}_2 \right)_n \text{CF}_2\text{CF}^- \right]_m \quad \text{OCF}_2\text{FOCF}_2\text{CF}_2\text{SO}_3^- \quad \text{CF}_3
\]

Figure 4-1. Structure of Nafion® where \(5 \leq n \leq 7\) and \(m\) is approximately 1000. Adapted from reference 173.

Nafion® was developed by DuPont in the early 1960s for use in chlor-alkali cells and was the first ionomer (synthetic polymer with ionic properties) ever synthesized. Other
applications of Nafion® include as a solid polymer electrolyte in fuel cells and batteries and a selective drying or humidifying agent for gases. Nafion® is also used as a super-acid catalyst in the production of fine chemicals.

As an ionic derivative of Teflon®, Nafion® has some unique properties:

- Mechanically stable and very resistant to chemical attack.
- High working temperatures, stable up to 230 °C.
- Ion-conductive, able to function as a cation exchange resin.
- Super-acid catalyst, readily donating protons due to the stabilizing effect of the electron withdrawing fluorinated backbone on the sulfonic acid.
- Nafion® is very selectively and highly permeable to water. The sulfonic acid groups in Nafion® have a very high water of hydration, so they very efficiently absorb water.

Extensive research has been performed on the structure of Nafion® membranes.175 As a result of this research Nafion® membranes are commonly considered as segregated domains containing hydrophobic (fluorocarbon) and hydrophilic (hydrated sulfonate) regions (Figure 4-2). When hydrated the SO3⁻ headgroups are thought to form water containing clusters approximately 40 Å in diameter. These clusters are then connected within the hydrophobic matrix by short channels 10 Å in diameter. It is from this ‘inverted micelle’ structure that Nafion® derives the exceptional ion selectivity and cation transport properties.

**Nafion® Supported Metal Catalysts**

Because of its stability and cation exchange properties, Nafion® has also been studied as a support for metal catalysts. Supported complexes are formed by covalently or electrostatically immobilizing metal species into a heterogeneous matrix. Typically the heterogeneous materials that are used as supports can be placed into three categories:
1. Inorganic matrix containing surface active hydroxyl groups such as Al₂O₃ and SiO₂
2. Organic polymers containing a pendant ligand such as polystyrene
3. Ion exchange membranes such as Nafion® and polyaniline

Figure 4-2. Cluster-network model for hydrated Nafion®. Adapted from reference 176.

The concept of immobilizing a soluble metal complex by attaching it to solid support was first introduced over thirty years ago. Even so this methodology still attracts considerable interest from the scientific community. The sustained interest in supported metal complexes is due to the distinct advantages of “heterogenized” complexes over traditional homogeneous species. Advantages of supported metal complexes include an increased reactivity and selectivity along with recyclability, stability and an ease of separation, inherent to heterogeneous systems.

As a result of the advantages listed above, supported metal complexes have been investigated for possible applications in numerous fields. Of these applications catalysis has received the most attention, especially for the synthesis of fine chemicals. The first example of a Nafion® supported metal catalyst was published in 1978 by Meidar,¹⁷⁷ who demonstrated that a Hg impregnated Nafion® membrane could catalyze the hydration of alkynes. This catalyst was easily separated from the mixture but upon reuse there was some loss of activity.¹⁷⁷ Since this report there have been several attempts at designing active Nafion® supported metal species as catalysts for organic synthesis.
With properties of an excellent support, a few cationic metal complexes have been successfully immobilized onto Nafion. In several instances catalytic activities comparable to homogeneous conditions have been observed for the Nafion® supported catalysts. In 1999 Seen reported the increased catalytic activity exhibited by a Nafion® supported Pd(II) complex during the methoxycarbonylation of ethene. Because this catalyst is limited by diffusion, a combination of low catalyst loading and high dispersion of Nafion® was used in order to increase the activity. When this Nafion® supported catalyst was used in water it was significantly more active than the unsupported catalyst, having a turnover frequency comparable to commercial applications.

**Chemically Modified Electrodes**

Chemically modified electrodes (CME) result from the modification of a conductive substrate to produce an electrode with properties that differ from that of the unmodified substrate. These electrodes have been studied from the mid-1960s when French investigated the behavior of a ferrocene modified carbon paste electrode (CPE). The composite nature of CPE makes these electrodes among the easiest to modify by simply admixing a third component with the graphite and binder. Other methods of preparing modified electrodes include adsorption, covalent attachment and coating the electrode with multi-layer films. CME are typically designed for applications such as catalysis or a sensitive sensor. An excellent review on the analytical application of sensors containing CME was published in 2003. Sensor applications of CME are beyond the scope of this dissertation and will not be reviewed further.

Catalysis can be performed with CME if favorable conditions are present for the flow of electrons between the electrode and the species to be oxidized or reduced. Scheme 4-1 shows a diagram of the reduction of A by the reduced form of the catalyst Q.
The reduction can occur within the film or at the film/solution interface by means of the reaction paths shown.

Scheme 4-1. Adapted from reference 181.

**Electrodes Modified with Ruthenium Complexes**

CME can be used to catalyze several reactions such as CO reduction, Cr(VI) reduction, NADH oxidation, the oxidation of small organic molecules such as methanol, formic acid, propene, ascorbic acid etc. These reactions were recently reviewed by Malinauskas,\textsuperscript{182} Andreev\textsuperscript{183} and Rolison.\textsuperscript{184} The first example of a ruthenium complex attached to an electrode is [(bpy)$_2$(H$_2$O)Ru(P4VP)$_n$$^{2+}$] where P4VP is poly-4-vinylpyridine.\textsuperscript{64} This ruthenium metallopolymer was covalently attached to the electrode surface and used as a catalyst during the electrooxidation of isopropanol to acetone. This complex was not very stable during the catalysis and slowly decomposed to an unidentified species.
Since the CME containing a ruthenium complex was published, several other electrodes modified with ruthenium complexes have been prepared. The methods of preparation have been varied and include encapsulation of the catalyst into ion-exchange membranes such as Nafion® and sulfonated polystyrene. Meyer reported that the dimer \([\text{Ru(bpy)}_2(\text{H}_2\text{O})]_2\text{O}^{4+}\) in solution is an active catalyst for the electrooxidation of water. When supported on polystyrene sulfonate this complex has no catalytic activity. Meyer proposed that the catalyst deactivation was due to the displacement of the aquo ligand and formation of a sulfonate complex. The loss of water will deactivate the catalytic reaction, by inhibiting the formation of the catalytically active oxo species.

The ruthenium bound CME can also be prepared by attaching the metal complex to a polymer film. The stability of electrodes prepared in this manner has been studied, and is dependent on the polymer and the method of preparation. In 2000 Meyer reported that the surface bound poly-cis-[\text{Ru(vbpy)}_2(\text{O})]_2^{2+}\) (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) is catalytically active during the electrooxidation of alkyl and aryl alcohols. In solution this complex is very unstable readily losing bipyridine to form the inactive trans-dioxo complex. The rigid nature of the polymer film retards ligand loss and increases the stability of the catalytically active cis-dioxo Ru(VI) species.

**Preparation of CME**

Typically the modified layer is assembled upon a very stable reproducible surface. This material is normally used as an electrode even when unmodified due to good
mechanical and chemical stability. Examples of typical materials include platinum, gold, tin oxide and carbon.

As classified by Murray,\textsuperscript{197} CME can be grouped into four categories based on the method used to modify them:

- Sorption
- Covalently modified electrodes
- Polymer coatings
- Heterogeneous multi-layer

CME prepared using sorption methods rely on chemical and physical interactions to form and maintain the monolayer.\textsuperscript{198} These electrodes have the advantage of being easily prepared but are not as stable as electrodes modified by other methods. Covalent modification of electrodes is another method for anchoring molecules to an electrode surface.\textsuperscript{198} Functional groups which have been employed include $\text{>C=O}$, $\text{>C-OH}$, $\equiv\text{Pt-OH}$ and $\equiv\text{Sn-OH}$. As with the adsorption method, these electrodes are limited to monolayer coverage, severely restricting the amount of modifier on the surface. The monolayer limitation can be overcome by preparing multi-layer CMEs. Multi-layer CME are prepared from uniform polymer coatings of ionomers, redox polymers, inorganic polymers, polymerization of mediators bearing monomers, etc.\textsuperscript{198} Another method of preparing multi-layer CME is the incorporation of mediators in a non-uniform matrix such as carbon paste, epoxy resin, clay, zeolite and other polymeric systems.\textsuperscript{198}

**Electrodes Modified with Bimetallic Complexes**

CME have been aggressively studied for the last 20 years (Figure 4-3). The modification of electrodes with bimetallic complexes however is one field that is still in its infancy, with only a handful of electrodes studied.\textsuperscript{192,199-203} The only reference to a
Figure 4-3. References to “chemically modified electrodes” in the scientific literature (SciFinder Scholar).

A heterobimetallic complex immobilized on an electrode is the Co(II)-Pt(II) porphyrin reported by Srour in 2005. When adsorbed to the surface of an edge plane graphite electrode a significant shift (600 mV) in the reduction potential of molecular oxygen was observed. This CME can act as a catalyst reducing all of the oxygen present to water (50 %) and hydrogen peroxide (50 %).

The electrochemical oxidation of methanol with Ru/Sn catalysts in solution was previously reported from this research group. The activity of the Ru/Sn heterobimetallic catalysts is dependent on the ancillary phosphine ligands. It was shown that bidentate phosphines greatly inhibited the catalytic activity of the complexes. The Ru/Sn complexes with monodentate phosphines are very efficient (90 % current efficiency) and selective (100 % DMM) when the electrooxidation is performed in neat
methanol. In order to continue the study of Ru/Sn Lewis acidic interactions, the synthesis and study of a series of Nafion® supported Ru/Sn complexes (Figure 4-4) was performed.

\[
\begin{align*}
(27) & \quad L = \text{PPh}_3, \quad X = \text{SnPh}_3 \\
(28) & \quad L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2, \quad X = \text{Cl} \\
(29) & \quad L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2, \quad X = \text{SnCl}_3 \\
(30) & \quad L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2, \quad X = \text{SnPh}_3 \\
(31) & \quad L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3\text{BF}_4, \quad X = \text{Cl} \\
(32) & \quad L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3\text{BF}_4, \quad X = \text{SnCl}_3
\end{align*}
\]

Figure 4-4. Structure of compounds 27 – 32.

**Synthesis**

**Synthesis of CpRu(PPh₃)₂(SnPh₃) (27)**

The Ru-SnPh₃ complex 27 was prepared by reacting CpRu(PPh₃)₂(SnCl₃) (20) in benzene with an excess of phenyl lithium (Eq 4.1) at room temperature.

CpRu(PPh₃)₂(SnPh₃) was isolated as an air and moisture stable dark yellow solid in 90 % yield. Replacing the chlorides in CpRu(PPh₃)₂(SnCl₃) with phenyl anions has a profound effect on the \(^{31}P\{^1H\} NMR data. The singlet for the equivalent phosphorus atoms is shifted downfield relative to CpRu(PPh₃)₂(SnCl₃) by approximately 8 ppm to 53 ppm. The P-Sn coupling is also affected; decreasing by 165 Hz to 270 Hz.
Synthesis of CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)

Attempts at synthesizing complex 28 through ligand displacement from CpRu(PPh$_3$)$_2$Cl led to product mixtures containing the monosubstituted complex. These product mixtures were difficult to separate and therefore an alternative route to 28 was needed. Complex 28 was instead synthesized by reacting Ru($\eta^2$-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl$_2$ with an excess of cyclopentadiene in refluxing ethanol (Eq. 4.2). After 3 days CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl was isolated in high yield (74 %) as a yellow solid. Complex 28 is very stable as a solid or in solution even upon prolonged exposure to air and moisture. The $^{31}$P{${}^1$H} NMR spectrum of CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl is very similar to that of CpRu(PPh$_3$)$_2$Cl, consisting of a singlet at 37 ppm.

\[
\begin{align*}
\text{CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl} & \quad + \quad 3 \text{ Cyclopentadiene} & \quad \text{Ethanol} & \quad 72 \text{ hours, Reflux} & \quad \text{CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl} \\
\end{align*}
\]

(4.2)

Synthesis of CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29)

The reaction between CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl and SnCl$_2$ in DCE (Eq 4.3) produced CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) in near quantitative yield. Complex 29 was isolated as a yellow solid that was stable to air and moisture not only in the solid state but also in solution. The $^{31}$P{${}^1$H} NMR spectrum is very similar to the previously synthesized Ru-SnCl$_3$ complexes, displaying only one singlet at 39 ppm with tin satellite couplings of 412 Hz.
Synthesis of CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) (30)

Complex 30 was prepared in a similar manner to CpRu(PPh₃)₂(SnPh₃), by reacting CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnCl₃) with phenyl lithium (Eq 4.4). After workup, CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) was isolated in 64% yield as a yellow solid. Complex 30 is stable in the presence of air and moisture, not only as a solid but also in solution. The singlet for the equivalent phosphorus atoms is shifted upfield relative to CpRu(PPh₃)₂(SnPh₃) by approximately 9 ppm to 44 ppm. The P-Sn coupling (²J_{P-Sn} = 262 Hz) of 30 is unaffected by the change in ligand environment.

Synthesis of CpRu(amphos)₂Cl (31)

CpRu(amphos)₂Cl was prepared in a similar manner to CpRu(TPPMS)₂Cl, by substitution of triphenylphosphine with amphos. The ligand substitution reaction was performed in refluxing toluene (Eq. 4.5). After four days of reflux 31 was isolated in 76
% yield as an orange solid. The stability of complex 31 is very similar to that of complex 28, showing no signs of decomposition even after prolonged exposure to air and moisture. The $^{31}$P{H} NMR spectrum of 31 is very similar to that of 28 consisting of a singlet at 36 ppm.

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Ru} & \quad \text{Cl} \\
\text{Ph}_2\text{P} & \quad \text{CH}_2\text{CH}_2\text{NMe}_3\text{BF}_4 \\
\text{PPh}_3 & \quad \text{Toluene} & \quad 96\text{ hours, Reflux}
\end{align*}
\]

Synthesis of CpRu(amphos)$_2$(SnCl)$_3$ (32)

The Ru/Sn complex CpRu(amphos)$_2$(SnCl)$_3$ was prepared in an analogous manner to CpRu(PPh$_3$)$_2$(SnCl)$_3$ by reacting 31 with a slight excess of SnCl$_2$ (Eq. 4.6) in refluxing ethanol. The resulting yellow solid is stable in air and in solutions exposed to air and moisture. As expected from the NMR spectrum of CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29), the $^{31}$P{H} NMR spectrum of CpRu(amphos)$_2$(SnCl)$_3$ consists of a singlet at 40 ppm with $^2$J$_{P-Sn}$ = 405 Hz.

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \\
\text{Ph}_2\text{P} & \quad \text{PPh}_2 \\
\text{SnCl}_3 & \quad \text{Ethanol} & \quad 24\text{ hours, Reflux}
\end{align*}
\]
As mentioned above, Nafion® is a cation exchange polymer capable of acting as a solid support for positively charged species. Because of this, cationic complexes analogous to CpRu(TPPMS)$_2$Cl (22) and CpRu(TPPMS)$_2$(SnCl$_3$) (23) were prepared. The cationic phosphine amphos, was selected as the ligand to replace TPPMS, forming CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_3$ BF$_4$)$_2$Cl (31) and CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_3$ BF$_4$)$_2$(SnCl$_3$) (32). The neutral complexes CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28) and CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29) were also synthesized; these complexes will be readily protonated by Nafion® to form positively charged species.

NMR Data

$^1$H and $^{31}$P{$^1$H} NMR spectroscopies were utilized to determine the ligand arrangement about the Ru center. Selected NMR data are presented in Table 4-1. The $^1$H and $^{31}$P{$^1$H} NMR spectral data are very similar to the previously reported complexes (Table 3-3). Only one singlet is observed in the $^{31}$P{$^1$H} NMR spectra for complexes 27 – 32. The chemical shifts of the cyclopentadienyl protons are a good indication of the electron density located on the Ru metal center. As observed in the $^1$H NMR of compounds 19 – 23 (Table 3-3), the Cp protons shift downfield as the electron density on Ru decreases. Hence for CpRuL$_2$Cl, the chemical shift of the Cp protons for

<table>
<thead>
<tr>
<th>Complex$^a$</th>
<th>Solvent</th>
<th>$^1$H NMR (ppm)</th>
<th>$^{31}$P{$^1$H} NMR (ppm)</th>
<th>$^2$J$_{P,Sn}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnPh$_3$) (27)</td>
<td>CDCl$_3$</td>
<td>4.27</td>
<td>53.0</td>
<td>270</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)</td>
<td>CDCl$_3$</td>
<td>4.29</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29)</td>
<td>CDCl$_3$</td>
<td>4.71</td>
<td>39.4</td>
<td>412</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnPh$_3$) (30)</td>
<td>CDCl$_3$</td>
<td>4.21</td>
<td>43.8</td>
<td>262</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>DMSO-d$_6$</td>
<td>4.48</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>acetone-d$_6$</td>
<td>5.00</td>
<td>39.5</td>
<td>405</td>
</tr>
</tbody>
</table>

$^a$ All NMR data obtained at room temperature.
L = amphos > Ph₂PCH₂CH₂NMe₂ > PPh₃ ≈ TPPMS. The same trend was observed for the complexes containing the SnCl₃ ligand.

**Homogeneous Studies**

**Cyclic Voltammetry**

Cyclic voltammograms of complexes 27 - 32 each display a single oxidation wave (Table 4-2). This oxidation process has previously been assigned to the Ru(II/III) couple for the monometallic [CpRu(PPh₃)₂Cl,₁⁶₇ (Ind)Ru(PPh₃)₂Cl,₁₆₈ CpRu(TPPMS)₂Cl] and heterobimetallic [CpRu(PPh₃)₂(SnCl₃), CpRu(TPPMS)₂(SnCl₃)] complexes (Table 3-3). Based on this assignment, the oxidation waves observed for complexes 27 - 32 have been assigned to the one-electron oxidation of Ru(II) to Ru(III).

The amphiphilic nature of the amino-phosphine ligands allow the electrochemical study of the Ru complexes 28 - 32 in polar and non-polar solvents. These ligands also stabilize complexes 28 - 32 in water. This increased stability was observed during the characterization of these molecules, and during the CV studies in aqueous solutions (Table 4-2). This contrasts to CpRu(TPPMS)₂Cl (22) and CpRu(TPPMS)₂(SnCl₃) (23), both of which are soluble but decompose quickly in water. Due to an inductive effect, the positive charge on the amphos ligand pulls electrons density away from the Ru metal center. Because of this the Ru(II/III) oxidation waves of complexes 31 and 32 occur at a slightly higher potential than 28 and 29, respectively.

The oxidation of the Ru/Cl complex CpRu(amphos)₂Cl (31) is chemically reversible (iₚa / iₚc ≈ 1), when analyzed in methylene chloride, methanol, water and acetonitrile (Table 4-2). The other monometallic complex CpRu(Ph₂PCH₂CH₂NMe₂)₂Cl (28) is also reversible when oxidized in methylene chloride, methanol and water.
<table>
<thead>
<tr>
<th>Complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Electrolyte</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_{pa} / i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (20)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.7 M TBAT / DCE</td>
<td>1.48</td>
<td>1.44</td>
<td>85</td>
<td>0.92</td>
</tr>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (20)</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>1.42</td>
<td>1.35</td>
<td>139</td>
<td>1.13</td>
</tr>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (20)</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.32, 1.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (27)</td>
<td>0.7 M TBAT / CH$_2$Cl$_2$</td>
<td>1.19</td>
<td>1.13</td>
<td>116</td>
<td>1.21</td>
</tr>
<tr>
<td>CpRu(PPh$_3$)$_2$(SnCl$_3$) (27)</td>
<td>0.1 M TBAT / MeOH</td>
<td>1.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)</td>
<td>0.7 M TBAT / CH$_2$Cl$_2$</td>
<td>1.13</td>
<td>1.05</td>
<td>134</td>
<td>1.04</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)</td>
<td>0.1 M TBAT / MeOH</td>
<td>0.97</td>
<td>0.90</td>
<td>142</td>
<td>1.13</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)</td>
<td>0.1 M KCl / H$_2$O</td>
<td>0.86</td>
<td>0.80</td>
<td>125</td>
<td>1.07</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl (28)</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>0.82, 1.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>0.7 M TBAT / CH$_2$Cl$_2$</td>
<td>1.18</td>
<td>1.12</td>
<td>124</td>
<td>1.10</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>0.1 M TBAT / MeOH</td>
<td>1.00</td>
<td>0.93</td>
<td>114</td>
<td>0.99</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>0.92</td>
<td>0.88</td>
<td>90</td>
<td>1.06</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>0.1 M KCl / H$_2$O</td>
<td>0.85</td>
<td>0.80</td>
<td>108</td>
<td>0.95</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>0.86</td>
<td>0.80</td>
<td>113</td>
<td>1.03</td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29)</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>1.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29)</td>
<td>0.7 M TBAT / CH$_2$Cl$_2$</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29)</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnPh$_3$) (30)</td>
<td>0.1 M TBAT / MeOH</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (31)</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>1.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>0.7 M TBAT / CH$_2$Cl$_2$</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>0.1 M TBAT / PC</td>
<td>1.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> All potentials reported vs NHE.  <sup>b</sup> Reference 169.
When analyzed in acetonitrile, the CV of 28 exhibits two irreversible peaks at 0.82 and 1.14 V. The first peak at 0.82 V was assigned to the one-electron oxidation of the Ru metal center in complex 28. This assignment was made by comparing the CV of 28 to that of 31. The second irreversible oxidation wave has not been conclusively assigned but is probably due to the oxidation of an acetonitrile adduct.

Figure 4-5. Cyclic voltammograms of 20 under nitrogen in 3.5 mL of CH₃CN / 0.1 M TBAT; glassy carbon working electrode; Ag/Ag⁺ reference electrode; 50 mV/s scan rate, solutions as specified in figure.

The CV of CpRu(PPh₃)₂(SnCl₃) (20) in acetonitrile (Table 4-2) is very similar to CpRu(Ph₂PCH₂CH₂NMe₂)₂Cl (28), displaying two irreversible oxidation waves, at 1.32 and 1.50 V. At a switching potential of 1.40 V, the first oxidation wave is chemically reversible (Figure 4-5). This first oxidation wave has been assigned to the Ru(II/III) couple of 20. This assignment was made by comparing the CVs of 20 in CH₃CN (Figure 4-2) to that in DCE (Figure 3-3). The second wave is irreversible, regardless of
the switching potential. This oxidation process is similar to the second oxidation wave observed for 28 in CH₃CN, and has been assigned to the oxidation of an acetonitrile complex. The formation of a solvent coordinated complex has been previously reported, during CV studies of an analogous ruthenium hydride complex, CpRu(PPh₃)₂H in acetonitrile (Eq. 4.7).

\[
\text{CpRu(PPh₃)₂H} \rightarrow 0.5 \{\text{CpRu(PPh₃)₂(CH₃CN)}\}^+ + 0.5 \{\text{CpRu(PPh₃)₂(H)₂}\}^+
\]

The CVs of the Ru/SnCl₃ complexes CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnCl₃) (29) and CpRu(amphos)₂(SnCl₃) (32) were studied in several solvents. A single irreversible oxidation wave was observed for 29 and 32 in MeNO₂, CH₂Cl₂ and CH₃CN. In methanol a significant increase in current was observed when 29 and 32 were added, but no oxidation waves were observed. The catalytic current of the methanol oxidation reaction obscures the Ru(II/III) redox couple.

The chloride ligands in complexes CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnCl₃) (29) and CpRu(PPh₃)₂(SnCl₃) (20) were substituted with the less electron withdrawing phenyl groups to yield complexes 30 and 27. A single oxidation wave, assigned to the Ru(II/III) couple was observed in the CV of complexes CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) (30) and CpRu(PPh₃)₂(SnPh₃) (27). The Ru(II/III) oxidation waves of the SnPh₃ complexes 30 and 27 are shifted to lower potentials than those of the corresponding SnCl₃ complexes. As predicted by Holt, and supported by the NMR and CV data, (SnPh₃)⁻ is a weaker Lewis acid than (SnCl₃)⁻.
Electrochemical Oxidation of Methanol

The cyclic voltammograms of the Ru/Sn complexes CpRu(PPh3)2(SnPh3) (27), CpRu(Ph2PCH2CH2NMe2)2(SnCl3) (29), CpRu(Ph2PCH2CH2NMe2)2(SnPh3) (30) and CpRu(amphos)2(SnCl3) (32) all exhibit a catalytic current in the presence of methanol. The onset of this catalytic current for the heterobimetallic complexes coincides with the oxidation of the metal center from Ru(II) to Ru(III), regardless of what solvent is being used. A similar current increase was observed in the cyclic voltammograms of CpRu(PPh3)2(SnCl3) (20) and CpRu(TPPMS)2(SnCl3) (23). For the monometallic complexes CpRu(Ph2PCH2CH2NMe2)2Cl (28) and CpRu(amphos)2Cl (31) no catalytic current was observed within the potential window (0 – 2.0 V) when methanol was introduced.

The electrochemical oxidation of methanol in 0.1 M TBAT/MeOH was performed at 1.4 V with 28 - 32. The anodic potential was chosen during previous studies, and used for these experiments so as to have a direct correlation to the previous results. At 1.4 V the Ru metal center of 28, 30 and 31 will be oxidized from Ru(II) to Ru(III). Although no oxidation wave was observed for 29 and 32 in methanol, by extrapolating from 28 and 31 the Ru(II/III) couple for 29 and 32 can be estimated as 1.56 and 1.62 V respectively. CpRu(Ph2PCH2CH2NMe2)2(SnCl3) (29) and CpRu(amphos)2(SnCl3) (32) are oxidized at an anodic potential of 1.4 V; this process can be observed in the CVs that display a current increase.

The oxidation products formed during the electrolysis are dimethoxymethane and methyl formate (Table 4-3). DMM and MF are the same products observed during earlier studies of Ru-TPPMS electrocatalysts in neat methanol. The evolution of
Table 4-3. Bulk electrolysis data for the oxidation of methanol by 27 - 32

<table>
<thead>
<tr>
<th>Complexa</th>
<th>TONb</th>
<th>Current Efficiencyc (%)</th>
<th>DMM (10^{-5} moles)</th>
<th>MF (10^{-5} moles)</th>
<th>Product Ratio (DMM/MF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(TPPMS)<em>{2}(SnCl</em>{3})d (23)</td>
<td>40.0 ± 2.6</td>
<td>90.1 ± 6.9</td>
<td>127 ± 6</td>
<td>13.0 ± 0.6</td>
<td>9.8 ± 1.0</td>
</tr>
<tr>
<td>CpRu(amphos)_{2}Cl (31)</td>
<td>8.85 ± 0.60</td>
<td>37.8 ± 1.5</td>
<td>28.7 ± 1.4</td>
<td>2.3 ± 0.1</td>
<td>12.6 ± 1.0</td>
</tr>
<tr>
<td>CpRu(amphos)<em>{2}(SnCl</em>{3}) (32)</td>
<td>10.3 ± 0.6</td>
<td>52.1 ± 2.1</td>
<td>27.9 ± 1.4</td>
<td>8.2 ± 0.4</td>
<td>3.4 ± 1.0</td>
</tr>
<tr>
<td>CpRu(Ph_{2}PCH_{2}CH_{2}NMe_{2})_{2}Cl (28)</td>
<td>9.66 ± 0.59</td>
<td>37.7 ± 1.9</td>
<td>27.2 ± 1.4</td>
<td>6.6 ± 0.3</td>
<td>2.5 ± 0.6</td>
</tr>
<tr>
<td>CpRu(Ph_{2}PCH_{2}CH_{2}NMe_{2})<em>{2}(SnCl</em>{3}) (29)</td>
<td>10.0 ± 0.6</td>
<td>47.6 ± 2.1</td>
<td>24.6 ± 1.2</td>
<td>10.6 ± 0.5</td>
<td>2.3 ± 1.0</td>
</tr>
<tr>
<td>CpRu(Ph_{2}PCH_{2}CH_{2}NMe_{2})<em>{2}(SnPh</em>{3}) (30)</td>
<td>2.14 ± 0.14</td>
<td>8.2 ± 0.4</td>
<td>7.5 ± 0.4</td>
<td>N.O.</td>
<td>∞</td>
</tr>
<tr>
<td>CpRu(PPh_{3})<em>{2}(SnPh</em>{3}) (27)e</td>
<td>0.80 ± 0.06</td>
<td>4.2 ± 0.1</td>
<td>2.8 ± 0.1</td>
<td>N.O.</td>
<td>∞</td>
</tr>
<tr>
<td>CpRu(PPh_{3})<em>{2}(SnCl</em>{3}) (20)d,e</td>
<td>3.37 ± 0.20</td>
<td>13.1 ± 0.7</td>
<td>8.65 ± 0.43</td>
<td>3.15 ± 0.16</td>
<td>2.7 ± 1.0</td>
</tr>
<tr>
<td>CpRu(PPh_{3})_{2}Cl (19)d,e</td>
<td>2.60 ± 0.15</td>
<td>7.3 ± 0.5</td>
<td>6.84 ± 0.34</td>
<td>2.26 ± 0.11</td>
<td>3.0 ± 1.0</td>
</tr>
</tbody>
</table>

a All electrolyses performed at 1.4 V in 0.1 M TBAT/MeOH with 10 mM catalyst for 5 hours.  
b Moles of product formed per mole of catalyst.  
c Calculated using Eq. 1.21.  
d Reference 169.  
e Performed at 1.7 V in 0.7 M TBAT/CH_{2}Cl_{2} with 10 mM catalyst, 0.35 M methanol for 5 hours.
DMM and MF was monitored as a function of time and plotted in Figures 4-6 and 4-7 respectively. For complexes 28, 29, 31 and 32, DMM is formed at a faster rate than MF,

Figure 4-6. Formation of DMM during the electrooxidation of methanol at 1.4 V with Ru catalysts as specified.

Figure 4-7. Formation of MF during the electrooxidation of methanol at 1.4 V with Ru catalysts as specified.
and its formation is favored all throughout the reaction. The Ru-aminophosphine complexes are not as active, efficient or selective as the Ru-TPPMS complexes (Table 3-5), forming smaller quantities of products with a lower current efficiency.

After 5 hours of electrolysis with 28, 29, 31 and 32, oxidative currents gradually decrease to approximately 60 % of the initial value. During this time the yellow solutions developed a dark brown color. Analysis of the resulting solutions by $^{31}$P{$^1$H} NMR was employed to determine what happened to the catalysts during the electrolysis. At the end of the electrolysis, two singlets corresponding to the major phosphorus species were observed. Based on the chemical shift, one species was identified as the oxide of the phosphine ligand. The other singlet had a chemical shift close to the starting material, and was presumed to be a structurally similar species. Similar reaction products were identified when the electrolysis was performed with the TPPMS complexes.

The role of tin during the catalysis is unclear. Two possibilities exist:

1. Activating the Ru metal center: Increasing the electrophilicity of Ru was suggested by Gusevskaya (Eq. 3.5) during the thermal dehydrogenation of methanol.

2. Binding site for methanol: A similar role was invoked by Shinoda (Scheme 3-3) during the thermal dehydrogenation of methanol.

Both possibilities are affected by the Lewis acidity of the tin(II) ligand. To determine the role of tin, the phenyl substituted complexes CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnPh$_3$) (30) and CpRu(PPh$_3$)$_2$(SnPh$_3$) (27) were used as catalysts during the electrooxidation of methanol. Both complexes catalyzed the electrooxidation of methanol, forming DMM (Table 4-3) as the only oxidation product. In neat methanol, CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnPh$_3$) (30) is a poor electrocatalyst, forming smaller quantities of products with a lower current efficiency than CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnCl$_3$) (29) and
CpRu(Ph₂PCH₂CH₂NMe₂)₂Cl (28). A similar trend was observed when the catalytic activity of CpRu(PPh₃)₂(SnPh₃) (27) was compared to CpRu(PPh₃)₂(SnCl₃) (20) and CpRu(PPh₃)₂Cl (19) (Table 4-3). The fact that the SnPh₃ complexes are less active than the SnCl₃ complexes implies that the Lewis acidity of the tin(II) ligand is an important factor in the activity of the catalysts. The mechanistic role of tin is still unclear since decreasing its Lewis acidity influences not only the electrophilicity of the neighboring Ru, but also the ability of tin to bind methanol.

The electrochemical oxidation of methanol was also investigated in nitromethane (MeNO₂), propylene carbonate (PC) and acetonitrile (CH₃CN) with CpRu(amphos)₂(SnCl₃) (32) and CpRu(PPh₃)₂(SnCl₃) (20). The CVs of 20 (Figure 4-5) and 32 (Figure 4-8) exhibited the anticipated catalytic current when methanol was introduced. The potential applied during the electrolysis is after the Ru(II/III) oxidation wave (Table 4-4), but within the solvent window of CH₃CN, MeNO₂ and PC. Although a catalytic current was observed in the CV when methanol was introduced, no oxidation products were detected during the electrolysis (Table 4-4).

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Electrolyte</th>
<th>Ru(II/III) Eₜₐ (V)</th>
<th>Anodic Potential (V)</th>
<th>TONb</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(PPh₃)₂(SnCl₃) (20)</td>
<td>0.1 M TBAT / CH₃CN</td>
<td>1.32</td>
<td>1.70</td>
<td>0</td>
</tr>
<tr>
<td>CpRu(PPh₃)₂(SnCl₃) (20)</td>
<td>0.1 M TBAT / MeNO₂</td>
<td>1.42</td>
<td>1.70</td>
<td>0</td>
</tr>
<tr>
<td>CpRu(amphos)₂(SnCl₃) (32)</td>
<td>0.1 M TBAT / CH₃CN</td>
<td>1.59</td>
<td>1.80</td>
<td>0</td>
</tr>
<tr>
<td>CpRu(amphos)₂(SnCl₃) (32)</td>
<td>0.1 M TBAT / MeNO₂</td>
<td>1.64</td>
<td>1.80</td>
<td>0</td>
</tr>
<tr>
<td>CpRu(amphos)₂(SnCl₃) (32)</td>
<td>0.1 M TBAT / PC</td>
<td>1.73</td>
<td>1.80</td>
<td>0</td>
</tr>
</tbody>
</table>

a All electrolyses performed with 10 mM catalyst and 0.35 M methanol for 5 hours. All potentials reported vs NHE. b Moles of product formed per mole of Ru complex.
Since CpRu(amphos)$_2$(SnCl$_3$) (32) and CpRu(PPh$_3$)$_2$(SnCl$_3$) (20) are catalytically active in methanol and DCE, their inactivity in CH$_3$CN, MeNO$_2$ and PC must be as a result of the solvents. Previous results with chelating phosphine ligands (dppm, dppe and dppp) have established the necessity of a vacant coordination site on Ru for the reaction to proceed. The methanol oxidation reaction is probably retarded by the formation of solvent coordinated adducts. The formation of solvent adducts was invoked during the CV studies of 20 and 28 in CH$_3$CN. The ability of a solvent to coordinate to a metal center is affected by the Lewis basicity / donor number of the solvent. Donor number is a qualitative measurement of Lewis basicity, developed by Gutmann in 1976. Strong Lewis bases have high donor numbers, and readily form adducts with Lewis acids. Acetonitrile and propylene carbonate are moderate Lewis bases (Table 4-5). Because of
Table 4-5. Donor number of selected Lewis bases

<table>
<thead>
<tr>
<th>Lewis Basea</th>
<th>Donor Number kcal. mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>0</td>
</tr>
<tr>
<td>DCE</td>
<td>0</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>2.1</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>14.1</td>
</tr>
<tr>
<td>PC</td>
<td>15.1</td>
</tr>
<tr>
<td>H₂O</td>
<td>18.0 (33.0ᵇ)</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>19.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>33.1</td>
</tr>
</tbody>
</table>

ᵃ Reference 206. ᵇ Bulk donor number (donor number of the Lewis base in the associated liquid)

this they should readily form adducts with the Lewis acidic metal centers of CpRu(amphos)₂(SnCl₃) (32) and CpRu(PPh₃)₂(SnCl₃) (20). By comparing the donor numbers of methanol and nitromethane it is evident that methanol is a better Lewis base than nitromethane. It should however be noted that these measurements were performed in dichloroethane as the solvent. A better value would be the donor number of nitromethane in nitromethane as solvent (bulk donor number). The bulk donor number of nitromethane is expected to be greater than the corresponding donor number in dichloroethane, compare water in Table 4-5. It is thought that the large excess of nitromethane, acetonitrile and propylene carbonate favors the formation of solvent adducts, overcoming the thermodynamic preference if any for methanol.

**Heterogeneous Studies**

**Preparation of Modified Toray Carbon Paper (MTCP) Electrodes**

Two methods were utilized for preparing the modified electrodes:

- **Method A)** The metal complex and Nafion® suspension were combined. After reaching equilibrium the resulting mixture is used to coat the TCP electrode.

- **Method B)** The TCP electrode is coated with the Nafion® membrane before immersing in a solution of the metal complex.
These electrodes are extremely stable in solvents commonly used in electrochemistry, such as water, propylene carbonate, nitromethane and acetonitrile. They are however unstable in chlorinated solvents, rapidly degrading in methylene chloride.

**MTCP-1.** 200 µL of a stock solution containing Nafion® (0.25 wt %) and CpRu(amphos)₂Cl (0.0167 wt %) dissolved in methanol was deposited on the surface of a TCP electrode. After drying, the modified electrode was washed with methanol and water before storing in aqueous KCl under an atmosphere of nitrogen.

**MTCP-2.** 200 µL of a stock solution containing Nafion® (0.833 wt %) and CpRu(amphos)₂(SnCl₃) (0.0167 wt %) dissolved in methanol was deposited on the surface of a TCP electrode. After drying, the modified electrode was washed with acetonitrile before storing in acetonitrile under an atmosphere of nitrogen.

**MTCP-3.** 200 µL of a 2.5 wt % Nafion® suspension was deposited on the surface of a TCP electrode. After drying, the modified electrode was immersed overnight in an acetonitrile or nitromethane solution of CpRu(amphos)₂Cl (0.1 wt %). Electrodes modified by this method were stored in this solution under an atmosphere of nitrogen when not in use.

**MTCP-4.** These electrodes were prepared in an analogous manner to MTCP-3 with CpRu(amphos)₂(SnCl₃) as the metal complex.

**MTCP-5.** These electrodes were prepared in an analogous manner to MTCP-3 with CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) as the metal complex.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>$E_{pa}$ (V vs NHE)</th>
<th>$E_{1/2}$ (V vs NHE)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_{pa} / i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>MTCP-1</td>
<td>0.1 M KCl / H$_2$O</td>
<td>0.90</td>
<td>0.81</td>
<td>185</td>
<td>1.15</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>MTCP-1</td>
<td>0.1 M TBAT / MeOH</td>
<td>0.97</td>
<td>0.90</td>
<td>142</td>
<td>1.08</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>MTCP-2</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.38</td>
<td>1.36</td>
<td>42</td>
<td>1.03</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>MTCP-3</td>
<td>0.1 M TBAT / MeOH</td>
<td>0.92</td>
<td>0.85</td>
<td>146</td>
<td>1.06</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>MTCP-3</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>1.06</td>
<td>0.93</td>
<td>264</td>
<td>1.15</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$Cl (31)</td>
<td>MTCP-3</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>0.82</td>
<td>0.77</td>
<td>110</td>
<td>1.13</td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>MTCP-4</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(amphos)$_2$(SnCl$_3$) (32)</td>
<td>MTCP-4</td>
<td>0.1 M TBAT / MeNO$_2$</td>
<td>1.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpRu(Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$(SnPh$_3$) (30)</td>
<td>MTCP-5</td>
<td>0.1 M TBAT / CH$_3$CN</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cyclic Voltammetry

Cyclic voltammetry was used to probe the stability of 

\[ \text{CpRu(Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)\text{SnPh}_3 \] (30), \( \text{CpRu(} \text{amphos})_2\text{Cl} \) (31) and 

\[ \text{CpRu(} \text{amphos})_2\text{SnCl}_3 \] (32) in the modified electrodes. Electrodes modified with 
\[ \text{CpRu(} \text{amphos})_2\text{Cl} \] (31) were stable in solutions of methanol, acetonitrile, nitromethane 
and water, with no evidence of leaching. These CVs were also very reproducible even 
upon repeated cycling and prolonged storage. When placed in 0.1 M TBAT/PC the 
complex rapidly leached from the electrode surface into solution. No leaching was 
observed when the electrodes were placed in propylene carbonate without supporting 
electrolyte. This indicated that the cation of the electrolyte was displacing the Ru 
complex from the Nafion® matrix. Attempts at stabilizing the electrodes by varying the 
supporting electrolyte (NaBPh₄, NH₄PF₆) were unsuccessful. Because of the rapid 
leaching observed in PC, this solvent was not used during further studies of the modified 
electrodes.

When attached to the electrode surface, a single chemically reversible oxidation 
wave was observed for MTCP-1 and MTCP-3 (Table 4-6). This redox process was 
assigned to the Ru(II/III) couple of \( \text{CpRu(} \text{amphos})_2\text{Cl} \) (31). The reversibility of this 
electron transfer process is a good indication that the complex and its oxidized form are 
both stable within the Nafion® matrix. When immobilized, the Ru(II/III) couple of 31 is 
typically shifted by 30 to 80 mV with respect to the Ru(II/III) couple of the complex in 
solution (Table 4-2).
Figure 4-9. Cyclic voltammograms of MTCP-2, electrode modified with CpRu(amphos)$_2$(SnCl$_3$) (32) under nitrogen in 3.5 mL of CH$_3$CN / 0.1 M TBAT; Ag/Ag$^+$ reference electrode; 50 mV/s scan rate.

The CVs of MTCP-2 and MTCP-4 are very stable and reproducible when analyzed in the aprotic solvents nitromethane and acetonitrile. For MTCP-2 in acetonitrile the oxidation of CpRu(amphos)$_2$(SnCl$_3$) (32) is reversible (Table 4-6, Figure 4-9). The Nafion$^\text{®}$ matrix stabilizes [CpRu(amphos)$_2$(SnCl$_3$)]$^+$, allowing it to be reduced reversibly. This was unexpected since in solution and in MTCP-4, the oxidation of 32 is irreversible (Table 4-3 and 4-6). No redox waves were initially observed in the CVs of MTCP-2 and MTCP-4 when analyzed in water or methanol. The absence of the Ru(II/III) oxidation wave was thought to be as a result of the catalytic current obscuring its presence. Upon repeated scans a redox couple similar to the Ru(II/III) couple of 32 is observed. This was the first indication that in the presence of methanol and water MTCP-2 and MTCP-4 may be unstable. $^{31}$P/{$^1$H} NMR was used to monitor the stability of CpRu(amphos)$_2$(SnCl$_3$)
(32) in the Nafion® suspensions prior to coating the TCP electrode. Based on the NMR studies complex 32 is stable for at least two days in the Nafion® suspension, prior to preparing MTCP-2. The actual decomposition pathway for the immobilized complex is uncertain, but it seems to require the passage of current in a protic solvent. The decomposition was also observed when the CV is performed in acetonitrile and nitromethane solutions containing methanol.

One attempt at stabilizing the complex during the CV studies in methanol was the use of CpRu(Ph2PCH2CH2NMe2)2(SnPh3) (30) in the modified electrodes (MTCP-5). This attempt however was unsuccessful and MTCP-5 also degraded when analyzed in water and methanol.

**Summary**

A series of Ru/Sn complexes containing the amphiphilic ligands Ph2PCH2CH2NMe2 and Ph2PCH2CH2NMe3BF4 was synthesized and studied. Complexes 28, 29, 31 and 32 are soluble and stable in both protic and aprotic solvents. Cyclic voltammetry of these complexes was performed in methylene chloride, acetonitrile, nitromethane, propylene chloride, methanol and water. The electrochemical oxidation of methanol was performed with 28, 29, 31 and 32 in neat methanol. The products formed during the electrolysis are DMM and MF. The aminophosphine complexes (28, 29, 31 and 32) are not as efficient or selective as the TPPMS complexes (22 and 23) studied in chapter 3. The decreased activity is attributed to the stronger Ru-P bond and the decreased cone angle of the aminophosphine complexes. These two factors will inhibit phosphine dissociation, and retard the methanol oxidation reaction.

Complexes containing the SnPh3 ligand CpRu(PPh3)2(SnPh3) (27) and CpRu(Ph2PCH2CH2NMe2)2(SnPh3) (30), form smaller quantities of oxidation products
than the corresponding SnCl₃ complexes CpRu(PPh₃)₂(SnPh₃) (20) and
CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) (29) respectively. This result indicates that the Lewis
acidity of the tin(II) metal center is important to the activity of the catalyst.

Chemically modified electrodes were prepared with Nafion® exchanged
membranes containing CpRu(amphos)₂Cl (31), CpRu(amphos)₂(SnCl₃) (32) and
CpRu(Ph₂PCH₂CH₂NMe₂)₂(SnPh₃) (30). Electrodes modified with 31 were studied in
solutions of water, methanol, nitromethane and acetonitrile. These electrodes were stable
and no evidence of leaching was observed. Electrodes containing the heterobimetallic
complexes could only be studied in nitromethane and acetonitrile. In solutions of water
and methanol, the heterobimetallic complexes quickly decompose. Because of the
instability of the electrodes in methanol and the retardation of the oxidation reaction by
nitromethane and acetonitrile, no catalytic studies were performed with these electrodes.
CHAPTER 5
EXPERIMENTAL PROTOCOLS

General Considerations

Standard Schlenk / vacuum techniques were used throughout. All NMR solvents were degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. $^1$H and $^{31}$P{$^1$H} NMR spectra are referenced to the residual proton in the deuterated solvent and to 85 % H$_3$PO$_4$, respectively. High-resolution mass spectrometry was performed by the University of Florida analytical service. Elemental analysis was performed by the Robertson Microlit Laboratories, Madison, NJ. ClCH$_2$CH$_2$N(CH$_3$)$_2$, cyclo-C$_5$H$_5$CH$_2$CH$_2$N(CH$_3$)$_2$, CpRu(PPh$_3$)$_2$Cl, Cp(PPh$_3$)Ru($\eta^1$-dppm)Cl, CpRu($\eta^2$-dppm)Cl, CpRu($\eta^2$-dppe)Cl, CpRu($\eta^2$-dppp)Cl, RuCl$_2$(PPh$_3$)$_3$, Ru($\eta^2$-Ph$_2$PCH$_2$CH$_2$NMe$_2$)$_2$Cl$_2$, (Ind)Ru(PPh$_3$)$_2$(SnCl$_3$), CpRu(PPh$_3$)$_2$(SnCl$_3$), (η$^5$-C$_5$H$_4$(CH$_2$)$_2$N(CH$_3$)$_2$H$^+$)Ru($\eta^2$-dppm)Cl, and IrCl(CO)$_2$(H$_2$N(C$_6$H$_4$)CH$_3$)$_2$ were prepared as previously described. TPPMS was prepared using a slight modification of the published procedure. Tetra-n-butylammonium triflate (TBAT), and RuCl$_3$·xH$_2$O were purchased from Sigma-Aldrich. (Ind)Ru(PPh$_3$)$_2$Cl was purchased from Strem Chemicals. Toray carbon paper (0.37 mm thickness) was purchased from fuelcellstore.com. Copper wire (0.5 mm diameter, 99.9999 %) was purchased from Alfa Aesar. All other starting materials were purchased in reagent grade purity and used without further purification.
Electrochemistry

Electrochemical experiments were performed at ambient temperature in a glove box under a nitrogen atmosphere using an EG&G PAR model 263A potentiostat/galvanostat. Cyclic voltammetry (CV) was performed with a normal three-electrode configuration consisting of a working electrode (glassy carbon 3 mm diameter or TCP electrode area 2 cm$^2$), a Pt flag counter electrode and a reference electrode. For experiments performed in 1,2-dichloroethane (DCE) or methanol, the reference electrode consisted of an acetonitrile solution of freshly prepared 0.01 M AgNO$_3$ and 0.1 M TBAT along with a silver wire. The Ag$^+$ solution and silver wire were contained in a 75 mm glass tube fitted at the bottom with a Vycor tip. For aqueous solutions a Ag/AgCl reference electrode (Bioanalytical Systems) was used. Constant potential electrolysis was carried out with similar equipment except for the working electrode being replaced with a vitreous carbon electrode. All potentials are reported vs. NHE and are not corrected for the junction potential of the reference electrode. The $E^0$ values for the ferrocene/ferrocenium couple in the electrolytes used is shown in Table 5-1.

Table 5-1. Formal potentials of the ferrocene/ferrocenium couple

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E^+/0$ (V vs NHE)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 M TBAT / DCE</td>
<td>0.50</td>
</tr>
<tr>
<td>0.7 M TBAT/CH$_2$Cl$_2$</td>
<td>0.50</td>
</tr>
<tr>
<td>0.1 M TBAT/MeOH</td>
<td>0.50</td>
</tr>
<tr>
<td>0.1 M TBAT/PC</td>
<td>0.58</td>
</tr>
<tr>
<td>0.1 M TBAT/CH$_3$CN</td>
<td>0.41</td>
</tr>
<tr>
<td>0.1 M TBAT/MeNO$_2$</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$^a$ Recorded at ambient temperature, scan rates = 50 mV/s.
Electrode Fabrication

Toray carbon paper (TCP) electrodes were fabricated as follows: TCP was cut into 1.5 cm x 1.0 cm blocks, treated with acetone, 0.1 M HCl and water to remove any impurities. The TCP blocks were then dried overnight at 60 °C. Electrical contact to the TCP was made through a copper wire attached with a conductive silver paste. After curing overnight at 60 °C, the electrode was cleaned as before with acetone, 0.1 M HCl and water, before drying at 60 °C for 5 hours. The silver electrical contact was then encapsulated with an insulating epoxy to give a TCP electrode with an area of approximately 2 cm². After curing overnight at 60 °C the electrode was cleaned again as described above and stored in an inert atmosphere.

Product Analysis

Electrolysis products were analyzed by gas chromatography on a Shimadzu GC-17A chromatograph containing a 15 m x 0.32 mm column of AT™-WAX (Alltech®, 0.5 µm film) on fused silica. The column was attached to the injection port with a neutral 5 m x 0.32 mm AT™-WAX deactivated guard column. The electrolysis products were quantitatively determined with the use of n-heptane as an internal standard. Products were identified by comparison to authentic samples.

Preparation of Modified Electrodes

Method A. Stock solutions of Nafion (0.5 - 2.5 wt %) and Ru complex (0.1 – 0.5 wt %) were prepared by slowly adding methanol solutions of the Ru complex to a rapidly stirred suspension of 5 wt % Nafion. The resulting mixture was left stirring under N₂ overnight to allow the ion exchange process to reach completion. The TCP electrodes were then coated with the Nafion/Ru mixture (50 µL increments), and evaporation of the
solvent assisted with a gentle flow of nitrogen. The electrodes were then dried at 60 °C for 30 minutes before rinsing with methanol, water and allowed to air dry at ambient temperature overnight. Electrodes modified by this method (MTCP-A) were stored under an atmosphere of nitrogen when not in use.

**Method B.** TCP electrodes were coated with 200 µL of a Nafion suspension (1 – 5 wt %) rinsed with water and dried overnight at 60 °C. The Nafion modified electrodes are then taken into the glove box before immersing overnight in a solution (0.1 – 0.5 wt %) of the Ru complex. Electrodes modified by this method (MTCP-B) were stored in this solution under an atmosphere of nitrogen when not in use.

**Synthesis**

\textbf{CpRu(PPh}_3\textbf{)(µ-Cl)(µ-dppm)HgCl}_2 \textbf{(16)}

A 50 mL Schlenk flask was charged with mercury acetate (0.21 g, 0.65 mmol) and 20 mL of DCE. To this suspension, CpRu(PPh}_3\textbf{(Cl)}(\textit{η}^1\textbf{-dppm}) \textbf{(6)} (0.56 g, 0.65 mmol) dissolved in 20 mL of DCE was slowly added while stirring. After two hours acetyl chloride (12 drops) dissolved in 20 mL of DCE was slowly added. All volatiles were removed in vacuo after an additional hour of stirring. The resulting yellow solid was then redissolved and filtered through Hyflo Super Cel with 50 mL of DCE. This orange solution was then concentrated to approximately 5 mL before hexanes (20 mL) was added. The resulting yellow solid was collected on a sintered glass frit and dried overnight at 80 °C under vacuum. Yield: 0.59 g, 81 %. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.81 – 6.50 (m, 35H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ + $\text{PPh}_3$), 4.85 (s, 5H, Cp), 3.25 – 2.95 (m, 2H, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$).

$^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 39.9 (d, Ru-$\text{PPh}_3$, $J_{PP}$ = 40 Hz), 35.0 (dd, Ru-$\text{PPh}_2\text{CH}_2\text{PPh}_2$, $J_{PP}$ = 40 Hz, 10 Hz), 30.1 (d, Hg-$\text{PPh}_2\text{CH}_2\text{PPh}_2$, $J_{PP}$ = 10 Hz).
**CpRu(PPh₃)(μ-Cl)(μ-dppm)Hg(OAc)₂ (18)**

Mercury (II) acetate (0.03 g, 0.10 mmol) and 5 mL of CH₂Cl₂ was placed in a 25 mL Schlenk flask. The Schlenk flask was then fitted with an addition funnel containing CpRu(PPh₃)(η¹-dppm)Cl (0.08 g, 0.10 mmol) in 5 mL of CH₂Cl₂. Approximately 10 minutes after the addition was complete, the mercury acetate was completely dissolved and stirring continued for an additional hour. The solution was then filtered through Hyflo Super Cel before evaporating to dryness at low pressure. The resulting solid was then recrystallized from CH₂Cl₂/hexanes. Yield: 95 %. ¹H NMR (CDCl₃): δ 31P{¹H} NMR (CDCl₃): δ 41.9 (d, Ru-PPh₃, JPP = 43 Hz), 36.9 (dd, Ru-PPh₂CH₂PPh₂, JPP = 43 Hz, 28 Hz), 24.1 (d, Hg-PPh₂CH₂PPh₂, JPP = 28 Hz).

**CpRu(TPPMS)₂Cl (22)**

In a 250 mL flask, CpRu(PPh₃)₂Cl (1.0 g, 1.4 mmol) and TPPMS (0.89 g, 2.3 mmol) in 100 mL of toluene were refluxed under N₂ for two days. The resulting orange solid was then collected on a medium frit, washed with approximately 200 mL of diethyl ether and dried under vacuum at 80 °C. Yield: 0.97 g, 90 %. ¹H NMR (DMSO-d₆): δ 7.72 – 7.52 (m, 4H), 7.25 – 7.08 (m, 24H), 4.07 (s, 5H, Cp). ³¹P{¹H} NMR (DMSO-d₆): δ 40.1 (s). HRMS (FAB): calc. for C₄₁H₃₃O₆Na₂P₂RuS₂ m/z 895.0033 [M – Cl⁻ - 2 H₂O]⁺, found 894.9935. Anal. Calc. for C₄₁H₃₇O₈Na₂ClP₂RuS₂: C, 50.96; H, 3.86. Found: C, 50.71; H, 3.68.

**CpRu(TPPMS)₂(SnCl₃) (23)**

CpRu(TPPMS)₂Cl (0.71 g, 0.76 mmol) and SnCl₂ (0.17 g, 0.89 mmol) in 25 mL ethanol were stirred under N₂ at room temperature overnight. The solution was then evaporated to dryness and the resulting yellow solid recrystallized from ethanol/diethyl
ether. Yield: 0.73 g, 85 %. \(^1\)H NMR (CD\(_3\)OD): \(\delta\) 7.86 – 7.70 (m, 4H), 7.35 – 7.08 (m, 24H), 4.65 (s, 5H, Cp). \(^{31}\)P\(^{1}\)H\) NMR (CD\(_3\)OD): \(\delta\) 46.0 (s, TPPMS, \(^2\)J\(_{P,Sn}\) = 422 Hz).

Anal. Calc. for C\(_{41}\)H\(_{37}\)O\(_8\)Na\(_2\)Cl\(_3\)P\(_2\)RuS\(_2\)Sn: C, 42.60; H, 3.23. Found: C, 42.87; H, 3.07.

**CpRu(\(\eta^2\)-dppm)(SnCl\(_3\)) (24)**

A 50 mL Schlenk was charged with CpRu(\(\eta^2\)-dppm)Cl (0.59 g, 1.0 mmol), anhydrous SnCl\(_2\) (0.21 g, 1.1 mmol) and 40 mL of ethanol. This orange mixture was then refluxed for 5 hours. The resulting bright yellow solid was then filtered and recrystallized from CH\(_2\)Cl\(_2\)/hexane before drying under vacuum at 60 °C. Yield: 0.66 g, 85 %. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.62 – 7.28 (m, 20H, Ph\(_2\)PCH\(_2\)PPh\(_2\)), 5.16 (m, 1H, Ph\(_2\)PCH\(_2\)PPh\(_2\)), 5.08 (s, 5H, Cp), 4.76 (m, 1H Ph\(_2\)PCH\(_2\)PPh\(_2\)). \(^{31}\)P\(^{1}\)H\) NMR (CDCl\(_3\)): \(\delta\) 8.3 (s, PPh\(_2\)CH\(_2\)PPh\(_2\)).

**CpRu(\(\eta^2\)-dppp)(SnCl\(_3\)) (26)**

A 50 mL round bottom flask was charged with CpRu(\(\eta^2\)-dppp)Cl (0.24 g, 0.39 mmol), anhydrous SnCl\(_2\) (0.09 g, 0.47 mmol) and 25 mL of ethanol before fitting with a reflux condenser. This orange mixture was then refluxed overnight under an atmosphere of nitrogen. The resulting bright yellow solid was then collected on a sintered glass frit and washed with ethanol before drying in vacuo at 60 °C. Yield: 0.29 g, 91 %.

\(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.48 – 7.22 (m, 20H, Ph\(_2\)PCH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\)), 4.84 (s, 5H, Cp), 2.8 – 2.7 (m, 4H, Ph\(_2\)PCH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\)), 1.54 (s, 2H, Ph\(_2\)PCH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\)). \(^{31}\)P\(^{1}\)H\) NMR (CDCl\(_3\)): \(\delta\) 33.9 (s, PPh\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\)). HRMS (FAB): calc. for C\(_{32}\)H\(_{31}\)P\(_2\)Ru m/z 579.0944 [M – SnCl\(_3\)]\(^+\), found 579.2200.
CpRu(PPh3)2(SnPh3) (27)

A 100 mL Schlenk flask was charged with CpRu(PPh3)2(SnCl3) (1.0 g, 1.1 mmol) and 50 mL of benzene, before fitting with an addition funnel containing 2.4 mL of phenyllithium (1.8M in di-n-butylether). Phenyllithium was then added dropwise to the yellow suspension, resulting in a purple solution. Stirring was continued for 4 hours at room temperature before quenching with 1 mL of ethanol. After removing the solvent, the resulting yellow solid was dried in vacuo for 2 hours. The yellow solid was then dissolved in approximately 100 mL of diethyl ether and filtered through a pad of Hyflo Super Cel before drying in vacuo at 60 °C overnight. Yield: 1.02 g, 90 %. \(^1\)H NMR (CDCl₃): \(\delta 7.19 – 6.98 \text{ (m, 45H)}, 4.27 \text{ (s, 5H, Cp)}\). \(^{31}\)P\(_1^1\)H NMR (CDCl₃): \(\delta 53.0 \text{ (s, PPh₃}, 2J_{PSn} = 270 \text{ Hz})\). HRMS (FAB): calc. for C₅₃H₄₄P₂RuSn m/z 964.0977 [MH⁺ – C₆H₆]⁺, found 964.0941.

CpRu(Ph₂PCH₂CH₂N(CH₃)₂)₂Cl (28)

A two necked 100 mL round bottom flask fitted with a reflux condenser and a rubber septum was charged with Ru(η²-Ph₂PCH₂CH₂NMe₂)₂Cl₂ (0.65 g, 0.95 mmol), cyclopentadiene (0.19 g, 2.8 mmol) and 50 mL of ethanol. This red mixture was then refluxed for three days under an atmosphere of nitrogen. After refluxing, the solvent was removed under vacuum and the resulting orange solid washed with 90 mL of n-hexanes before recrystallizing with CH₂Cl₂/n-hexanes. Yield: 0.50 g, 74 %. \(^1\)H NMR (CDCl₃): \(\delta 7.47 – 7.15 \text{ (m, 20H)}, 4.29 \text{ (s, 5H, Cp)}, 3.12 \text{ (m, 2H), 2.94 (m, 2H), 2.63 (s, 12H, N(CH₃)₂), 2.42 (m, 2H), 2.20 (m, 2H)}\). \(^{31}\)P\(_1^1\)H NMR (CDCl₃): \(\delta 36.6 \text{ (s, Ph₂PCH₂CH₂NMe₂)}\). HRMS (FAB): calc. for C₃₇H₄₆ClN₂P₂Ru m/z 717.1872 [MH⁺], found 717.1889.
CpRu(Ph₂PCH₂CH₂N(CH₃)₂)₂(SnCl₃) (29)

A 25 mL Schlenk flask was charged with CpRu(Ph₂PCH₂CH₂N(CH₃)₂)₂Cl (0.84 g, 1.11 mmol), SnCl₂ (0.33 g, 1.75 mmol) and 20 mL of 1,2-dichloroethane. The resulting mixture was stirred at room temperature for two days before refluxing for 6 hours. After removing the solvent under vacuum, the orange solid was dissolved in CH₂Cl₂ and filtered through a pad of Hyflo Super Cel. A yellow solid was then precipitated with n-hexanes before recrystallizing with CH₂Cl₂/n-hexanes. Yield: 0.97 g, 96 %. ¹H NMR (CDCl₃): δ 7.44 – 7.19 (m, 20H), 4.71 (s, 5H, Cp), 3.09 (m, 4H), 2.86 – 2.74 (m, 14H), 2.56 (m, 2H). ³¹P{¹H} NMR (CDCl₃): δ 39.4 (s, Ph₂PCH₂CH₂NMe₂, 2JₚSn = 412 Hz).

HRMS (FAB): calc. for C₃₇H₴₅Cl₂N₂P₂RuSn m/z 871.0500 [M-Cl-]⁺, found 871.0543.

CpRu(Ph₂PCH₂CH₂N(CH₃)₂)₂(SnPh₃) (30)

A 50 mL Schlenk flask was charged with CpRu(Ph₂PCH₂CH₂N(CH₃)₂)₂(SnCl₃) (0.25 g, 0.28 mmol) and 50 mL of toluene before cooling to -78 °C. The Schlenk flask was then fitted with an addition funnel containing 0.70 mL of phenyllithium (1.7M in di-n-butylether) and 2 mL of toluene. Phenyllithium was then added dropwise, resulting in the formation of a purple solution. Stirring was continued for 4 hours at room temperature before quenching with 1 mL of ethanol. After drying in vacuo, the resulting yellow solid was dissolved in n-hexanes and filtered through a pad of Hyflo Super Cel. Complex 30 was then isolated by chromatography on SiO₂ with 99:1 (chloroform/triethylamine) as eluent. Yield: 0.19 g, 64 %. ¹H NMR (CDCl₃): δ 7.52 – 7.09 (m, 35H), 4.21 (s, 5H), 2.3 – 2.1 (m, 4H), 1.81 (s, 12H), 1.6 – 1.7 (m, 4H). ³¹P{¹H} NMR (CDCl₃): δ 43.8 (s, Ph₂PCH₂CH₂N(CH₃)₂, 2JₚSn = 262 Hz).
CpRu(Ph₂PCH₂CH₂N(CH₃)₃BF₄)₂Cl (31)

A 500 mL two-necked round bottom flask containing CpRu(PPh₃)₂Cl (1.00 g, 1.37 mmol) and 150 mL of toluene was fitted with a reflux condenser and a pressure equalizing addition funnel before heating to reflux. To the refluxing orange mixture, a solution of amphos (0.99 g, 2.8 mmol) in 50 mL of methylene chloride was added dropwise. After four days of reflux, the solvent was removed under vacuum and the resulting yellow solid was washed with 200 mL of petroleum ether and 100 mL of toluene before recrystallizing from CH₂Cl₂ / diethyl ether. Yield: 0.96 g, 76 %. ¹H NMR (DMSO-d₆): δ 7.49 – 7.21 (m, 20H), 4.48 (s, 5H, Cp), 3.21 – 2.85 (m, 24H), 2.57 (m, 2H). ³¹P{¹H} NMR (DMSO-d₆): δ 35.9 (s, amphos). HRMS (FAB): calc. for C₃₉H₅₁BClF₄N₂P₂Ru m/z 833.2294 [M-BF₄]+, found 833.2287.

CpRu(Ph₂PCH₂CH₂N(CH₃)₃BF₄)₂(SnCl₃) (32)

CpRu(amphos)₂Cl (0.20 g, 0.22mmol) and SnCl₂ (0.50 g, 0.33mmol) in 50 mL of ethanol were refluxed under N₂ overnight. The solution was then evaporated to dryness and the resulting yellow solid was recrystallized from ethanol/diethyl ether. Yield: 0.21 g, 88 %. ¹H NMR (acetone-d₆): δ 7.65 – 7.43 (m, 20H), 5.00 (s, 5H, Cp), 3.49 (m, 2H), 3.11 (s, 18H, N(CH₃)₂), 2.94 (m, 4H), 2.44 (m, 2H). ³¹P{¹H} NMR (acetone-d₆): δ 39.5 (s, Ph₂PCH₂CH₂NMe₃BF₄, ²Jₚ,Sn = 405 Hz).

Ph₂PCH₂CH₂N(CH₃)₂

1.25 g of Li chips and 100 mL of THF were placed in a 250 mL Schlenk flask fitted with a pressure equalizing addition funnel. To the vigorously stirred Li suspension, Ph₂PCl (10 g, 0.045 moles) in 50 mL of THF was slowly added. After stirring at R.T. for 12 hours, the resulting Ph₂PLi solution was transferred to a two necked round bottom
flask fitted with a rubber septum and an addition funnel. While stirring the deep red Ph2PLi solution, ClCH2CH2N(CH3)2 (5.0 g, 0.036 moles) in 50 mL of THF was slowly added before heating for 12 hours at 60 °C. The resulting mixture was then hydrolyzed with 50 mL of degassed water, before adding 200 mL of diethyl ether. The organic layer was extracted with 250 mL of water and dried over MgSO4 before the solvent was removed under vacuum to yield an oil. Purification of the oil was achieved using flash chromatography through a column of neutral alumina with diethyl ether as the eluent. Yield: 7.86 g, 84 %. The compound was identified by comparison to literature data.220

Ph2PCH2CH2N(CH3)3BF4

Me3OBF4 (1.65 g, 0.011 mol) and 80 mL of CH2Cl2 were added to a 250 mL Schlenk flask, fitted with a pressure equalizing addition funnel. The flask was then cooled to -98 °C before a solution of Ph2PCH2CH2N(CH3)2 (3.01 g, 0.012 mol) in 30 mL of CH2Cl2 was added dropwise. When the addition was complete the mixture was stirred at -98 °C for 5 hours then at rt overnight. The resulting white solid was collected on a sintered frit and washed exhaustively with diethyl ether, before recrystallizing from CH2Cl2 / diethyl ether. Yield: 3.36 g, 84 %. 1H NMR (acetone-d6): δ 7.42 – 7.55 (m, 10H, Ph2P), 3.68 (m, 2H, Ph2PCH2CH2NMe3), 3.38 (s, 9H, Ph2PCH2CH2NMe3), 2.85 (m, 2H, Ph2PCH2CH2NMe3). 31P {1H} NMR (acetone-d6): δ -19.5 (s, Ph2PCH2CH2NMe3).

A 100 mL round bottom flask was charged with

(η^5-C5H4(CH2)2N(CH3)2H^+)Ru(η-dppm)(μ-CO)2IrCl2]Cl

1.3 g, 2.0 mmol), IrCl(CO)2(H2N(C6H4)CH3) (0.81 g, 2.0 mmol) and 50 mL of toluene. This mixture was then refluxed for 24 hrs and the resulting yellow precipitate collected on a sintered glass
frit. The crude product was then placed into a Soxhlet extractor and impurities extracted overnight with benzene, before drying overnight in vacuo at 60 °C. Yield: 1.25 g, 65 %.

$^1$H NMR (DMSO-d$_6$): $\delta$ 7.52-7.18 (m, 20H, $Ph_2PCH_2PPh_2$), 5.30 (s, 2H, $Cp$), 5.07 (s, 2H, $Cp$), 3.17 (m, 2H, $Ph_2PCH_2PPh_2$), 2.70 (m, 10H, $C_5H_4(CH_2)_2N(CH_3)_2H^+$). $^{31}$P$^1$H NMR (d$_6$-DMSO): $\delta$ 59.8 (d, Ru-$Ph_2PCH_2PPh_2$, J$_{PP}$ = 59 Hz), 12.4 (d, Ir-$PPh_2CH_2PPh_2$, J$_{PP}$ = 59 Hz). IR (KBr) 1800, 1780 cm$^{-1}$. HRMS (FAB) calcd for C$_{36}$H$_{37}$Cl$_2$IrNO$_2$P$_2$Ru m/z 942.0349 [M-Cl]$^+$, found 942.0377.

Crystallographic Structure Determination of CpRu(PPh$_3$)(µ-Cl)(µ-dppm)HgCl$_2$ (16)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoK$_\alpha$ radiation ($\lambda$ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the $\omega$-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in SHELXTL5, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of the complex and two dichloroethane molecules of crystallization. One of those molecules had one of its chlorine atoms disordered and was refined in two parts (Cl6 & Cl6'). Their site occupation factors were dependently refined to 0.67(2) for Cl, and consequently 0.33(2) for Cl6'. A total of 581 parameters were refined in the final cycle of refinement using 10968 reflections with I >
2σ(I) to yield R₁ and wR₂ of 2.07 % and 5.23 %, respectively. Refinement was done using F².
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Corey Ricardo Carlo Anthony was born in Kingston, Jamaica on December 31st, 1976. His interest in the sciences was sparked at an early age by his sisters and their toy chemistry kit. Corey spent his formative years at St. Theresa Preparatory School before attending St. George’s College High School where his love for chemistry took root. After completing high school Corey went on to pursue a tertiary level education at the University of the West Indies at Mona. He thoroughly enjoyed his college years and graduated in 1998 with a Bachelor of Science degree in pure and applied chemistry. Corey then got his first full time job at the Jamaica Forensic Science Laboratory as a forensic science examiner. He worked at the forensic lab for two years before enrolling at the University of Florida. In spring of 2001 he joined the McElwee-White research group and began his Ph.D. studies in organometallic chemistry. After six years of research, he graduated from the University of Florida with a Doctorate of Philosophy in chemistry.