THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

MARK A. GAPINSKI

ENTITLED

INTRAMOLECULAR ELECTRON TRANSFER STUDIES OF

1',6'-DIBENZYLBIFERROCENIUM HEXAFLUOROPHOSPHATE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Intramolecular Electron Transfer Studies of 1',6'-Dibenzylbiferrocanium Hexafluorophosphate

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There are many people that were helpful during the course of my research. However, one person in particular stands out. To say that Michael Dean (Mad Dog) Lowery was helpful would be an incredible understatement. His help, guidance and teaching were invaluable.

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Above all I thank Vicki Lynn Merkel for everything. She is an undying inspiration in everything I do. She is dearly missed.

It is to Vicki Lynn that I dedicate this work.
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I. INTRODUCTION

Electron transfer is a very fundamental and important process. It is important in many areas; chemical reactions, photosynthesis, and catalysis just to name a few. Intramolecular electron transfer is a good way to study the overall process of electron transfer.

The study of intramolecular electron transfer in mixed-valence transition-metal complexes was pioneered by Taube and Cowan. The underlying idea is to determine the rate of intramolecular electron transfer between two well separated metal sites in a mixed-valence complex. In this work the metal sites are iron (Fe) atoms. The primary technique utilized is $^{57}$Fe Mossbauer spectroscopy. A good explanation of Mossbauer spectroscopy and its theoretical principles can be obtained from numerous sources. Much work has been done recently in this area using ferrocene derivatives. The structures of several ferrocene derivatives are shown in Figure 1.

The three main factors controlling intramolecular electron transfer are 1) the distance between the metal sites, 2) the bridging ligands between the metal sites, and 3) the environment around the metals. When the distance between metal sites is increased and if unconjugated bridging ligands are used the electron transfer rate is decreased. In these recent studies the distance between the metal sites and the bridging ligands were constant but the metals' environment changed. This was
accomplished by changing the substituents (represented as X in Figure 1) on the cyclopentadienyl rings. Almost all of this work to this point has been done with linear trihalide salts. From this work three basic classes of systems have been discovered:

1) Systems, with symmetric crystal structures, that are detrapped on all time scales. (X=I, Br).

2) Systems with asymmetric crystal structures, that are trapped on all time scales. (X=Cl).

3) Systems that are trapped on some faster time scales and show temperature dependence as to whether or not they are detrapped on the Mossbauer time scale. (X= alkyls).

My research dealt with the temperature dependent dialkyl substituted biferrocene systems. I however investigated hexafluorophosphate (PF$_6^-$) salts as opposed to the previously studied linear trihalide salts. In particular I synthesized, characterized and investigated the intramolecular electron transfer properties of 1',6'-dibenzylbiferrocenium hexafluorophosphate whose structure is shown in Figure 2.

II. EXPERIMENTAL

A. Compound Preparation

Chloromercuriferrocene,$^{18-19}$ bromoferrocene,$^{18-25}$ 1-benzoyl-1'-bromoferrocene,$^{26-29}$ 1',6'-dibenzoylbiferrocene$^{26-28}$ and 1',6'-dibenzylbiferrocene$^{28}$ were prepared with guidance provided
Figure 1. 1',6'-Disubstituted biferrocene.
Figure 2. $1',6'$-Dibenzylbiferrocenium Hexafluorophosphate (PF$_6^-$).
by literature. These synthetic preparations, however, were changed extensively and the techniques utilized are presented here.

i. Chloromercuriferrocene.

In a three-neck round-bottom flask fitted with a mechanical stirrer, reflux condenser and addition funnel ferrocene was dissolved in methanol and ethyl ether. This solution was then brought to reflux. To the addition funnel was added mercuric acetate that had been dissolved in boiling methanol. This mercuric acetate solution was added to the refluxing ferrocene solution over a period of approximately one hour. This reaction mixture was allowed to reflux for an additional five hours at which point the heating was discontinued.

To the reaction mixture was then added lithium chloride in boiling methanol over a period of approximately fifteen minutes. After all of the lithium chloride solution had been added the heating was resumed and the reaction mixture was refluxed for one additional hour. The heating was then discontinued and the mixture was allowed to cool to room temperature with stirring. Once cool the mixture was filtered. The yellow-orange precipitate was air dried and the filtrate was evaporated on a rotary evaporator. The resulting solid was combined with that of the filtration. These combined solids were extracted three times with boiling hexane. The dark orange filtrate was evaporated on a rotary evaporator to give recovered ferrocene. The solid that was
insoluble in the boiling hexane is a mixture of chloromercuriferrocene and dichloromercuriferrocene. The former was extracted from the latter with four portions of boiling n-butanol. The red filtrate was cooled to yield yellow-gold crystals of chloromercuriferrocene (Mp. 196-197 °C) which were filtered, washed with hexane and air dried.

ii. Bromoferroocene.

In a three-neck round-bottom flask fitted with a mechanical stirrer and an addition funnel chloromercuriferrocene was dissolved in methylene chloride and then degassed with argon for approximately five minutes. A solution of N-bromosuccinimide in methylene chloride was placed in the addition funnel and also degassed with argon for approximately five minutes.

After degassing, the reaction flask was placed in an ice bath. Once the reaction flask had reached the temperature of the ice bath the N-bromosuccinimide solution was added dropwise over a period of approximately one hour with stirring. This resulted in a green solution which was kept stirred for approximately fifteen hours.

The reaction was worked up by adding an aqueous solution of sodium bisulfite to the reaction flask and forcing the layers to mix with rapid stirring for approximately one hour. At this point an aqueous solution of sodium carbonate was added and rapidly stirred for an additional hour. The resulting mixture separated
into two layers. The upper, aqueous layer that contained a white precipitate was discarded. The lower, methylene chloride layer was filtered and the filtrate was extracted with water. The methylene chloride was dried over magnesium sulfate and filtered through a short (ca. 1 inch) column of neutral alumina to remove the drying agent and a small amount of green material which is left on the alumina.

The methylene chloride was removed on a rotary evaporator leaving a dark yellow-brown oil which was immediately chromatographed on neutral alumina and eluted with hexane. The leading bright yellow band was collected and the solvent was removed on a rotary evaporator leaving a dark yellow-brown oil. The resulting oil was recrystallized by suspending it in a minimum of warm methanol with stirring. While the stirred solution slowly cooled crystals began to form. As soon as the first crystals began to form the stirring was discontinued and the solution was left to sit for thirty minutes as the yellow-gold crystals grew. (Mp. 28-30 C).

iii. 1-Benzoyl-1'-bromoferrocene.

In a three-neck round-bottom flask fitted with a mechanical stirrer and an ice-jacketed addition funnel was dissolved bromoferrocene in dried methylene chloride. This reaction flask was placed into an ice bath. Into the addition funnel was dissolved aluminum chloride in dried methylene chloride. To the addition
funnel solution was added benzoyl chloride via syringe. Once the reaction flask and addition funnel had achieved ice bath temperature the solution in the addition funnel was added dropwise to the stirred reaction flask over a period of approximately one hour. The solution in the reaction flask turned from yellow to violet-purple during the addition. After the addition was completed, the mixture stirred at ice temperature for one hour. At this time the ice bath was removed and the mixture was stirred for an additional ninety minutes at room temperature. The reaction was worked up by pouring the reaction mixture into ice water and then extracting with methylene chloride. The methylene chloride solution was washed with a saturated aqueous solution of sodium bicarbonate and then washed repeatedly with water. The resulting organic solution was dried over magnesium sulfate and the drying agent was filtered off. The solvent was removed on a rotary evaporator and the crude product was immediately chromatographed on neutral alumina. The first band was eluted with hexane and discarded. The second band was eluted with 10/1 benzene/ethyl acetate. The solvent was evaporated to yield a red oil that was purified by rechromatography.

iv. 1',6'-Dibenzoylbiferrocene.

A mixture of 1-benzoyl-1'-bromoferrocene and activated copper were heated to 120-130 C for approximately 36 hours under argon. The activated copper was prepared by treating a fine copper
powder with iodine and 1/1 acetone/conc. hydrochloric acid and then washing with acetone and drying under a vacuum.

After 36 hours the reaction flask was allowed to cool to room temperature and the mixture was extracted with methylene chloride until the extractions were colorless. The solution was then removed on a rotary evaporator. Although the literature procedure called for chromatography, a very pure red-brown crystalline product was obtained by dissolving the crude product in a minimum of boiling benzene and allowing the solution to slowly cool to room temperature without evaporation. The crystals grew over a period of approximately three days. (Mp. 167 °C) Anal. Calcd: C, 70.62; H, 4.53; Fe, 19.32. Found: C, 70.78; H, 4.58; Fe, 19.18.

v. 1',6'-Dibenzylbiferrocene.

1',6'-dibenzoylbiferrocene was dissolved in ethyl ether in a three-neck round-bottom flask that was fitted with a mechanical stirrer, reflux condenser and an ice-jacketed addition funnel. While the solution was purging with argon, a three-fold molar excess of lithium aluminum hydride was added to the reaction flask. Gas was evolved during the addition so care was taken to prevent pressure build up. Upon addition, the reaction solution also changed color from red to yellow.

A layer of glass wool covered with glass beads was placed in the addition funnel before a three-fold molar excess ethyl ether solution of aluminum chloride was added. This solution was
dripped into the stirred reaction flask over a period of approximately one hour. The reaction mixture was then refluxed for one hour and then allowed to cool to room temperature. Once cool, water was dripped into the stirred reaction solution until gas was no longer evolved. The reaction mixture was extracted with ethyl ether and the solvent was removed on a rotary evaporator. The resulting crude product was immediately chromatographed on neutral alumina and eluted with hexane. The solvent was removed again on a rotary evaporator and the product was recrystallized from hot hexane. (Mp. 152 C) Anal. Calcd: C, 74.21; H, 5.49; Fe, 20.30. Found: C, 72.62; H, 5.57; Fe, 19.82.

vi. 1',6'-Dibenzylbiferrocenium Hexafluorophosphate.

The following reaction was carried out in plastic lab-ware due to the fact the hexafluorophosphoric acid decomposes glass and contaminates samples. To a solution of 1',6'-dibenzylbiferrocene in methanol was added a catalytic amount of sublimed quinone. To this solution was added an equal molar solution of hexafluorophosphoric acid with stirring. The product came out of this solution with stirring and was filtered and air dried. Anal. Calcd: C, 58.74; H, 4.35; Fe, 16.06. Found: C, 58.40; H, 4.13; Fe, 15.79.
B. Physical Methods.

$^{57}$Fe measurements were obtained on a constant-acceleration-type instrument that has been described previously.\textsuperscript{30-31} The absolute temperature precision is estimated to be +/- 3 K and the relative precision is +/- 0.5 K. The Mössbauer spectra were fit to Lorentzian lineshapes with a previously documented computer program.\textsuperscript{32}

Differential scanning calorimetry (DSC) studies were obtained on a Perkin-Elmer Model DSC7 Differential Scanning Calorimeter that was controlled by a Perkin-Elmer Model TAC7 Instrument Controller. The data was manipulated with a Perkin-Elmer Model 7500 Professional Computer and then plotted on a Perkin-Elmer Graph Plotter 2.

Electron paramagnetic resonance (EPR) studies were obtained on a Bruker Model 230 Electron Paramagnetic Spectrometer.

Elemental analyses were performed by the Microanalytical Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign.

III. RESULTS AND DISCUSSION.

A. Previously Studied Dialkyl Substituted Biferrocenium Trihalides.

There have been many studies on mixed-valence biferrocene
systems with trihalides as the counter-ion.\textsuperscript{9-14} Much of this work is presented by T.-Y. Dong.\textsuperscript{33} In my studies I examined one of the three classes of systems that were presented earlier in this work; temperature dependent dialkyl substituted biferrocenes. This temperature dependence refers to whether or not the system is seen to be trapped or detrapped on the Mossbauer time scale.

The dialkyl substituted biferrocenium trihalides are seen to be temperature dependent as to when the system becomes detrapped. This temperature dependence was explained by Dong et al.\textsuperscript{11-12} as due to the linear trihalide counter-ions being thought of as a set of conformations as opposed to one single conformation which is exhibited in Figure 3. This is to say that the two bond lengths in linear trihalide counter-ions are unequal. Single crystal x-ray structures of the trihalide systems showed that the linear counter-ions are packed in alternating stacks with the biferrocenium cations as shown in Figure 4. It was stated, qualitatively, in the micromodulation theory \textsuperscript{11-12} that as the temperature was increased the trihalide counter-ion oscillated between the two configurations. (A quantitative theoretical model is up coming.)\textsuperscript{34} This was coupled with the intramolecular electron transfer between the two Fe sites and therefore the detrapping of the system. This theory is substantiated very well by the dialkyl substituted biferrocenium trihalide Mossbauer data showing temperature dependence\textsuperscript{33} which is presented in Figures 5-8.
Figure 3. Trihalide (triiodide) counter-ion conformations.
Figure 4. Stereoview of the packing arrangement of biferrocenium triiodide.
Figure 5. Variable-temperature $^{57}$Fe Mossbauer spectra for:
   biferrocenium triiodide, left panel; and
   biferrocenium dibromoiiodide, right panel.
Figure 6. Variable-temperature $^{57}$Fe Mossbauer spectra for 1',6'-diethylbiferrocenium triiodide.
Figure 7. Variable-temperature $^{57}$Fe Mossbauer spectra for 1',6'-di-n-butylbiferrocenium triiodide.
Figure 8. Variable-temperature $^{57}$Fe Mossbauer spectra for 1',6'-dibenzylbiferrocenium triiodide.
B. 1',6'-Dibenzylbiferrocenium Hexafluorophosphate (PF$_6^-$).

i. $^{57}$Fe Mossbauer Spectroscopy.

Mossbauer spectroscopy is extremely useful in probing the oxidation states of the two Fe atoms in mixed-valence biferrocene systems. If a spectrum has two distinct sets of doublets, the system is said to be trapped on the Mossbauer time scale at the given temperature. (The Mossbauer time scale is $10^{-7}$ sec.$^{-1}$) The inner doublet is attributable to one iron (Fe) center being seen as a distinct Fe (III) and the outer doublet is attributable to the other iron (Fe) center being seen as a distinct Fe (II). In a detrapped system only a single doublet will be seen which is attributable to the electron transferring between the two iron (Fe) centers faster than the Mossbauer time scale, consequently both iron (Fe) centers are seen as equivalent Fe (II.5)'s. The distance between the two peaks of a doublet is referred to as the quadrupole splitting. The quadrupole splittings for Fe (II) and Fe (III) are generally very different; approximately 2.00 and 0.35 mm/sec respectively. As a system becomes detrapped, the two sets of doublets merge into one sharp doublet with an averaged quadrupole splitting. By varying the temperature at which the spectra are obtained, the temperature at which the system becomes detrapped can be determined. (In this work "detrapped" refers to the Mossbauer time scale.)

My studies dealt with changing the counter-ion from a linear
trihalide to a spherical hexafluorophosphate (PF$_6^-$). Dong \textit{et al.} 9-11,13 have studied the trihalide system of 1',6'-dibenzylbiferrocene. In my studies, by replacing the trihalide counter-ion with hexafluorophosphate in a previously studied system, 1',6'-dibenzylbiferrocene, the counter-ion's role in intramolecular electron transfer was being investigated. As was seen with the trihalide system, the hexafluorophosphate system also exhibited temperature dependence. The 1',6'-dibenzylbiferrocenium hexafluorophosphate became detrapped at approximately 175 K. This system's variable temperature $^{57}$Fe Mossbauer data is presented in Figures 9-15, and a plot of quadrupole splitting versus temperature is presented in Figure 16.

The trihalide and hexafluorophosphate salts of 1',6'-dibenzylbiferrocene exhibit very similar Mossbauer spectra. Both systems show two sets of doublets moving together, without line broadening, to give one sharp doublet at higher temperatures. This detrapping occurs, however, approximately 95 degrees higher in the trihalide system. Although the systems' spectra are similar it can not be assumed that the spherical PF$_6^-$ counter-ion undergoes the same conformational change as the trihalides. However, it is proposed in this work that the PF$_6^-$ counter-ion, like the trihalide, is responsible for the rate of intramolecular electron transfer.
Figure 9. $^{57}$Fe Mossbauer spectrum for $1',6'$-dibenzyl-biferrocenium hexafluorophosphate, (100 K).
EFFECT IN PERCENT

BENZYLBIFC PF6 AT 100 K

VELOCITY IN [MM/SEC]
Figure 10. $^{57}$Fe Mossbauer spectrum for 1',6'-dibenzyl-biferrocenium hexafluorophosphate, (150 K).
BENZYLBRIFC PF6 AT 150 K

VELOCITY IN [MM/SEC]
Figure 11. $^{57}$Fe Mossbauer spectrum for 1',6'-dibenzyl-biferrocenium hexafluorophosphate, (160 Hz).
BENZYLINDENE AT 100 K

VELOCITY IN (MM/SEC)
Figure 12. $^{57}\text{Fe}$ Mossbauer spectrum for 1',6'-dibenzyl-biferrocenium hexafluorophosphate, (165 K).
BENZYLAIFFC PF6 AT 165 K

VELOCITY IN (MM/SEC)
Figure 13. $^{57}$Fe Mossbauer spectrum for 1',6'-dibenzyl-
biferrocenium hexafluorophosphate, (175 K).
BENZYLBF6 PF6 AT 175 K

VELOCITY IN (MM/SEC)
Figure 14. $^{57}\text{Fe}$ Mossbauer spectrum for 1',6'-dibenzyl-
biferrocenium hexafluorophosphate, (185 K).
Benzylbifc PFO at 185 K

Velocity in (mm/sec)
Figure 15. $^{57}$Fe Mossbauer spectrum for 1',6'-dibenzyl-biferrocenium hexafluorophosphate, (200 K).
BENZYLBF-CN PF8 AT 200 K

VELOCITY IN (MM/SEC)
Figure 16. Quadrupole Splitting versus Temperature for 1',6'-
Dibenzylbiferrocenium Hexafluorophosphate ($PF_6^-$).
FIGURE 1

Q.S. vs. Temp for Bisbenzylbiferrocenium PF6

Q.S. (mm/sec)

temperature (K)
ii. Differential Scanning Calorimetry.

Differential Scanning Calorimetry (DSC) was utilized to investigate 1',6'-dibenzylbiferrocenium PF$_6^-$. A good explanation of DSC's theories and applications is presented by McNaughton and Mortimer.$^{35}$ DSC measures the heat capacity for a sample over a given temperature range. Any changes in heat capacity will be seen as a peak at the temperature at which the change occurred. If there were a change in structure of 1',6'-dibenzylbiferrocenium PF$_6^-$, as is theorized for the trihalides, a change in heat capacity and consequently a peak would be seen. (This is actually seen in biferrocenium triiodide (I$_3^-$).)$^{36}$ DSC studies did not show any dramatic changes in heat capacity in the temperature range over which the system becomes detrapped. The sample did, however, show a small feature that may be a glass transition in this temperature range. A glass transition is a small, gradual change in heat capacity, manifested as a small broad feature in the run, that occurs when a system goes from a state of some disorder to that of slightly greater disorder. This DSC study, which suggests that there is some type of structural change occurring, is presented in Figure 17.

IV. CONCLUSIONS.

In Dong et al.'s$^{11-12}$ micromodulation theory it was the fact that the trihalide counter-ions were going through a
Figure 17. Differential scanning calorimetric thermal analysis of 1',6'-dibenzylbiferrocenium hexafluorophosphate.
**PERKIN-ELMER**

7 Series Thermal Analysis System

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conformational change that facilitated the electron transfer. It is also a structural change in the PF$_6^-$ system that explains the facilitated electron transfer and subsequent detrapping of the system. The PF$_6^-$ counter-ion must undergo a change to increase its disorder over the temperature range that the system becomes detrapped. The DSC study gives some evidence that supports this theory. This increase in disorder of the PF$_6^-$ ion is also seen in studies by Albert and Gutkowsky$^{37}$ as well as by Niemela and Tuohi$^{38}$ in ammonium PF$_6^-$. It was proposed that one of ammonium hexafluorophosphate's observed phase transitions was due to the increase in disorder of the PF$_6^-$ anion. This change was seen in approximately the same temperature range where 1',6'-dibenzylbiferrocenium PF$_6^-$ becomes detrapped.

Work has also been done on simple alkali metal salts of PF$_6^-$ by G. R. Miller.$^{39}$ Miller studied the dynamic structure of these salts. He determined that the surrounding ions, distance between ions, geometric arrangement of ions in the crystal and the temperature all help determine the dynamic structure. He also stated that if a phase transition occurred the arrangement and distance between ions can change greatly. However, a phase transition for these salts was hypothesized but never proven.

The PF$_6^-$ anion, being spherical, is not be given to distorting itself in an oscillatory conformational way that the trihalides do. It is proposed by this work that the PF$_6^-$ anion changes in a way to allow it to move more freely in the lattice. As was stated by Miller,$^{39}$ a phase transition would change the environment in
the salt, which would lead to a symmetric environment. This ac­
counts for the detrapping of the system. At a given temperature, 
depending on the cation, the PF$_6^-$ anion starts to move between 
the two Fe sites faster than the Mossbauer time scale.

V. Further Studies Needed.

Single crystal growth techniques were used in an attempt to 
learn more about the structure of 1',6'-dibenzylbiferrocenium 
PF$_6^-$. However all of the methods that were used to grow crystals 
were unsuccessful. Currently many disubstituted biferrocenium 
PF$_6^-$ systems are being investigated. Yet at present, no single 
crystals have been obtained due to the rapid decomposition of 
these systems in solution. Single crystal structures were very 
useful in the development of the micromodulation theory for tri­
halide counter-ion systems. A single crystal of a PF$_6^-$ system 
would most likely be equally useful in explaining the PF$_6^-$ 
systems.

A low temperature (7.1 K), 9.438 GHz powder electron para­
magnetic resonance (EPR) spectrum has been obtained for 1',6'-di­
benzylbiferrocenium PF$_6^-$ and is presented in Figure 18. More EPR 
studies are necessary, however, for these studies to be useful. 
Temperatures above 175 K should be investigated to help determine 
the electron transfer rate.

Much time was spent refining the synthetic preparations of the 
disubstituted biferrocenium hexafluorophosphates and consequently
Figure 18. Electron Paramagnetic Resonance (EPR) Spectrum (9.438 GHz.) for 1',6'-Dibenzylbiferrocenium Hexafluorophosphate at 7.1 K.
MAGNETIC FIELD (GAUSS)
time limited my intramolecular electron transfer rate studies of
them. Currently, others are synthesizing and studying more
systems in this series. Their discoveries, in conjunction with
mine, should result in a more complete theory on the effect the
PF₆⁻ anion has on intramolecular electron transfer rates in disub-
stituted biferrocene systems. In addition, the disubstituted bi-
ferrocene systems should be studied with other types of anions
such as BF₄⁻, BPh₄⁻, FeCl₄⁻, FeBr₄⁻, and TCNQ to name a few. These
studies should give still a more complete theory on intramolec-
ular electron transfer.
REFERENCES AND NOTES


Current work on other disubstituted biferrocenium PF₆⁻ is being done by Michael D. Lowery and Robert J. Weinb of Professor David N. Hendrickson's research group at the University of Illinois at Urbana-Champaign.
Mark A. Gapinski was born on August 17, 1965 in Chicago, Illinois. He grew up in Deerfield, Illinois where he attended Holy Cross Elementary and Junior High School. In September 1979 he entered Deerfield High School and in June 1983 he graduated with honors as an Illinois State Scholar.

That August he entered the University of Illinois at Urbana - Champaign where he studied chemistry. In August 1986 he entered the research group of Professor David N. Hendrickson to undertake an undergraduate senior research project in inorganic chemistry.

The author is a member of the scholastic honoraries, Alpha Lambda Delta and Phi Eta Sigma.