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The Use of Lanthanide Triflates as a Method for Reducing Ytterbium(III) to Ytterbium(II)

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To the Graduate Council:

I am submitting herewith a thesis written by Latasha Michelle Garrett entitled "The Use of Lanthanide Triflates as a Method for Reducing Ytterbium(III) to Ytterbium(II)." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

George Schweitzer, Major Professor

We have read this thesis and recommend its acceptance:

Ben Xue, Jamie Adcock

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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The Use of Lanthanide Triflates as a Method for Reducing Ytterbium(III) to Ytterbium(II)

A Thesis
Presented for the
Master of Science
Degree
University of Tennessee at Knoxville

Latasha Michelle Garrett
December 2008

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ABSTRACT

High purity lutetium (99.999%) is employed in the manufacture of cerium-doped lutetium oxyorthosilicate. Such lutetium is in high demand because the cerium-doped lutetium oxyorthosilicate is the best gamma-detecting scintillator known. Solvent extraction is the most widely used method for separating the rare earths on an industrial scale at 99.999% purity. However, this process is time consuming and requires 80-100 separation stages. The major difficulty in pure lutetium production is the separation from the adjacent element, ytterbium. If ytterbium(III) could be reduced to ytterbium(II), this would permit a different chemistry between ytterbium(II) and the trivalent state elements, allowing a more facile separation process by opening the separation gap between ytterbium and lutetium. This has been previously achieved through the use of mercury cathodes or amalgams. Unfortunately, any process involving mercury is unacceptable industrially because of the toxicity of mercury. Literature has shown that reduction with magnesium metal can be carried out with proper selection of solvent. A maximum amount of $85\% \pm 5\%$ can be obtained. The ideal system would be one which would remove all of the ytterbium(III). This project was performed to develop a more efficient reduction by the use of the triflate system. Anhydrous solutions were used in the project because of the capability of water to oxidize ytterbium(II) to ytterbium(III). With the set of systems that were attempted, about 50% ytterbium(II) was achieved. The hypothesis that the absence of water would increase the percent recovery of ytterbium did not solve the problem.

TABLE OF CONTENTS

CHAPTER I	1
Introduction	1
Overview	1
Rare Earth Reduction History	3
Proposed Project	10
CHAPTER II.....	12
MATERIALS AND METHODS.....	12
Materials	12
Apparatus	12
Methods	21
CHAPTER III.....	25
Results and Discussion.....	25
Solubility tests	25
Isolated analysis	28
Ytterbium triflate reduction	29
Initial reduction with magnesium	29
New Order of Addition	30
Effect of Temperature.....	33
THF Removal	37
Reduction Time	43
Form of Magnesium.....	45
Lutetium triflate and magnesium.....	46
combined triflate studies.....	47
CHAPTER IV	50
Conclusion.....	50
REFERENCES.....	52
Vita.....	56

LIST OF TABLES

Table 1: List of Solvents and Reagents.....	13
Table 2: Lutetium and Ytterbium Solubility Tests	26
Table 3: Ytterbium Triflate in the Absence of Magnesium.....	28
Table 4: Lutetium Triflate in the Absence of Magnesium.....	28
Table 5: Initial trials of Yb(III) Triflate Reduction with Mg Powder	30
Table 6: Effects of Different Reaction Times	30
Table 7: New Procedure for Reducing Ytterbium(III) Triflate.....	31
Table 8: Ytterbium(III) Triflate Reduction in the presence of Grignard in Ether	32
Table 9: Reduction of Soluble Ytterbium(III) Triflate.....	33
Table 10: Temperature Effects on Triflate System	38
Table 11: Removal of Additional Tetrahydrofuran	40
Table 12: Effect of Concentration Excluding Tetrahydrofuran	40
Table 13: Removal of Tetrahydrofuran from Grignard.....	42
Table 14: Different Amounts of Tetrahydrofuran Removed	42
Table 15: Best Reduction Time	43
Table 16: Best Reduction Time II	43
Table 17: Reduction Time of Two Days	44
Table 18: Multiple Additions of Grignard and Magnesium	44
Table 19: Best Reduction Time with Mg Ribbon	45
Table 20: Magnesium Ribbon versus Magnesium Powder	46
Table 21: Lutetium triflate with Magnesium Powder	47
Table 22: Lutetium triflate with Magnesium Ribbon.....	47
Table 23: Ytterbium(III) and Lutetium(III) Triflate Mixed	48

LIST OF FIGURES

Figure 1: Fractional Distillation Apparatus.....	16
Figure 2: Basic System for Ytterbium(III) Reduction.....	18
Figure 3: Experimental Set Up for Removal of THF	19
Figure 4: Carbon Filter Apparatus	20
Figure 5: Perkin Elmer AAnalyst 100.....	22
Figure 6: Relationship between Ytterbium and Lutetium Mixed	49

CHAPTER I INTRODUCTION

OVERVIEW

Positron emission tomography (PET) is a medical imaging technique used to produce a three-dimensional picture of metabolic activity in the human body. It is a very important method used for diagnosing cells whose metabolic activity is abnormal, such as cancerous ones.¹ Cerium-doped lutetium oxysilicate, Lu_2OSiO_4 , or (LSO) crystals are commonly used as scintillators for gamma-ray detection in PET instruments. LSO has excellent scintillation properties which include a high-efficiency light output, a short fluorescence decay time, a high density, and a high atomic number. One of the disadvantages of LSO is that the expensive lutetium(III) oxide used in its preparation cannot have a chemical purity less than 99.999% to be effective.² This high purity requires a suitable method for separating lutetium cleanly from the other lanthanide elements, which tend to be its major contaminants.

Lutetium is the very last lanthanide element (rare earth element) in the periodic table with the highest atomic number, and it is amongst the rarest of the lanthanide elements. Just as all the lanthanide elements, with the possible exception of cerium, its chemistry predominantly involves the trivalent state in aqueous solutions.³ This stability can be explained by observing the pattern of the ionization energies needed to form the various oxidation states.⁴

As a result of the similarities of the lanthanides, these elements are extremely difficult to separate, especially from their neighboring elements. Previous methods for separating these elements involved fractional crystallization of selected partially-soluble compounds, which required thousands of steps with little purity obtained. Ion-exchange chromatography and counter-current solvent extraction have become the current methods for separating the lanthanide elements, the latter technique being the preferred industrial method. Separation and purification of lutetium is not an easy task due to the adjacent element, ytterbium. The separation factor in all methods is very small. For example, continuous counter-current solvent extraction requires 80-100 stages to obtain 99.999% purity of lutetium. However, if ytterbium could somehow be completely removed from the system, thulium becomes the nearest element to lutetium with a separation factor twice that of ytterbium and lutetium. As a result, separation of lutetium would require only 30-40 stages, which is a great economic advantage for industrial companies.⁵

Although most of the lanthanide elements prefer the trivalent state, a few elements such as europium, ytterbium, and samarium can exist in aqueous solution with divalent oxidation states, even though their half lifetimes might be short.⁶ This provides a means for separation because the chemistry of the divalent state lanthanide elements is different from trivalent state elements.

RARE EARTH REDUCTION HISTORY

In 1929, Klemm and Schuth were the first to develop a method for preparing a divalent compound of ytterbium. The preparation was carried out by treating ytterbium(III) oxide with a stream of chlorine-disulfur dichloride ($\text{Cl}_2\text{-S}_2\text{Cl}_2$) at 600°C . The product was solid ytterbium(II) chloride. Although this technique was successful, it was not performed in aqueous solution.⁷

A year later, R.W. Ball and L.F. Yntema were able to produce ytterbium(II) sulfate in aqueous solution from its trivalent state. A mixture of rare earth oxides, which contained a small amount of ytterbium, was dissolved in hydrochloric acid. The solution was diluted to 400 mL and 400 mL of sulfuric acid was added after evaporating the excess hydrochloric acid. Then, the solution was placed in an electrolytic cell containing a mercury cathode and a platinum anode to generate the divalent ytterbium which precipitated as the sulfate. The above solution was placed in the cathode compartment while the anode compartment contained 0.05 M hydrochloric acid. The voltage between the electrodes was 110 volts with a direct current of 0.1 ampere and a cathode density of $0.025 \text{ ampere/cm}^2$. A green color was observed for ytterbium(II) sulfate and was found to be a distinguishing feature for the ytterbium(II) ion. The success of this technique was dependent upon the high overvoltage of the mercury cathode and the insolubility of ytterbium(II) sulfate. Even though only 1 to 2% ytterbium was in the starting material, the authors reported obtaining an ytterbium product of 98% purity. The amount of ytterbium(II) sulfate recovered was not given in the article.⁸

At some point in 1932, W. Prandtl was able to produce YbSO_4 in solution using the same method discussed by Ball and Yntema. A mercury cathode and platinum anode were used for this electrolytic cell. The voltage between the electrodes was 110 volts with a current between 0.2 and 0.4 amperes at a temperature of about 50°C . The percentage recovery of ytterbium sulfate was not reported.⁹

During 1936, D.W. Pearce, C.R. Naesar, and B.S. Hopkins modified the electrolysis cell used by Yntema. The anode was a narrow piece of platinum foil, which was enclosed in a glass tube that was turned upward to prevent released gases from entering the anode compartment. The mercury cathode was also enclosed in a cone-shaped tube, which allowed different amounts of mercury to be exposed during electrolysis. The temperature of the system was controlled by surrounding the cathode compartment with a water jacket. The last part of the system to be varied was the addition of a stopcock so the cell could be drained. The authors reported that ytterbium(III) was reduced to its divalent state. The most efficient method found for reduction and separation was with 0.13 M ytterbium(III) chloride dissolved in 0.6 M sulfuric acid. The current density of the cell was 0.16 ampere/cm^2 with a voltage of 110 volts. Under these conditions, approximately 90% of the ytterbium was removed during one electrolysis cycle. It was assumed that the remaining 10% of ytterbium in solution reached an equilibrium between the two oxidation states and ceased further reduction. The authors also reported that a drop in temperature assisted with removal of ytterbium from its neighboring elements.¹⁰

The following year, J.K. Marsh obtained a high yield of ytterbium(II) sulfate by substituting amalgamated lead for the mercury cathode with a lead pipe anode. Electrolysis took place in a porous pot that was placed in a 400 mL beaker. The porous pot included the anode and 1M sulfuric acid. The beaker contained the cathode compartment as well as ytterbium(III) sulfate solution produced from ytterbium(III) oxide and 1M sulfuric acid. A maximum of six cells was used in sequence with a voltage of 100 and a cathode current of 0.3 amp/cm^2 was applied to the cell. A 95% yield of ytterbium(II) sulfate was reported with a increase in purity from 30% to 100% with four additional precipitations.¹¹

During the same year, A. Brukl was interested in obtaining pure ytterbium and the previously discussed electrolytic reduction experiments were performed. A mercury cathode and platinum anode were used along with sulfuric acid to produce a precipitation of ytterbium(II) sulfate. The production of large amounts of ytterbium was found to be dependent upon the solubility of ytterbium(II) sulfate in sulfuric acid.¹²

In 1937, L. Holleck and W. Noddack used a strontium amalgam to reduce rare earth metals. This was an innovative procedure that allowed displacement without the use of an electrolytic cell. Strontium amalgam was used to reduce ytterbium and a co-precipitate of ytterbium sulfate and strontium sulfate was produced. An eighty percent recovery of ytterbium(II) sulfate was obtained.¹³ Over the next couple of years, L. Holleck developed a method for reducing all the rare earth elements. The trichlorides of lanthanum to lutetium including scandium and yttrium were reduced when heated at 800°C with a stream of hydrogen for about 14 hours. The majority of the lanthanide

chloride reduced to a dichloride while part of the trichloride reduced to its metal state, which was found to increase from lanthanum to lutetium and from lanthanum to yttrium to scandium. Samarium, europium, and ytterbium were the only stable divalent chlorides formed.¹⁴

In 1940, G.W. Walters and D.W. Pearce were the first to report the electrode potential for ytterbium(III) / ytterbium(II) to be -0.578 volts by using a mercury-platinum electrode.¹⁵ On the other hand, H.A. Laitinen found an error in the experimental approach used to determine the electrode potential for ytterbium. It was reported that the potential found by Walters and Pearce was a “mixed potential”, which represented two different systems. With polarographic determinations and with a dropping mercury electrode, it was concluded that the potential of ytterbium(III) / ytterbium(II) lies between -1.05 and -1.17 volts. A half wave potential of -1.15 volts was obtained with a ytterbium amalgam and ytterbium salt. The half wave value was suggested to more likely be the electrode potential for ytterbium(III) / ytterbium(II).¹⁶ In 1974, D. A. Johnson estimated the electrode potential of ytterbium(III) / ytterbium(II) to be -1.10 volts with an ionic model and thermodynamic data. Estimated values were found to be in agreement with qualitative observations and calculated values from spectroscopic data.¹⁷ During 1976, L.R. Morss estimated the potential value to be -1.04 volts.¹⁸ A few years later, D. Ferri and colleagues estimated the value to be -1.155 volts.¹⁹

During 1960, M. Peltier and P. Rombau obtained a patent for separating the trivalent and divalent lanthanide ions by treating them with ammonium hydroxide. The divalent lanthanides did not precipitate, but the remaining lanthanide elements in the

trivalent state were insoluble. The authors also found that the addition of sulfate resulted in the precipitation of $\text{Ln}(\text{SO}_4)$ and $\text{Ln}(\text{OH})_3$. In the presence of acid, the hydroxides were dissolved and the sulfates were separated by filtration.²⁰

In 1963, L.B. Asprey, F.H. Ellinger, and E. Staritzky also prepared divalent sulfate, carbonate, and fluoride compounds for samarium, europium, and ytterbium. The divalent sulfates were prepared using the Hg cathode. Double displacement reactions were used to produce the divalent carbonate and fluoride compounds. The percent recovery of the divalent compounds was not reported, but the crystalline samples were analyzed by X-ray diffraction and optical crystallography. Measurements were found to be imprecise due to the instability of the divalent compounds obtained.²¹

The research discussed above has shown that mercury cathodes provide successful procedures for reducing rare earth metals in aqueous media. However, mercury is a toxic metal that is exceedingly harmful to the human body. Amalgams are alternate methods for reduction without the use of an electrolytic cell; however, amalgams are also mercury-based. Due to the toxicity of mercury, it cannot be used industrially as a means for reducing the rare earth metals. This has sparked an interest in developing other methods for reducing rare earth metals.

For the first time in 1948, Clifford and Beachell developed a novel method for reducing lanthanide elements to their divalent state with the use of magnesium. An interest in using non-aqueous solvents was pursued in order to decrease the chance of reoxidation to the trivalent state. Hydrated samarium trichloride was dissolved in ethanol and a small amount of 12 M hydrochloric acid. Although several active metals

were added to the solution, magnesium was the only one successful in obtaining reduced samarium. Other metals attempted were zinc, manganese, aluminum, beryllium, thorium, calcium, lithium, and sodium. Samarium dichloride was separated from the rare earths with the exception of europium and ytterbium in the presence of the mentioned solvents and magnesium. The most favorable results were found when a 50/50 mixture of dioxane and ethanol was saturated with strontium and barium chlorides using magnesium. Results were also found to be successful with the use of the organic solvents, acetone and isopropanol.²²

In 1972, B. Mikheev and colleagues repeated the above experiment with the use of magnesium metal. The following were combined: 50 mg of magnesium metal and 1 mL of 7M hydrochloric acid in ethanol was added to a 1 mL ethanol solution that contained about 100 mg/mL of SmCl_3 . A similar experiment was also performed with europium(III) chloride. The purpose of the experiment was to examine the co-crystallization effects when very small quantities of other divalent elements are present. The authors mixed the trichlorides for samarium, europium, and ytterbium in the presence of an aqueous ethanolic solution and magnesium. The results revealed a co-crystallization of europium chloride and ytterbium chloride on the surface of the magnesium. The authors did not report the percent recovery of the divalent compounds.²³

L.I. Maksai and M.G. Sayun formed ytterbium sulfate in 1974 by using an ytterbium amalgam. The amalgam was placed in a chloride/acetate buffer solution that contained sodium sulfate while stirring for ten to fifteen minutes. Ytterbium sulfate was

formed as a product. The authors reported a 95.5% recovery of ytterbium in the divalent state.²⁴

The following year, B.F. Myasoedov and colleagues stated that the following elements: Eu, Sm, Tm, Er, and Am in the trivalent state, could be reduced in acetonitrile with the use of potential-controlled electrolysis and polarography. The authors also observed oxidation of the divalent cations in the presence of water. This oxidation occurred at different rates and was found to be related to the stability of the divalent cation.²⁵

During 1998, Siler reduced ytterbium(III) to ytterbium(II) in non-aqueous solvents without changing the oxidation state of lutetium in the same system. The best results were produced with the use of 50 mesh magnesium powder and 50/50 mixture of dioxane/ethanol as solvents. The idea of reducing trivalent ytterbium in the discussed solvents came from previously discussed authors, A.F. Clifford and H.C. Beachell. About fifty percent of ytterbium was reduced to its +2 state. This separation of ytterbium(II) and lutetium(III) was unsuccessful, it having been attempted by removing the reducing metal and the adhering product, removing the suspension of product after centrifuging or removal of the solution containing the product.²⁶

In 2000, R.J. Mack reduced ytterbium(III) to ytterbium(II) by electrolytic reduction using a lead cathode in different types of media. The experimental conditions with the most favorable results comprised of approximately 0.11 M $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ in 50:50 ethanol:dioxane with a direct current of about 20 mA, a pH of approximately 2.0, and

precipitation with 3.0 M $(\text{NH}_4)_2\text{SO}_4$. It was reported that approximately 30.0% of divalent ytterbium was recovered.²⁷

In 2007, Jones was also able to reduce ytterbium(III) to ytterbium(II) with use of magnesium in different types of media. The best system consisted of ytterbium(III) chloride in a 3:1 mixture of ethanol: dioxane, acetic acid, tetramethylammonium sulfate and 50 mesh magnesium powder under nitrogen at about 0°C. It was reported that 85% of Yb(II) was recovered from the system.²⁸

In 1994, Hanamoto, T., Sugimoto, Y., Sugino, A., and Inanaga, J. reduced samarium(III) and ytterbium(III) using a triflate system in the presence of ethylmagnesium bromide and tetrahydrofuran at room temperature under argon. Reduced products were used to study its reducing ability in a pinacol coupling reaction. The interest of this article was in using divalent lanthanides compounds as catalysts in organic reactions. Samarium and ytterbium triflates were successful in producing a good percent yield during the reactions.²⁹

PROPOSED PROJECT

Most of the experiments that were described in the history of rare earth reduction were carried out on a lab scale. The interest of this research project was to develop a method that has potential use for an industrial process. The mercury electrodes and amalgam cathodes were successful systems developed for reducing rare earths and recovering a large percent. However, as discussed earlier, mercury is toxic and not

industrially suitable. Magnesium metal has the potential [$E^\circ (\text{Mg}^{+2} / \text{Mg}^0) = -2.36 \text{ V}$]³⁰ to reduce rare earths in non-aqueous as well as aqueous solvents.

The main goal of this work was to prepare a method that will reduce ytterbium(III) to ytterbium(II) without changing the oxidation state of lutetium(III) under the same conditions. Lanthanide triflates were compounds of particular interest because they can be prepared anhydrous, excluding water, which can oxidize ytterbium(II) back to its trivalent state.

Lanthanide(III) trifluoromethanesulfonates for ytterbium and lutetium are to be prepared in order to attempt the reduction of ytterbium(III) to ytterbium(II). Previous studies have found that Eu, Yb, and Sm triflate salts can be reduced to their divalent states in non-aqueous solutions.³¹ The efficiencies for the reduction were not reported. Similar conditions to those used by Hanamoto et al. will be used in preliminary investigations. Particular attention will be paid to quantitative yields, and conditions will be altered to attempt to improve the system.

CHAPTER II MATERIALS AND METHODS

MATERIALS

All solvents that were used for the experiments were reagent grade. Solvents were also selected based on the absence of water. The water used was deionized. All manipulations for the triflate system were carried out under nitrogen to prevent atmospheric contamination. Table 1 lists the different solvents and reagents used in the experiments. The purity of these chemicals was an important aspect because the presence of impurities has been known to interfere with redox reactions. All solvents were anhydrous with the exception of diethyl ether, which was treated in order to remove water from the system. Anhydrous tetrahydrofuran was placed in a sealed container with molecular sieves. Triflic acid was also re-purified with the use of amorphous carbon.

APPARATUS

There were five different apparatus used during the course of this research: fractional distillation, a test tube, modified test tube with attached vacuum, column, and atomic emission spectrometer. A fractional distillation apparatus was assembled to remove water from ethyl ether. Figure 1 shows a general depiction of the apparatus. Water and contaminants are capable of oxidizing ytterbium (II) and water can react violently with Grignard reagents. A sand bath was used as the heating source for the distillation.

Table 1: List of Solvents and Reagents

CHEMICAL	SUPPLIER	PURITY
Water		Deionized
Tetrahydrofuran (THF)	Acros Organics	Reagent grade, >99.9%
Ethyl ether	Fisher Scientific Co.	99.9%
Ethylmagnesium bromide, 3M in ether	Alfa Aesar	N/A
Ethylmagnesium bromide, 1M in tetrahydrofuran	Sigma Aldrich	N/A
1,4-dioxane	Sigma Aldrich	99.8%
Ethanol	Aaper Alcohol and Chemical Co.	95%, 190 proof
Magnesium metal, ribbon	Fisher Scientific Co.	99+%
Magnesium metal, 50 mesh	Sigma Aldrich	Reagent Plus ≥ 99%
Hydrochloric acid	Fisher Scientific Co.	Certified ACS plus, 99.95%
Nitric acid	Fisher Scientific Co.	Certified ACS plus, 99.95%
Potassium Chloride	J.T. Baker Chemical Co.	99.6%
Ytterbium(III) oxide	Alfa Aesar	99.9%
Lutetium(III) oxide	Alfa Aesar	99.9%
Molecular sieves	Sigma Aldrich	N/A

Table 1, cont.

CHEMICAL	SUPPLIER	PURITY
Trifluoromethanesulfonic acid (triflic acid)	Fisher Scientific	99%
Triethyl orthoformate (TEOF)	Sigma Aldrich	98%
Sodium tetraphenylborate	Sigma Aldrich	≥99.5%
Ytterbium(III) chloride hexahydrate	Sigma Aldrich	99.9%
Activated Carbon	Atlas Powder Co.	N/A
Dichloromethane	Acros Organics	99.9%
Acetonitrile	Fisher Scientific	N/A
1,4-dioxane	Sigma Aldrich	99.8%
1,3-dioxane stabilized w/o BHT	Alfa Aesar	99.5%

Table 1, cont.

CHEMICAL	SUPPLIER	PURITY
N,N-Dimethylformamide	Acros Organics	99.8%
Dimethyl Sulfoxide	Fisher Scientific	99.7%
Methyl Sulfoxide	Sigma Aldrich	99.9+%
1-chlorobutane	Acros Organics	99+%
Isobutanol	Fisher Scientific	99%
Ethyl Chloroacetate	Acros Organics	99%
Methyl Alcohol	Mallinckrodt AR	99.9%
Acetic Acid	Fisher Scientific	99.9%

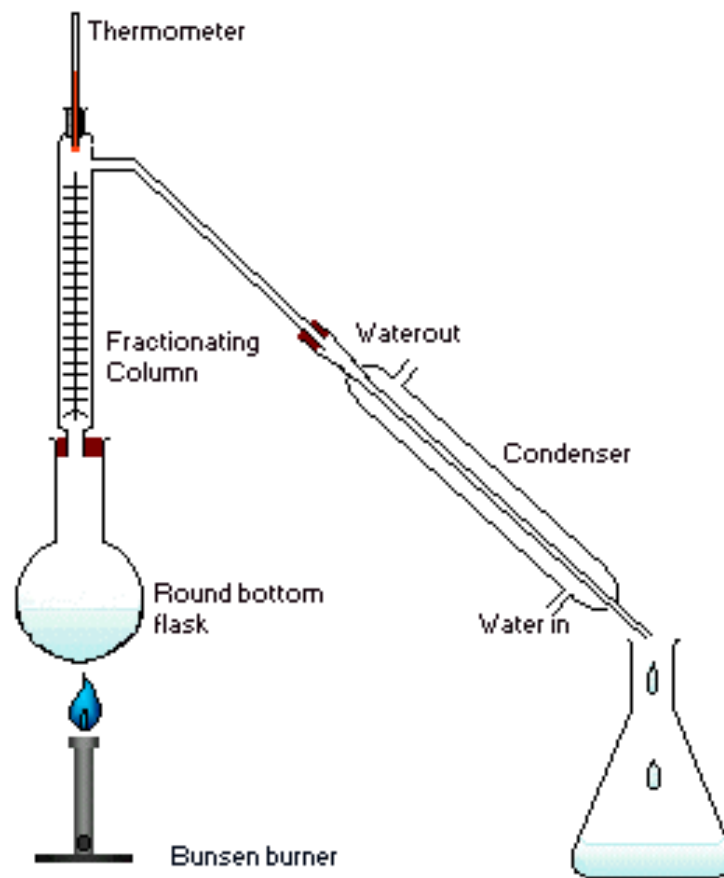


Figure 1: Fractional Distillation Apparatus

The temperature of the sand remained steady between 45-50.0 °C. After about 2 hours, the temperature of the ether reached 31.0 °C. The distillation of the ether was complete after approximately 6 hours. The ether was transferred to a glass bottle containing molecular sieves and the bottle was capped.

Figure 2 shows the basic system used for reducing ytterbium(III) to ytterbium(II) in non-aqueous solution. This set-up involved the test tube solution studies, which were encapsulated and allowed to react with continuous stirring. The triflate and magnesium were added to the test tube along with a stir bar. A rubber septum was placed over the test tube so that the environment of the system could be controlled. The test tube was flushed with nitrogen and solvents were added to the system via syringe. Samples were allowed to stir for an hour at room temperature before green solid was observed. A green precipitate indicated the presence of ytterbium(II).

Figure 3 is an illustration of the apparatus used for removing small amounts of tetrahydrofuran from the Grignard reagent in the presence of triflate. The triflate was placed in a test tube and capped with a rubber septum. The system was flushed with nitrogen and the Grignard reagent in tetrahydrofuran was added by syringe. Before the addition of magnesium, the vacuum tube was attached to a syringe and the needle was placed in the test tube. A portion of the solution was allowed to evaporate while the pressure of the system was decreased by vacuum.

Figure 4 shows a simple set-up used for removal of contaminants found in trifluoromethanesulfonic (triflic) acid. Triflic acid is a hygroscopic, colorless liquid at room temperature that can decompose to form a yellow solution color under certain

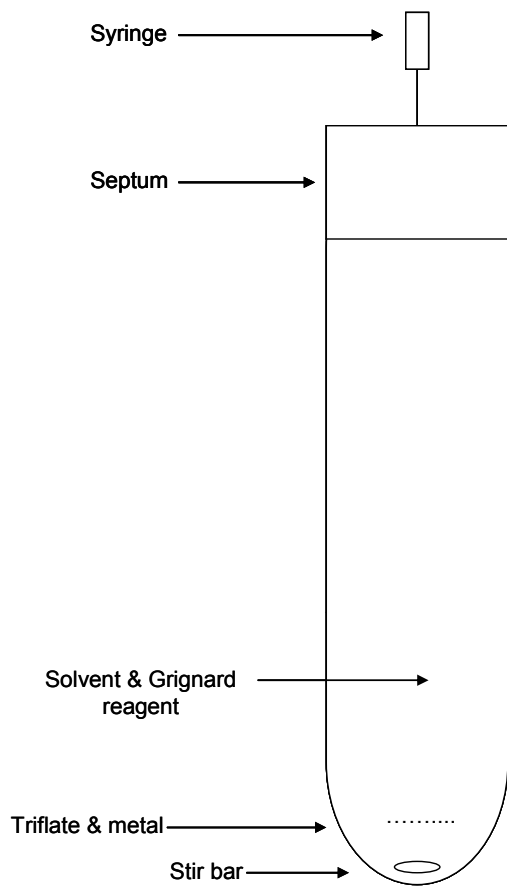


Figure 2: Basic System for Ytterbium(III) Reduction

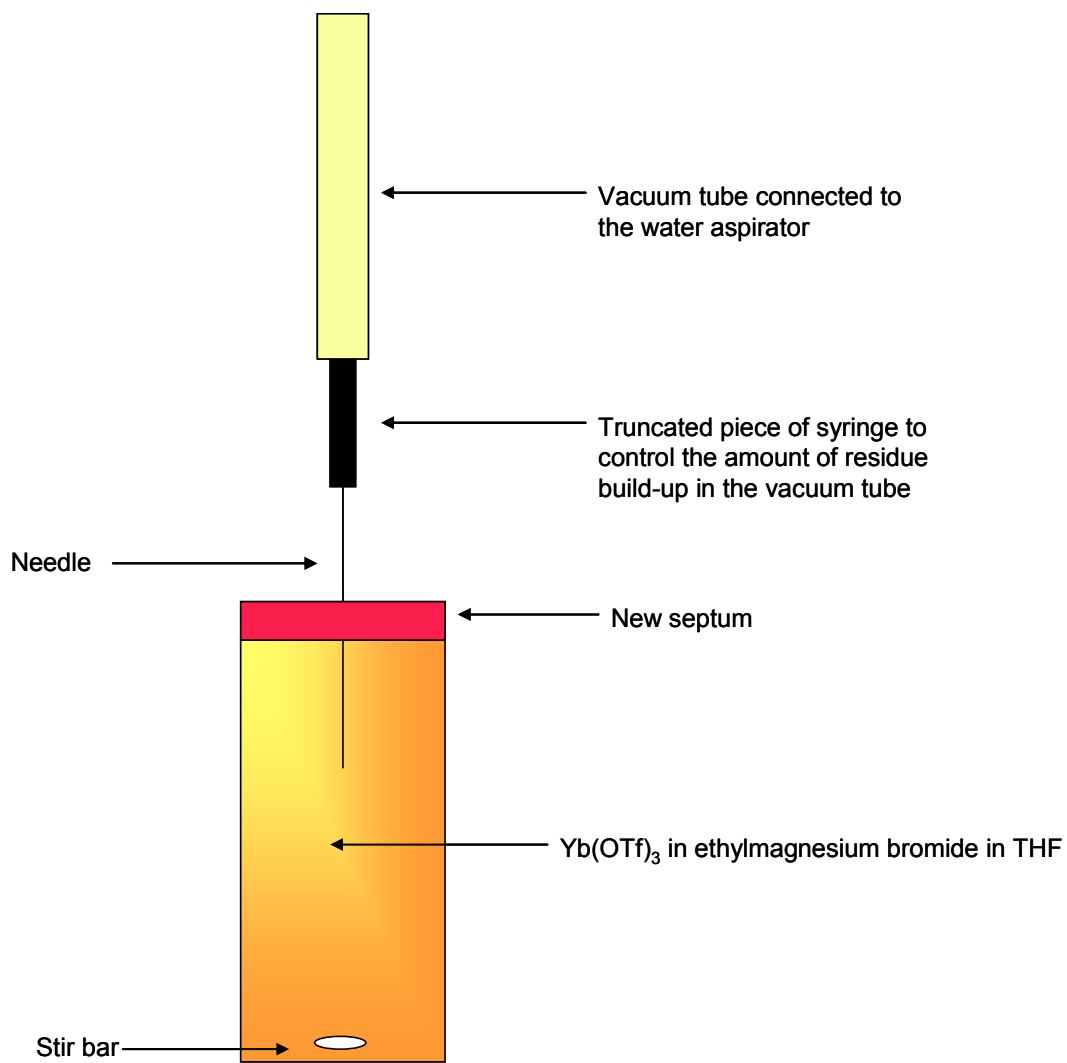


Figure 3: Experimental Set Up for Removal of THF

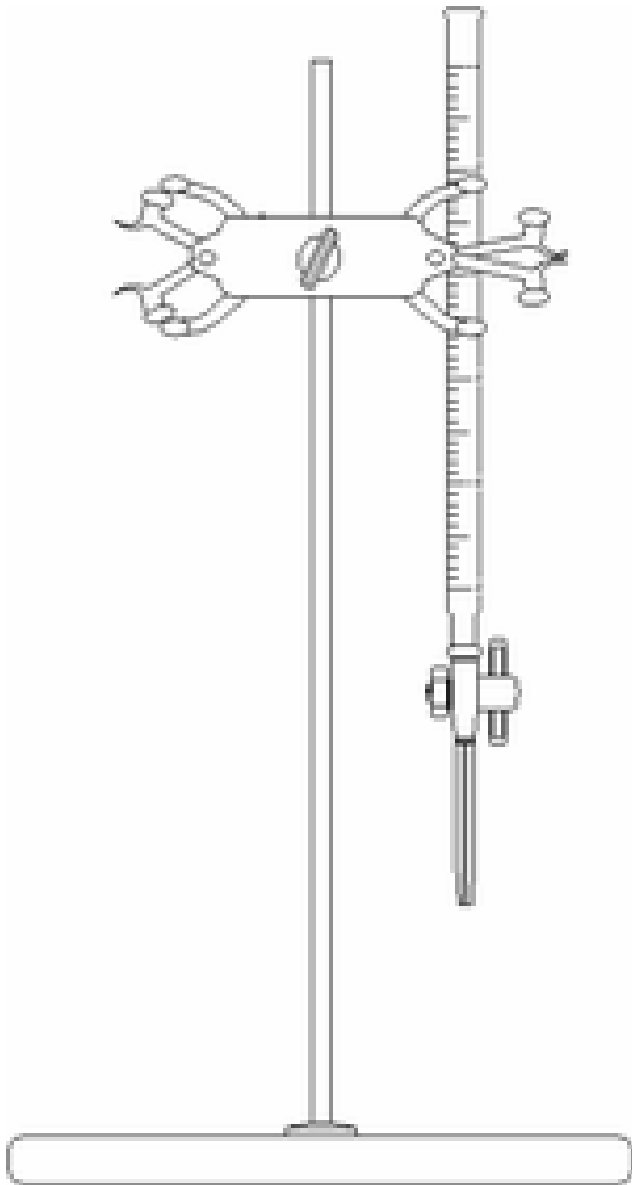


Figure 4: Carbon Filter Apparatus

circumstances such as change of temperature. A carbon column was prepared by filling a buret with activated carbon. A piece of filter paper was cut to fit into the base of the barrel so the solid did not pass through the column. The powdered carbon served as the stationary phase. Then the triflic acid was added to the column and allowed to run by gravity flow. This process was completed after about two days.

Samples were analyzed with the Perkin Elmer AAnalyst 100 by atomic emission spectroscopy. An image of this instrument can be found in Figure 5. The wavelengths used for ytterbium and lutetium analyses were 398.8 nm and 451.9 nm, respectively. Standards used during the analyses were prepared by diluting 1000 ppm SpecPure AAS standards. In atomic emission, a sample is placed under a high energy source so as to produce excited atoms that are capable of emitting light. The energy source used in this case was a flame. For the experiments performed, emission techniques were used to determine how much of an element was present in a sample. For a "quantitative" analysis, the intensity of light emitted at the wavelength of the element to be determined was measured.

METHODS

The initial step for this project was the preparation of anhydrous ytterbium and lutetium triflates. The triflate salts were prepared by adding lanthanide oxides, Ln_2O_3 , in excess to aqueous trifluoromethanesulfonic acid (triflic acid). 5.0 grams of Ln_2O_3 was mixed with 8.0 mL of 50% (v/v) aqueous triflic acid. The system was sealed with parafilm and left to stir at room temperature until a pH of 5 was reached. Then the clear solution was



Figure 5: Perkin Elmer AAnalyst 100

removed by centrifuging to separate the lanthanide triflate solution from the insoluble, white oxide. The solution was placed in a Petri dish and placed under vacuum for about 20 hours to remove water. Then the crystals were placed in the oven for about 48 to 120 hours at 110°C for further drying. Lastly, a small amount of lanthanide triflate was placed in a test tube with the addition of about 2.0 mL of water. Triflate preparation was complete when no insoluble products were present in the aqueous solution.

Basic preparation of samples was achieved by dissolving the anhydrous triflate in an anhydrous solvent and the Grignard reagent with the addition of magnesium to reduce the ytterbium(III) triflate to its divalent state. Solvents and Grignard reagents were added to the system via a syringe. When magnesium powder was added to the system after it had been flushed with nitrogen, it was placed in a syringe with an one inch-16 gauge needle. Solvents of choice had to dissolve both the triflate and the Grignard reagent. The best system was determined by changing the order of addition, the temperature of the system, the concentration of the triflate, the reduction time, and the form of the magnesium. Positive results for the production of ytterbium(II) were indicated when a green precipitate and/or a yellow-orange solution was observed in the system. All experiments were repeated a minimum of three times to ensure reproducibility.

The concentrations of ytterbium and lutetium ions were computed by measurements obtained by atomic emission spectroscopy. After centrifuging the ytterbium samples that were reduced with magnesium powder, the solution exhibited a yellow-orange color with gray (magnesium powder) and green solid. In the case of

magnesium ribbon, a yellow solution color was observed with a green solid and the magnesium strip. In both cases, the green solid contained divalent ytterbium triflate while the solution contained trivalent ytterbium triflate, tetrahydrofuran, ethylmagnesium bromide and possibly ytterbium(II) complexed with tetrahydrofuran. The liquid part was quantitatively transferred to a volumetric flask and diluted with 1% nitric acid with a few drops of concentrated nitric acid. The solid part was dissolved in the same solutions in a separate volumetric flask. 0.1% potassium chloride was added to each sample to minimize the chances of ionization interferences. After preparation, samples were analyzed by atomic emission spectroscopy. If ytterbium or lutetium concentrations were higher than the standards, samples were diluted from their original preparation. The concentrations of the solid sample and liquid sample were calculated from the absorbance measurements. The concentration was then used to measure the distribution between the two phases. Lutetium samples were prepared using a similar procedure. However, there was a colorless solution and no green solid. In the presence of magnesium powder, only gray solid was observed. A white solid was observed with the magnesium strip. Eventually, ytterbium and lutetium triflate were mixed together and the same procedures for individual experiments with ytterbium and lutetium were followed.

CHAPTER III RESULTS AND DISCUSSION

SOLUBILITY TESTS

It was important to find a solvent that would dissolve both the lanthanide triflate and the Grignard reagent so that the effects of magnesium powder could be observed in a homogenous solution. Lutetium and ytterbium triflate were found to behave in a similar manner for the solubility studies. The general technique involved placing about 0.04 grams of lanthanide triflate in a test tube. A stir bar was placed in the test tube to assist with the mixing of the different reagents. Then the test tube was capped with a rubber septum and flushed with nitrogen for about 10 seconds. 0.5 mL of solvent was added to the test tube via syringe. The sample was allowed to stir for about 15 minutes. If the triflate dissolved in the solvent, 0.5 mL of Grignard reagent was added to the system. If the triflate did not dissolve in the reagent, the test was considered complete and the solvent was considered unsuccessful for the system. Results for these studies are listed in Table 2.

Lanthanide triflate was found to be soluble in several organic solvents. However, with the addition of the Grignard reagent, only three solvents passed the solubility tests: acetonitrile, tetrahydrofuran, and 1,3-dioxane. Two different Grignard reagents were tested in the reduction reactions, ethylmagnesium bromide in 1.0 M THF, and ethylmagnesium bromide in 3.0 M ether. Since the triflate was soluble in tetrahydrofuran, additional tests were performed to further verify this property.

Table 2: Lutetium and Ytterbium Solubility Tests

Solvent	Solubility of Ln(OTf)₃	Solubility in Grignard
Tetrahydrofuran	Soluble	Soluble
Acetonitrile	Soluble	Soluble
1,4-dioxane	Soluble	Insoluble; cloudy white precipitate formed
1,3-dioxane stabilized w/o BHT	Soluble	Soluble
N,N-dimethylformamide	Soluble	Insoluble; cloudy 2 minutes after addition
Dimethyl Sulfoxide	Soluble	Insoluble; cloudy, yellow precipitate
Methyl Sulfoxide	Soluble, yellow solution	Insoluble; cloudy tan precipitate
Dichloromethane	Insoluble; cloudy	-
1-chlorobutane	Insoluble	-
Isobutanol	Soluble	Insoluble; cloudy
Acetic Acid	Soluble	Insoluble; slightly cloudy
Methyl Alcohol	Soluble	Insoluble; cloudy
Ethyl Chloroacetate	Insoluble; cloudy	-
Ethyl Ether	Insoluble; cloudy	-
Ethanol	Soluble	Insoluble; precipitate

Tetrahydrofuran was found to be soluble in both Grignard reagents. However, in some cases, tetrahydrofuran produced a very small amount of insoluble particles once added to the triflate. The volumes of the organic solvents and Grignard reagent were increased to see if this would help dissolve the remaining particles. The results observed were unchanged. The triflates were then placed in the oven at 110°C for about 24 hours for further drying to ensure the removal of water. The results continued to remain unchanged. Impurities obtained during the preparation of triflate were also considered as a result of the insoluble materials, but even with the preparation of additional triflate, insoluble particles were still observed. Control experiments were prepared with anhydrous tetrahydrofuran and Grignard reagent mixed together. The solution formed an insoluble compound even in the absence of triflate. Due to the several punctures in the Grignard bottle, it was suggested that the Grignard reagent had been exposed to air and therefore contained impurities. Upon the arrival of the new Grignard reagents, tetrahydrofuran was found to be soluble in the presence of triflate and Grignard.

Tetrahydrofuran was considered to be an excellent solvent for this system since one of the Grignard reagents used in the system was also dissolved in tetrahydrofuran. It is an aprotic solvent that cannot donate a hydrogen bond, but it can donate an electron pair. Since it is a moderately polar solvent, it can dissolve a wide range of nonpolar and polar molecules. It is also a good choice to use with the Grignard reagent because it does not contain acidic hydrogen that could go through an acid-base reaction with the Grignard reagent. Last, but not least, it would be a good solvent to use

industrially since it does not have any major human risks. Even though in some instances, there were very small amounts of insoluble material present in the system, samples were prepared with several modifications in order to increase the efficiency of the system. These modifications will be discussed more in the ytterbium triflate studies section.

ISOLATED ANALYSIS

Ytterbium and lutetium triflate samples were prepared without the addition of magnesium powder to ensure that the insoluble particles observed were not precipitated lanthanide triflate. The results for these experiments can be found in Tables 3 and 4. The percent recoveries listed in both tables are the amounts recovered in the solid phase. Data show that the majority of ytterbium and lutetium triflate remained in the liquid phase in the absence of magnesium.

Table 3: Ytterbium Triflate in the Absence of Magnesium

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-1	~0.02 g	0.3 mL	0.5 mL	5.2
Y-2	~0.02 g	0.3 mL	0.5 mL	4.2
Y-3	~0.02 g	0.3 mL	0.5 mL	4.5

Table 4: Lutetium Triflate in the Absence of Magnesium

<i>Components</i>	<i>Lu(OTf)₃</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Percent Recovery</i>
L-1	~0.02 g	0.3 mL	0.5 mL	2.6
L-2	~0.02 g	0.3 mL	0.5 mL	3.9
L-3	~0.02 g	0.3 mL	0.5 mL	3.6

YTTERBIUM TRIFLATE REDUCTION

Initial reduction with magnesium

Previous studies by Hanamoto et al. found that ytterbium(III) triflate could be partially reduced to its divalent state in the presence of the Grignard reagent. Based on the isolated studies that excluded magnesium powder, ytterbium(III) triflate remained mostly in the liquid phase with a minimal amount of ytterbium recovered in the solid phase. For the initial reduction experiments with magnesium, approximately 0.02 grams of triflate and 0.02 grams of 50 mesh magnesium powder were placed in a test tube, flushed with nitrogen, and then 0.5 mL of anhydrous tetrahydrofuran and 1.0 mL of Grignard reagent were added via syringe. Samples were allowed to react for two days before atomic emission preparation. The sole purpose of these initial experiments was to ensure the reduction of ytterbium(III) by the triflate method. Table 5 shows a table with the components and the most reliable results for this system. Green solid was present in these samples and the percent recovery of ytterbium in the solid phase was 78 and 81%. Since results were similar for both types of Grignard reagents, the Grignard in tetrahydrofuran was chosen because it appeared to react less with the air during solution transfer for atomic emission preparation.

Several trial experiments confirmed the reduction of ytterbium(III) triflate to ytterbium(II) triflate in the presence of magnesium powder. The next step was design experiments to analyze the best reaction time for the reduction process. Triflate samples were prepared the same as in the initial experiments, but samples were allowed to react for 1, 3, 5 and 7 days for samples Y-6 through Y-9, respectively.

Table 5: Initial trials of Yb(III) Triflate Reduction with Mg Powder

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Mg powder</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Grignard ether</i>	<i>Percent Recovery</i>
Y-4	~0.02 g	~0.02 g	0.3 mL	0.5 mL	n/a	78
Y-5	~0.02 g	~0.02 g	0.3 mL	n/a	0.5 mL	81

Table 6: Effects of Different Reaction Times

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Mg powder</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Reaction Time</i>	<i>Percent Recovery</i>
Y-6	~0.02 g	~0.02 g	0.3 mL	0.5 mL	1 day	51
Y-7	~0.02 g	~0.02 g	0.3 mL	0.5 mL	3 days	72
Y-8	~0.02 g	~0.02 g	0.3 mL	0.5 mL	5 days	71
Y-9	~0.02 g	~0.02 g	0.3 mL	0.5 mL	7 days	72

Table 6 lists the components and results for these samples. All samples had a percent recovery of ytterbium in the solid phase that was over 50%. Samples that were allowed to reduce for more than one day had percentages of about 70%, which was much higher than the one day reduction results.

According to the atomic emission results, the reaction time does not affect the reduction of ytterbium(III) as long as the system is allowed to react for more than 1 day. The percent recovery of ytterbium(II) in the solid phase was insignificantly different for days 3, 5, and 7.

New Order of Addition

With the implementation of the initial method, a few particles continued to remain in the test tube in the absence of magnesium powder as described in the solubility tests section. This problem was thought to be resolved, but the Grignard reagent must have become contaminated again with the continuous needle punctures by the syringe. To account for this issue, a new technique was attempted by centrifuging the test tubes

after the triflate, tetrahydrofuran, and Grignard reagent were mixed. Any components that were insoluble in the solutions were separated from the liquid after centrifuging. The septum was removed from the test tube and the supernatant was removed by syringe and transferred to a sealed test tube that contained magnesium powder and nitrogen. Samples were left to stir at room temperature for 3 days. After centrifuging, green solid was visible in the test tube after about a 1-hour reaction time with a yellow-orange solution color that darkened in color over time. These samples are identified as Y-10 and Y-11 in Table 7. These experiments were repeated, but the septum was not removed from the test tube when transferring the supernatant. The results for these samples were similar to the former technique. Results for these experiments are shown in Table 7 as Y-12 through Y-15. Y-10 and Y-11 had slightly lower yields compared to these samples. This is most likely due to Y-10 and Y-11 samples having more exposure to air during the transfer of solution because the septum was completely removed from the test tube.

The same experiments were repeated with the Grignard in ethyl ether instead of the tetrahydrofuran to see if any differences in results would be observed. These samples were allowed to reduce for three days as well and Table 8 shows the data

Table 7: New Procedure for Reducing Ytterbium(III) Triflate

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Mg powder</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-10	~0.02 g	~0.02 g	0.3 mL	0.5 mL	38
Y-11	~0.02 g	~0.02 g	0.3 mL	0.5 mL	50
Y-12	~0.02 g	~0.02 g	0.3 mL	0.5 mL	64
Y-13	~0.02 g	~0.02 g	0.3 mL	0.5 mL	79
Y-14	~0.02 g	~0.02 g	0.3 mL	0.5 mL	52
Y-15	~0.02 g	~0.02 g	0.3 mL	0.5 mL	53

Table 8: Ytterbium(III) Triflate Reduction in the presence of Grignard in Ether

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Mg powder</i>	<i>Anhydrous THF</i>	<i>Grignard ethyl ether</i>	<i>Percent Recovery</i>
Y-16	~0.02 g	~0.02 g	0.3 mL	0.5 mL	63
Y-17	~0.02 g	~0.02 g	0.3 mL	0.5 mL	56
Y-18	~0.02 g	~0.02 g	0.3 mL	0.5 mL	71
Y-19	~0.02 g	~0.02 g	0.3 mL	0.5 mL	64
Y-20	~0.02 g	~0.02 g	0.3 mL	0.5 mL	74

collected for these experiments. On average, the percent recovered for ytterbium in the solid phase with the use of Grignard in ethyl ether was slightly higher than with Grignard in tetrahydrofuran. The difference of these averages was insignificant and the Grignard in tetrahydrofuran remained as the preferred organic reagent.

The percent recovery of ytterbium in the solid phase was greatly increased when the supernatant was removed from the test tube with the septum via syringe. However, this method was still exposed to air once the syringe was removed from the test tube. Therefore, modifications were made to improve this system by performing the supernatant transfer in a nitrogen bag. Samples were prepared as the previous techniques with the modification formerly described. Table 9 shows the results from these experiments. The percent recoveries recorded were similar to results observed with the technique that removed the supernatant by syringe with the septa before the addition of magnesium powder. These results were considered positive because almost half or more of ytterbium was found in the solid phase, but they remain similar to previous experiments. Although this modification kept divalent ytterbium from air exposure, the final yields of divalent ytterbium did not significantly increase compared to the initial experiments.

Table 9: Reduction of Soluble Ytterbium(III) Triflate

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Mg powder</i>	<i>Anhydrous Tetrahydrofuran</i>	<i>Grignard Tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-21	~0.02 g	~0.02 g	0.3 mL	0.5 mL	46
Y-22	~0.02 g	~0.02 g	0.3 mL	0.5 mL	52
Y-23	~0.02 g	~0.02 g	0.3 mL	0.5 mL	60

Isolated experiments were also performed with the organic solutions used in the triflate system to better understand the products that are formed from the reactions. After the reaction of ytterbium(II) triflate, a brownish orange solution and green and gray solid were observed after centrifuging the test tube. The brownish orange solution was proposed to be oxidized tetrahydrofuran or ytterbium(II) complexed to tetrahydrofuran. In the absence of triflate, tetrahydrofuran did not produce a brownish orange solution. Instead, it produced a colorless solution. This observation verified that oxidized tetrahydrofuran is not likely to be one of the products found in solution, but it is more likely to be ytterbium(II) complexed to tetrahydrofuran.

Effect of Temperature

As a result of the additional steps required in the previous system, the effects of the order of addition and the temperature were considered. The most favorable results were observed when the following steps were applied: (1) ytterbium (III) triflate was added to a test tube, (2) then the test tube was flushed with nitrogen, (3) followed by the addition of the Grignard reagent and then magnesium powder via syringe at 0°C. On average, about 50% of ytterbium remained in the solid phase with a 48 hour reduction

time having the most favorable percent recovery of ytterbium in the solid phase after three trials.

Originally, samples were prepared at room temperature during the addition of each component. The effect of temperature became a factor of consideration because the addition of the Grignard reagent was found to produce an exothermic reaction. Since ytterbium(II) is easily oxidized to its trivalent state, it was suggested that a lower temperature would allow for the redox reactions to be controlled. By controlling the rate of the redox reactions by lowering the temperature, one could also decrease the rate of oxidation of divalent ytterbium as well.

Experimentally, a lower temperature appeared to produce a larger proportion of green solid, but the percent recovery was not higher than previous studies that were performed at room temperature. Experiments that were repeated at room temperature with the lower temperature samples produced less ytterbium(II) triflate in the solid phase. The results for the room temperature experiments were previously higher than these experiments that were performed at room temperature.

Results for these experiments are listed in Table 10. Y-24 and Y-25 were prepared by adding 0.04 grams of ytterbium(III) triflate to a test tube. Then magnesium powder was added, the test tube was capped, and flushed with nitrogen. 0.3 mL of anhydrous tetrahydrofuran, and 1.0 mL of Grignard in tetrahydrofuran was added by syringe at room temperature. Y-24 was analyzed after one day of reacting at room temperature and a very low percent recovery was obtained. Y-25 was placed on ice for about 15 minutes after reacting for five days at room temperature. When analyzed, a

26% yield of ytterbium(II) in the solid phase was achieved. Y-26 was prepared by mixing anhydrous tetrahydrofuran and Grignard in tetrahydrofuran in a test tube that had been capped and flushed with nitrogen. The system was cooled to 0°C before the addition of the organic solutions. Once the system reached room temperature, ytterbium triflate was added to the system by syringe. The sample was left to stir at room temperature for one day before adding magnesium powder to the system via syringe. A yield of 50% was obtained for ytterbium(II) in the solid phase. Y-27 and Y-28 were prepared the same as Y-24 and Y-25 except both samples were placed on ice for about 15 minutes after reacting at room temperature for one day. No green solid was observed for these samples. Y-29 and Y-30 were prepared in the following order: ytterbium(III) triflate, capped test tube, flushed with nitrogen, addition of anhydrous tetrahydrofuran, system cooled to 0°C, addition of magnesium powder, and addition of Grignard in tetrahydrofuran. These samples remained at the cooled temperature for 30 minutes. No green solid was present. After stirring for 30 minutes at room temperature, green solid was observed. The percent recovery was 34% and 38% for these samples, which reacted for a shorter time than the samples prepared at room temperature and produced a larger amount of divalent ytterbium. Y-26 had a higher recovery, but it also reacted for five days before analysis. Y-31 was prepared as Y-29 and Y-30, but it was cooled to 0°C for four hours. After reacting at room temperature for about 30 minutes, green solid was present and 54% of ytterbium(II) was obtained in the solid phase. Y-32 and Y-33 were prepared in a similar manner as Y-31 except these samples were not placed at room temperature after reacting at 0°C for three hours. Green solid was

present and the yields were low for these samples. Y-34 and Y-35 were prepared by adding the magnesium after the addition of Grignard in tetrahydrofuran at 0°C. Both samples were allowed to react at this low temperature for about 24 hours. Green solid did not become visible until the sample was allowed to react at room temperature. After reacting for seven days, samples were cooled to 0°C again to see if a greater portion of green solid could be obtained. A yield of 55 and 41 was achieved for Y-34 and Y-35, respectively. The table lists the observations for each sample. After samples were left at a temperature of 0°C for a period of time, they were placed back at room temperature the remaining reacting time unless otherwise stated in the table. Samples that did not produce a green solid were not analyzed since a reduction to ytterbium(II) was not visually observed. The percent recovery of ytterbium(II) samples that produced a green solid are listed in the last column of the tables. The reduction time was different for each of these samples as observed by the table. The final observation day represents the total reaction time.

Experiments were performed with a variation in the amount of time samples were allowed to react at a low temperature. As the data above showed, some samples were left at 0°C for minutes, hours, or days. This time did not make a significant difference in the percent recovery in the solid phase of divalent ytterbium. As long as the sample was at the low temperature during the addition of the Grignard reagent, which produced heat during its addition, the results were similar to samples left at 0°C for approximately 24 hours. It was found that 15 to 30 minutes was a reasonable amount of time to cool the reaction for the triflate system. Y-26, Y-31, and Y-34 samples produced the highest

yield of ytterbium(II) in the solid phase. Each of these samples was prepared by placing the system at 0°C while adding the Grignard reagent via syringe.

THF Removal

The next experiments examined the exclusion of anhydrous tetrahydrofuran from the system. This only eliminated the additional tetrahydrofuran that was added to the system because the Grignard reagent was dissolved in 1.0M tetrahydrofuran. 0.4 grams of ytterbium(III) triflate was added to the system, flushed with nitrogen, 0.5 mL of anhydrous tetrahydrofuran was added to samples Y-36 and Y-37, and 1.0 mL of Grignard reagent was added to samples Y-36 through Y-39. Lastly, 50 mesh magnesium powder was added immediately afterwards to the system. The Grignard reagent and magnesium powder were added to the system at 0°C via syringe and maintained at this temperature for about 30 minutes until warmed to room temperature. Samples were left to react for two days. When samples were prepared without the additional tetrahydrofuran, a higher percent recovery was found compared to the control samples that were prepared with tetrahydrofuran. Results for these samples are shown in Table 11. Y-36 and Y-37 had a percent recovery of about 40% and Y-38 and Y-39 had a recovery of 56% of ytterbium(II) in the solid state. Samples that excluded the additional tetrahydrofuran produced favorable results.

Table 10: Temperature Effects on Triflate System

Sample	Observations	Percent Recovery
Y-24	Day 0: After the addition of the Grignard, the test tube was very hot. Day 1: Solution was yellow green; small amount of green solid; grey solid	16
Y-25	Day 0: After the addition of the Grignard, the test tube was very hot and the solution with solid was green during Grignard addition and the green color faded. Day 1: Solution was brownish orange; green solid; grey solid Day 4: brownish orange solution; black solid Day 5: Placed on ice for 15 min, brownish orange solution, green solid was larger	26
Y-26	Day 0: The solution was slightly warm after adding the Grignard. The color of the solution was yellow green. Day 1: Colorless solution; After the addition of Mg, colorless solution, green and grey solid; Day 4: Slightly brownish orange solution; Greater amount of green solid; black solid present Day 5: Placed on ice for 15 min, brownish orange solution, green solid was larger	53
Y-27	Day 0: Brownish yellow solution, grey and black solid after 3 hours of stirring. Day 1: Placed on ice for 15 min, no green solid present	n/a
Y-28	Day 0: Brownish yellow solution, grey and black solid after 3 hours of stirring. Day 1: Placed on ice for 15 min, no green solid present	n/a
Y-29	Day 0: after 30 min at 0°C, light green solution, no green solid. after stirring for 30 min at RT, yellow solution, yellow solid Day 1: green solid present	34
Y-30	Day 0: after 30 min at 0°C, light green solution, no green solid. after stirring for 30 min at RT, clear solution, grey solid Day 1: green solid present	38

Table 10, cont.

Y-31	<p>Day 0: after 30 min at RT, yellow-green solution, grey solid; after ice, a little green solid was present</p> <p>Day 1: green solid present</p>	54
Y-32	<p>Day 0: after 3 hours on ice, green solid was present (very small amount)</p>	21
Y-33	<p>Day 0: after 3 hours on ice, green solid was present (very small amount)</p>	14
Y-34	<p>Day 0: after 5 hours on ice, No green solid was present. Samples were left at 0°C overnight.</p> <p>Day 1: No change observed. Samples were left to stir at RT.</p> <p>Day 7: Brownish orange solution and green and grey solid. Samples were placed at 0°C to see if greener solid could be recovered.</p> <p>Day 8: Samples were prepped for analysis. The solid appeared to be greener. There was black, green, and grey solid present.</p>	55
Y-35	<p>Day 0: after 5 hours on ice, No green solid was present. Samples were left at 0°C overnight.</p> <p>Day 1: No change observed.</p> <p>Day 7: Brownish orange solution and green and grey solid.</p> <p>Day 8: green solid present</p>	41

Table 11: Removal of Additional Tetrahydrofuran

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Anhydrous THF</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-36	~0.04 g	0.5 mL	1.0 mL	44
Y-37	~0.04 g	0.5 mL	1.0 mL	41
Y-38	~0.04 g	-	1.0 mL	56
Y-39	~0.04 g	-	1.0 mL	56

Table 12: Effect of Concentration Excluding Tetrahydrofuran

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-40	~0.04 g	1.5 mL	68
Y-41	~0.06 g	1.5 mL	56
Y-42	~0.08 g	1.5 mL	47

More samples were prepared without the additional tetrahydrofuran and with a variation in the triflate weight. Samples were prepared with 0.04, 0.06, and 0.08 grams of triflate labeled as Y-40, Y-41, and Y-42, respectively, in Table 12. Each test tube was flushed with nitrogen and 1.5 mL of Grignard in tetrahydrofuran and magnesium powder was added by syringe at 0°C. Samples were allowed to react at 0°C for about 30 minutes and then allowed to react at room temperature for two days. Compared to previous experiments, the volume of the Grignard reagent was slightly increased due to the exclusion of tetrahydrofuran to the system. Data for these samples found that 0.04 grams of triflate gave the best results. These results can be found in Table 12. As the concentration of the ytterbium triflate increased, the percent recovery slightly decreased, but all values remained similar to previous results. Based on these experiments, 0.04 grams of ytterbium(III) triflate was chosen as the preferred concentration for this system.

Since results were improved when tetrahydrofuran was excluded, it was proposed that the removal of some of the tetrahydrofuran from the Grignard reagent could possibly produce more favorable results. The method previously discussed (refer to Figure 3) was employed for these experiments. The system was evacuated in order to remove some of the tetrahydrofuran from the Grignard reagent. Samples were prepared by dissolving 0.04 grams of triflate in 1.5 mL of Grignard in tetrahydrofuran. The test tube was flushed with nitrogen after the addition of triflate and the Grignard reagent was added while the test tube was placed at 0°C. Then samples were placed partially evacuated, in order to remove tetrahydrofuran. Solvents boil at a lower boiling point than when the liquid is at atmospheric pressure. Placing this system under vacuum reduced the pressure so that tetrahydrofuran from the Grignard reagent could be partially evaporated. As Figure 3 portrays, a syringe was placed in the vacuum tube and taped so air could not enter and to secure the syringe in the tube. The syringe was placed inside the test tube through the septum. When the vacuum was turned on, the solution began to bubble and the solvent began to evaporate. It was noted that tetrahydrofuran boils at about 66°C and the Grignard reagent is unstable in its crystal form; therefore, all of the solvent was not removed. Initial experiments had an evacuation time of approximately 2 hours. At the end of the evacuation, magnesium powder was added to each sample by syringe at 0°C. These samples were maintained at this temperature for about 30 minutes and then warmed to room temperature. Results for these experiments are shown in Table 13. The table shows the initial results found with the removal of tetrahydrofuran from the Grignard reagent. During this first

Table 13: Removal of Tetrahydrofuran from Grignard

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-43	~0.04 g	1.5 mL	34
Y-44	~0.04 g	1.5 mL	40
Y-45	~0.04 g	1.5 mL	59

Table 14: Different Amounts of Tetrahydrofuran Removed

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Solvent Removed</i>	<i>Percent Recovery</i>
Y-46	~0.04 g	1.5 mL	75	37
Y-47	~0.04 g	1.5 mL	50	47
Y-48	~0.04 g	1.5 mL	10	36

trial, about 10% of solution remained in the test tube after the removal of most of the tetrahydrofuran. Y-43, Y-44, and Y-45 were subject to reduction for 1, 2, and 3 days, respectively. The percent recovery increased with the reduction time. A 3-day reduction time was used for further studies.

Table 14 depicts the percent recovery when different amounts of tetrahydrofuran were removed from the system. 75%, 50%, and 10% were analyzed to see how the amount of solvent removed affected the amount of ytterbium(II) recovered in the solid phase. Based on data, the removal of tetrahydrofuran from the Grignard reagent did not seem to have a significant influence on the system compared to results obtained with the addition of the Grignard reagent in tetrahydrofuran.

The percent recovery of ytterbium in the solid state did not significantly increase after the removal of tetrahydrofuran from the Grignard reagent. The average value remained about the same compared to previous results. Results remained similar to previous results with this small change to the system. However, the additional

anhydrous tetrahydrofuran that was initially added to the system was considered unproductive for the triflate system.

Reduction Time

The best reduction time was re-analyzed after finding that 0.04 grams of ytterbium triflate in 1.5 mL of Grignard reagent produced the highest percent recovery of ytterbium in the solid state. The best results were produced after ytterbium(III) triflate reacted with the Grignard reagent and magnesium powder for two days. Tables 15 and 16 show the results for these experiments. Although day 2 produced the highest yield and was chosen as the best reduction time, the yields observed for day 1, 3, and 4 were very close to results observed with a 2 day reduction time.

Samples were prepared by adding 1.5 mL of Grignard reagent to 0.04 grams of triflate in a test tube flushed with nitrogen. The Grignard reagent was added to the

Table 15: Best Reduction Time

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Reduction time</i>	<i>Percent Recovery</i>
Y-49	~0.04 g	1.5 mL	1 day	48
Y-50	~0.04 g	1.5 mL	2 days	58
Y-51	~0.04 g	1.5 mL	3 days	57
Y-52	~0.04 g	1.5 mL	4 days	56

Table 16: Best Reduction Time II

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Reduction time</i>	<i>Percent Recovery</i>
Y-53	~0.04 g	1.5 mL	1 day	60
Y-54	~0.04 g	1.5 mL	2 days	64
Y-55	~0.04 g	1.5 mL	3 days	55
Y-56	~0.04 g	1.5 mL	4 days	59

Table 17: Reduction Time of Two Days

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-57	~0.04 g	1.5 mL	63
Y-58	~0.04 g	1.5 mL	66
Y-59	~0.04 g	1.5 mL	62

Table 18: Multiple Additions of Grignard and Magnesium

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
Y-60	~0.04 g	1.5 mL	38
Y-61	~0.04 g	1.5 mL	39

system at 0°C for about 30 minutes and then samples were transferred to room temperature for two days. Results for these experiments are found in Table 17. The percent recovery average is close to 65%.

Since removing excess tetrahydrofuran from the system did not improve results, other experiments were tried to improve the system. Molecular sieves were added to the system to make sure any water that could have been introduced to the system was eliminated. Even with this change to the system, the percent recovery of ytterbium(II) triflate was not increased compared to previous methods performed. There was about 50% recovery in the solid state, which was the same as some of the other results. The system was supersaturated with 1.0 g of ytterbium(III) triflate and 1.0 mL of Grignard in tetrahydrofuran. These results did not show any significant changes to previous results. Multiple additions of magnesium powder and Grignard reagent were also added to the system after a reaction time of 1 day. However, these additions did not appear to reduce any remaining ytterbium(III) to ytterbium(II) based on data. The results for these reactions are shown in Table 18.

Form of Magnesium

Magnesium strip was used to prepare samples in place of magnesium powder. It was assumed that magnesium powder would be the more suitable reducing agent because it has a greater surface area than the magnesium strip. However, this greater surface area also results in a faster reaction, which may need to be slowed down in this particular system. Preparation of samples was similar to preparation for reduction with magnesium powder, except the magnesium strip was placed in the test tube after the addition of the ytterbium triflate. The strip was also abraded before its addition to the system. Table 19 shows the experimental data for determining the best reduction time of ytterbium(III) triflate with magnesium ribbon.

The data reveal that the percent recovery slightly increases with reduction time. Another experiment was performed with both forms of magnesium to see how a longer reduction time would affect the results. Samples were allowed to react for nine days before prepping for atomic emission analysis. Table 20 displays the results for these

Table 19: Best Reduction Time with Mg Ribbon

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Reduction time</i>	<i>Percent Recovery</i>
Y-62	~0.04 g	1.5 mL	1 day	34
Y-63	~0.04 g	1.5 mL	2 days	38
Y-64	~0.04 g	1.5 mL	3 days	41
Y-65	~0.04 g	1.5 mL	4 days	42
Y-66	~0.04 g	1.5 mL	5 days	50

Table 20: Magnesium Ribbon versus Magnesium Powder

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Form of Magnesium</i>	<i>Percent Recovery</i>
Y-67	~0.04 g	1.5 mL	Powder	59
Y-68	~0.04 g	1.5 mL	Ribbon	59

experiments. After a reduction time of about nine days, the percent recovery for ytterbium in the solid phase was approximately the same for both forms of magnesium.

LUTETIUM TRIFLATE AND MAGNESIUM

Due to the similarity in chemistry of the lanthanide elements, lutetium triflate was found to be soluble and insoluble in the same solvents that were tried for ytterbium triflate. The best system found for ytterbium triflate was used to test the chemistry of lutetium triflate. Based on the Pourbaix diagram, magnesium does not have the potential to reduce lutetium. Lutetium triflate was prepared by adding 0.04 grams of lutetium triflate to a test tube, flushing the test tube with nitrogen, and adding 1.5 mL of Grignard reagent and magnesium powder via syringe at 0°C. All samples were allowed to reduce for two days since optimal results were found with ytterbium(III) triflate with this reduction time. Results were higher for ytterbium triflate when tetrahydrofuran was removed, but lutetium triflate samples were prepared with tetrahydrofuran for comparison purposes. The percent recovery for lutetium in the solid phase is listed in Table 21. Results were similar for all samples with L-4 and L-5 having slightly lower percent recoveries compared to L-6 and L-7 samples that excluded tetrahydrofuran.

Table 21: Lutetium triflate with Magnesium Powder

<i>Components</i>	<i>Lu(OTf)₃</i>	<i>Tetrahydrofuran</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery</i>
L-4	~0.04 g	0.5 mL	1.5 mL	9
L-5	~0.04 g	0.5 mL	1.5 mL	8
L-6	~0.04 g	-	1.5 mL	15
L-7	~0.04 g	-	1.5 mL	10

Table 22: Lutetium triflate with Magnesium Ribbon

<i>Components</i>	<i>Lu(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Reaction time</i>	<i>Percent Recovery</i>
L-8	~0.04 g	1.5 mL	1 day	9
L-9	~0.04 g	1.5 mL	2 days	9
L-10	~0.04 g	1.5 mL	3 days	12
L-11	~0.04 g	1.5 mL	4days	19

When magnesium powder was replaced with magnesium strip, the amount of lutetium that remained in the liquid phase did not change significantly. Table 22 gives the results for these experiments. Results show that the longer the reaction time, the higher the amount of lutetium found in the solid state. The percent recovery lists the amount of lutetium in the solid state, which was less than 20 percent for all samples.

COMBINED TRIFLATE STUDIES

After establishing a system that converts about half of ytterbium(III) to its divalent state in the solid phase and retains trivalent lutetium in the liquid phase, both triflates were mixed together to investigate the chemistry of combining them together. If the two compounds produce the same results found when they were isolated, the first step will have been accomplished before developing a means of separation of the divalent ytterbium triflate from lutetium(III) triflate. In the presence of both triflates (0.04 grams of

each), ytterbium(III) triflate continued to reduce to its divalent state and the majority of lutetium triflate remained in its trivalent state in the liquid phase. The percent recovery values were slightly higher for the combined results compared to the isolated results. Table 23 displays the components and results for these experiments. The percent recovery of ytterbium(II) triflate is the amount recovered in the solid phase. The percent recovery of lutetium(III) triflate is the amount recovered in the liquid phase. As these experiments were repeated, the ytterbium(II) triflate results remained reproducible, but the lutetium(III) triflate results slightly increased. Instead of ranging between 85-95% in the liquid phase, about 70-80% of lutetium remained in the liquid phase. Figure 6 shows a graph of ytterbium(II) triflate and lutetium(III) triflate recovered in the solid phase. As the graph shows, a little more than half of the ytterbium is converted to the solid state and very little lutetium is found in the solid state.

Table 23: Ytterbium(III) and Lutetium(III) Triflate Mixed

<i>Components</i>	<i>Yb(OTf)₃</i>	<i>Lu(OTf)₃</i>	<i>Grignard tetrahydrofuran</i>	<i>Percent Recovery Yb(OTf)₂ (solid phase)</i>	<i>Percent Recovery Lu(OTf)₃ (aqueous phase)</i>
YL-1	~0.04 g	~0.04 g	1.5 mL	63	96
YL-2	~0.04 g	~0.04 g	1.5 mL	55	85
YL-3	~0.04 g	~0.04 g	1.5 mL	57	86

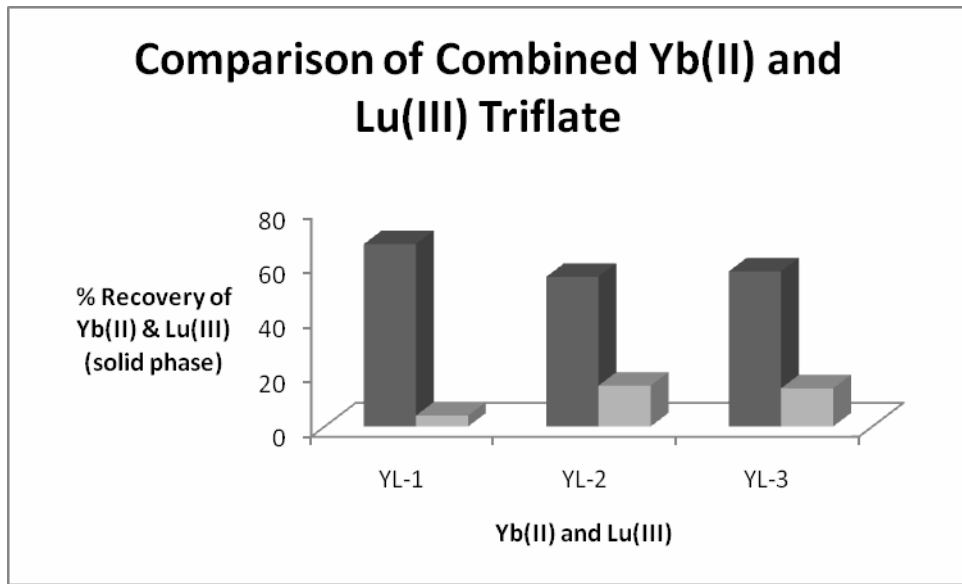


Figure 6: Relationship between Ytterbium and Lutetium Mixed

CHAPTER IV CONCLUSION

The most common use of PET scanners is for the identification of abnormally active tissue. The production of the lutetium oxyorthosilicate used in PET scanners requires a high purity of lutetium. This high purity is very difficult to achieve due to the similar chemical properties and mainly the adopted trivalent oxidation state of the lanthanide elements. However, it is possible to change the environments of ytterbium and lutetium so that the separation process is more efficient. We found that the reduction of ytterbium(III) triflate provides a convenient method for the production of ytterbium(II) triflate. Under the same conditions as ytterbium(III), lutetium(III) triflate remained in its trivalent state. The difference of properties of the two compounds would allow a more effective separation between ytterbium(II) and lutetium(III).

Past research has shown that the electrolytic reduction of ytterbium(III) to ytterbium(II) can be successfully achieved with the use of a mercury cathode or mercury amalgams. However, the toxicity of mercury makes the use of the method undesirable in an industrial setting.

Triflates have shown to be great catalysts in organic chemistry for several reactions and has also shown to be a great compound for reducing ytterbium(III). The most effective system that could be used industrially was the following: approximately 0.04 grams of ytterbium(III) triflate was dissolved in 1.5 mL of Grignard in tetrahydrofuran at 0°C for about 30 minutes after capping and flushing the system with nitrogen. Then about 0.04 grams of 50 mesh magnesium was added and the system was allowed to stir at room temperature for about two days. About fifty percent of

ytterbium(III) was reduced to its divalent state in the presence of a Grignard reagent in tetrahydrofuran and magnesium powder. If allowed to reduce for about five days, substitution with magnesium strip gave a reduction of about fifty percent also.

It was believed that the major difficulty in producing a large quantity of ytterbium(II) was its ability to oxidize back to the trivalent state due to its potential. Although the triflate system allowed the removal of water from the system, a problem continues to exist with the system. It is possible that the system was exposed to some oxygen due to the punctures from the syringe. On the other hand, it is also likely that the system may reach an equilibrium that will not allow the reaction to push forward. Further research will definitely have to address this issue by discovering a compound that will favor the forward reaction.

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