

(non-linear optical properties). To investigate this possibility we will study the interaction of the cluster with other metal containing systems. We are investigating the effect of substituting ferrocenyl phosphine ligands for carbonyl ligands (CO). Newly synthesized compounds will be probed by Infrared Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), and Electrochemical analysis, to reveal the structure, degree of attachment, oxidation potentials, and electron communication between the cluster and the ligands. This research not only furthers our knowledge of the chemistry of these systems, but also provides important data about the possible applications of these cluster's material, optical, and electrochemical properties.

Proposed Research

This research is a continuation of work begun during summer 2000 and two semesters of C409 (Independent Research). This project involves the synthesis and analysis of several previously unsynthesized compounds and the further synthesis, purification, and investigation of a few preliminarily synthesized compounds. This preliminary research indicates that the desired compounds can be synthesized and reveals that thorough and more intense investigation will provide original, significant, and publishable information [5].

The starting material (Figure 1, X = OMe) is synthesized in the lab from commercially available $\text{Ru}_3(\text{CO})_{12}$. The new compounds are produced by the substitution of the carbonyl ligands on the starting material with ferrocenyl phosphine ligands ("ligand" is a term for any group attached to a metal center such as the CO groups in Figure 1). Substitution with these ligands yields compounds that, when analyzed, provide a wealth of information regarding their structure and electrochemical activities.

The ligand substrates are triphenyl phosphine (PPh_3) and ferrocene (Fc). The well-known properties of the new ligand (phosphine and ferrocene) allow for precise and accurate substitution, electrochemical analysis, and structure determination of the new clusters products [2].

The ferrocenyl phosphine ligands (Figure 2) have been synthesized and purified previously, and $(\text{PPh})_2\text{Fc}$ is available commercially. The substitution reaction that occurs between the cluster and the ligand is illustrated in Figure 3. It has been shown previously that up to three equivalents of the ligand (L) can be reacted with the cluster and replace the corresponding number of axial carbonyls [3].

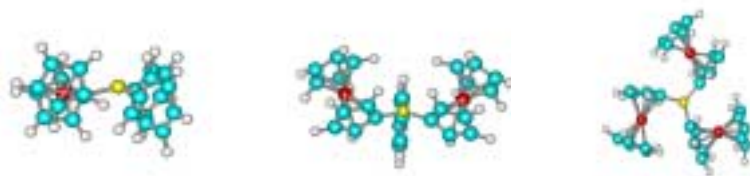
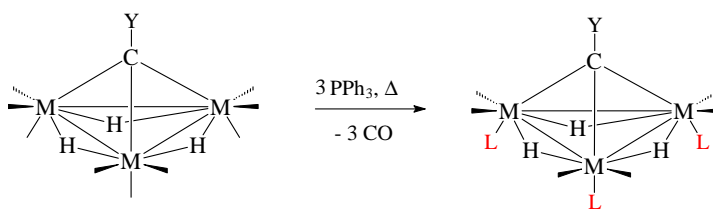


Figure 2. Ferrocenyl Phosphine Ligands

While a maximum of three ligand attachments are possible, the size of the ferrocenyl phosphine ligands may reduce the number of substitutions. A yield of mono- or di-substituted product would not be detrimental to the analysis process, rather, the information obtained from the various degrees of substitution would be invaluable to determine the changes in reactivity, communication, and optical aspects of the cluster [4].



Once synthesized, these clusters will be purified and analyzed. Thin Layer Chromatography (TLC) and crystallization will be used to purify the synthesized

Figure 3. Reaction of the Cluster with Phosphine Ligands compounds. Once purified, the compounds will be analyzed by IR, NMR, and electrochemical methods. A preliminary NMR of the PFc_3 substituted cluster is shown in Figure 4. The chemical shift in the -16 ppm region reveal that this synthesis produced a mono-substituted product.

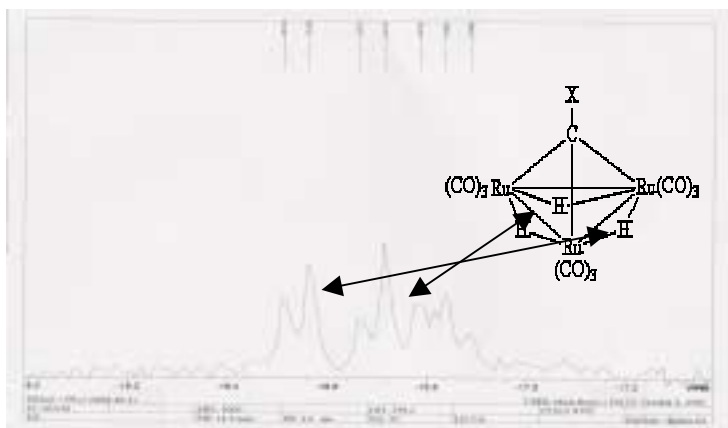


Figure 4. ^1H NMR Spectrum of $\text{H}_3\text{Ru}_3(\text{COMe})(\text{CO})_8(\text{PFc})$

The electrochemical data of PFc_3 (Figure 5) reveals complex electric interaction between the ligand and the cluster and further investigation will allow us to further understand the extent to which the reactivity of the cluster is altered.

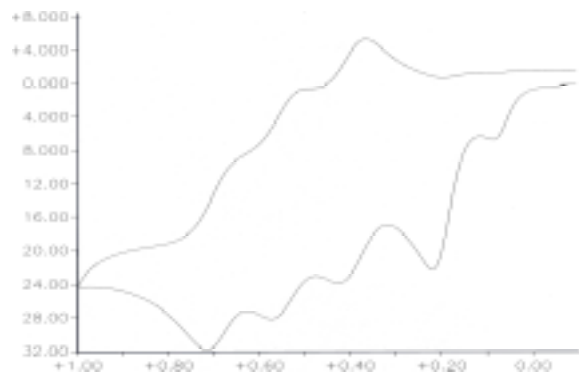


Figure 5. Electrochemistry of $\text{H}_3\text{Ru}_3(\text{COMe})(\text{CO})_8(\text{PFc})$

The preliminary research provides a foundation for research that will provide data regarding electron communication, optical properties, and altered reactivity of the cluster and ligands. It is expected that this project will lead to results that can be presented at research meetings and be published. The ability to spend a summer to focus on researching this area would greatly advance the understanding of these clusters and provide knowledge as to the potential application of these clusters in electronic and data storage devices. The summer SMART award would allow me to gain experience in a lab that normal classroom settings are unable to provide. My knowledge of chemistry has greatly increased during the past semester I have spent in Dr. Feighery's lab, and receiving this grant would allow me to continue to gain the lab experience necessary to succeed in graduate school.

References

- (1) "Metal-Metal Bonds and Clusters in Chemistry and Catalysis" ed. J.P. Fackler, Jr., Plenum Press, New York, 1990.
- (2) Keister, J.B., Payne, M.W., and Muscatella, M.J., *Organometallics*, **1983**, 2, 220.
- (3) Sollott, G.P., Mertwoy, H.E., Portnoy, S., and Snead, J.L., *Journal of Organic Chemistry*, **1963**, 28, 1090.
- (4) Rahman, Z.A., Beanan, L.R., Bavaro, L.M., Modi, S.P., Keister, J.B., and Churchill, M.R., *Journal of Organometallic Chemistry*, **1984**, 263, 75.
- (5) These results were presented at the IUSB Student Research Conference --
"Ferrocenyl Phosphine Ligand Substitution On Triruthenium Carbonyl Clusters"
(March 9, 2001).

Proposed Research Schedule

The time I have spent researching in Dr. Feighery's lab has had an immense impact on my education at IUSB. My knowledge and understanding of practical research, organometallic chemistry, and various chemical analyzing techniques has expanded tremendously with the hands-on learning experience that I have been afforded. I plan on continuing this research for the rest of my undergraduate career, and complete my senior honors thesis in this area of chemistry. I look forward to working in Dr. Feighery's lab this summer so that I may be able to accomplish a great amount of work that I have been unable to do during the school year due to time constraints. The expected summer research schedule (20 hours/week, 200 hours total) is outlined below:

Weeks 1 - 2

Synthesis and purification of the starting material $\text{H}_3\text{Ru}_3(\text{COMe})(\text{CO})_9$.

$\text{Ru}_3(\text{CO})_{12}$ is used to produce the starting material by a published procedure which requires a series of several air sensitive reactions each requiring many hours and/or days [3]. In order to ensure sufficient starting material will be available, 3-4 separate batches will be prepared (1500-2000 mg). The several step reactions have many byproducts which will affect the ferrocenyl phosphine reactions. Therefore, the desired component is separated from the byproducts by Thin Layer Chromatography.

Weeks 2 - 6

Reactions of ferrocenyl phosphine ligands (PPh_2Fc , PPhFc_2 , PFc_3 , $(\text{PPh}_2)_2\text{Fc}$) with the starting cluster.

These reactions also involve several steps and may form unimportant byproducts. Therefore, several different reactions will be simultaneously performed for all ligands in order to ensure reaction success and several various degrees of ligand substitution. It is expected that these reactions will take the most time to determine the optimal conditions.

Weeks 6 - 8

Separation and purification of the ferrocenyl phosphine substituted clusters.

In order to analyze the products by NMR and electrochemical analysis, analytically pure compounds must be obtained. It is also necessary to separate the compounds in order to ensure the integrity of the desired compounds. TLC will be the most commonly used purification technique, although recrystallization will also be implemented.

Weeks 8 - 10

Characterization of products using IR, NMR, and electrochemistry.

Three of the most important analyzing techniques in organometallic chemistry will be used to analyze these products and obtain conclusive results. IR, NMR, and electrochemical analysis reveal the structure, electrical communication, and changes in reactivity due to the ligand substitution.