2010

Novel Synthesis of Polyhydrogenated Fullerenes

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NOVEL SYNTHESIS OF POLYHYDROGENATED FULLERENES

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By
ANGELA M. CAMPO

B.S. in Chemistry, Wright State University 2001

2010
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Angela M. Campo
ENTITLED Novel Synthesis of polyhydrogenated fullerenes BE ACCEPTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

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Novel synthesis of polyhydrogenated fullerenes

Hydrogenated fullerenes are of interest as a starting material in metal fulleride synthesis. By reacting \( C_{60}H_2 \) with various metals, alloyed metal fullerides could be produced. To achieve this goal, first a reliable synthesis of \( C_{60}H_2 \) must be determined. \( C_{60}H_2 \) is difficult to synthesis exclusively; \( C_{60}H_4 \) and \( C_{60}H_6 \) are also produced. Reduction of \( C_{60} \) with \( NaBH_4 \) produced a mixture of products as well as excessive unreacted \( C_{60} \). Attempts to modify this reaction to achieve \( C_{60}H_2 \) exclusively were unsuccessful. A novel route was explored by reducing \( C_{60} \) with thiophenol. This reaction produced \( C_{60}H_2 \) after 4 days. In an effort to speed up the reaction time, \( C_{60} \) was reduced with \( Zn(Cu) \) and thiophenol as a proton source. This reaction appeared to yield a mixture of 1,2 \( C_{60}H_2 \) and 1,4 \( C_{60}H_2 \).
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1 Introduction

As advanced aircraft and satellite systems have increased in complexity, thermal management issues have become performance limiting. By increasing the power requirements of aircraft systems, such as high power radar, the waste thermal energy has become more troublesome. Aerospace engineers have typically removed waste heat by using hydraulic fluid for dissipation and the fuel as a heat sink. The use of aircraft fuel, such as JP-8, as a heat sink is very effective and has the added benefit of increased fuel efficiency of the engine due to the heated fuel. But there are downsides to using the fuel as a heat sink. The decomposition of JP-8 can occur in the form of coking at relatively low temperatures. Excessive coking can lead to increased maintenance and down time for the aircraft. Continual heating of the fuel can lead to thermal cracking as well as additional coking. \(^1\) Long missions can suffer when fuel is the main cooling system for the aircraft as the amount of fuel decreases during the flight thereby steadily reducing the amount of available heat sink.

The advent of the More Electric Aircraft (MEA) concept has introduced even more thermal challenges. Traditionally hydraulic fluid, such as polyalphaolefin (PAO) fluid, cools actuators and is able to dissipate localized heat loads across the entire hydraulic system. MEA designs have replaced the hydraulic system with electric actuators, which significantly reduced the active cooling of the aircraft. MEA designers have struggled to overcome this thermal management dilemma. Adding cooling systems would defeat the purpose of eliminating heavy fluid loops in the aircraft. Future aircraft that employ hydraulic systems would still have inadequate thermal management because PAO fluid is not designed for heat transport; rather it is designed for lubrication and its bulk modulus. A lower viscosity PAO fluid is commonly used as a radar coolant. As radar technology becomes more powerful, new coolant technology will also
need to be researched as the existing PAO coolants cannot remove heat from a radar system fast enough to prevent damaging heat spikes. When looking at high performance aircraft design, the combination of hydraulic fluid and fuel as thermal management tools has reached the limit. Future aircraft designs will need to incorporate new cooling technology to supplement the tried and true techniques. In Figure 1 the increasing thermal load in aircraft is illustrated.

![Figure 1 Thermal loads for existing and future aircraft](image)

Figure 1 Thermal loads for existing and future aircraft

Figure courtesy of Air Force Research Laboratory Thermal Steering Committee

Ram air cooling consists of small openings along the body of the aircraft to scoop air in and force it through the heat exchangers, rejecting it on the opposite side. Ram air has become less effective for cooling due to several reasons; at high altitudes the air density is reduced which in return reduces cooling, air temperature increases with air speed, and the addition of ram air ports also increases drag. It is evident that ram air and fuel will not be able to meet the thermal management needs for future systems. More importantly there is a projected order of magnitude increase in thermal load between the F-35 STOVL, which is already plagued with thermal management issues, and the concept for long range strike bombers (LSRRII). This increase in thermal load is mostly driven by advanced electronics and directed energy weapons (DEW)
instead of the more conventional aerodynamic and mechanical inefficiencies. These unprecedented and often low quality heat thermal loads will require a unique variety of solutions to address the massive amount of thermal energy that needs to be dissipated. Thermoelectric devices could supplement current aircraft cooling systems and could play key roles in thermal management of future aircraft.

Thermoelectric devices can be used for refrigeration and power generation processes, however, their efficiency is limited by existing materials. Development of new thermoelectric materials would benefit other applications such as satellites. In power generation and energy harvesting modes thermoelectrics perform best in an environment where the temperature difference between the hot and cold surface can be maximized. Thermoelectric generators are ideal for spacecraft because they are reliable, low weight, unaffected by radiation or orientation, and could also be used to heat or cool on demand instead of harvesting energy. The heat generated inside the satellite and the extreme cold of space is the perfect application for thermoelectric usage. NASA has employed Radioisotope Thermoelectric Generators (RTG) for long duration energy production in deep space probes. An RTG consists of a heat source, which is commonly heat produced from the radioactive decay of plutonium-238 (\(^{238}\text{Pu}\)), and a thermoelectric generator. For example, the Cassini spacecraft employed three RTGs for power generation. The original mission of the Cassini spacecraft was to study Saturn. The spacecraft required a power source capable of producing 600-700 W for at least 11 years\(^6\). Solar arrays could not be used for this mission because the array would have to be prohibitively large due to the distance of Saturn from the sun. Even if an array could be constructed to generate enough power, the weight of the array would be so massive that the Cassini would not have had enough fuel to reach Saturn. It may seem that RTGs have solved the difficult problem of producing power in deep space, but this technology is dependent on a limited supply of \(^{238}\text{Pu}\). The inability of the Department of Energy (DOE) to produce \(^{238}\text{Pu}\) has forced NASA to delay missions that
require RTGs. If more efficient thermoelectric materials were available, less $^{238}$Pu would be needed for each RTG, which means the dwindling supply of $^{238}$Pu could be stretched further.

### 1.1 Thermoelectricity

In 1821 Thomas Johann Seebeck found that a circuit constructed out of two dissimilar metals, with junctions at differing temperatures, would produce an electric potential. This phenomenon is referred to as the Seebeck Effect, see Figure 2, and is the operational principle of thermocouples.

**Figure 2 Representation of the Seebeck effect**

Thermoelectric devices depend on the Seebeck Effect to generate electricity. This relationship is defined in Equation 1. $T_L$ and $T_H$ are the temperatures of the metal junctions while $S_A$ and $S_B$ are the Seebeck coefficients of each metal. It is evident that the Seebeck Effect is driven by the temperature difference of the materials.

**Equation 1**

\[
V = \int_{T_L}^{T_H} (S_B(T) - S_A(T)) dT
\]

Thermoelectric devices can be used not only to harvest electricity from a heat source, but to also cool and refrigerate. The Peltier Effect is the inverse of the Seebeck effect. If a voltage is applied to a circuit of two dissimilar metals, the junction would either be heated or cooled based
on the direction of the current. A Peltier device in essence works as a small heat pump. By manipulating the Peltier and Seebeck effects, one device can be used to switch between energy harvesting and cooling which would be desirable for thermal management applications.

The dimensionless thermoelectric figure of merit, $ZT$, is commonly used to assess the effectiveness of a material for thermoelectricity. The contributors to the $ZT$ of a material are described mathematically in Equation 2.

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

The contributors of $ZT$ are defined as follows: $\sigma$ is the electrical conductivity (S/cm), $S$ is the Seebeck Coefficient (V/K), $T$ is the temperature (K), and $\kappa$ is the thermal conductivity (W/m*K). If the $ZT$ of a material is high, this usually corresponds to a good thermoelectric material. Today, most commercial thermoelectric devices have a $ZT < 1$. If a $ZT$ of 3 could be achieved, inexpensive thermoelectric cooling could replace traditional compressor based refrigeration, air conditioning, and heat pumping. There are multiple inherent physical characteristics of a material that determine the $ZT$ of a material. It is difficult to reduce thermal conductivity in a given material without also reducing the electrical conductivity, as these characteristics are both dependant on the carrier concentration.
Figure 3 Interdependence of physical characteristics of thermoelectric materials


Figure 3 illustrates the nature of thermoelectric materials. If one wanted to optimize the ZT, that would occur at a lower carrier concentration than if one wanted to optimize the thermoelectric power factor (labeled as $\alpha^2 \sigma$ in Figure 3). Due to this quandary of interdependent characteristics, development of new more efficient thermoelectric materials is difficult. In this thesis, new chemical approaches to reduce thermal conductivity while maintaining good electrical conductivity will be explored. In the next section, methods to reduce thermal conductivity will be discussed.

1.1.1 Decreasing thermal conductivity

Thermal conductivity in a solid is the movement of thermal energy through a given material. If a solid is crystalline, thermal energy is transported by the movement of phonons across the lattice. The thermal conductivity is defined by Equation 3.
Equation 3 \[ \kappa = \frac{1}{3} C v l \]

The variables for Equation 3 are defined as the following: \( \kappa \) is the thermal conductivity (W/m*K), \( C \) is the heat capacity (J/m\(^3\)K), \( v \) is the phonon group velocity (m/s), and \( l \) is the mean free path of the phonon. By disrupting phonon movement, the thermal conductivity can be reduced. Amorphous materials, which have no lattice, have inherently low thermal conductivity due to the lack of phonon propagation. Current thermoelectric materials, such as bismuth telluride (Bi\(_2\)Te\(_3\)) disrupt phonon transport by using nanograin of their constituent materials, which are then pressed into a bulk material. The nanograin interfaces act as scattering sites for phonons which reduce the mean free path. Each particle that the phonon encounters slows the velocity at which the phonon is moving through the material. The mean free path of the phonon is the average distance a phonon travels before it reaches a scattering point. This production of nanograin is the method of choice for the most efficient commercially available Bi\(_2\)Te\(_3\), which has a ZT of about 1.4.\(^{10}\)

Another method to reduce thermal conductivity is to introduce rattlers in a structure. Rattlers were first proposed by G.A Slack\(^ {11}\), who found that when he compared filled skutterudites to unfilled skutterudites the thermal conductivity was decreased. Skutterudites are a class of compounds that have the general chemical formula of (Co,Ni,Fe)As\(_3\). Slack postulated that the atoms inside the skutterudite would “rattle” the lattice when hit by phonons.\(^ {12}\) Rattling disturbs phonon transport, therefore reducing the thermal conductivity of the material. This same phenomenon was noticed in clathrates that contained guest atoms.\(^ {13}\) Clathrates have a cage structure, such as a fullerene, that may or may not hold a guest atom/compound inside the cage.

Filled skutterudites and clathrates have also been investigated as possible phonon glass – electron crystal (PGEC) materials. A PGEC material has inherent phonon blocking ability, which results in a low thermal conductivity like that of glass, and also has high electrical conductivity.
which is commonly seen in crystalline materials. A PGEC material does not have to be crystalline; just possess good electrical conductivity like a crystal. PGEC materials can be engineered by starting with materials that have inherently good electrical conductivity and low thermal conductivity. By inserting rattlers into the crystal structure the thermal conductivity should be reduced even further.

The NASA Jet Propulsion Laboratory (JPL) investigated state-of-the-art thermoelectric materials compared to structures with rattlers, referred to as filled skutterudites. NASA found that filled skutterudites had a better ZT than unfilled skutterudites, which was not surprising due to the rattling effect of the doped atoms. The filled skutterudites in the study outperformed more traditional thermoelectric materials such as lead telluride (PbTe).

1.1.2 Current thermoelectric materials

As mentioned earlier, Bi$_2$Te$_3$ is the most common commercial thermoelectric material. It is often used as the benchmark for thermoelectric performance since it has been characterized extensively. The production of Bi$_2$Te$_3$ materials has reached a bottleneck stage, since tellurium is in limited supply and the demand is increasing. Tellurium is considerably less abundant than platinum or gold and only mined as a by-product of other materials such as copper and gold. The majority of tellurium in the United States is used for steel alloys and cadmium telluride solar cells, which have also seen rapidly increasing production. According to the U.S. Geological Survey, the cost of tellurium has increased from $13/kg in 2003 to $215/kg in 2008. This trend shows signs of continuing due to the increased demand of cadmium telluride for solar cells. Other promising thermoelectric materials, such as TAGS, an alloy consisting of $(\text{GeTe})_{0.85}(\text{AgSbTe}_2)_{0.15}$ and lead telluride (PbTe) are also affected by this increased tellurium demand. Since so many commercial and developmental thermoelectric materials contain tellurium, research on new thermoelectric materials that avoid tellurium as a major constituent is especially welcome.
Aside from material shortages, the current leading thermoelectric materials have serious health hazards. PbTe is a chronic health hazard, as lead is an accumulative poison. Antimony based thermoelectric materials, such as TAGS are hazardous as well. Antimony shows signs of being as toxic as arsenic, but toxicological testing has not been completed in this area. Initial studies have suggested proceeding with caution when using antimony due to the unknown nature of how the human body would detoxify this substance. 16

1.1.3 Fullerene based compounds as thermoelectric materials

Fullerenes are an interesting starting point when engineering a novel thermoelectric material. Unlike current thermoelectric materials, initial toxicity tests indicate that C_{60} carries only a minimal toxicity concern 17 In addition, their structure enables them to host atoms and/or small molecules endohedrally. These trapped materials can act as rattlers to reduce thermal conductivity. Rattlers can also be introduced to fullerene-based materials in the voids found between fullerenes in their crystal structure. Figure 4 illustrates one example of molecules existing in the lattice with fullerenes.

![Figure 4 Ferrocene molecules between C_{60}]({http://dx.doi.org/10.1039/C39920001764})

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Given what is observed in Figure 4, there is more than enough room for C\textsubscript{60} to host a few metal ions and still be able to maintain electrical conductivity. This comes as no surprise considering that the interstitial cavities of C\textsubscript{60} account for up to 27% of the unit cell volume.\textsuperscript{19} \(\text{C}_{60}\text{M}_x\) (\(M = \text{metal, } x = 1-6\)) structures could reduce thermal conductivity by the rattling of the metals but still without negatively impacting electrical conductivity of the C\textsubscript{60}. In particular, \(\text{C}_{60}\text{M}^a\text{M}^b\) would be ideal because two different rattling modes would be introduced as well as an alloying effect.\textsuperscript{20} Alloying increases scattering points in a material, which reduces phonon transport. An example of this would be the decrease in the thermal conductivities of Fe-Mn-Al austenitic alloys that occurs with an increase of the aluminium percentage.\textsuperscript{21} Although \(\text{C}_{60}\text{M}_x\) molecules have been found in the literature, their preparation has been accomplished by electrochemical or sealed tube reaction techniques.

2 Historical

2.1 Fullerene chemistry

The discovery of fullerenes and their availability has spawned intense study in many different fields.\textsuperscript{22-25} Initially, it was believed that C\textsubscript{60} was a super aromatic material, meaning that electrons resonated throughout the structure. Later studies proved this to be untrue; the electrons only resonate within the 6 member rings.\textsuperscript{26} The main driving force behind C\textsubscript{60} reactions is to relieve strain in the molecule. C\textsubscript{60} consists of all sp\textsuperscript{2} carbon atoms with two different bond lengths, the bonds at the hexagon junctions are 1.39 Å and the bonds at the junction of a hexagon and a pentagon are 1.44 Å. The carbon atoms in graphite are also sp\textsuperscript{2} hybridized but do not have the same strain as fullerenes since the carbon atoms in fullerenes must be bent to create the structure. There is a great reduction of strain when addition to the C\textsubscript{60} molecule occurs; changing sp\textsuperscript{2} hybridized carbons to sp\textsuperscript{3} hybridized carbons. The double bonds only exist in the six membered rings because this arrangement produces the lowest energy structure. Early research
determined that the reactivity of C_{60} was comparable to an electron deficient alkene. The majority of reactions occur at the fusion of two 6 membered rings, the location of the double bonds. In general, if an alkene can undergo a given reaction, then C_{60} will most likely also undergo that same reaction. See Scheme 1 for selected reactions of C_{60}.

![Scheme 1 Representative C_{60} reactions](image)

One notable exception, C_{60}I_2 has never been formed, whereas I_2 can be added across a typical alkene. It has been postulated that C_{60}I_2 is unstable due to the bulkiness of iodine and that the C_{60}-I bond would be very weak.

C_{60} has surprising solubility characteristics. One would expect that solvents that typically dissolve alkenes or benzenes would also readily dissolve C_{60}, but this is not the case. C_{60} has low solubility in many common laboratory solvents. Figure 5 is a partial listing of solvents that dissolve at least 1mg/mL of C_{60} at room temperature.
**Figure 5 Solubility of C₆₀ in various solvents at room temperature**

C₆₀ is insoluble in polar solvents, hydrogen bonding solvents, and the majority of alkanes. In the few alkanes in which C₆₀ is soluble, such as hexane (0.043 mg/mL), the solubility is so low it would not be suitable to be used as a solvent in a C₆₀ reaction. Thus, solvent selection for fullerene reactions can be difficult. Toluene is usually a good choice as it has a moderately high boiling point of 110.6°C, is easily removed under vacuum, and does not interfere in most reactions.

In the next section, the electrochemical behaviour of C₆₀ will be examined. These data shed light on why multiple additions to C₆₀ are common.
2.2 Electrochemical assessment

$C_{60}$ has a high electron affinity, which is easily shown by its first reduction potential. However, it is more remarkable that $C_{60}$ exhibits six evenly spaced one-electron reversible step reductions. See Figure 6. Given that the steps are separated by at least -0.5 V, a chemical reducing agent should be able to stop the reduction at a specific step.  

![Figure 6 Multiple reductions of $C_{60}$](image)


Many research groups have studied the electrochemical properties of $C_{60}$ and substituted $C_{60}$ compounds. Based on protonation studies, $C_{60}^-$ is a relatively weak base, whereas $C_{60}^{2-}$ is a relatively strong base. $C_{60}$ anions are very air sensitive and have varying solubilities. Most anions are soluble in tetrahydrofuran (THF) whereas $C_{60}$ has minimal solubility in THF. This difference in solubility could be used to synthetic advantage. The difference in solubilities between $C_{60}$ and $C_{60}^{n-}$ was exploited in a paper by Mingfei Wu. The $C_{60}$ anion was generated in an aqueous NaOH/THF solution. $C_{60}$ and zinc powder were suspended between the THF and aqueous layer. As the anion formed, it migrated to the THF layer. Only $C_{60}^-$ was formed in this manner, but $C_{60}^{2-}$ was formed by switching to DMSO. In this manner the anions can be easily formed and isolated due to the difference in solubility of the starting material and the reactants.
This method may be good at producing fullerene anions, but does not provide an easy route to alloyed fulleride compounds.

$C_{60}$ was researched heavily in the superconductor field. In the early 1990’s, alkali fullerides were produced by electrochemical means in hopes of finding a superconducting material. $K_2C_{60}$ was the first alkali fulleride found to be a superconductor. This discovery opened the floodgates of research, leading to the identification of many more alkali fulleride superconductors. See Table 1 for alkali and alkaline doped fullerenes that are superconductors.

Table 1 Alkali and alkaline doped $C_{60}$ superconductors

This research was of particular interest to this project because it suggests the breadth of fullerides that can be found. Superconductors are poor thermoelectric materials because their Seebeck Coefficient is zero. See Equation Set 3
In Superconductors the following is true:

\[ V = IR = 0 \]

\[ S = \frac{\Delta V}{\Delta T} = 0, \quad ZT = \frac{\sigma S^2 T}{\kappa} = 0 \]

This list provides a good starting point; however, there are some obvious holes in the table. Zinc fullerides have not been reported in the literature. Zinc is promising for possible thermoelectric fullerides as it is low in toxicity, inexpensive and available in large quantities, and would have a full outer shell once it bonded with C\textsubscript{60}. Recently, Snyder et al \(^3\) found that Zn\textsubscript{4}Sb\textsubscript{3} behaves as an ideal PGEC material because disorder is created by the zinc in the antimony lattice. It is conceivable that zinc would behave in a similar manner in the C\textsubscript{60} lattice.

The research on metal fullerides also showed another area of interest. The majority of metal fullerides are produced in electrochemical cells versus a solution based synthetic route. Electrochemical reactions are difficult to scale up in industry for a variety of reasons such as mass transfer limitations to bulk electrodes and the limited number of chemists that are trained in electrochemical techniques. A solution based synthetic route would be preferred for there to be a good chance of scale up production and future transition to a thermoelectric device manufacturer.

There was one example of K\textsubscript{x}C\textsubscript{60} synthesis by reacting C\textsubscript{60} with potassium metal. The authors were unsure how many potassium additions they made to the C\textsubscript{60} and the method involved a large excess of potassium metal which was hand extracted at the end of the reaction. A synthetic procedure that could produce the desired metal fulleride in decent yield and be
scalable in industry would be a significant advance. However, no such procedure appears to exist in the literature to date.

In this study, C₆₀H₂ is the target molecule as it would be an excellent precursor to form C₆₀HM and C₆₀HM⁺M⁰ with M being various metals. It has been shown that C₆₀H₂ is acidic with a pKa of 4.7, which is similar to acetic acid. This presents the possibility of producing metal fullerides through acid-base reactions utilizing C₆₀H₂ as the acid. This seems preferable to direct reaction with alkali metals where stoichiometric control could be problematic. The proposed route is illustrated below in Scheme 2.

**Scheme 2 Proposed synthesis of C₆₀MₓMᵦ**

Step 1: Synthesis of C₆₀HM from various metal carbonates, for example, sodium bicarbonate.

Step 2: Utilize a differing metallic base to create the alloyed fulleride

By using C₆₀H₂, stoichiometric control can be achieved with the metal fullerides. Pure C₆₀H₂ could be reacted with a variety of organometallic reagents to achieve various metal
fullerides. The first step is to prepare C$_{60}$H$_2$, however its preferential formation may be problematic. There are no reports in the literature that described a route to produce only C$_{60}$H$_2$ with a significant yield. Hydrogenation of fullerenes generally produces a mixture of products including C$_{60}$H$_2$, C$_{60}$H$_4$, C$_{60}$H$_6$, and even higher hydrogenated fullerenes. Electrochemical studies on the protonation of C$_{60}$ anions have shed some much needed light on this subject. In an electrochemical cell, the following reactions occur:

1. $C_{60}^- + e^- = C_{60}^{2-}$
2. $C_{60}^{2-} + RCOOH = C_{60}H^- + RCOO^-$
3. $C_{60}H^- + e^- = C_{60}H^{2-}$
4. $C_{60}H^{2-} + RCOOH = C_{60}H^- + RCOO^-$
5. $C_{60}H^- + e^- = C_{60}H^{2-}$

It is quite apparent that the C$_{60}^-$ anion will readily take on another electron to become C$_{60}^{2-}$. This is not surprising given the potential for C$_{60}$ to be reduced to a -6 charge. One interesting concept Cliffel et al$^{34}$ found is that C$_{60}^{2-}$ only partially protonates to C$_{60}H^-$, which is then rapidly reduced to C$_{60}H^{2-}$. After each proton addition the hydrogenated fullerene is reduced again, setting the stage for further protonation. This electrochemical study explains why C$_{60}$H$_2$ is difficult to produce as the only hydrogenated product. The following section will discuss the advantages and disadvantages of several methods to produce C$_{60}$H$_2$.

2.3 Preparation of C$_{60}$H$_2$

Early research$^{23}$ on hydrogenated fullerenes found that if C$_{60}$H$_2$ is stored as a solution in toluene and under oxygen and C$_{60}$ free conditions, then C$_{60}$H$_2$ has an indefinite shelf life. But if care is not taken in storing C$_{60}$H$_2$, it will readily decompose. Various methods to prepare C$_{60}$H$_2$ can be found in the literature,$^{35-39}$ the majority of which involve air-free techniques. Many of the methods had poor yields or difficulties in separation of the desired product. Separation of C$_{60}$H$_2$,
C_{60}H_{4}, and C_{60}H_{6} can be difficult without the aid of a preparatory HPLC system. Without an HPLC, the removal of unreacted C_{60} from a reaction is best achieved by exploiting the solubility of C_{60} in methylecyclohexane in which C_{60}H_{2} has very limited solubility.

Hydroboration was the first technique for producing C_{60}H_{2} reported in the literature. This procedure could produce C_{60}H_{2} in 10 – 30 % yields. The downside of this reaction is not only the low yield, but the additional danger of producing diboranes. Rhodium catalyzed hydrogenation also produced C_{60}H_{2} in a low yield, 14 %, while utilizing an expensive reagent. Hydrozirconation and hydrazine reductions also produced the desired compound but require either expensive reagents or a highly toxic material. Ultrasonic irradiation produced only C_{60}H_{2} but in extremely low yield, ~2.5%, but attempts to increase the yield by lengthening the sonication time resulted in the destruction of the fullerene cage. The most promising approaches include reduction via sodium borohydride (NaBH_{4}) and dissolving metal reduction via zinc-copper couple (Zn(Cu)). Each of these approaches produced a mixture of products. In the current study, each approach will be modified in an attempt to produce exclusively C_{60}H_{2}. Below, each approach will be discussed along with the modifications proposed to push each reaction toward sole C_{60}H_{2} production.

2.3.1 A Simple preparation of dihydrofullerene and its reversion to fullerene (C_{60})

Hydrogenated fullerenes can be synthesized by reducing C_{60} with NaBH_{4}/ethanol in toluene. See Scheme 3 for NaBH_{4} reduction of C_{60}.

Scheme 3 Reduction of C_{60} via NaBH_{4}
The formation of $C_{60}H_2$ varies with reaction time and the concentration of NaBH$_4$. See Table 2 for reaction conditions versus $C_{60}H_2$ produced.

<table>
<thead>
<tr>
<th>$C_{60}$ : NaBH$_4$</th>
<th>1 : 0.5</th>
<th>1 : 0.5</th>
<th>1 : 1</th>
<th>1 : 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>45</td>
<td>60</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Unreacted $C_{60}$ (%)</td>
<td>20</td>
<td>12</td>
<td>35</td>
<td>39</td>
</tr>
<tr>
<td>$C_{60}H_2$ (%)</td>
<td>66</td>
<td>63</td>
<td>55</td>
<td>52</td>
</tr>
<tr>
<td>$C_{60}H_{2n}$ (n≥2)(%)</td>
<td>14</td>
<td>25</td>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 2 Reaction conditions for reduction of $C_{60}$ by NaBH$_4$

Based on the information in Table 2, it is evident that the reaction is dependent on the time and ratio of NaBH$_4$. It is surprising that when the amount of NaBH$_4$ in the reaction is increased, that the percentage of unreacted $C_{60}$ increases. Increasing the NaBH$_4$ will decrease the amount of desired product, but it should also decrease the undesired $C_{60}H_{2n}$ products. Based on literature results in Table 2, increasing the reaction time should increase the hydrogenated fullerene products.

2.3.2 Dissolving metal reduction

Zinc copper couple, Zn(Cu), can be used to transfer electrons to $C_{60}$ which can then be protonated by a proton source in the reaction such as water or acid. This method is one of the most widely cited methods for producing various hydrogenated fullerenes. As with the NaBH$_4$ reduction, this method produces the unwanted $C_{60}H_4$ and $C_{60}H_6$ side products that must be removed by preparatory HPLC. Meier et al used the dissolving metal reduction, with small changes in the conditions, to achieve only $C_{60}H_6$. It should be noted that $C_{60}H_6$ could be used in the preparation of $C_{60}M_x$ in place of $C_{60}H_2$ if that compound cannot be isolated in decent yields. See Scheme 4 below for the reduction of $C_{60}$ to $C_{60}H_2$ by Zn(Cu). One avenue to research with reduction via Zn(Cu) is alternative proton sources. In the various papers from the Meier group on this reduction, they stated that only water and various acids were reported to protonate $C_{60}$. When
water is used as a proton source for C₆₀, less protonation occurs than when acids are used. Alcohols were found by Meier not to be effective as a proton source, but thiols are not mentioned.

Scheme 4 Reduction of C₆₀ by Zn(Cu) and water

C₆₀Hₓ materials have been shown to revert to C₆₀. This has been accomplished by exposing C₆₀Hₓ to O₂ while in the presence of a reducing agent and also by heating C₆₀H₂ to drive off the protons. In the Bettinger paper, a solution of C₆₀H₂ in 1,2-dichloro-[D₄]-benzene was heated between 443 - 459 K to yield C₆₀. The thermal breakdown of C₆₀H₂ was found to be a very similar mechanism to that of ethane thermolysis. See Scheme 5

Scheme 5 Thermolysis mechanism of C₆₀H₂

Initiation: C₆₀H₂ → C₆₀H + H

Propagation: C₆₀H₂ + H → C₆₀H + H₂

Propagation: C₆₀H → C₆₀ + H

The thermal breakdown of C₆₀H₂ indicates that it may be possible to synthesize C₆₀Hₓ products, create a fulleride metal salt, and then thermally drive off the remaining hydrogens. This would provide an alternative approach to synthesize various metal fullerides while avoiding the time consuming and costly separation of the various C₆₀Hₓ species (such as a mixture of C₆₀H₂, C₆₀H₄, and C₆₀H₆).
2.4 This project

The goals of this project are the following:

1. Develop a procedure to hydrogenate C\(_{60}\) to the desired level only, such as C\(_{60}\)H\(_2\) exclusively or at the very least with a high yield.
   a. Adjust the reaction conditions of known methods in the literature to hopefully produce C\(_{60}\)H\(_2\) exclusively
   b. React thiophenol with C\(_{60}\) without the presence of a base to attempt to produce C\(_{60}\)H\(_2\)

2. Establish a procedure to easily isolate the desired hydrogenated product from unreacted materials without the aid of a preparatory HPLC.

3. Develop a procedure to synthesize various metal fullerides from hydrogenated fullerenes.

2.4.1 Novel synthesis of C\(_{60}\)H\(_2\) via reduction of C\(_{60}\) with various thiols.

Various methods to synthesize C\(_{60}\)H\(_2\) have been found in the literature and a few have been discussed in this paper. What is lacking in the literature is an easily scaled procedure to produce exclusively C\(_{60}\)H\(_2\), which would avoid preparatory HPLC separation. In the literature\(^{45,46}\) the following scheme was found:

**Scheme 6 Formation of C\(_{60}\)H\(_2\) via reduction of C\(_{60}\) by H\(_2\)S**

\[
\text{CS}_2 + \text{Al}_2\text{O}_3/\text{trace water} \rightarrow \text{H}_2\text{S}
\]

\[
\text{H}_2\text{S} + \text{C}_{60} \rightarrow \text{C}_{60}\text{H}_2 + \text{S}
\]

Given the above reactions, it is conceivable that C\(_{60}\) would react with a thiol to produce C\(_{60}\)H\(_2\). See Scheme 7 below.
While this method should produce the desired $C_{60}H_2$, it would also provide a novel synthesis of disulfides.

3 Experimental

3.1 Chemicals and instrumentation

Solvents were procured from Aldrich and the oxygen removed by purging with nitrogen for at least 30 minutes prior to use. $C_{60}$, 99.9%, was procured from MER Corporation and used as received. The zinc-copper couple (Zn(Cu)) was obtained from Sigma-Aldrich and used as received. Distilled water was placed into a vial fitted with a septum and purged with argon or nitrogen for at least 30 minutes prior to use. Thiophenol quality was determined via NMR analysis and found to be free of disulfides, therefore, it was used as received.

Ultraviolet-visible spectral data (UV/Vis) were collected with a Shimadzu Multi-Spec 1501 UV Spectrometer. Matched quartz 3 ml cells were used with septum caps. Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 300 NMR Spectrometer for all $^1H$, $^{13}C$, and $^{13}C$ Distortionless Enhancement by Polarization Transfer (DEPT) 90 experiments. DEPT 90 $^{13}C$ experiments are useful for determining the C-H groups present in the sample while suppressing CH$_2$, CH$_3$, and quaternary carbons. DEPT $^{13}C$ experiments are more sensitive than the standard $^{13}C$ experiment. Assignments of chemical shifts are based on literature values.
3.2 Preparation for analytical samples

All UV-Vis samples were prepared from 1 mL aliquots taken from the reaction mixture under air free conditions. Aliquots were diluted in the quartz UV/Vis cell. Toluene was used as a blank for UV-Vis samples. Only reactions utilizing Zn(Cu) were filtered with a syringe filter prior to injection into the UV-Vis cell. NMR samples were prepared from solid product that was dissolved in either o-dichlorobenzene (ODCB)-d₄ or toluene-d₈. NMR samples were prepared in a glass vial, sonicated, and then filtered prior to data acquisition. FTIR samples were prepared as KBr windows.

3.3 General reaction procedure

Glassware was assembled and cooled under nitrogen. Toluene used in the reactions was purged with nitrogen for at least 15 minutes prior to use. All liquid reactants were also purged for at least 15 minutes with nitrogen. C₆₀ was weighed onto weighing paper and then transferred to the reaction flask while under nitrogen. Once the thiol of choice and toluene were in the Schlenk flask with the C₆₀, the flask was sonicated for 10 minutes. All visible C₆₀ was dissolved after sonication. Each reaction was heated to reflux for 4 days, unless stated otherwise. Nitrogen flow was turned to positive pressure after the toluene reached reflux. Pre and post analysis by UV/Vis spectroscopy was conducted for each sample. Pre samples were collected after sonication and a brief amount of time stirring to ensure the reaction mixture was uniform. Aliquots taken for UV/Vis did not need to be filtered except those taken from reactions with Zn(Cu).

3.4 Synthesis of C₆₀H₂ via reduction of C₆₀ by NaBH₄, 1:1 ratio

Following the literature protocol, a stock solution of NaBH₄ (0.052 g) in ethanol (50 mL) was prepared in a volumetric flask and 8 mL was injected into a prepared flask of C₆₀ (72 mg, 0.1 mol) in dry toluene (200 mL). The reaction mixture turned slightly pink from the original
deep purple color. The solution was allowed to stir at 60 °C for 45 minutes at which point an aliquot was taken by syringe to determine if C₆₀H₂ had formed. The desired compound was formed but appeared to be in low yield, the reaction was then allowed to run overnight to determine if all of the C₆₀ would be eventually consumed. The total reaction time was ~ 11 hours and C₆₀ was still present in the reaction flask. Final UV/Vis (toluene, λ): C₆₀ peaks: 410, 599, C₆₀H₂ peaks: 426, 714.

3.4.1 Modification of reduction of C₆₀ by NaBH₄, using 1:2.5 of C₆₀: NaBH₄ ratio

The same procedure was used as in Section 3.4, but the amount of NaBH₄ was increased. This reaction was also conducted on a smaller scale; 0.036 g of C₆₀ was used along with 125 mL of toluene and 5 mL of NaBH₄/ethanol stock solution. With the addition of NaBH₄/ethanol, the reaction turned slightly pinkish purple from the original deep purple color. This reaction ran for a total of 2 hours. UV/Vis (toluene, λ): C₆₀ peaks: 410, 599, C₆₀H₂ peaks: 436, 714. $^1$H NMR (toluene-$d_8$): 5.93

3.4.1.1 Column purification of C₆₀H₂

As cited in the literature 39, the reaction mixture from Section 3.4.1 was passed through a silica gel column utilizing CS₂ as the mobile phase. No instructions were given in the paper on how to best conduct this column considering that the product is air sensitive. The column was assembled under an argon purge and the top was fitted with a rubber septum. A vacuum adapter was fitted with a rubber septum and then connected to a Schlenk flask. The bottom tip of the column was punched through the vacuum adapter rubber septum. Argon was purged into the column system from the top of the column and the vacuum adapter.

Once the glassware was assembled a slurry of alumina and dry CS₂ was prepared. Under an argon purge, the septum on the top of the column was removed and the slurry was quickly poured in. The septum was replaced and the column was purged with argon for 1.5 hours. During this time, the column was observed for a color change, which would indicate that CS₂ was
reacting with the alumina to produce $\text{H}_2\text{S}$. The column changed color from a slight peach to a noticeable yellow, indicating the presence of sulfur. The reaction mixture was loaded via cannula, followed by an injection of 15 mL of dry $\text{CS}_2$. $\text{CS}_2$ was injected in 30 mL increments after each fraction was taken. A brown band and purple band were visible in the column. The first fraction was collected until the entire purple band had been collected. The purple band was most likely to contain $\text{C}_{60}$. All catch flask changes were conducted under an argon purge through the column and the flask. The brown band was difficult to distinguish in the column and the remaining fractions were collected in 30 mL increments until no bands remained in the column. A total of 6 fractions were collected. All fractions were sealed in their respective Schlenk flasks, wrapped in foil to prevent light exposure, and then stripped of solvent under vacuum. UV/Vis analysis of the fractions indicated the presence of $\text{C}_{60}$ in all fractions. Fraction 2 appeared to have the least amount of $\text{C}_{60}$, according to UV/Vis (toluene, $\lambda$): $\text{C}_{60}$ peaks: 410 $\text{C}_{60}\text{H}_2$ peaks: 436. $^1\text{H}$ NMR (toluene-$d8$): 6.34, 6.22

3.4.2 Modification of reduction of $\text{C}_{60}$ by $\text{NaBH}_4$, 10X of $\text{NaBH}_4$ used

The same procedure was used as in section 3.4.1, except that a large excess of $\text{NaBH}_4$ (10X) was used to see if all $\text{C}_{60}$ could be consumed in the reaction. 20 mL of NaBH$_4$ stock solution was added to 0.07 g of C$_{60}$ in 300 ml of dry toluene. UV/Vis (toluene, $\lambda$): 433

3.5 Synthesis of $\text{C}_{60}\text{H}_x$

3.5.1 Novel synthesis of $\text{C}_{60}\text{H}_2$: reduction of $\text{C}_{60}$ with thiophenol

$\text{C}_{60}$ (0.3g) and a stir bar were added to a 200 mL dry Schlenk flask, which was fitted with a condenser. Dry toluene was purged with nitrogen for at least 15 minutes prior to being transferred via cannula into the prepared Schlenk flask. Thiophenol was purged with nitrogen for at least 30 minutes prior to use, after which 4.5 mL of thiophenol was injected into the flask. The Schlenk flask was placed in an ultrasonic bath for 10 minutes to dissolve the $\text{C}_{60}$. After
sonication, the solution was deep purple in color and no undissolved C_{60} was visible. The Schlenk flask was purged with nitrogen for 10 minutes and the condenser was fitted with a gas adapter at the top under a fast flow of nitrogen. The nitrogen flow on the flask was increased, the septum removed, and the flask was quickly fitted with a condenser. An oil bath was used to heat the reaction to reflux and the mixture was continuously stirred and heated at reflux for four days. There was a characteristic color change from the deep brilliant purple of C_{60} dissolved in toluene to a clear reddish brown. The color change was noted on day three, but was faint. On day four the flask was obviously reddish brown in color. Dry acetone was added to the flask in a 10:1 ratio to precipitate the fullerene based materials. The solution was filtered under nitrogen. The resulting brown-black powder was further dried under vacuum to remove as much residual toluene as possible. **UV/Vis (toluene, \lambda):** 435 nm, 709 nm.

3.5.2 Reaction of C_{60} with 1-Octadecanethiol in toluene.

C_{60} (0.3073 g) and 2.4351 g of 1-Octadecanethiol were used for this reaction, as well as about 150 mL of purged toluene. The reaction mixture was prepared according to the general reaction procedure. On the 4th day, a 1 mL aliquot was taken for UV-Vis analysis, which confirmed that no reaction had occurred.

3.5.3 Reaction of C_{60} with triphenyl methanethiol (TPMT) in toluene

C_{60} (0.3106 g), TPMT (2.2556 g), and about 120 mL of sparged toluene were combined in a Schlenk flask. The reaction was prepared according to the general reaction procedure. By the end of the 4th day no color change was observed. An aliquot was taken for UV/Vis analysis and it confirmed no reaction occurred; only C_{60} peaks were present in the spectrum.

3.5.4 Reaction of C_{60} with 4-nitrothiophenol in toluene

C_{60} (0.3106 g), 4-nitrothiophenol (1.2872 g), and about 120 mL of sparged toluene were combined in a Schlenk flask. The reaction was prepared according to the general reaction
procedure. By the end of the 4th day no color change was observed. An aliquot was taken for UV/Vis analysis and it confirmed no reaction occurred; only $C_{60}$ peaks were present in the spectrum.

3.5.5 Synthesis of $C_{60}H_6$

The reaction was prepared following Meier’s protocol in the literature. $C_{60}$ (0.6 g) and Zn(Cu) (5 g) was transferred to a 200 mL dry Schlenk flask. The flask was fitted with a rubber septum. Dry toluene was purged with nitrogen for at least 15 minutes. Toluene (125 mL) was transferred via cannula into the prepared Schlenk flask. Purified water (0.75 mL) was purged with nitrogen for 15 minutes. The water was then injected into the reaction flask. The flask was sonicated for 5-10 minutes to help dissolve the $C_{60}$. The reaction flask was fitted to a condenser under nitrogen purge and then lowered into a preheated 50°C oil bath. After 3 hours the reaction was cooled and filtered in a nitrogen atmosphere. The solid was rinsed with toluene twice. The solvent was removed from the filtrate under vacuum. The resulting dark brown solid was dried in the drying pistol for at least 8 hours to remove residual toluene. UV/Vis (toluene, $\lambda$): 439 nm, 710 nm.

3.5.6 Removal of thiophenol from reaction mixture

The purification procedures discussed in the literature by Meier involved the use of an HPLC. In lieu of that equipment, thiophenol will need to be removed after the reaction precipitating the fullerenes. When using the Zn(Cu) to produce hydrogenated fullerenes, post reaction the resulting mixture must be filtered to remove the Zn(Cu). The filtrate was then reduced in volume under vacuum. Nitrogen-purged acetone was then added to the filtrate in a 10:1 acetone: filtrate ratio. The sealed flask was wrapped with foil and stored in the refrigerator overnight. The acetone forces the fullerene compounds to precipitate while keeping the thiophenol in solution. The acetone mixture was filtered with a Schlenk filter under vacuum. The resulting solid was dried in the drying pistol.
3.5.7 Modification of Meier’s C_{60}H_{6} preparation

C_{60} (0.7533 g) and Zn(Cu) (5.1461 g), was added to a prepared Schlenk flask. The reaction was prepared in the same manner as C_{60}H_{6} in section 3.5.5 with the exception that thiophenol was used as the proton source instead of water. The reaction flask was fitted to a condenser under nitrogen purge and then lowered into a preheated 50°C oil bath. After 3 hours the reaction was cooled and filtered in a nitrogen atmosphere to remove the Zn(Cu). The solid rinsed with toluene twice. Roughly 350 mL of solution was in the flask after washings. 700 mL of sparged acetone was added to the flask to precipitate the fullerene compounds. The flask was filled with argon, sealed, and placed in the refrigerator overnight. The solution was filtered under nitrogen, the resulting dark brown solid was dried in the drying pistol for at least 8 hours to remove residual toluene.

4 Results and discussion

4.1 Challenges in this project

This project had three main challenges; air sensitivity of the products, separation of the desired product from the reaction mixture, and difficulties in identifying products due to the inability to separate them.

4.1.1 Air sensitivity of hydrogenated fullerenes

Various sources in the literature describe hydrogenated fullerenes as air sensitive; \textsuperscript{35} C_{60}H_{2} readily reacts with oxygen to form C_{60}. This major inconvenience can be partially mitigated by utilizing Schlenk techniques during the preparation of hydrogenated fullerenes. The air sensitivity of hydrogenated fullerenes also complicates their chemical analysis. Samples
quickly degrade, even if precautions are taken to deoxygenate samples and/or solvents because oxygen is often caught in the lattice of fullerene structures. 48

4.1.2 Separation of hydrogenated fullerenes

During the literature review phase of this project, the hope was to find a synthetic route to form C_{60}H_2 as the only hydrogenated fullerene product. There was no published method of separation that did not rely on HPLC with a Cosomil BuckyPrep column. The reactions that appeared to form only C_{60}H_2, according to UV/Vis, could not be verified by NMR spectroscopy. A “separation” was mentioned by Wang in the NaBH_4 reduction paper 39, which was one of the reasons the NaBH_4 reduction was chosen. Wang did not give any procedure on the column separation of C_{60}H_2 from the reaction mixture, he simply stated the stationary and mobile phases. Further literature searching was done to determine why this column would be an appropriate method to purify C_{60}H_2. It is assumed that the reasoning for the column is based on the production of H_2S within the column, which would then react with C_{60} to produce C_{60}H_2. In our hands, the column purification was attempted twice and did not remove C_{60} from the reaction mixture. All fractions contained C_{60} in varying amounts. It is possible that further refinement of this technique may lead to less C_{60} in the reaction mixture, but the column is undesirable to conduct due to the large amount of waste CS_2 that is created and also the hazard of H_2S.

4.1.3 Difficulties in obtaining NMR spectra

C_{60} is not very soluble in commonly acquired solvents as explained earlier in this thesis. In the literature, three solvents were used for NMR studies; toluene, CS_2/acetone, and o-dichlorobenzene. CS_2/acetone is the most common NMR solvent used in the literature but in-house samples proved to have difficulty staying in solution. The ratio of CS_2 to acetone used in the literature was 9:1. At this concentration the C_{60}/C_{60}H_x mixture was able to be dissolved, but the NMR was not able to lock on the acetone. Acetone was added to the tube dropwise in hopes
of achieving a lock with the lowest amount of additional acetone necessary. The NMR lock was never achieved with this solvent mixture and, eventually, the additional acetone caused the C$_{60}$/C$_{60}$H$_x$ to precipitate in the NMR tube.

The number of scans necessary for $^{13}$C NMR analysis of fullerene compounds was not found in the literature. It was alluded to by Hirsch$^{24}$ that a large number of scans would be necessary to increase the signal to noise. Initial attempts at $^{13}$C NMR analysis of C$_{60}$, in toluene-$d_8$, experimented with 1-2 hours of scans, which proved to be insufficient as the only peaks visible were those from toluene. According to Silverstein$^{49}$, the minimum sample needed for $^{13}$C at 75.5 MHz would be 10 mg in 0.4 mL of solvent in a 5-mm o.d. NMR tube. At best, when dissolving C$_{60}$ in toluene there is only $\sim$1.12 mg in 0.4 mL. Given that the natural abundance of $^{13}$C is only about 1.16 % that of $^1$H, using a solvent that does not dissolve at least 10 mg of C$_{60}$ or C$_{60}$H$_x$ in 0.4 mL introduces a risk of the NMR data being unsatisfactory. See Table 3 below for comparisons with other NMR solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility of C$_{60}$, mg/ml$^{27}$</th>
<th>mg of C$_{60}$ dissolved in 0.4 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.16</td>
<td>0.064</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.7</td>
<td>0.68</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.8</td>
<td>1.12</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>7.9</td>
<td>3.16</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>27</td>
<td>10.8</td>
</tr>
</tbody>
</table>

**Table 3 Solubility comparison of C$_{60}$ in common NMR solvents**

The solubility of C$_{60}$ has been determined in the literature, but little is known about the solubility of hydrogenated fullerenes. It is assumed that the same solubility trends that are present in C$_{60}$ should be present in C$_{60}$H$_x$ compounds, considering the chemical similarities. Two known exceptions include CS$_2$ and methylcyclohexane$^{40}$, in which hydrogenated fullerenes are significantly more soluble than C$_{60}$. 
The general trend with hydrogenated fullerenes is that their signals move upfield with increasing level of hydrogenation. The solvent used also affects the peak position substantially; CS$_2$/acetone will produce a peak the furthest downfield ($\delta$ 7.17), followed by CS$_2$/CDCl$_3$ ($\delta$ 7.01), o-dichlorobenzene ($\delta$ 6.85), toluene ($\delta$ 5.93), and benzene is the most upfield at $\delta$ 5.915. See Appendix 1 for a table of NMR peak data for various hydrogenated fullerenes in the literature.

Without the aid of an HPLC, there is no known method in the literature to isolate one hydrogenated fullerene from another. At the time this thesis was written, the exact hydrogenated products from each reaction are not known with a high level certainty. In the next section, the results for each reaction will be discussed.

4.2 Reaction results and discussion

4.2.1 NaBH$_4$ reduction of C$_{60}$

This reaction was conducted several times at varying ratios as a method to prepare C$_{60}$H$_2$. When using a 1:1 (C$_{60}$: NaBH$_4$) ratio, the production of C$_{60}$H$_2$ was noted in the UV/Vis but was not confirmed by $^1$H NMR spectroscopy. As mentioned in the experimental section, the reaction mixture was passed through an alumina column with CS$_2$ as the eluent. The fractions that were collected all contained C$_{60}$, but the amount decreased with each successive fraction. See Figure 7 for UV/Vis spectra of fractions 3 through 6. Fraction 1 contained CS$_2$ and toluene only. Fraction 2 contained C$_{60}$, based on the light purple color, but according to UV/Vis spectroscopy it must have been below the threshold, as only CS$_2$ and toluene were present. Fraction 6 also consisted of mostly solvent.
The column did appear to reduce the amount of C$_{60}$ in later fractions, but could never completely eliminate it. Each fraction was stripped of solvent and dried under vacuum.

The amount of NaBH$_4$ was increased in an attempt to push more C$_{60}$ to react. See Figure 8 for representative UV/Vis data. The C$_{60}$ peaks are located at 407 nm and 597 nm, whereas, the C$_{60}$H$_2$ peaks are located at 436 nm and 713 nm.
A large excess of NaBH₄ was reacted with C₆₀ in an attempt to hydrogenate all of the C₆₀. According to UV/Vis spectroscopy, all of the C₆₀ was consumed, but the products are unknown (See Figure 9) as there are no distinguishable peaks in the UV/Vis spectrum.

Figure 8 UV/Vis data of the 1:2.5 reaction of C₆₀:NaBH₄
The peak at 433 nm is not consistent with $C_{60}H_2$. If a more hydrogenated fullerene were present, the peak would be expected at a higher wavelength, such as 439 nm for $C_{60}H_6$. Further research on adapting this reaction was halted because it showed little promise in producing reasonable yields of the desired hydrogenated fullerenes. Except for the 10X reaction, significant $C_{60}$ peaks were noted in the UV/Vis data.

### 4.2.2 Reduction of $C_{60}$ by various thiols

The idea of using a thiol to reduce $C_{60}$ was very promising. There was support in the literature for $H_2S$ reacting with $C_{60}$ to form $C_{60}H_2$. Thiols were chosen because many were readily available in high purity, free of major safety concerns, and were not P-listed materials. P-listed materials are dangerous to the environment and are significantly more expensive to dispose of as waste. $C_{60}$ was heated in toluene for 4 days as a control reaction, as expected no $C_{60}H_2$ was produced. See Table 4 for the test matrix of thiols.
<table>
<thead>
<tr>
<th>Thiol</th>
<th>Type of thiol</th>
<th>C₆₀H₂ formed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptoacetic acid</td>
<td>Aliphatic</td>
<td>No, confirmed by UV-Vis</td>
</tr>
<tr>
<td>Thiophenol</td>
<td>Aromatic</td>
<td>Yes, UV-Vis confirmation.</td>
</tr>
<tr>
<td>1-Octadecanethiol</td>
<td>Aliphatic</td>
<td>No, confirmed by UV-Vis</td>
</tr>
<tr>
<td>Triphenyl methanethiol</td>
<td>Benzylic</td>
<td>No, confirmed by UV-Vis</td>
</tr>
<tr>
<td>4-Nitrothiophenol</td>
<td>Aromatic with electron withdrawing group</td>
<td>No, confirmed by UV-Vis</td>
</tr>
</tbody>
</table>

Table 4 Matrix of thiols to reduce C₆₀

The first thiol attempted was mercaptoacetic acid. For this reaction the stoichiometry was based on a 1:2 C₆₀: thiol ratio. After a few hours, the reaction did not experience a color change, which typically indicates the conversion of C₆₀ to a hydrogenated fullerene. UV/Vis spectroscopy confirmed that no reaction occurred.

Scheme 8 Reduction of C₆₀ by thiophenol

Thiophenol was chosen as the next thiol, see Scheme 8. The experience gained from previous fullerene hydrogenation reactions led to some changes for this reaction. The amount of thiol was increased to 10X. This is consistent with the 5-27 fold excess used to achieve maximum yield in fullerene Grignard reactions.²⁴ Also the reaction time was lengthened and the temperature was increased. Thiophenol and C₆₀ were dissolved in toluene and heated to reflux for 2 days, at which point the color change was first noticed. Subsequent thiophenol reductions varied in reaction time. The color change would occur anywhere from 2-5 days into the reaction.
Avent et al., also found that their reaction time varied, for unknown reasons, from batch to batch when reducing $C_{60}$ with hydrogen. See Figure 10 for UV/Vis data for the product of the thiophenol reduction of $C_{60}$.

![UV/Vis data of the products of the thiophenol reduction of $C_{60}$](image)

**Figure 10 UV/Vis data for the products of the thiophenol reduction of $C_{60}$**

The appearance of the $C_{60}H_2$ peak at 436 nm indicates the success of the reaction. The corresponding peak at 714 nm is further validation that a hydrogenated fullerene is present. The $C_{60}$ peak at 599 nm is reduced in the post reaction sample but still visible. Multiple attempts were made to acquire $^1$H NMR data for the products of all the thiophenol reductions of $C_{60}$. Early attempts used $d_8$-toluene and CS$_2$/acetone as the solvent as there was a literature precedent to suggest those solvents would be appropriate. The $^{13}$C spectra routinely displayed peaks for toluene and thiophenol, but no $C_{60}$ or $C_{60}H_2$. The decision was made to try another NMR solvent, such as $o$-dichlorobenzene, that dissolves greater amounts of both $C_{60}$ and the hydrogenated products. The downside to this change of solvent was the absence of any literature chemical shift.
reference values. Many of the other solvents had more than one source citing the NMR data, increasing the chance that it is valid.

Scheme 9 Attempted reduction of C\textsubscript{60} by 1-octadecanethiol

As outlined in Scheme 9 the 1-octadecanethiol reactions with C\textsubscript{60} were heated and stirred for 4 days each time with no C\textsubscript{60}H\textsubscript{x} being formed; UV/Vis revealed no peaks corresponding to C\textsubscript{60}H\textsubscript{x}.

Scheme 10 Attempted reduction of C\textsubscript{60} by triphenyl methanethiol

The triphenyl methanethiol reactions with C\textsubscript{60} were also heated and stirred for 4 days with no visual change (See Scheme 10). UV/Vis spectroscopy confirmed that no hydrogenated products were present, but did show a subtle change as depicted in Figure 11.
There is a slight shift in the UV/Vis spectrum for the triphenyl methanethiol reaction mixture. The C$_{60}$ peak at ~407 nm is shifted slightly to 410 nm in the post reaction sample. It is possible that a fullerene anion is being formed. In the literature C$_{60}$ anions have exhibited distinct bands in UV/Vis that differentiate them from the uncharged fullerene. For example, C$_{60}$ in CH$_2$Cl$_2$ has peaks at 257 nm and 330 nm. Once C$_{60}$ is reduced to C$_{60}^-$, the peaks shift to 262 nm and 339 nm, C$_{60}^{2-}$ exhibits a further shift to 263 nm and 340 nm. It is possible that C$_{60}^-$ is being formed in this reaction but more investigation would be necessary to determine that. The steric hindrance of triphenyl methanethiol might have contributed to the reaction not occurring. Future work in the area should consider using another benzylic thiol, but one that is less hindered.
Scheme 11 Attempted reduction of C_{60} by 4-nitrothiophenol

The use of 4-nitrothiophenol was expected to produce C_{60}H_2; see Scheme 11. The nitro group is electron withdrawing and should pull the electron density away from the aromatic ring, which in turn, would pull the electron density from the thiol. This should have made the thiol hydrogen easier to abstract. Thus, it was surprising, after 4 days, that no reaction was evident.

4.2.3 C_{60}H_6

It became evident that isolating C_{60}H_2 would be difficult and time consuming, even if the thiophenol reduction produced only C_{60}H_2. The thiophenol reduction averaged 4 days to react and always contained unreacted C_{60}. A route in the literature to produce C_{60}H_6 as the main product was considered. This reaction was performed by Meier’s et al.\textsuperscript{47} and was noted for producing C_{60}O as the only known side product. C_{60}H_2 and C_{60}H_4 could be present, but in very small quantities. C_{60}H_6 could be used a precursor to metal fullerenes, but the pK_a information is not readily found in the literature. Without pK_a data it will be difficult to decide which base to use to preferentially remove specific numbers of hydrogens. Alloying fullerenes will be difficult to produce reproducibly without having detailed pK_a information for the six hydrogens on C_{60}H_6. In order to see if it could be a possible precursor to metal fullerenes, C_{60}H_6 was chosen to be prepared as outlined in Scheme 12.
Scheme 12 Zn(Cu) reduction of C\textsubscript{60} to form C\textsubscript{60}H\textsubscript{6}.

The reaction proceeded as expected and the formation of C\textsubscript{60}H\textsubscript{6} was confirmed using UV/Vis spectroscopy (See Figure 12).

The C\textsubscript{60} peaks in the pre-reaction sample are located at 407 nm and 598 nm. After reacting for 3 hours, the C\textsubscript{60} appears to be exhausted and the C\textsubscript{60}H\textsubscript{6} peaks at 439 nm and 713 nm are present. The C\textsubscript{60}H\textsubscript{6} match the literature values in the Meier paper.
An adaptation of the Meier method was attempted with thiophenol as the proton source to produce C_{60}H_{6}, see Scheme 13. The reaction was set up with C_{60} dissolved in toluene with thiophenol as a proton source. After 5 days, the UV/Vis revealed no reaction occurred. At this time, Zn(Cu) was added to see if it would encourage the reaction to occur. This mixture was heated and stirred for two days. The hydrogenated fullerenes were evident from the UV-Vis spectra shown in Figure 13.
After the initial five days of the reaction, a small peak, representative of hydrogenated fullerene, is present. In all previous attempts with the thiophenol reduction, the hydrogenated fullerene peak had a much stronger absorbance. There is a sizeable increase after the addition of Zn(Cu). The product was precipitated with acetone to remove the thiophenol and dried under vacuum. An NMR sample was prepared with o-dichlorobenzene and $^1$H and $^{13}$C DEPT 90 spectra were acquired. See Figures 14 and 15.

Figure 13 UV/Vis of Zn(Cu) reduction of C$_{60}$ with thiophenol
Figure 14. 300 MHz ¹H NMR spectrum of C₆₀Hₓ.

The ¹H NMR spectrum is difficult to interpret for a number of reasons. First, the lock solvent was set to CDCl₃ even though o-dichlorobenzene was used. This was done because o-dichlorobenzene was not in the list of lock solvents on the instrument. Attempts to manually lock were unsuccessful. With CDCl₃ as the “lock” solvent, the NMR successfully locked and shimmed, but the peaks could be shifted. The two peaks that could be hydrogenated fullerenes are located at δ 6.74 and δ 6.58. The literature value for C₆₀H₂ in o-dichlorobenzene is δ 6.85. Assuming no shift in the data, this spectrum would indicate two different hydrogenated fullerenes are present that have more than two hydrogens. There appears to be no literature NMR data for C₆₀H₄ and C₆₀H₆ compounds using o-dichlorobenzene as the lock solvent. The ¹³C NMR data presented a different possibility for the identification of the sample, as shown in Figure 15.
The peaks of interest in the $^{13}$C DEPT spectrum were located at $\delta$ 53.00 and $\delta$ 59.30. The literature peak for $C_{60}H_2$, in $o$-dichlorobenzene, is $\delta$ 53.32. The $^1H$ spectrum did not indicate 1, 2 $C_{60}H_2$ based on the peak positions, but the $^{13}$C DEPT 90 appears to confirm its presence. If the peak at $\delta$ 53.00 is assumed to be 1,2 $C_{60}H_2$, the peak at $\delta$ 59.30 must be a different isomer of $C_{60}H_2$ because the higher hydrogenated fullerenes would have peaks upfield from those of 1,2 $C_{60}H_2$. There are 23 isomers of $C_{60}H_2$, with 1,2 $C_{60}H_2$ being the lowest in energy. The only other low energy structure is 1,4 $C_{60}H_2$. It is unlikely that a $C_{60}H_2$ structure would be formed other than 1,2 $C_{60}H_2$ or 1,4 $C_{60}H_2$, due to their high energy of formation. The tentative peak assignments for $\delta$ 53.00 and $\delta$ 59.30 are 1, 2-$C_{60}H_2$ and 1,4-$C_{60}H_2$, respectively. At this time, the peaks cannot be assigned with any degree of certainty for a number of reasons. First, the sample appears to be a mixture. HPLC separation of the products should be attempted and then NMR measurements repeated. It is possible that the 1,4 isomer is a kinetic product, which could be
determined by conducting NMR experiments with various temperatures to see if one isomer disappears. The last hurdle in identifying the peaks is to verify that the separated products have the correct mass for the tentative assignments. Access to matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry is necessary to determine accurate molecular weights for hydrogenated fullerenes.

4.3 Future work

This project brought up more questions than it solved. Can C_{60}H_{2} be made exclusively and isolated without an HPLC? Maybe, but more work will need to be done to verify that it is indeed possible. Would C_{60}H_{6} be a better starting point for metal fulleride synthesis? The advantage of using C_{60}H_{6} is that this molecule is easier to synthesize, in part because it is accompanied by fewer side products than the C_{60}H_{2} reactions. C_{60}H_{6} can be produced with good yield and few impurities by using the Zn(Cu) approach.\textsuperscript{47} If C_{60}H_{6} is pursued, a \( pK_a \) study would need to be conducted to assess whether different metal bonds can be formed in a reproducible manner at the desired stoichiometry.

The first avenue to explore would be to reproduce all of the reactions that created a hydrogenated product and then isolate the products with an HPLC. If two different isomers of C_{60}H_{2} were indeed produced, refinement of the reaction conditions may preferentially produce a single isomer.

Extraction of reaction mixtures with methylcyclohexane could also be attempted in lieu of an HPLC separation. This would separate the hydrogenated fullerene mixture from the unreacted C_{60}.

5 Conclusions

The preparation of C_{60}H_{2} can be achieved by a number of reactions. Without the assistance of HPLC separation, isolation of C_{60}H_{2} is quite challenging. Reduction of C_{60} by
NaBH₄ does not appear to be a viable route to producing C₆₀H₂. The amount of unreacted C₆₀ appears to be significant compared to any hydrogenated product. The most promising approach still appears to be reduction of C₆₀ via Zn(Cu) and water. Future work on this project will involve fine-tuning of the proton source used and limiting the reaction time. It is possible that thiophenol could prove to be a proton source that will reliably produce C₆₀H₂ without producing C₆₀H₄ or C₆₀H₆. Based on UV-Vis peak positions and NMR data, it would indicate that this project has succeeded in producing 1, 2-C₆₀H₂ and possibly 1, 4-C₆₀H₂ when C₆₀ is reduced by Zn(Cu) in the presence of thiophenol.

The hydrogenation of C₆₀ with thiophenol may be novel, but at this time it does not appear to be a viable route for large-scale production of hydrogenated fullerenes. The length of time the reaction requires is excessive compared to other methods known in the literature. However, if this method proves to afford only one hydrogenated compound, it may be useful.
## Appendix 1 NMR Peak Data for Various Hydrogenated Fullerenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1\text{H}$ NMR, ppm</th>
<th>$^{13}\text{C}$ NMR, ppm</th>
<th>Method/Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$</td>
<td>n/a</td>
<td>143, (d$_8$-toluene)</td>
<td></td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>5.93, s (d$_8$-toluene)</td>
<td></td>
<td>Hydroboration$^{36}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>6.03</td>
<td></td>
<td>Reduction by H$_2$S$^{42}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>6.97, s (CS$_2$/CDCl$_3$)</td>
<td></td>
<td>Reduction by diimide$^{42}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>7.01, s (CS$_2$/CDCl$_3$)</td>
<td></td>
<td>Hydrolysis of fullerene ketone$^{37}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>5.915, s (d$_6$-benzene)</td>
<td></td>
<td>Hydrolysis of fullerene ketone$^{37,37}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>6.850, s, (d$_{0-o}$-dichlorobenzene)</td>
<td>53.32, 136.36, 140.38, 141.61, 141.96, 141.98, 142.55, 143.31, 144.73, 145.44, 145.52, 146.11, 146.33, 146.39, 147.40, 147.79, 152.49 (d$_{0-o}$-dichlorobenzene)</td>
<td>Hydrolysis of fullerene ketone$^{37,37}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>7.17, s (CS$_2$/acetone-$d_6$)</td>
<td>54.10, 136.92, 141.05, 142.20, 142.52, 142.57, 143.14, 143.66, 143.91, 145.28, 145.99, 146.10, 146.61, 146.87, 146.93, 147.90, 148.38, 153.28 (CS$_2$/acetone-$d_6$)</td>
<td>Zn(Cu) reduction$^{38}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>6.97, s (CS$_2$/CDCl$_3$)</td>
<td></td>
<td>Reduction by diimide$^{42}$</td>
</tr>
<tr>
<td>1, 2 C$_{60}$H$_2$</td>
<td>6.13, s (d$_6$-benzene)</td>
<td></td>
<td>Reduction by diimide$^{42}$</td>
</tr>
<tr>
<td>1, 4 C$_{60}$H$_2$</td>
<td>7.23, s (CS$_2$/CDCl$_3$)</td>
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<td>Produced by reduction with diborane, diimide, chromium(II) acetate, and hydrogen with Pt/C$^{42}$</td>
</tr>
<tr>
<td>1,2,3,4 C$_{60}$H$_4$</td>
<td>AA<code>BB</code> centered at 5.03 (d$_8$-toluene)</td>
<td></td>
<td>Henderson angew chem. 1994</td>
</tr>
<tr>
<td>1,2,18,36 C$_{60}$H$_4$</td>
<td>5.36, s (d$_6$-toluene) 5.05, q(d$_6$-toluene)</td>
<td></td>
<td>Henderson angew chem. 1994</td>
</tr>
<tr>
<td>1,2,18,36 C$_{60}$H$_4$</td>
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<tr>
<td>1,2,33,50 C$_{60}$H$_4$</td>
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<td>Reduction by Zn(Cu)$^{38}$</td>
</tr>
<tr>
<td>C$_{60}$H$_6$</td>
<td>6.00, s (CS$_2$/CDCl$_3$)</td>
<td>52.28, 141.55, 142.60, 144.18, 145.71, 151.45, 151.65, 153.66, 153.97, 158.05, Reduction by Zn(Cu)$^{38}$</td>
<td></td>
</tr>
<tr>
<td>C$_{60}$H$_6$, isomer 1</td>
<td>5.18, s, (d$_6$-toluene) 6.0, s, (CS$_2$/CDCl$_3$)</td>
<td>158.05, 153.97, 153.66, 151.65, 151.45, 144.18, 142.60, 141.55, 52.28 (CS$_2$/CDCl$_3$), $^1$H-$^{13}$C decoupled</td>
<td>Reduction by Zn(Cu)$^{47}$</td>
</tr>
</tbody>
</table>
References


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